Chapter 3

Creators and Creations in Chemistry and Materials Science

Alle Arnzneien sind auf der Erde, aber es fehlen die Menschen, die sie pflücken würden. Sie sind zur Ernte gereift, aber die Schnitter sind nicht gekommen. Wenn einmal die Schnitter der rechten Arznei da sein werden, dann werden wir ohne Hinderung durch leere Sophistik die Aussätzigen reinigen und die Blinden sehend machen. Denn diese Kraft liegt in der Erde und sie wächst überall. [...]

All the remedies are on earth, but we lack the people to gather them. They are ready to be harvested, but the reapers have not come. But one day the reapers of the right remedies shall come, and undeterred by empty sophistry we will cleanse the lepers and make the blind see. For this power is concealed in the earth, and it grows everywhere. [...]

Die Natur ist so sorgfältig und genau in ihren Dingen, daß man sie ohne große Kunst nicht verwenden kann; denn sie bringt nichts an den Tag, was an sich vollendet wäre. Alles hat der Mensch zu vollenden. Diese Vollendung heißt: Alchemie... Und der ist ein Alchemist, der alles, was in der Natur den Menschen zum Nutzen wächst, zu seinem von ihr bestimmten Ende führt. [...] Deswegen soll mehr Fleiß darauf verwendet werden, um mehr daraus zu gestalten! [...]

Nature is so careful and exact in her creations that they cannot be used without great skill; for she does not produce anything that is perfect in itself. Man must bring everything to perfection. This work of bringing things to their perfection is called alchemy... And he is an alchemist who carries what nature grows for the use of man to its destined end. [...] For this reason more diligence should be spent on alchemy, in order to obtain still greater results! [...]

Gott hat Eisen geschaffen, aber nicht das, was daraus gemacht werden soll... Das Weitere hat Er dem Feuer anbefohlen und dem Vulcanus, der des Feuers Herr ist... Daraus folgt, daß das Eisen zuerst von seinen Schlacken gereinigt und dann zu dem geschmiedet werden muß, was aus ihm entsehen soll. Das nennt sich Alchemie, das ist der Schmelzer—der Schmied—, der Vulcanus heißt. Was das Feuer tut, ist Alchemie—auch im Ofen, oder auch im Küchenherd.

God created iron but not that which is to be made of it... He enjoined fire, and Vulcan, who is the lord of fire, to do the rest... From this it follows that iron must be cleansed of its dross before it can be forged. This process is alchemy; its founder is the smith Vulcan. What is accomplished by fire is alchemy—whether in the furnace or in the kitchen stove.

Paracelsus. ca. 1536. In Jolande Jacobi, ed. 2002. *Paracelsus: Lebendiges Erbe.* St. Goar: Reichl. pp. 96–97. English translation adapted from Norbert Guterman.

As with biology, during the nineteenth century, intellectual leadership in chemistry and materials science passed from scientists in other countries (primarily France, the United Kingdom, and Sweden) to German-speaking scientists.[1]

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[1] In addition to specific references that are cited in different areas throughout this chapter, this chapter makes use of general biographical and project information from: ACLS 2000; Albrecht et al. 1992; Ash and Söllner 1996; Bar-Zohar 1967; Bower 1987; Bunch and Hellemans 2004; Challoner 2009; Cornwell 2003; Crim 2018; EB 1911, 2010; Gillispie 1970–1990; Gimbel 1990a; Glatt 1994; Hall 2019a; István Hargittai 2006, 2011; Linda Hunt 1991; Impey et al. 2008; Jacobsen 2014; Koertge 2007; Kurowski 1982; Lasby 1971; Lusar 1956, 1971; Medawar and Pyke 2000; Mick 2000; Murray 2003; Nachmansohn 1979; NDB 1953–2020; Neufeld 2012; Nouzille and Huwart 1999; O'Reagan 2014, 2019; Porter 1994; Charles Walker 1946; Peter Watson 2010; Weitensfelder 2009.

For coverage of major portions of the history of chemistry and materials science in the German-speaking world, see: Abelshauser et al. 2004; Brock 1993; Bugge 1955; Coffey 2008; Deichmann 2001; Drummer and Zwilling 2007; Engels et al. 1989; Farber 1961; Haber 1958, 1971; Ihde 1984; Johnson 1990; Kahlert 2002; Karlsch2016; Lesch 2000; Maier 2015; Marsch 1994a; Neufeldt 2003; Partington 1935, 1957, 1964; Peppas 2013; Rosner 2004; Sasuly 1947; Scerri 2006; Schwenk 2000; Soukup 2007; Teltschik 1992; Ungewitter 1938; Weeks and Leicester 1968; Welsch 1981; Werner 2017.

I have deliberately left a blank space where images of some creators or creations should go. Those are people or projects that I felt were important enough that they should definitely be shown in this book, yet I have not yet been able to locate a suitable image that I have permission to use, despite my searches in Europe and in the United States. If readers have any relevant images and could send them to me, I would be very grateful and will include them in future editions of this book. Even where a suitable photo cannot be located, I believe that leaving a blank space pays tribute both to the scientific importance of that creator or creation and to how that historical fact has been very nearly forgotten.

As covered in this chapter, creators from the predominantly German-speaking central European research world then made enormous contributions to:

3.1. Inorganic chemistry

3.2. Organic chemistry

3.3. The chemistry of foods and drinks

3.4. Chemical explosives

3.5. Chemical warfare agents and pesticides

3.6. Physical chemistry

3.7. Film photography

3.8. Materials science

3.9. Other aspects of chemistry

German-speaking creators also made numerous contributions to other chemistry-related areas such as biochemistry (Chapter 2), earth science (Chapter 4), quantum and statistical physics (Chapter 5), and nuclear chemistry (Chapter 8).

In 1946, the American journalist Charles Lester Walker provided a useful contemporary perspective on chemistry- and materials-related creations that were transferred out of the German-speaking world [Charles Walker 1946]:

> Mica was another thing. None is mined in Germany, so during the war our Signal Corps was mystified. Where was Germany getting it?
>
> One day certain piece of mica was handed to one of our experts in the U.S. Bureau of Mines for analysis and opinion. “Natural mica,” he reported, “and no impurities.”
>
> But the mica was synthetic. The Kaiser Wilhelm Institute for Silicate Research had discovered how to make it and—something which had always eluded scientists—in large sheets.
>
> We know now, thanks to FIAT teams, that ingredients of natural mica were melted in crucibles of carbon capable of taking 2,350 degrees of heat, and then—this was the real secret—cooled in a special way. Complete absence of vibration was the first essential. Then two forces directly perpendicular to each other were applied. One, vertically, was a controlled gradient of temperature in the cooling. At right angles to this, horizontally, was introduced a magnetic field. This forced the formation of the crystals in large laminated sheets on that plane.

> "You see this . . ." the head of Communications Unit, TIIB, said to me. It was metal, and looked like a complicated doll's house with the roof off. "It is the chassis or frame, for a radio. To make the same thing, Americans would machine cut, hollow, shape, fit—a dozen different processes. This is done on a press in one operation. It is called the 'cold extrusion' process. We do it with some soft, splattery metals. But by this process the Germans do it with cold steel!
>
> Thousands of parts now made as castings or drop forgings or from malleable iron can now be made this way. The production speed increase is a little matter of one thousand per cent."
>
> This one war secret alone, many American steel men believe, will revolutionize dozens of our metal fabrication industries.
>
> In textiles the war secrets collection has produced so many revelations, that American textile men are a little dizzy. There is a German rayon-weaving machine, discovered a year ago by the American 'Knitting Machine' Team, which increases production in relation to floor space by one hundred and fifty percent. Their "Links-Links" loom produces a ladderless, runproof hosiery. New German needle-making machinery, it is thought, will revolutionize that business in both the United Kingdom and the United States. There is a German method for pulling the wool from sheepskins without injury to hide or fiber, by use of an enzyme. Formerly the "puller"—a trade secret—was made from animal pancreas from American packing horses. During the war the Nazis made it from a mold called aspergil paraciticus, which they seeded in bran. It results not only in better wool, but in ten per cent greater yield.
>
> Another discovery was a way to put a crimp in viscose rayon fibers which gives them the appearance, warmth, wear resistance, and reaction-to-dyes of wool. The secret here, our investigators found, was the addition to the cellulose of twenty-five per cent fish protein.
>
> But of all the industrial secrets, perhaps, the biggest windfall came from the laboratories and plants of the great German cartel, I. G. Farbenindustrie. Never before, it is claimed, was there such a store-house of secret information. It covers liquid and solid fuels, metallurgy, synthetic rubber, textiles, chemicals, plastics. drugs, dyes. One American dye authority declares:
>
> *It includes the production know-how and the secret formulas for over fifty thousand dyes. Many of them are faster and better than ours. Many are colors we were never able to make. The American dye industry will be advanced at least ten years.*

A 29 July 1945 press release from the U.S. Foreign Economic Administration confirmed Walker's assessment of how advanced German science and engineering were, and also cited many additional examples, mainly in chemistry and materials science [NARA RG 40, Entry UD-75, Box 12, Folder Publicity, Advance Release FEA-575]:

Among the new developments uncovered so far are the following:

A plane with a ceiling several thousand feet higher than any American plane.

Process for welding side seams on tin cans by machine instead of by hand, as in this country.

New applications of radiation devices in fields not heretofore explored in the U.S.

New and improved X-ray tubes for cancer therapy and industrial purposes.

Flexible high tension cables that withstand double the voltage of American made cables of the same size.

Tungsten substitutes for use in the manufacture of armor-piercing shells and cutting tools for machining metals.

Power circuit breakers with construction details unfamiliar in the U.S.

New uses of waste cellulose materials for the manufacture of fats for animal feed.

Improved techniques in the fermentation of yeast from wood sugar in the production of both human and cattle food.

Improved techniques for the production of synthetic petroleum products.

Hydrogenation plants operating at extremely high pressures.

New catalysts permitting the Germans to convert oil to high octane gasoline more quickly than was known here.

Details on German refinements in the gas synthesis method of producing liquid fuels and lubricants from coal.

New processing methods in the field of synthetic rubber.

New data on continuous polymerization processes in plastics manufacture.

New data on acetylene and electro-chemical processes.

Information on high temperature alloys unknown in the U.S.

Production of high grade nitro-cellulose from lower grade wood pulp with stability superior to the same product made from high grade pulp in the U.S.

Gottfried Plumpe, a historian of science who wrote one of the most comprehensive studies of I.G. Farben's chemical research programs [Plumpe 1990], summarized his findings about why the German chemical industry was so innovative [Caron 1995, pp. 163–173]:

> When the companies merged to form the IG Farben in 1926 they had a total of 25 large laboratories employing over 3,700 people. [...]
>
> Cooperation with external researchers and research institutes traditionally played an important role in developing the innovative potential of the company. It is no exaggeration to say that there was a close network of cooperation between chemical companies and universities, and that this formed the basis for the development of the German chemical industry. Outstanding examples from the years prior to the merger include the synthesis of indigo and ammonia, the development of the first medicines and chemotherapy. Famous names from this period include Adolf von Baeyer, Fritz Haber, Wilhelm Filehne, Paul Ehrlich and Hermann Staudinger.
>
> The basic research carried out by external institutes was essential for industrial R&D. The universities also ensured a supply of qualified personnel both for the research laboratories and for the production plants. A close and trusting relationship between the company and universities was thus an integral part of IG Farben's research strategy. The importance accorded to this is reflected by the fact that the Board of Management itself rook charge of maintaining these contacts. The founding fathers of IG, men like Carl Duisberg, Carl Bosch and Arthur von Weinberg, regarded themselves at least partially as scientists and undertook this task personally. In 1931, when the Central Committee was set up, it was agreed unanimously that one of its nine members should have special responsibility for these research contacts.
>
> IG Farben has often been accused of having no uniform R&D strategy, unlike the Anglo-American corporations. I do not believe that this is true. IG management most definitely did have a basic objective—we need only think of its declared aim of becoming a diversified company capable of synthesizing all organic products. Given the size of the company and above all the diversity of its activities this objective could never manifest itself in the form of a single "grand design". The most important factor behind the company's R&D policy was the fact that all members of the management team shared the basic conviction that R&D was essential for the company's future and that there was general agreement on the basic aims.
>
> In the relatively prosperous years following the merger, when the company was earning high profits, this meant that almost every project received authorization and financial support. Costs expanded accordingly, with research expenses reaching ten per cent of sales in the 1920s, the highest level in the company's short history.
>
> [...] About a third of all university graduates working for IG were employed in research. In 1929/30 there were about 1,100 scientists on the payroll. By 1932 the number had fallen by about 100, partly through redundancies and partly through natural wastage. During the 1930s the number of researchers gradually rose again, reaching a high point of 1,300 in 1940. During the war it fell back to 1,000. This decline becomes more significant if we compare it with the development of the total workforce. In 1929 research scientists

> represented just one per cent of the workforce. This rose to 1.5 per cent during the Depression because considerably more labourers and clerical staff lost their jobs than researchers. By 1939 researchers only represented 0.8 per cent of the workforce and by 1944 this had dropped to 0.5 per cent. [...]
>
> It is never as easy to quantify the results of R&D and their economic impact as it is to describe organizational structures. It is a well-known fact that the number of patents is only a very rough indicator because it says nothing about the importance of the processes and products they refer to. Nevertheless, the figures give some indication of activity. IG Farben obtained an extremely large number of patents, roughly corresponding to its spending on R&D.
>
> The number of patent applications rose in the 1920s, dropped during the Depression and then increased again through the 1930s. Between 1928 and 1930 IG Farben submitted more than 2,000 patent applications a year in Germany and almost 10,000 worldwide. In the thirties IG Farben had more patents than any other company in the world. At the start of 1939 it held over 5,000 patents in Germany and about 34,000 in other major countries throughout the world, including 5,300 in the USA, about 4,000 in the UK, 3,700 in France, 2,300 in Italy and nearly 900 in Japan. The majority—a good third of the German patents—concerned dyestuffs, while 13 per cent were for organic intermediates and solvents, about 10 per cent each were for inorganic products and medicines, eight per cent for photographic products and fibres and about six per cent for the hydrogenation of mineral oil.

Plumpe also gave an overview of the wide range of innovations that came from the German chemical industry [Caron 1995, pp. 163–173]:

> A few details of the innovations made by IG Farben should give a clearer idea of what all this meant. In the 1920s by far the largest project was the synthesis of mineral oil, which was brought to a successful conclusion in 1932. The basic principle comprised catalytic hydrogenation of solid carbon from lignite or hard coal, yielding aviation and motor fuel, lubricants and hydrogenation gas. The high energy requirement meant that these processes were less economical than those based on petrochemical feedstocks, and they were only used in Germany during the Nazi period. However, the R&D work in this field provided a wealth of material that was of wider use to the petrochemical industry and is still important today.
>
> The second most important project was the synthesis of rubber, a project which the companies had worked on prior to the merger and which was taken up again in 1926. The project was largely abandoned during the Depression, but in 1935 came the breakthrough with the development of styrene butadiene rubber. A modified form of this synthetic rubber is the most important commodity rubber produced today. IG Farben was also a pioneer in the development of plastics. Its achievements include polystyrene (1929), the development of polyvinylchloride (PVC) into a usable engineering plastic (1931) and the discovery of polyurethane in 1937. IG also developed a polyamide-based synthetic fibre (Perlon) at around the same time as Du Pont (1935) and in 1941 it produced the first polyacrylonitrile fibre.

Until the discovery of penicillin, IG was also a world leader in the field of chemotherapy. Milestones in this field include the development of antimalarial drugs based on quinolone derivatives, for example, Plasmochin (1924), Atebrin (1930) and, above all, the first antibacterial sulphonamide (1935). A pioneering innovation in the field of crop protection, phosphoric acid ester (mid-1930s), also belongs to the IG era.

The development of organic intermediates was extremely important for many areas of the chemical industry from dyestuffs through pharmaceuticals and crop protection agents to films and plastics. The products developed are too numerous to be listed here, but it is no exaggeration to say that the success of IG was largely due to its dominant position in this field and that the organic intermediates were the foundation stone for the development of modern chemical technology. In order to give a complete picture of the breadth of research in the IG Farben, its work on inorganic and metal chemistry and its pioneering role in the development of colour photography should also be mentioned.

Since there are no precise data on the contribution made by new products to the company's sales and earnings, it is not easy to quantify their importance, and above all their economic impact. However, I feel that the company's steady diversification is evidence of the importance of research in its development. Even when the merger was agreed in 1926 the name "Farbenindustrie" (dyestuffs industry) was hardly appropriate for the company as a whole. Nitrogen fertilizers were already generating a larger proportion of sales than dyestuffs, and the establishment of new commercial activities based on successful innovations accelerated this trend, making IG Farben one of the most diversified chemical companies by the 1940s.

3.1 Inorganic Chemistry

German-speaking scientists made a huge number of important discoveries in inorganic chemistry, including:[2]

3.1.1. Identifying large numbers of the elements.

3.1.2. Creating the periodic table of the elements.

3.1.3. Making a wide variety of other chemical innovations.

3.1.1 Discoveries of Elements

Once chemists realized in the eighteenth century that chemicals were composed of distinctive elements, there was an international race to purify, characterize, and name as many chemical elements as possible. Several important scientists in that race were in Sweden, France, and the United Kingdom, but arguably the largest share of element discoveries came from scientists in the German-speaking world. The major German-speaking discoveries are summarized below. Note that some elements are listed more than once, if they were independently discovered by different scientists, or first discovered earlier but then characterized in much more detail later.

Carl Wilhelm Scheele (Pomerania, 1742–1786), shown in Fig. 3.1, was the earliest and most successful German-speaking discover of elements. He discovered at least ten elements: hydrogen (1771), nitrogen (1771), oxygen (1771), fluorine (1771), phosphorus (1774), chlorine (1774), manganese (1774), molybdenum (1778), barium (1774), and tungsten (1781).

As illustrated in Fig. 3.2, Martin Klaproth (German states, 1743–1817) discovered six elements: titanium (1795), strontium (1791), zirconium (1789), tellurium (1798), cerium (1803), and uranium (1789).

Friedrich Wöhler (German, 1800–1882) discovered five elements: beryllium (1828), aluminum (1827), silicon (1850), titanium (1850), and yttrium (1828); see Fig. 3.3. He was the first to synthesize several important inorganic molecules such as silane, silicon nitride, and calcium carbide. By synthesizing urea and other organic molecules, he was also one of the founders of organic chemistry and biochemistry.

Robert Bunsen (German, 1811–1899) and Gustav Kirchhoff (German, 1824–1887), shown together in Fig. 3.4, discovered cesium in 1860 and rubidium in 1861 using novel methods of spectroscopic analysis. Bunsen also created the carbon-zinc battery; with Peter Desaga (German, 1812–1879), he created the Bunsen burner.

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[2] Brock 1993; Bugge 1955; Coffey 2008; Engels et al. 1989; Farber 1961; Ihde 1984; Johnson 1990; Kahlert 2002; Maier 2015; Neufeldt 2003; Partington 1935, 1957, 1964; Scerri 2006; Weeks and Leicester 1968; Werner 2017.

As shown in Fig. 3.5, Jean de Marignac (Swiss, 1817–1894) measured atomic weights with greater precision than others had previously and also discovered three elements: samarium (1880), gadolinium (1880), and ytterbium (1878).

Berta Karlik (Austrian, 1904–1990) and Traude Bernert (Austrian, 1915–1998) discovered short-lived astatine in natural ore samples in 1942; see Fig. 3.5.

Carl Auer von Welsbach (Austrian, 1858–1929, Figs. 3.6 and 6.16), was phenomenally successful on fronts in science, engineering, and business. He discovered four elements: praseodymium (1885), neodymium (1885), ytterbium (1905), and lutetium (1905). He also invented the gaslight mantle (1885), osmium wire (1890), metal filament incandescent lamps (1898), and the flint metal lighter (1903). Based on those inventions and discoveries, he founded the Auergesellschaft, Treibacher Industrie, and Osram companies.

As illustrated in Fig. 3.7, Otto Berg (German, 1873–1939), Walter Noddack (German, 1893–1960), and Ida Tacke Noddack (German, 1896–1978) discovered rhenium and technetium in 1925. In 1934, Ida Tacke Noddack also correctly predicted both neutron-induced uranium fission and methods of producing and purifying neptunium and plutonium, which do not exist naturally (p. 1548).

Other German-speaking discoverers of elements are shown in Figs. 3.8–3.11:

- Hennig Brand (German states, 1630–1692, Fig. 3.8) discovered phosphorus in 1669.
- Clemens Winkler (German, 1838–1904, Fig. 3.8) discovered germanium in 1886.
- Albertus Magnus (German states, 1193–1280, Fig. 3.8) discovered arsenic in 1250.
- Carl Jacob Löwig (German, 1803–1890, Fig. 3.8) discovered bromine in 1825.
- Karl Ernst Claus (Baltic German, 1796–1864, Fig. 3.8) discovered ruthenium in 1844.
- Friedrich Stromeyer (German states, 1776–1835) and Karl Hermann (German states, 1765–1846) discovered cadmium in 1817; see Fig. 3.9.
- Ferdinand Reich (German, 1799–1882) and Hieronymous Theodor Richter (German, 1824–1898) discovered indium in 1863; see Fig. 3.9.
- Franz-Joseph Müller von Reichenstein (Austrian, 1740–1825) discovered tellurium in 1782; see Fig. 3.10.
- Jacques-Louis Soret (Swiss, 1827–1890) and Marc Delafontaine (Swiss, 1838–1911) discovered holmium in 1878; see Fig. 3.10.
- Dirk Coster (Dutch, 1889–1950) and George de Hevesy (Hungarian, 1885–1966) discovered hafnium in 1922; see Fig. 3.10.

- Georgius Agricola, also known as Georg Bauer (German states, 1494–1555, Fig. 3.10), discovered bismuth around 1540. He conducted extensive work on metallurgy.

- Friedrich Ernst Dorn (German, 1848–1916, Fig. 3.11) discovered radon in 1900.

- Gerhard Carl Schmidt (German, 1865–1949, Fig. 3.11) discovered the radioactivity of thorium in 1898; Marie Curie later confirmed that result.

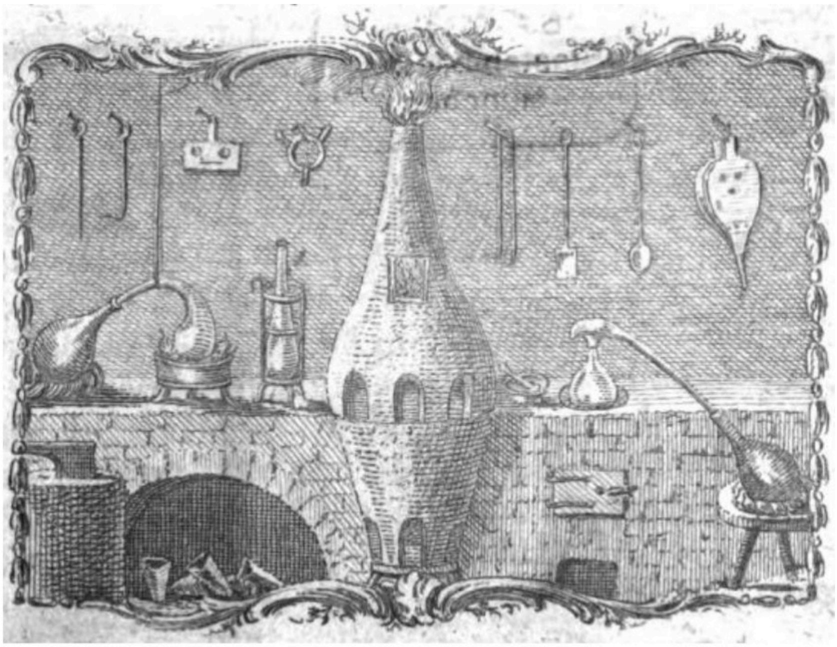
- Kasimir Fajans (Polish, 1887–1975) and Oswald Helmuth Göhring (German, 1889–1915) discovered the first isotope of protactinium in 1913; see Fig. 3.11.

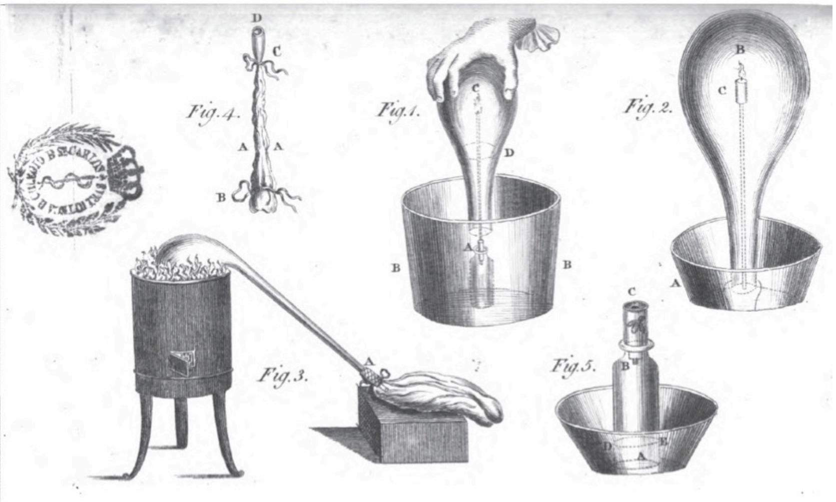
- Otto Hahn (German, 1879–1968) and Lise Meitner (Austrian, 1878–1968) discovered a longer-lived protactinium isotope in 1917; see Fig. 3.11.

German-speaking scientists also discovered all three of the building blocks of atoms: electrons, protons, and neutrons (Section 5.2.3).

Even in English-speaking countries and after so much time, the symbol for the atomic number (the number of protons in the nucleus, or the number of electrons in a neutral atom) is still Z, for the German word “Zahl” or number.

Carl Wilhelm Scheele
(1742–1786)
discovered
hydrogen (1771),
nitrogen (1771),
oxygen (1771),
fluorine (1771),
phosphorus (1774),
chlorine (1774),
manganese (1774),
molybdenum (1778),
barium (1774),
tungsten (1781)

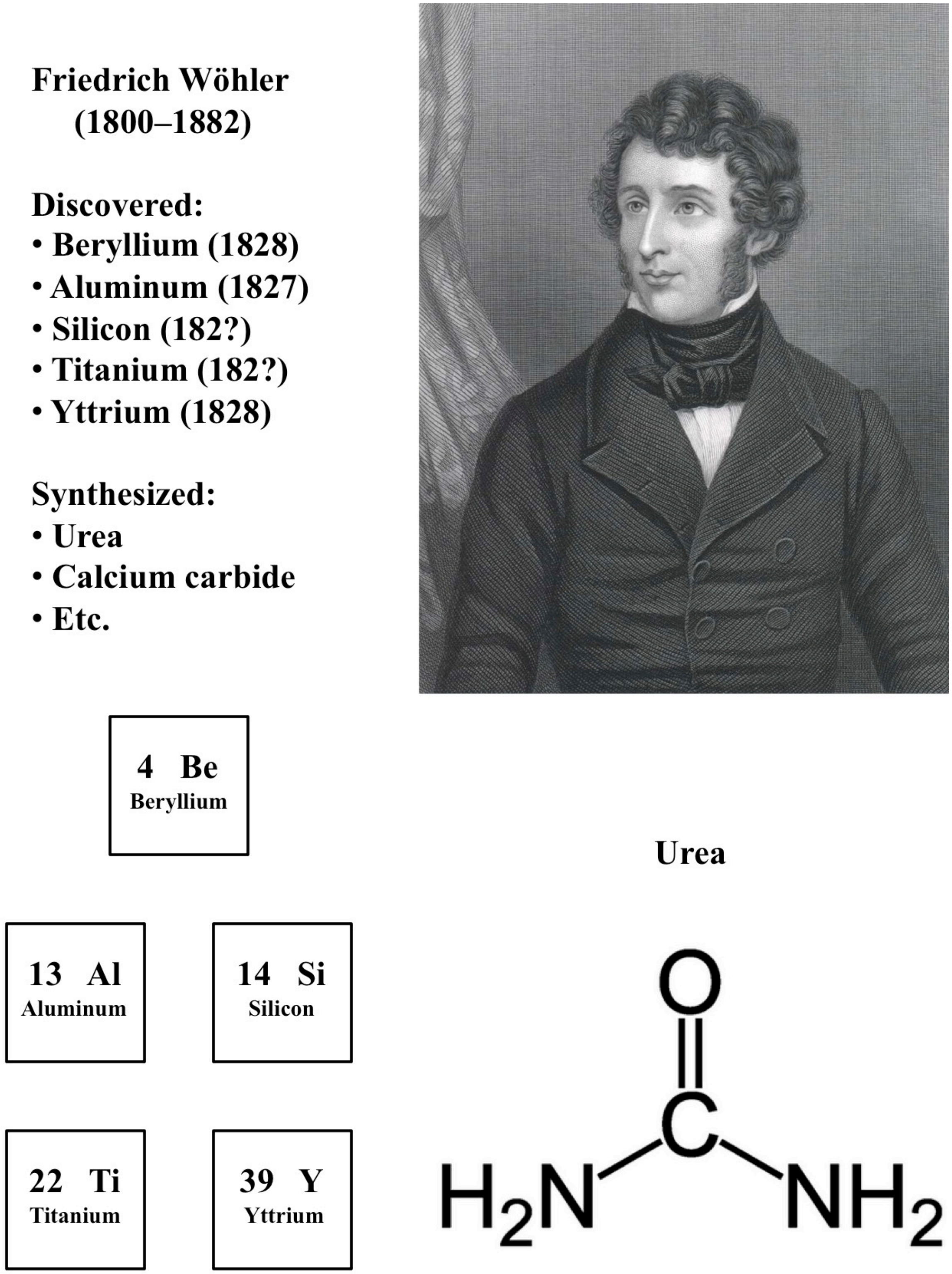




1 H **Hydrogen**	**7 N** **Nitrogen**	**8 O** **Oxygen**	**9 F** **Fluorine**	**15 P** **Phosphorus**
17 Cl **Chlorine**	**25 Mn** **Manganese**	**42 Mo** **Molybdenum**	**56 Ba** **Barium**	**74 W** **Tungsten**

Figure 3.1: Carl Wilhelm Scheele discovered ten elements during the period 1771–1781.

Figure 3.2: Martin Klaproth discovered six elements (including uranium) during the period 1789–1803.

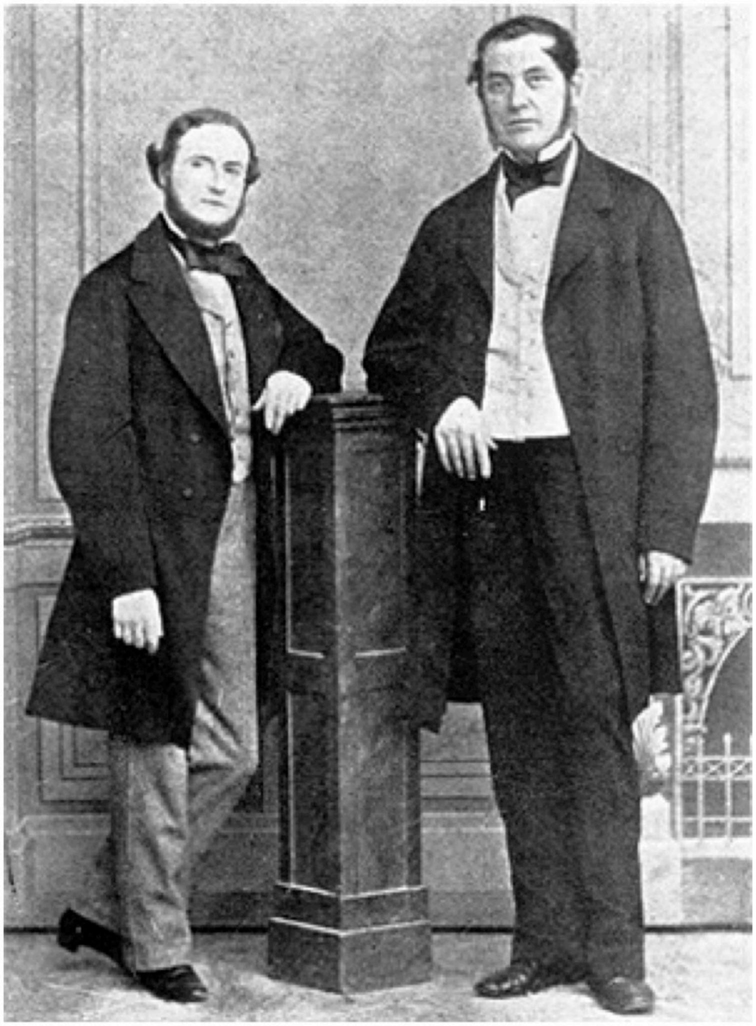


Friedrich Wöhler
(1800–1882)

Discovered:
- **Beryllium (1828)**
- **Aluminum (1827)**
- **Silicon (182?)**
- **Titanium (182?)**
- **Yttrium (1828)**

Synthesized:
- **Urea**
- **Calcium carbide**
- **Etc.**

Figure 3.3: Friedrich Wöhler discovered five elements, and was also the first to synthesize important molecules such as urea and calcium carbide.



Gustav Kirchhoff
(1824–1887)
discovered
cesium (1860),
rubidium (1861)

Robert Bunsen
(1811–1899) discovered
cesium (1860), rubidium (1861);
Bunsen burner;
carbon-zinc battery; etc.

Peter Desaga
(1812–1879)
Bunsen burner

37 Rb Rubidium	55 Cs Cesium

Figure 3.4: Robert Bunsen and Gustav Kirchhoff discovered cesium in 1860 and rubidium in 1861 using novel methods of spectroscopic analysis. Bunsen also created the carbon-zinc battery; with Peter Desaga he created the Bunsen burner.

Jean de Marignac (1817–1894)

Measured atomic weights with greater precision

Discovered:
- **Samarium (1880)**
- **Gadolinium (1880)**
- **Ytterbium (1878)**

62 Sm
Samarium

64 Gd
Gadolinium

70 Yb
Ytterbium

Berta Karlik (1904–1990)
and Traude Bernert
(not shown, 1915–1998)

Discovered astatine (1942)

85 At
Astatine

Figure 3.5: Jean de Marignac measured atomic weights with greater precision and discovered samarium, gadolinium, and ytterbium 1878–1880. Berta Karlik and Traude Bernert discovered short-lived astatine in natural ore samples in 1942.

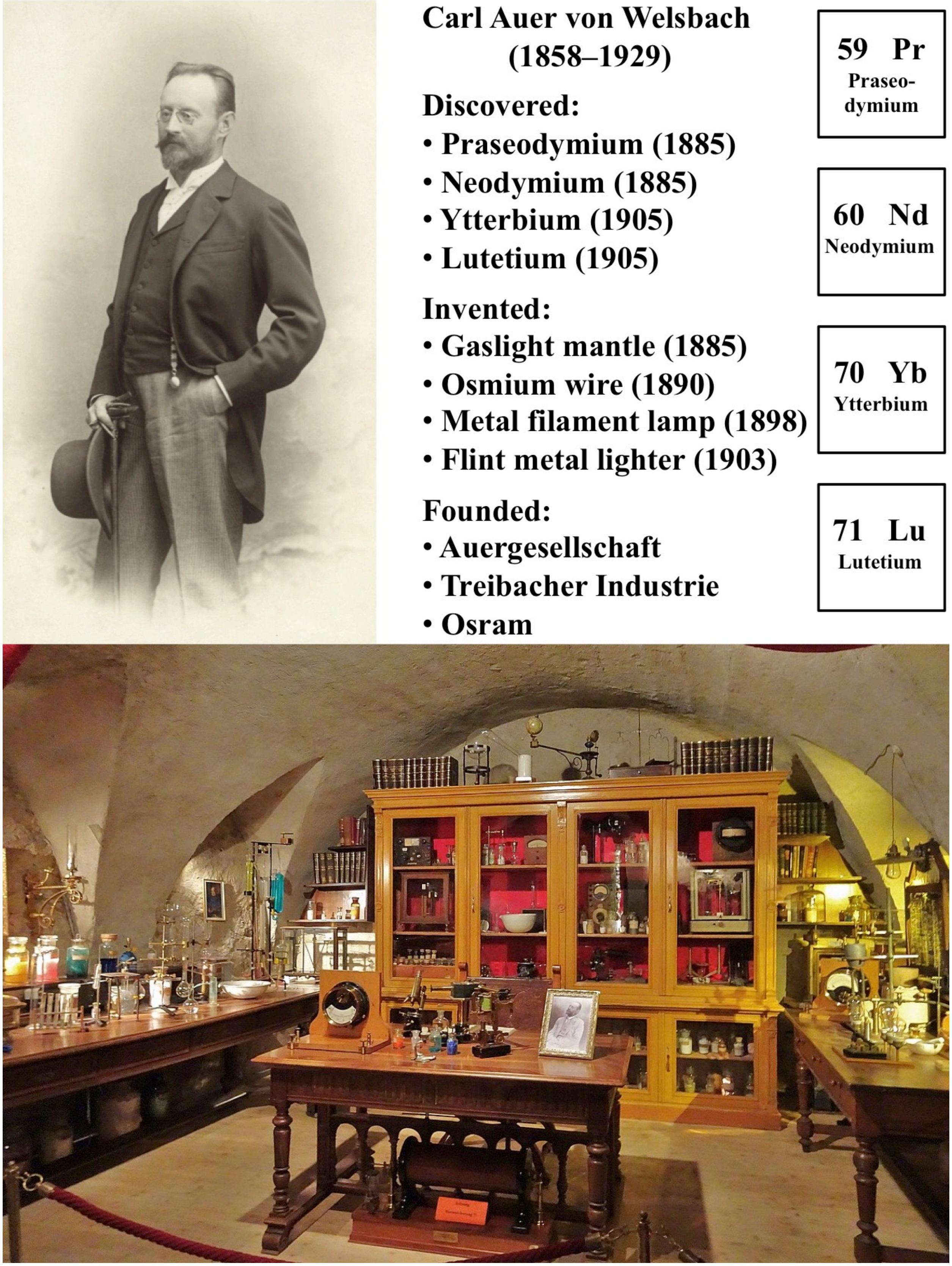


Figure 3.6: Carl Auer von Welsbach discovered four elements; invented the gaslight mantle, osmium wire, the metal filament incandescent lamp, and the flint metal lighter; and founded Auergesellschaft, Treibacher Industrie, and Osram.

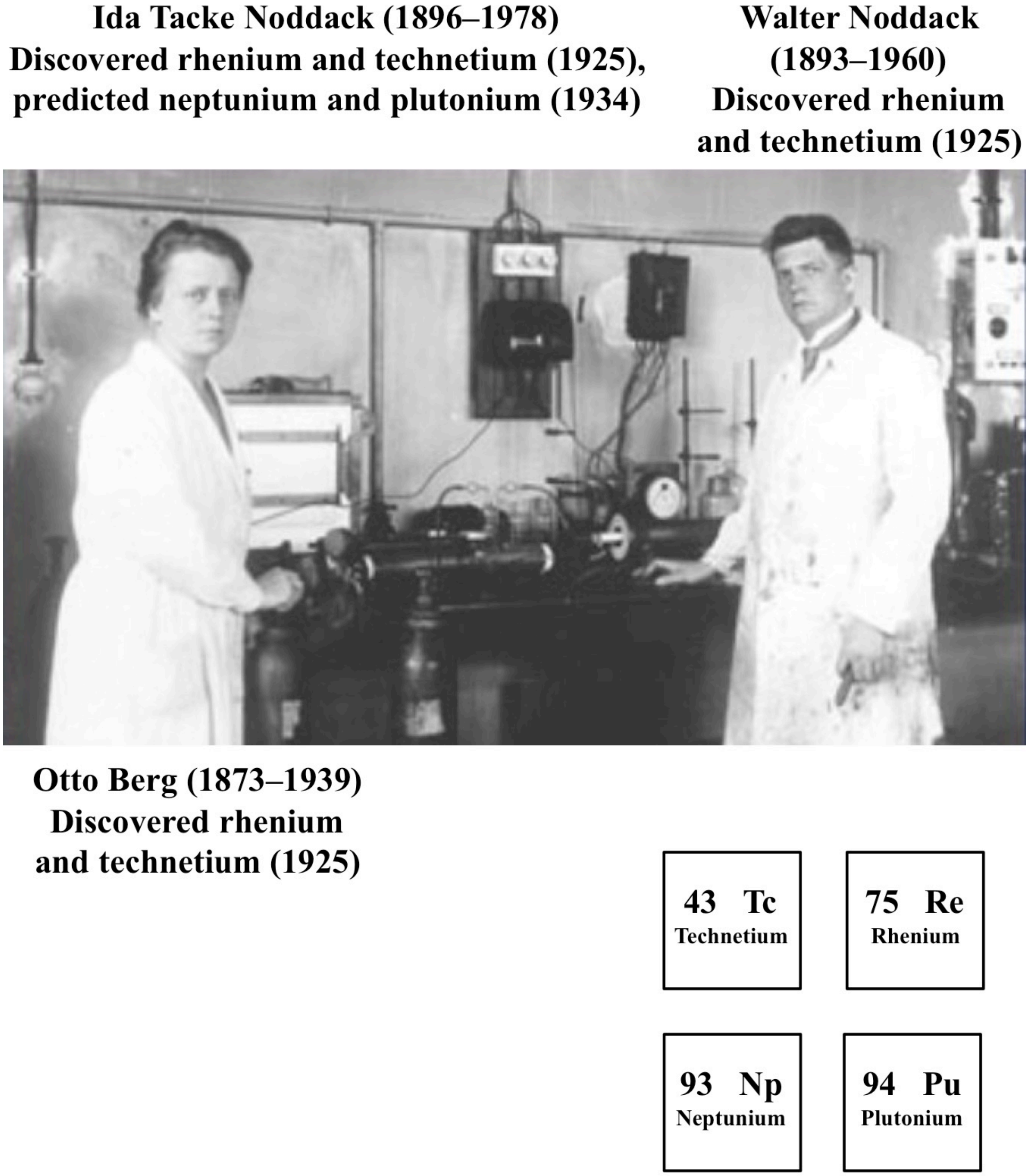
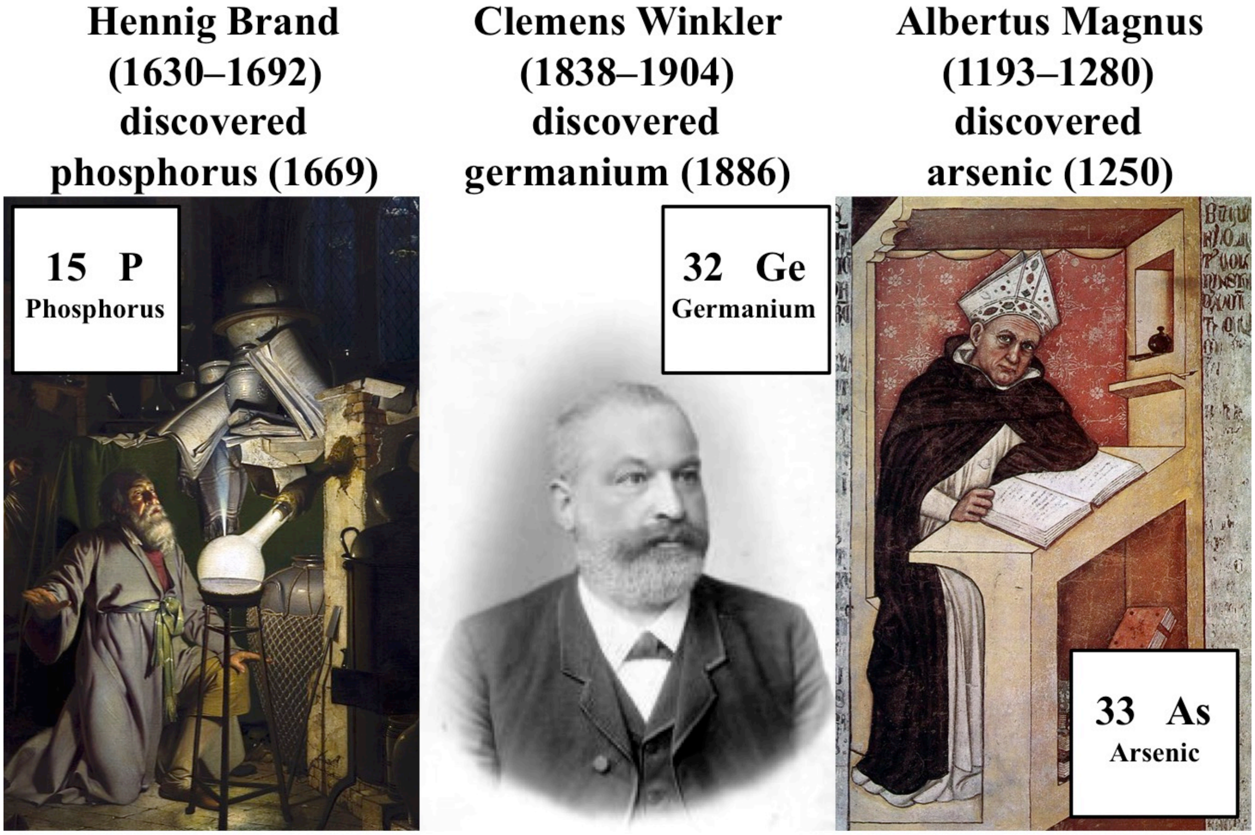


Figure 3.7: Otto Berg, Walter Noddack, and Ida Tacke Noddack discovered rhenium and technetium in 1925. In 1934, Ida Tacke Noddack also correctly predicted how to produce neptunium and plutonium, which do not exist naturally.



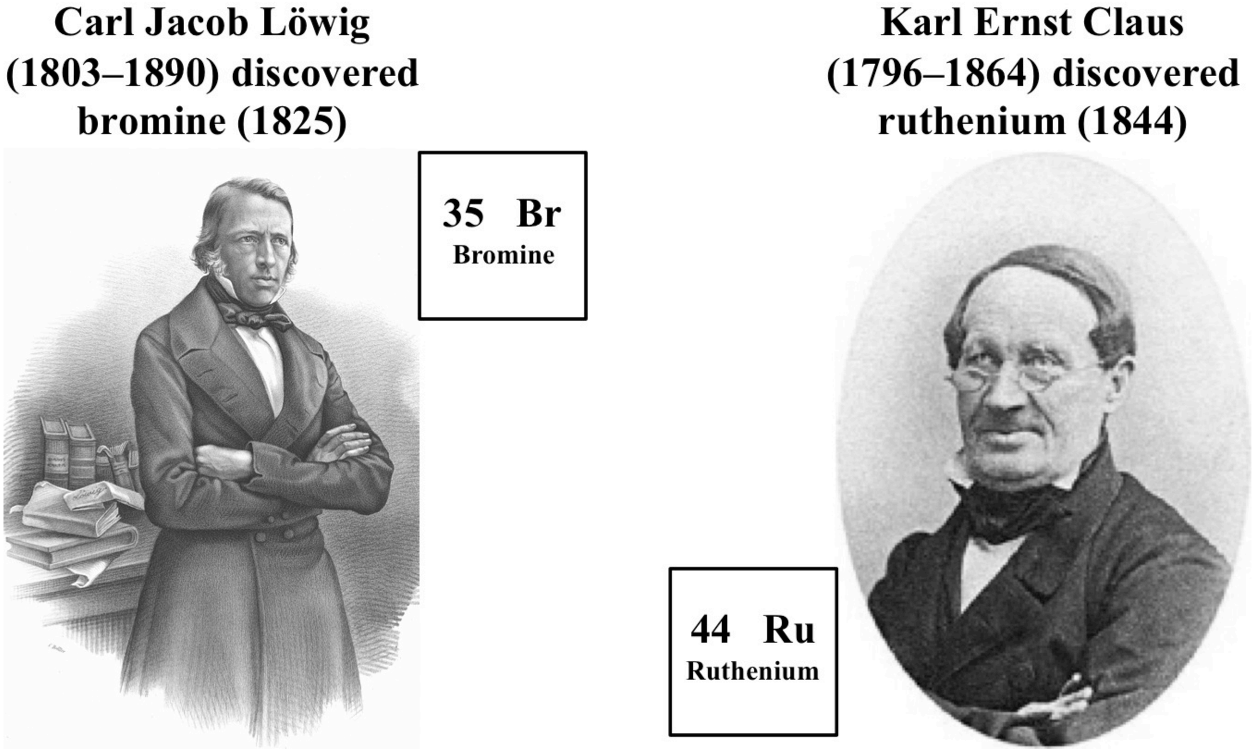


Figure 3.8: Hennig Brand discovered phosphorus in 1669. Clemens Winkler discovered germanium in 1886. Albertus Magnus discovered arsenic in 1250. Carl Jacob Löwig discovered bromine in 1825. Karl Ernst Claus discovered ruthenium in 1844.

Johann Friedrich Stromeyer (1776–1835) discovered cadmium (1817)

48 Cd
Cadmium

Karl Hermann (1765–1846) discovered cadmium (1817)

Ferdinand Reich (1799–1882) discovered indium (1863)

49 In
Indium

Hieronymous Theodor Richter (1824–1898) discovered indium (1863)

Figure 3.9: Friedrich Stromeyer and Karl Hermann discovered cadmium in 1817. Ferdinand Reich and Hieronymous Theodor Richter discovered indium in 1863.

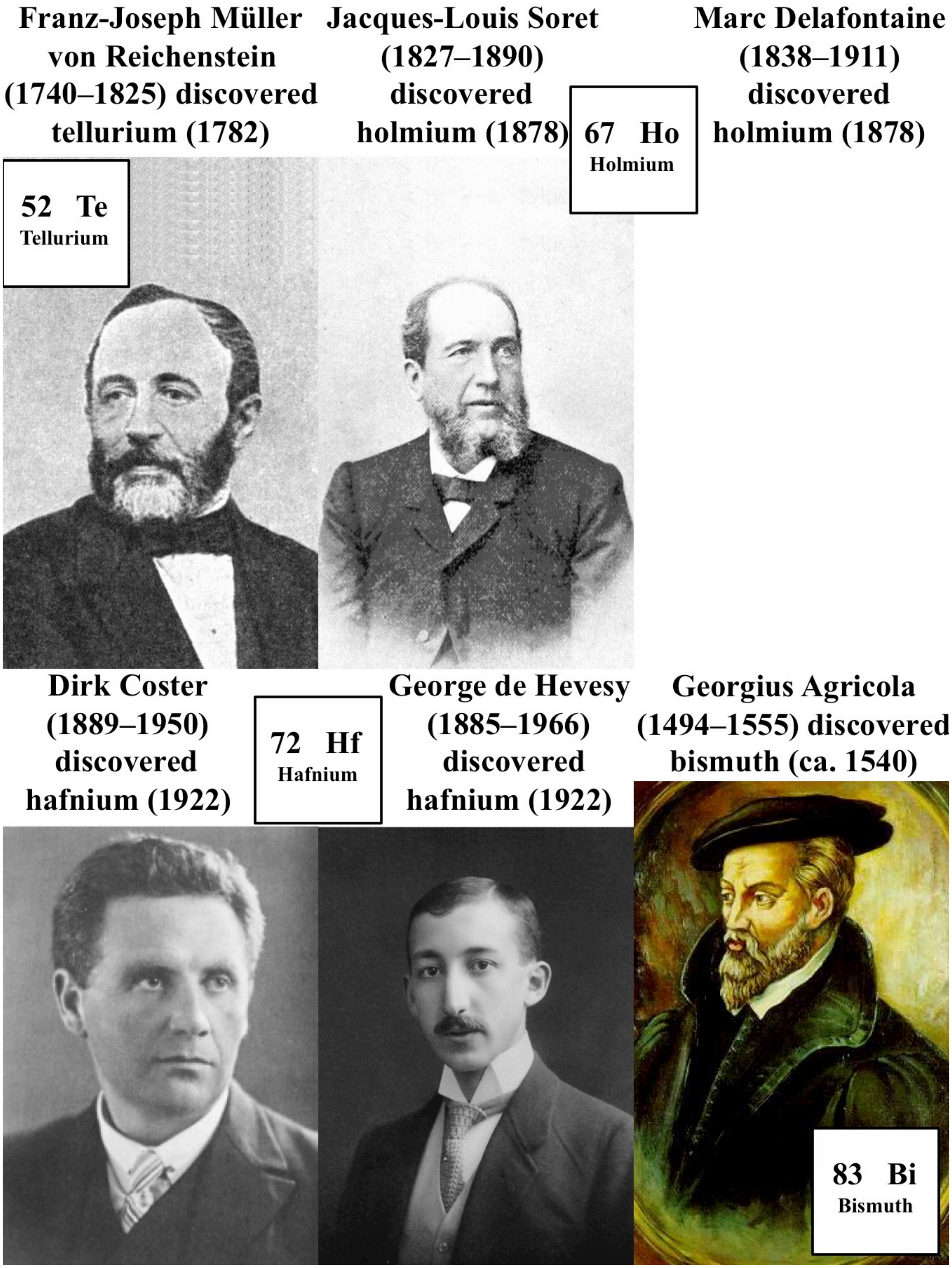


Figure 3.10: Franz-Joseph Müller von Reichenstein discovered tellurium in 1782. Jacques-Louis Soret and Marc Delafontaine discovered holmium in 1878. Dirk Coster and George de Hevesy discovered hafnium in 1922. Georgius Agricola discovered bismuth around 1540.

Friedrich Ernst Dorn (1848–1916) discovered radon (1900)

86 Rn
Radon

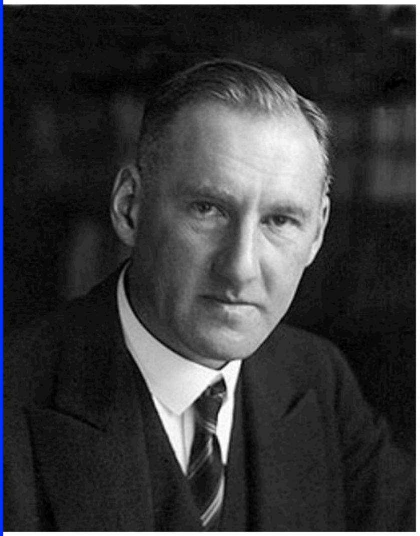
Gerhard Carl Schmidt (1865–1949) discovered radioactivity of thorium (1898)

90 Th
Thorium

Kasimir Fajans (1887–1975)

Oswald Helmuth Göhring (1889–1915)

Discovered protactinium (1913)



Otto Hahn (1879–1968)

91 Pr
Protactinium

Lise Meitner (1878–1968)

Discovered longer-lived protactinium isotope (1917)

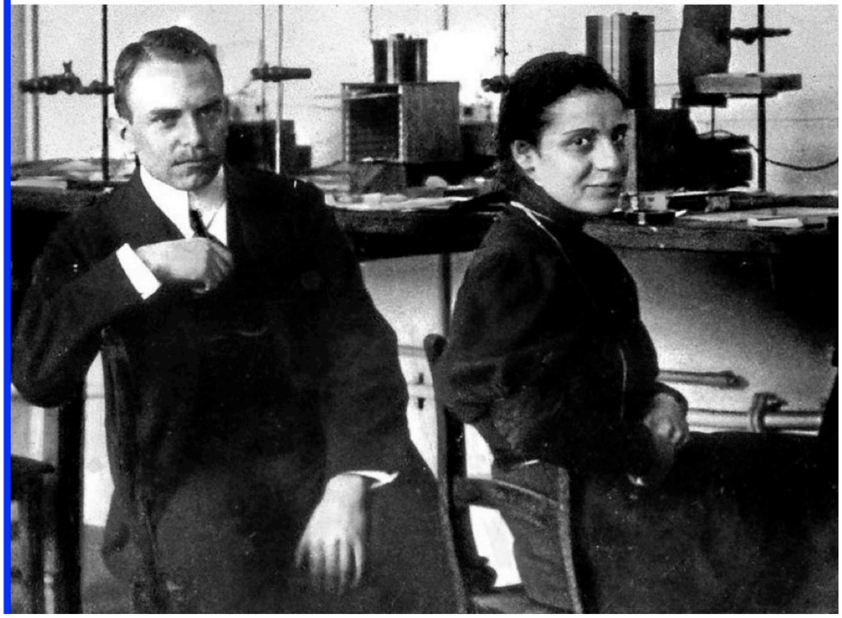


Figure 3.11: Friedrich Dorn discovered radon in 1900. Gerhard Schmidt discovered the radioactivity of thorium in 1898. Kasimir Fajans and Oswald Göhring discovered the first isotope of protactinium in 1913. Otto Hahn and Lise Meitner discovered a longer-lived protactinium isotope in 1917.

3.1.2 Creation of the Periodic Table of the Elements

Johann Wolfgang Döbereiner (German states, 1780–1849), shown in Fig. 3.12, was the first to realize that elements could be grouped by similar chemical properties. Among elements that were known then in 1829, he found three examples of each type, later dubbed triads. He also discovered platinum catalysts and used those to invent an improved lamp, which became widely used as the world's first fluid-filled instant lighter.

As illustrated in Fig. 3.13, Leopold Gmellin (German states, 1788–1853) expanded Döbereiner's triads into a connected table of known elements in 1843. Some other pioneers of periodic properties of the elements included Max Joseph von Pettenkofer (German, 1818–1901, who also made important contributions to urban hygiene), Peter Kremers (German?, 18??–19??), and Ernst Lenssen (German?, 1837–1870?).

Julius Lothar Meyer (German, 1830–1895) produced the first truly scientific periodic table of the elements in 1862 and published it in his 1864 chemistry textbook, as shown in Fig. 3.14. Meyer's 1864 textbook discussed in detail how the known elements fit into a periodic table that explained all of the measured masses, densities, and valences of the elements (Fig. 3.15). It also predicted new elements that would fill in gaps in the periodic table. Meyer presented data demonstrating the periodic properties of atomic volumes, with peaks corresponding to the beginning of each row of the periodic table. In 1868 he updated his periodic table with additional elements that had been newly discovered (Fig. 3.16).

Dmitri Mendeleev (Russian, 1834–1907) left Russia to study chemistry with Robert Bunsen and Gustav Kirchhoff in Heidelberg in 1860–1861, studied in Switzerland, and then returned to Russia. During his chemistry studies in Germany and Switzerland, Mendeleev almost certainly would have been exposed to the early periodic tables of Döbereiner, Gmellin, and others (though of course the available documents do not record students' discussions from that time). Moreover, it is highly likely that Mendeleev would have heard about the early work of Julius Lothar Meyer, especially since Meyer also studied with Bunsen and Kirchhoff in Heidelberg around the same time that Mendeleev was there. In addition to any personal transfers of information, Meyer's 1864 chemistry textbook that publicly presented and explained the periodic table was widely circulated in Europe, and copies would presumably have been available in Russia after Mendeleev returned home.

After returning to Russia, Mendeleev did not even begin to work on his version of the periodic table until 1869, nine years after his personal immersion in the academic world of German chemistry, and five years after the publication of Meyer's detailed textbook that explained the organization, contents, and scientific evidence for the periodic table. Then Mendeleev did not finalize his version of a periodic table for another decade, until 1879 [Scerri 2006, pp. 105, 112]. Mendeleev never even attempted to offer a credible explanation for how his version of the periodic table resulted from his earlier studies and the earlier researchers. Rather, he quite incredibly claimed that the entire periodic table simply came to him suddenly in a dream, that he had never heard of any earlier versions of the periodic table, and that the entire concept of a periodic table was his alone.

While Mendeleev is widely called the originator of the period table nowadays, the evidence clearly demonstrates that Döbereiner's and Gmellin's work preceded Mendeleev's by decades, and that Julius Lothar Meyer produced and published highly detailed versions of the periodic table backed by large amounts of experimental evidence and accurate predictions years before Mendeleev, even including details that Mendeleev's later table did not. Furthermore, the available evidence suggests that Mendeleev simply plagiarized his "discovery" from the earlier German-speaking scientists.

Johann Wolfgang Döbereiner (1780–1849)
Discovered platinum catalyst (18??)

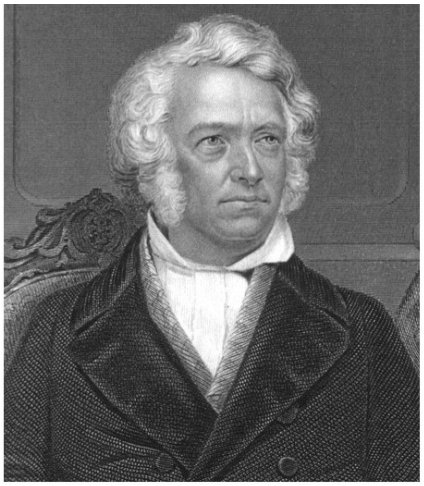
Döbereiner's lamp
(18??)

Döbereiner's periodic arrangement of elements into triads (1829)

Li	**Ca**	**P**	**S**	**Cl**
Na	**Sr**	**As**	**Se**	**Br**
K	**Ba**	**Sb**	**Te**	**I**

Figure 3.12: Johann Wolfgang Döbereiner was the first to realize that elements could be grouped by similar chemical properties. Among elements that were then known in 1829, he found three examples of each type, later dubbed triads. He also discovered platinum catalysts and invented an improved lamp.

Leopold Gmelin
(1788–1853)
expanded
Döbereiner's triads
into a connected table of
known elements (1843)



O N H
F Cl Br I Li Na K
S Se Te Mg Ca Sr Ba
P As Sb Be Ce La
C B Bi Zr Th Al
Ti Ta W Sn Cd Zn
Mo V Cr U Mn Ni Fe
Bi Pb Ag Hg Cu
Os Ir Rh Pt Pd Au

Some other pioneers of periodic properties of the elements:

Max Joseph von
Pettenkofer (1818–1901)
(also urban hygiene)

Peter Kremers
(18??–19??)

Ernst Lenssen
(1837–19??)

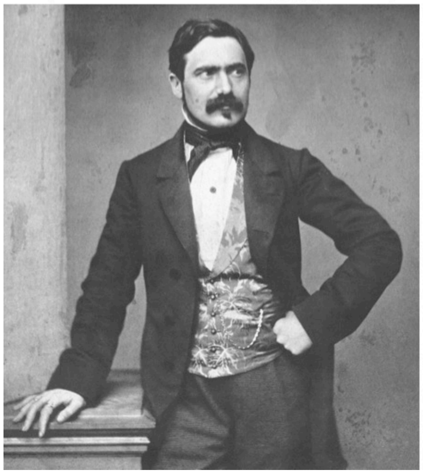
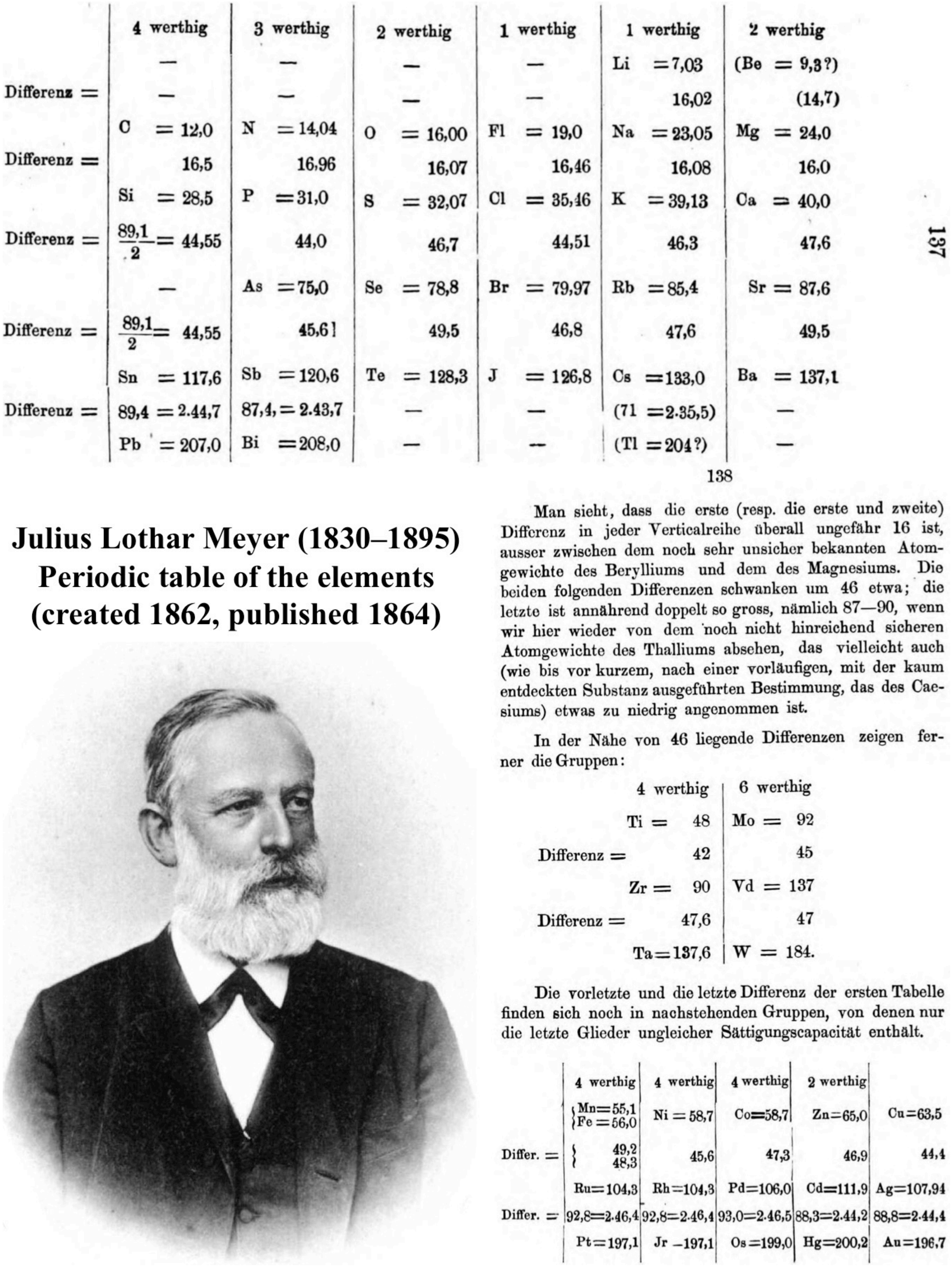


Figure 3.13: Leopold Gmelin expanded Döbereiner's triads into a connected table of known elements in 1843. Some other pioneers of periodic properties of the elements included Max Joseph von Pettenkofer, Peter Kremers, and Ernst Lenssen.



	4 werthig	3 werthig	2 werthig	1 werthig	1 werthig	2 werthig
	—	—	—	—	Li =7,03	(Be = 9,3?)
Differenz =	—	—	—	—	16,02	(14,7)
	C = 12,0	N = 14,04	O = 16,00	Fl = 19,0	Na = 23,05	Mg = 24,0
Differenz =	16,5	16,96	16,07	16,46	16,08	16,0
	Si = 28,5	P = 31,0	S = 32,07	Cl = 35,46	K = 39,13	Ca = 40,0
Differenz =	$\frac{89,1}{2}$ = 44,55	44,0	46,7	44,51	46,3	47,6
	—	As = 75,0	Se = 78,8	Br = 79,97	Rb = 85,4	Sr = 87,6
Differenz =	$\frac{89,1}{2}$ = 44,55	45,6	49,5	46,8	47,6	49,5
	Sn = 117,6	Sb = 120,6	Te = 128,3	J = 126,8	Cs = 133,0	Ba = 137,1
Differenz =	89,4 = 2.44,7	87,4, = 2.43,7	—	—	(71 = 2.35,5)	—
	Pb = 207,0	Bi = 208,0	—	—	(Tl = 204?)	—

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Julius Lothar Meyer (1830–1895)
Periodic table of the elements
(created 1862, published 1864)

Man sieht, dass die erste (resp. die erste und zweite) Differenz in jeder Verticalreihe überall ungefähr 16 ist, ausser zwischen dem noch sehr unsicher bekannten Atomgewichte des Berylliums und dem des Magnesiums. Die beiden folgenden Differenzen schwanken um 46 etwa; die letzte ist annährend doppelt so gross, nämlich 87—90, wenn wir hier wieder von dem noch nicht hinreichend sicheren Atomgewichte des Thalliums absehen, das vielleicht auch (wie bis vor kurzem, nach einer vorläufigen, mit der kaum entdeckten Substanz ausgeführten Bestimmung, das des Caesiums) etwas zu niedrig angenommen ist.

In der Nähe von 46 liegende Differenzen zeigen ferner die Gruppen:

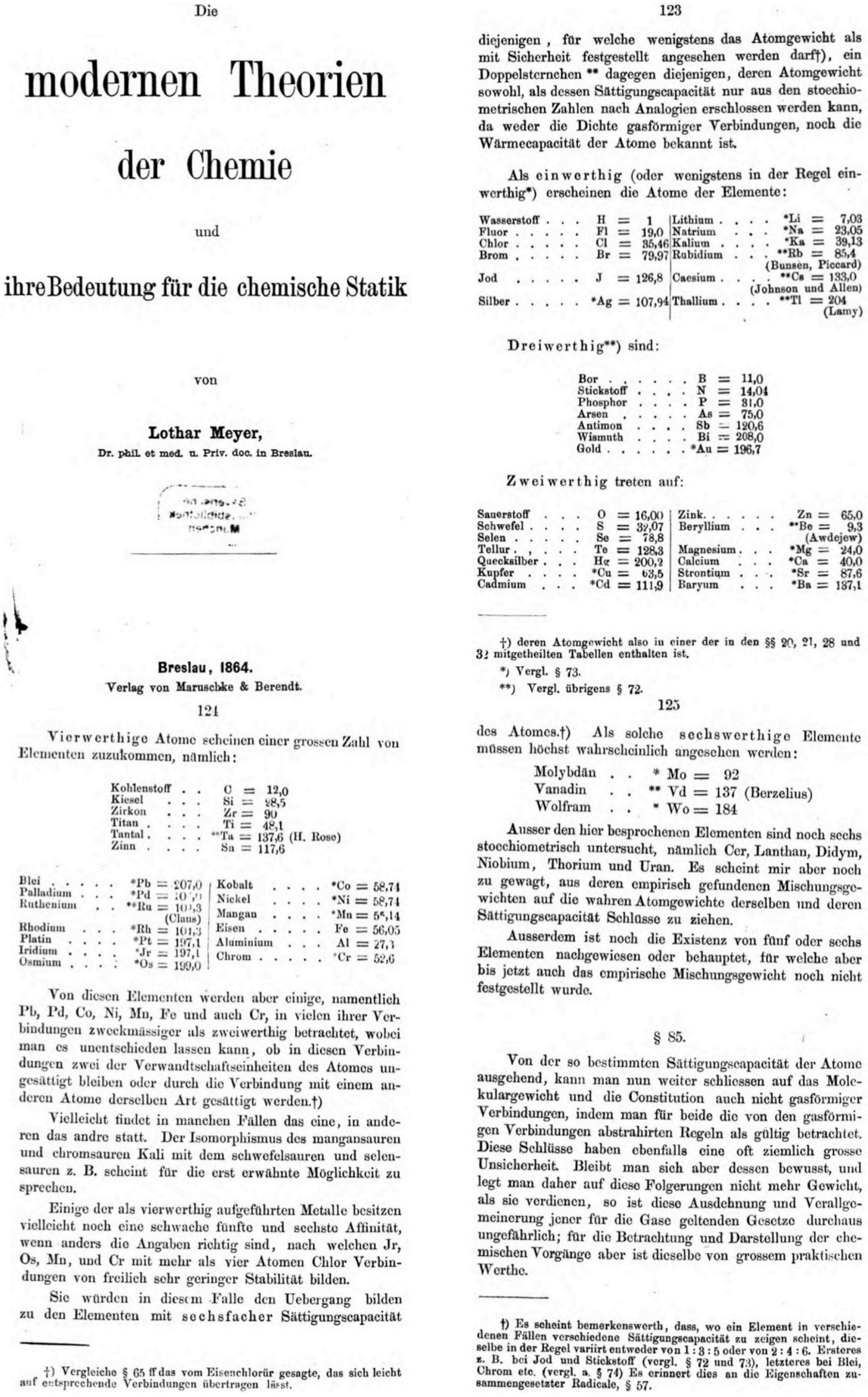
	4 werthig	6 werthig
	Ti = 48	Mo = 92
Differenz =	42	45
	Zr = 90	Vd = 137
Differenz =	47,6	47
	Ta = 137,6	W = 184.

Die vorletzte und die letzte Differenz der ersten Tabelle finden sich noch in nachstehenden Gruppen, von denen nur die letzte Glieder ungleicher Sättigungscapacität enthält.

	4 werthig	4 werthig	4 werthig	2 werthig	
	Mn = 55,1 Fe = 56,0	Ni = 58,7	Co = 58,7	Zn = 65,0	Cu = 63,5
Differ. =	49,2 48,3	45,6	47,3	46,9	44,4
	Ru = 104,3	Rh = 104,3	Pd = 106,0	Cd = 111,9	Ag = 107,94
Differ. =	92,8 = 2.46,4	92,8 = 2.46,4	93,0 = 2.46,5	88,3 = 2.44,2	88,8 = 2.44,4
	Pt = 197,1	Jr – 197,1	Os = 199,0	Hg = 200,2	Au = 196,7

Figure 3.14: Julius Lothar Meyer produced the first scientific periodic table of the elements in 1862 and published it in his 1864 chemistry textbook.

Lothar Meyer's 1864 chemistry textbook showed in detail how the known elements fit into a periodic table that explained all of the measured masses, densities, and valences of the elements. It also predicted new elements that would fill in gaps in the periodic table.



Die

modernen Theorien

der Chemie

und

ihre Bedeutung für die chemische Statik

von

Lothar Meyer,
Dr. phil. et med. u. Priv. doc. in Breslau.

Breslau, 1864.
Verlag von Maruschke & Berendt.

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Vierwerthige Atome scheinen einer grossen Zahl von Elementen zuzukommen, nämlich:

Kohlenstoff . .	C =	12,0
Kiesel . . .	Si =	28,5
Zirkon . . .	Zr =	90
Titan	Ti =	48,1
Tantal	**Ta =	137,6 (H. Rose)
Zinn	Sn =	117,6

Blei	*Pb =	207,0	Kobalt	*Co =	58,74
Palladium . . .	*Pd =	10[illegible]	Nickel	*Ni =	58,74
Ruthenium . .	**Ru =	104,3 (Claus)	Mangan	*Mn =	55,14
Rhodium . . .	*Rh =	104,3	Eisen	Fe =	56,05
Platin	*Pt =	197,1	Aluminium . . .	Al =	27,3
Iridium	*Jr =	197,1	Chrom	*Cr =	52,6
Osmium	*Os =	199,0			

Von diesen Elementen werden aber einige, namentlich Pb, Pd, Co, Ni, Mn, Fe und auch Cr, in vielen ihrer Verbindungen zweckmässiger als zweiwerthig betrachtet, wobei man es unentschieden lassen kann, ob in diesen Verbindungen zwei der Verwandtschaftseinheiten des Atomes ungesättigt bleiben oder durch die Verbindung mit einem anderen Atome derselben Art gesättigt werden.†)

Vielleicht findet in manchen Fällen das eine, in anderen das andre statt. Der Isomorphismus des mangansauren und chromsauren Kali mit dem schwefelsauren und selensauren z. B. scheint für die erst erwähnte Möglichkeit zu sprechen.

Einige der als vierwerthig aufgeführten Metalle besitzen vielleicht noch eine schwache fünfte und sechste Affinität, wenn anders die Angaben richtig sind, nach welchen Jr, Os, Mn, und Cr mit mehr als vier Atomen Chlor Verbindungen von freilich sehr geringer Stabilität bilden.

Sie würden in diesem Falle den Uebergang bilden zu den Elementen mit sechsfacher Sättigungscapacität

---

†) Vergleiche § 65 ff das vom Eisenchlorür gesagte, das sich leicht auf entsprechende Verbindungen übertragen lässt.

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diejenigen, für welche wenigstens das Atomgewicht als mit Sicherheit festgestellt angesehen werden darf†), ein Doppelsternchen ** dagegen diejenigen, deren Atomgewicht sowohl, als dessen Sättigungscapacität nur aus den stoechiometrischen Zahlen nach Analogien erschlossen werden kann, da weder die Dichte gasförmiger Verbindungen, noch die Wärmecapacität der Atome bekannt ist.

Als einwerthig (oder wenigstens in der Regel einwerthig*) erscheinen die Atome der Elemente:

Wasserstoff . . .	H =	1	Lithium	*Li =	7,03
Fluor	Fl =	19,0	Natrium . . .	*Na =	23,05
Chlor	Cl =	35,46	Kalium	*Ka =	39,13
Brom	Br =	79,97	Rubidium . . .	**Rb =	85,4 (Bunsen, Piccard)
Jod	J =	126,8	Caesium	**Cs =	133,0 (Johnson und Allen)
Silber	*Ag =	107,94	Thallium	**Tl =	204 (Lamy)

Dreiwerthig**) sind:

Bor	B =	11,0
Stickstoff	N =	14,04
Phosphor	P =	31,0
Arsen	As =	75,0
Antimon	Sb =	120,6
Wismuth	Bi =	208,0
Gold	*Au =	196,7

Zweiwerthig treten auf:

Sauerstoff . . .	O =	16,00	Zink.	Zn =	65,0
Schwefel	S =	32,07	Beryllium . . .	**Be =	9,3 (Awdejew)
Selen	Se =	78,8			
Tellur	Te =	128,3	Magnesium . . .	*Mg =	24,0
Quecksilber . . .	Hg =	200,2	Calcium . . .	*Ca =	40,0
Kupfer	*Cu =	63,5	Strontium . . .	*Sr =	87,6
Cadmium . . .	*Cd =	111,9	Baryum . . .	*Ba =	137,1

---

†) deren Atomgewicht also in einer der in den §§ 20, 21, 28 und 32 mitgetheilten Tabellen enthalten ist.

*) Vergl. § 73.

**) Vergl. übrigens § 72.

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des Atomes.†) Als solche sechswerthige Elemente müssen höchst wahrscheinlich angesehen werden:

Molybdän . .	* Mo =	92
Vanadin . .	** Vd =	137 (Berzelius)
Wolfram . .	* Wo =	184

Ausser den hier besprochenen Elementen sind noch sechs stoechiometrisch untersucht, nämlich Cer, Lanthan, Didym, Niobium, Thorium und Uran. Es scheint mir aber noch zu gewagt, aus deren empirisch gefundenen Mischungsgewichten auf die wahren Atomgewichte derselben und deren Sättigungscapacität Schlüsse zu ziehen.

Ausserdem ist noch die Existenz von fünf oder sechs Elementen nachgewiesen oder behauptet, für welche aber bis jetzt auch das empirische Mischungsgewicht noch nicht festgestellt wurde.

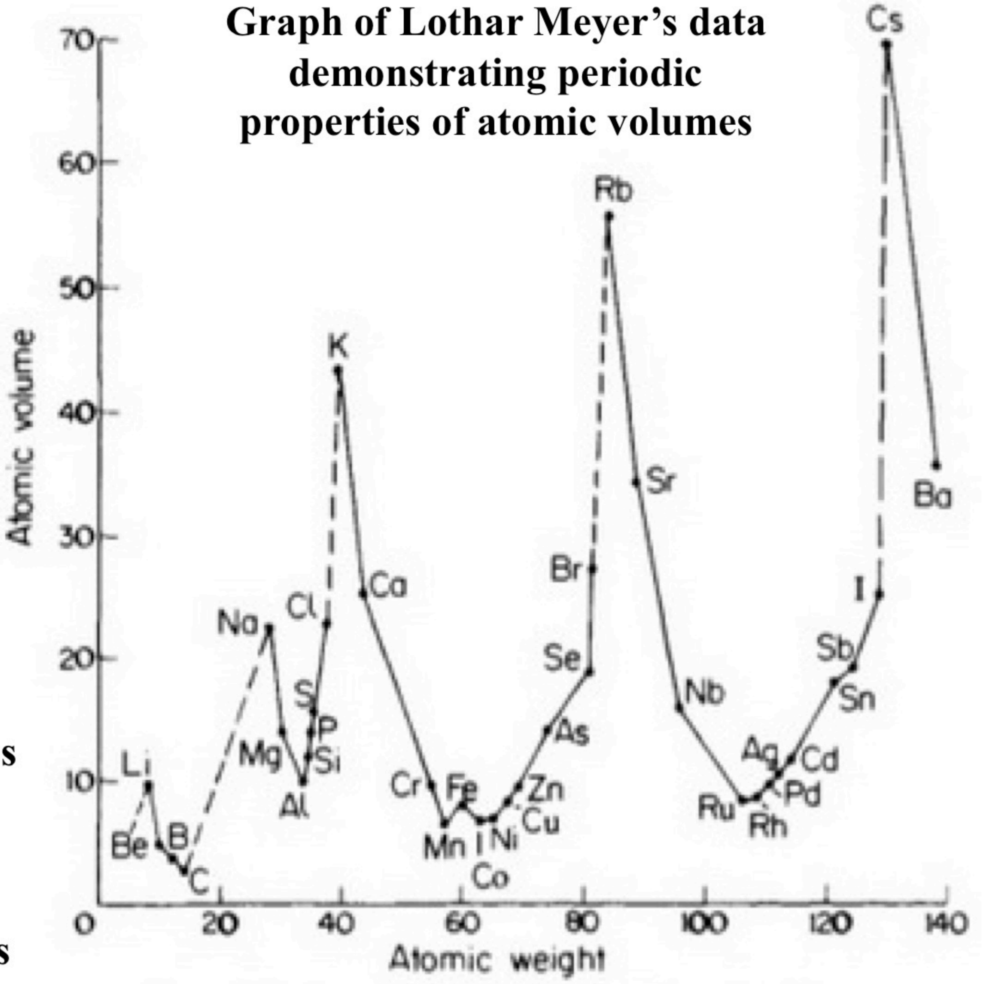
§ 85.

Von der so bestimmten Sättigungscapacität der Atome ausgehend, kann man nun weiter schliessen auf das Molekulargewicht und die Constitution auch nicht gasförmiger Verbindungen, indem man für beide die von den gasförmigen Verbindungen abstrahirten Regeln als gültig betrachtet. Diese Schlüsse haben ebenfalls eine oft ziemlich grosse Unsicherheit. Bleibt man sich aber dessen bewusst, und legt man daher auf diese Folgerungen nicht mehr Gewicht, als sie verdienen, so ist diese Ausdehnung und Verallgemeinerung jener für die Gase geltenden Gesetze durchaus ungefährlich; für die Betrachtung und Darstellung der chemischen Vorgänge aber ist dieselbe von grossem praktischen Werthe.

---

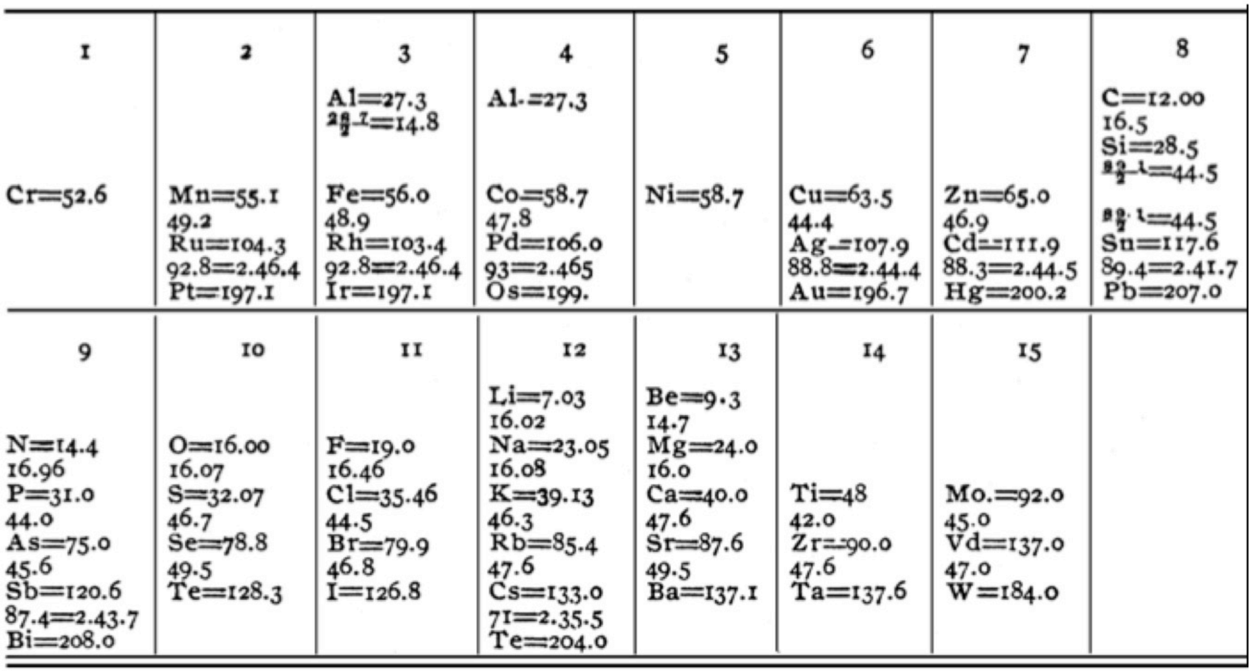
†) Es scheint bemerkenswerth, dass, wo ein Element in verschiedenen Fällen verschiedene Sättigungscapacität zu zeigen scheint, dieselbe in der Regel variirt entweder von 1 : 3 : 5 oder von 2 : 4 : 6. Ersteres z. B. bei Jod und Stickstoff (vergl. § 72 und 73), letzteres bei Blei, Chrom etc. (vergl. a. § 74) Es erinnert dies an die Eigenschaften zusammengesetzter Radicale, § 57.

Figure 3.15: Lothar Meyer's 1864 chemistry textbook showed in detail how the known elements fit into a periodic table that explained all of the measured masses, densities, and valences of the elements. It also predicted new elements that would fill in gaps in the periodic table.



Graph of Lothar Meyer's data demonstrating periodic properties of atomic volumes

Lothar Meyer's 1868 update to his 1864 periodic table of the elements



I	2	3	4	5	6	7	8
Cr=52.6	Mn=55.I 49.2 Ru=104.3 92.8=2.46.4 Pt=197.I	Al=27.3 $\frac{29.6}{2}$=14.8 Fe=56.0 48.9 Rh=103.4 92.8=2.46.4 Ir=197.I	Al.=27.3 Co=58.7 47.8 Pd=106.0 93=2.465 Os=199.	Ni=58.7	Cu=63.5 44.4 Ag=107.9 88.8=2.44.4 Au=196.7	Zn=65.0 46.9 Cd=III.9 88.3=2.44.5 Hg=200.2	C=I2.00 16.5 Si=28.5 $\frac{89.1}{2}$=44.5 $\frac{89.1}{2}$=44.5 Sn=117.6 89.4=2.4I.7 Pb=207.0
9	10	11	12	13	14	15	
N=14.4 16.96 P=31.0 44.0 As=75.0 45.6 Sb=120.6 87.4=2.43.7 Bi=208.0	O=16.00 16.07 S=32.07 46.7 Se=78.8 49.5 Te=128.3	F=19.0 16.46 Cl=35.46 44.5 Br=79.9 46.8 I=126.8	Li=7.03 16.02 Na=23.05 16.08 K=39.13 46.3 Rb=85.4 47.6 Cs=133.0 7I=2.35.5 Te=204.0	Be=9.3 14.7 Mg=24.0 16.0 Ca=40.0 47.6 Sr=87.6 49.5 Ba=137.I	Ti=48 42.0 Zr=90.0 47.6 Ta=137.6	Mo.=92.0 45.0 Vd=137.0 47.0 W=184.0	

Figure 3.16: Lothar Meyer presented data demonstrating the periodic properties of atomic volumes, with peaks corresponding to the beginning of each row of the periodic table. In 1868 he updated his periodic table with newly discovered elements.

3.1.3 Other Important Contributions to Inorganic Chemistry

Fritz Haber (German, 1868–1934) invented and Carl Bosch (German, 1874–1940) scaled up the Haber-Bosch process for chemically synthesizing ammonia on an industrial scale for fertilizers and explosives (rather than having to rely on limited natural sources, such as harvesting bat guano from caves) [Hager 2008; Stoltzenberg 1994, 2005; Szöllösi-Janze 2015]. See Fig. 3.17. Haber won the 1918 Nobel Prize in Chemistry for this work. Å. G. Ekstrand, President of the Royal Swedish Academy of Sciences, praised Haber's accomplishment [https://www.nobelprize.org/prizes/chemistry/1918/ceremony-speech/]:

> Geheimrat Professor Haber. This country's Academy of Sciences has awarded you the 1918 Nobel Prize for Chemistry in recognition of your great services in the solution of the problem of directly combining atmospheric nitrogen with hydrogen. A solution to this problem has been repeatedly attempted before, but you were the first to provide the industrial solution and thus to create an exceedingly important means of improving the standards of agriculture and the well-being of mankind. We congratulate you on this triumph in the service of your country and the whole of humanity.

In 1962, Rudolf Hoppe (German, 1922–2014) created the first chemical compounds containing noble gases, which had previously been believed to be chemically inert. See Fig. 3.18.

As shown in Figs. 3.19–3.22, many other German-speaking scientists made important contributions to inorganic chemistry:

Richard Abegg (German, 1869–1910, Fig. 3.19) pioneered valence theory (including what is now know as Abegg's rule) and also measured the effects of solutes on freezing point depression, osmotic pressure, and other properties.

Wilhelm Biltz (German, 1877–1943, Fig. 3.19) made careful measurements of many inorganic molecular weights and vapor pressures.

Otto Linné Erdmann (German states, 1804–1869, Fig. 3.19) conducted experiments with nickel and indigo and also measured a number of atomic weights.

Otto Robert Fricke (German, 1895–1950, Fig. 3.19) was especially known for his work with oxide hydrates.

Wilhelm Hampe (German, 18??–19??, Fig. 3.19) studied the properties of metal-halogen compounds.

Siegfried Herzog (German, 1918–2011, Fig. 3.19) conducted research on a variety of compounds containing metals or transition metals.

Kurt Issleib (German, 1919–1994, Fig. 3.20) created and studied a wide range of phosphorus compounds, including phosphorus-containing drug molecules.

Wilhelm Klemm (German, 1896–1985, Fig. 3.20) made important discoveries in many areas of inorganic chemistry, including intermetallic compounds, rare earths, transition elements, oxides, fluorides, and magnetochemistry. As a student, teacher, or collaborator, he worked with many other major inorganic chemists, such as Wilhelm Biltz, Rudolf Hoppe, Eduard Zintl, and others.

Wilhelm Manchot (German, 1869–1945, Fig. 3.20) was especially known for his work on a variety of carbon monoxide reactions, but he also conducted research on silicides and other areas of inorganic chemistry.

Eilhard Mitscherlich (German states, 1794–1863, Fig. 3.20) discovered isomorphism in crystals, experimented with several acids and salts, studied catalysis, and measured the vapor pressures of many volatile compounds.

Paul Pfeiffer (German, 1875–1951, Fig. 3.20) conducted research on ionic compounds and crystals. He discovered salen ligands (complex molecular structures) as well as the Pfeiffer effect of molecules on optical rotation of polarized light.

Carl Friedrich Rammelsberg (German, 1813–1899, Fig. 3.20) studied phosphoric acid and made a large number of important discoveries in chemical mineralogy that were relevant to both geology and industrial mining.

Günther Rienäcker (German, 1904–1989, Fig. 3.21) focused especially on heterogeneous catalysts, their mechanisms, and their applications.

Otto Ruff (German, 1871–1939, Fig. 3.21) was noted for his work in fluorine chemistry, high-temperature chemistry, and several other areas of inorganic chemistry.

Robert Schwarz (German, 1887–1963, Fig. 3.21) conducted important research on the chemistry of silicon, germanium, halogens, and peroxides.

Arthur Simon (German, 1893–1962, Fig. 3.21) harnessed Raman spectroscopy to determine molecular structures. He also developed an electric furnace and a cryostat for chemical experiments.

Georg Ernst Stahl (German states, 1659–1734, Fig. 3.21) conducted some of the first detailed chemical studies of reduction-oxidation reactions and fermentation reactions.

Alfred Stock (German, 1876–1946, Fig. 3.21) studied a number of areas of inorganic chemistry, including boron hydrides, silicon hydrides, beryllium, and mercury toxicity. He created the Stock system (e.g., “iron(II) chloride” for $FeCl_2$) for naming binary chemical compounds that is still in use today.

Erich Thilo (German, 1898–1977, Fig. 3.22) created and studied novel inorganic polymers composed of silicates, as opposed to more conventional carbon-based polymers.

Hans von Wartenberg (German, 1880–1960, Fig. 3.22) developed techniques and compiled a large amount of important data regarding high-temperature chemistry. He also did important work in silicon chemistry.

Alfred Werner (Swiss, 1866–1919, Fig. 3.22) won the Nobel Prize in Chemistry in 1913 for his discoveries regarding the coordination chemistry of bonding and stereochemistry in inorganic molecules. T. Nordström, President of the Royal Swedish Academy of Sciences, explained the importance of Werner’s work [https://www.nobelprize.org/prizes/chemistry/1913/ceremony-speech/]:

> The number of atoms or groups of atoms which can be linked in a first sphere with the elementary atom functioning as centre, or which in other words can be coordinated into complex radicals under direct linkage with an atom, Werner calls the coordination number. This is a dearly defined numerical concept which is superior to other numerical

> concepts designed to characterize affinity saturation in that it is to some extent independent of the nature and valence of the interconnected elementary atoms, in so far as it has the same value for the great majority of elements. Only two such numerical values have been demonstrated as yet, i.e. four for some elements, and six for the others.
>
> By this approach of which only some principal characteristics can be mentioned here, Werner explains the structure and origin of complex inorganic compounds. By widening and deepening the concept of valence which incorporates his view he has succeeded in bringing atomistic and molecular compounds together under a common point of view. He has drawn a large number of diverse compounds into the range of his comprehensive expert mental work and has thereby been able to establish a uniform system for large groups of inorganic compounds. Werner's approach has also exerted significant influence on research in organic chemistry.
>
> Werner's theory has been supported in an extremely important and valuable manner by the stereochemical researches which he carried out as a sideline, mostly in connection with his work on the constitution of chemical compounds.
>
> By virtue of his theory of the asymmetrical carbon atom, van't Hoff became the real founder of the stereochemistry of organic compounds, and it is Werner's indisputable merit to have introduced this approach to inorganic chemistry as well. Even in his earlier investigations into certain metal ammonias he was able to show that numerous cases of isomerism in complex cobalt and platinum compounds could only be satisfactorily explained by steric approach. For complex radicals of a certain type he put forward a steric theory—the octahedron theory—which predicted that certain of these compounds must occur in two stereoisomeric forms, a prediction which has been confirmed by experiment. By far the greatest interest in this field attaches also to the discovery he made in the last few years, that certain cobalt, chromium, iron, and radium compounds with an asymmetrical metal atom in the complex radical can be divided into two forms which behave like mirror images and show differences of the same kind as those in organic mirror-image isomers, i.e. they are optical antipodes of each other. This discovery is a splendid support for Werner's theory. It has been called the most important discovery in chemistry in recent times, and his stereochemical work makes him the founder of inorganic stereochemistry.
>
> As to Werner's research work as a whole we can with good reason agree with the remark of an eminent research worker, that Werner's theoretical and experimental work in inorganic chemistry has opened up new paths of chemical research and is of positively revolutionary significance. It is substantially his researches which have during the last few decades set the trend of development in inorganic chemistry and have newly inspired this branch of science which had been somewhat neglected during the last quarter of the 19th century, by giving it new impulses which have borne fruit in numerous different special studies by various research workers.

Lothar Wöhler (German, 1870–1952, Fig. 3.22) spent his career studying oxidative reactions for explosives, catalysts, and other applications.

Eduard Zintl (German, 1898–1941, Fig. 3.22) made important discoveries regarding intermetallic compounds; his name remains associated with Zintl phases and Zintl ions.

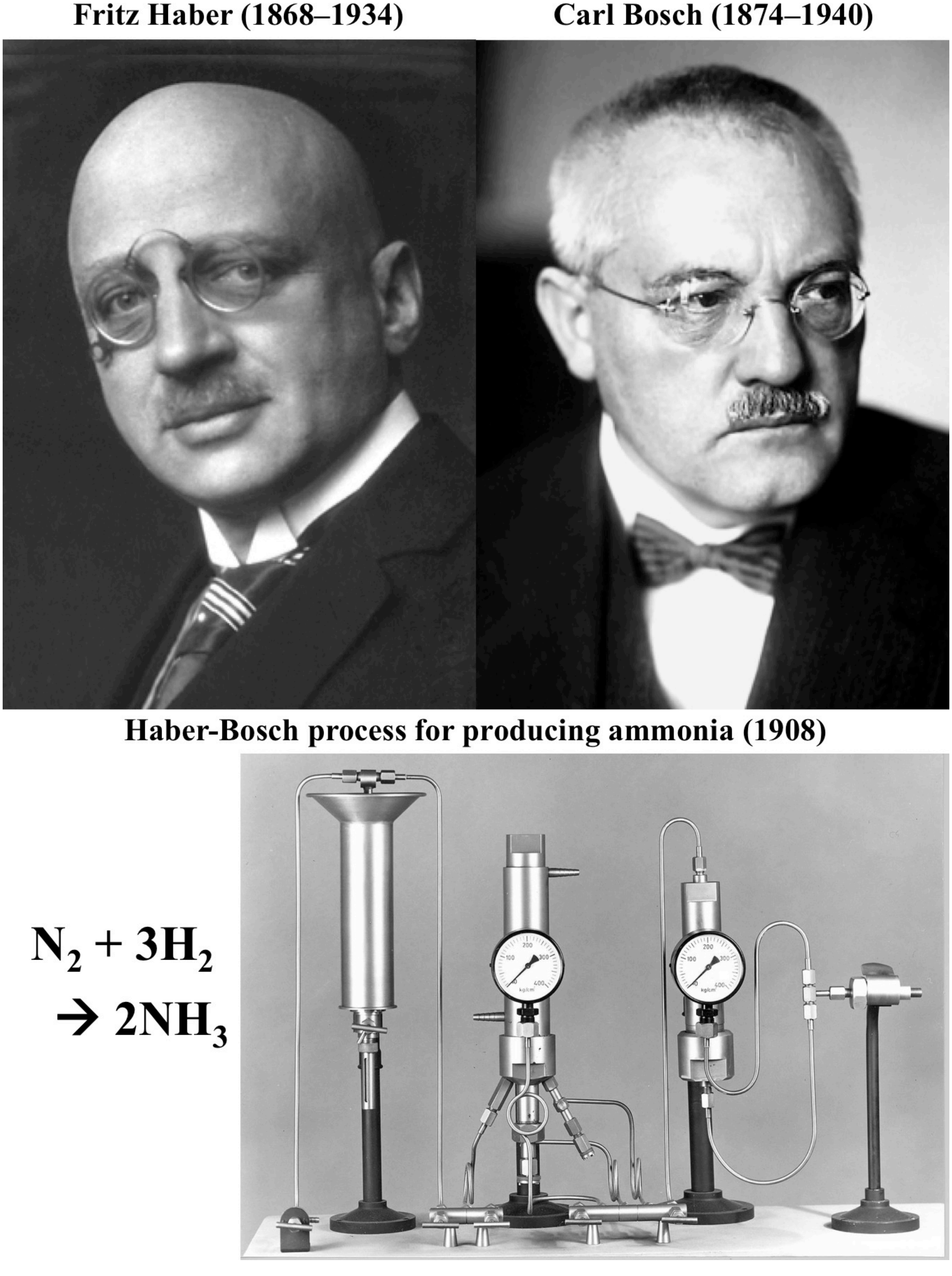
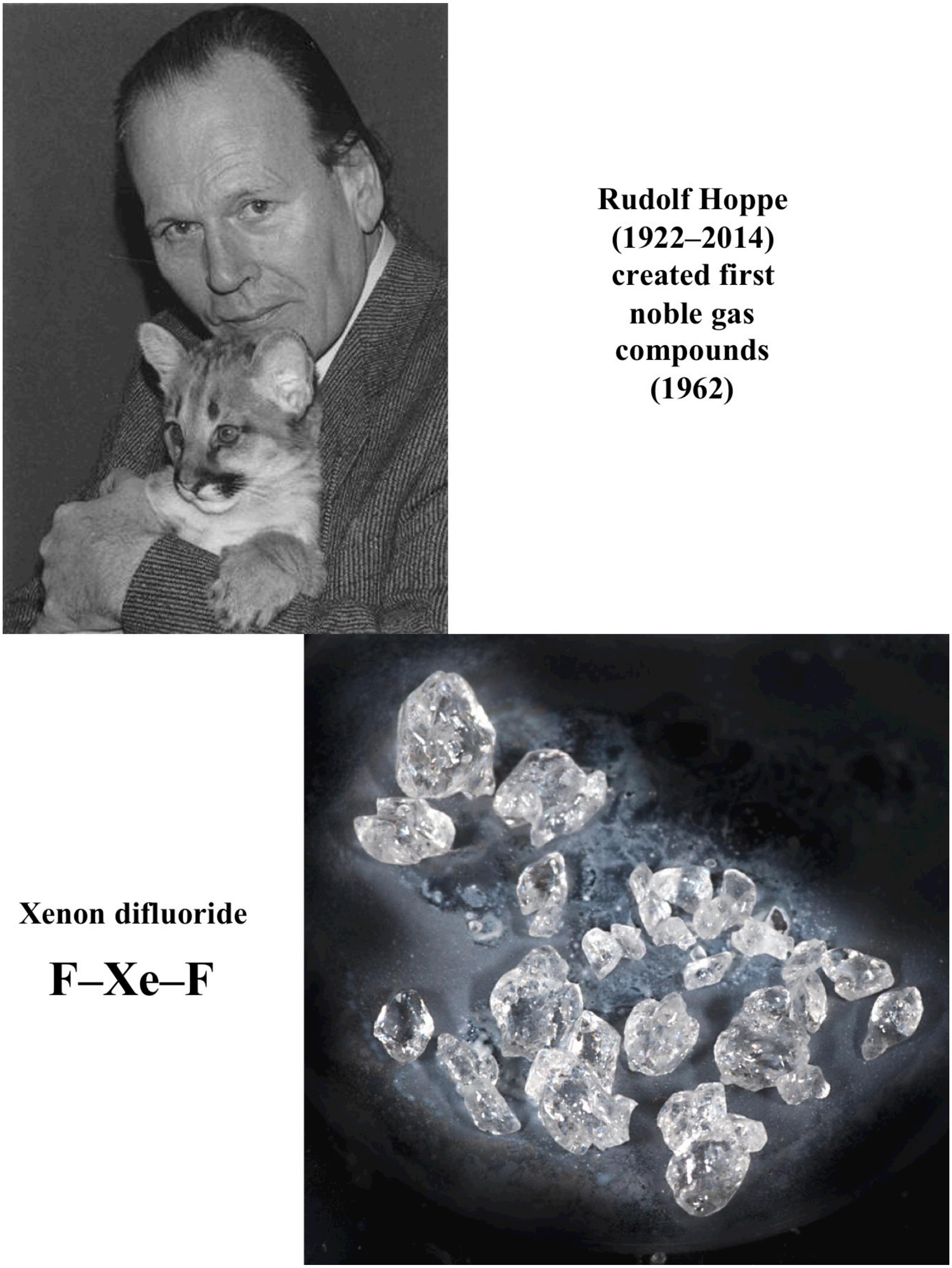


Figure 3.17: Fritz Haber invented and Carl Bosch scaled up the Haber-Bosch process for producing ammonia for fertilizers and explosives.



Rudolf Hoppe
(1922–2014)
created first
noble gas
compounds
(1962)

Xenon difluoride

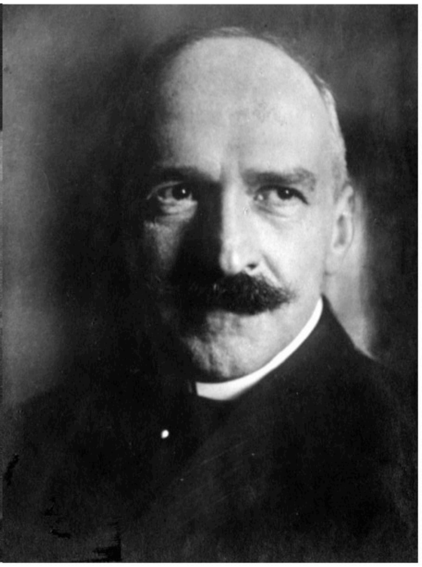
F–Xe–F

Figure 3.18: In 1962, Rudolf Hoppe created the first chemical compounds containing noble gases, which had previously been believed to be chemically inert.

Richard Abegg
(1869–1910)
Valence theory, freezing point depression

Wilhelm Blitz
(1877–1943)
Inorganic molecular weights and vapor pressures

Otto Linné Erdmann
(1804–1869)
Nickel, indigo, atomic weights



Otto Robert Fricke
(1895–1950)
Oxide hydrates

Wilhelm Hampe
(18??–19??)
Properties of metal-halogen compounds

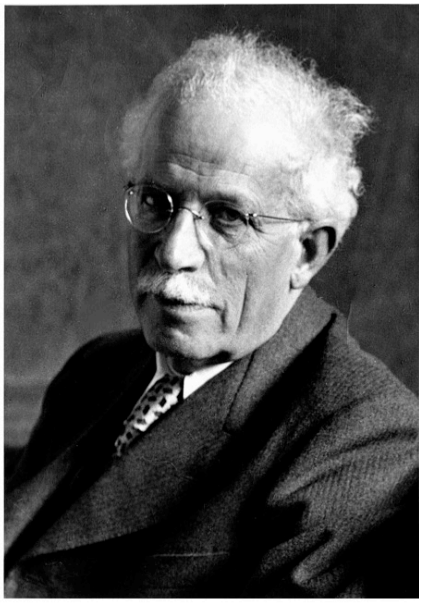
Siegfried Herzog
(1918–2011)
Metal compounds

Figure 3.19: Other creators who made important contributions to inorganic chemistry included Richard Abegg, Wilhelm Blitz, Otto Linné Erdmann, Robert Fricke, Wilhelm Hampe, and Siegfried Herzog.

Kurt Issleib
(1919–1994)
Phosphorus
compounds

Wilhelm Klemm
(1896–1985)
Intermetallic
compounds,
rare earths,
transition elements

Wilhelm Manchot
(1869–1945)
Carbon monoxide
reactions



Eilhard Mitscherlich
(1794–1863)
Isomorphism
in crystals

Paul Pfeiffer
(1875–1951)
Ionic compounds
and crystals

Carl Friedrich
Rammelsberg
(1813–1899)
Phosphoric acid,
crystals

Figure 3.20: Other creators who made important contributions to inorganic chemistry included Kurt Issleib, Wilhelm Klemm, Wilhelm Manchot, Eilhard Mitscherlich, Paul Pfeiffer, and Carl Friedrich Rammelsberg.

Günther Rienäcker
(1904–1989)
Heterogeneous catalysts

Otto Ruff
(1871–1939)
Fluorine chemistry

Robert Schwarz
(1887–1963)
Chemistry of silicon, germanium, halogens, and peroxides

Arthur Simon
(1893–1962)
Raman spectroscopy to determine molecular structures

Georg Ernst Stahl
(1659–1734)
Reduction-oxidation reactions, fermentation

Alfred Stock (1876–1946)
Boron hydrides, silicon hydrides, beryllium, mercury toxicity, Stock system for naming compounds

Figure 3.21: Other creators who made important contributions to inorganic chemistry included Günther Rienäcker, Otto Ruff, Robert Schwarz, Arthur Simon, Georg Ernst Stahl, and Alfred Stock.

Erich Thilo
(1898–1977)
Silicate polymers

Hans von Wartenberg
(1880–1960)
Silicon chemistry, high-temperature chemistry

Alfred Werner
(1866–1919)
Coordination chemistry
Nobel Prize in Chemistry 1913

Lothar Wöhler
(1870–1952)
Explosives and other oxidative reactions

Eduard Zintl
(1898–1941)
Intermetallic compounds

Figure 3.22: Other creators who made important contributions to inorganic chemistry included Erich Thilo, Hans von Wartenberg, Alfred Werner, Lothar Wöhler, and Eduard Zintl.

3.2 Organic Chemistry

German-speaking scientists dominated the development of organic chemistry, or the chemistry of molecules that contain significant numbers of carbon atoms.[3] Organic chemistry is especially important since carbon-rich molecules include everything from biological molecules and pharmaceuticals to synthetic polymers and dyes.

This section covers some of the German-speaking creators and their creations that were involved in:

3.2.1. Synthetic dyes and the origins of organic chemistry

3.2.2. General organic chemistry

3.2.3. Organometallic chemistry

3.2.4. Synthetic fuels

3.2.5. Liquid crystals

3.2.6. Technology transfer out of the German-speaking world

3.2.1 Synthetic Dyes and the Origins of Organic Chemistry

One of the strongest motivations for the development of organic chemistry in the German-speaking world was the creation of synthetic fabric dyes that could be cheaper than natural dyes and could come in a greater variety of colors. That industry was quite lucrative, yet it also led to the generation of many would-be dyes that had pharmaceutical, explosive, or other desirable properties. All of those applications drove the need to understand the science of organic molecules and reactions, and to develop methods of synthesizing and mass-producing any desired organic molecule.

Ulrich Wengenroth, a scientific historian at the Deutsches Museum in Munich, summarized the importance of the German-speaking world for organic chemistry, and vice versa [Landes et al. 2010, pp. 290–291]:

> The showcase of German science-based industry was undoubtedly organic chemistry. From the 1880s until well after World War II German companies held a commanding position in most products based on carbon hydrates, especially when it came to high-value products like pharmaceuticals. The success story began with synthetic dyestuffs in the 1880s. Although the first synthetic dyestuffs were created in France and England, the latter in a laboratory set up by a student of the German chemist Liebig, it was German firms, supported by academic chemists from universities and engineers from

---

[3] Abelshauser et al. 2004; Brock 1993; Bugge 1955; Coffey 2008; Deichmann 2001; Drummer and Zwilling 2007; Engels et al. 1989; Farber 1961; Haber 1958, 1971; Ihde 1984; Johnson 1990; Kahlert 2002; Karlsch2016; Lesch 2000; Maier 2015; Marsch 1994a; Neufeldt 2003; Partington 1935, 1957, 1964; Peppas 2013; Rosner 2004; Sasuly 1947; Schwenk 2000; Soukup 2007; Teltschik 1992; Ungewitter 1938; Welsch 1981; Werner 2017.

> polytechnics, that turned synthetic dyestuffs into an industry with a highly methodical and scientific approach. The main strategy was always the same: analyze a natural product and then find ways to synthesize it cheaply from the tar derivatives the heavy industries and gasworks would abundantly supply. The overabundant supply of first-rate human capital for industrial research, plus the additional incentive of not having access to natural resources for colonies, created a situation that proved to be immensely fortunate. Only the Swiss chemical industry, also with a good supply of academically trained scientists and no colonies, could match the progress of German organic chemistry. It was one of the first examples after the Industrial Revolution when the absence of natural resources proved to be beneficial. Apart from the availability of highly qualified human capital, the German dyestuffs industry benefited from having hit a treasure trove of potential products, and the most innovative entrepreneurs were smart enough to see and fully utilize that potential.
>
> Serendipity had it that hydrocarbons are at the root of three major product families: dyestuffs, synthetic materials, and pharmaceuticals. In looking for one, chemists would inevitably find the others. They just had to find out what the properties of the respective stuff were they had hit upon. This was done by massive testing on a hitherto unprecedented scale by hundreds of professionals in the laboratories of the big three (Hoechst, Bayer, BASF) of the German chemical industry. In the words of Carl Duisberg, head of Bayer, there was "nowhere any trace of a flash of genius" in the labs, just academic toil and screening. Eventually his company found more than 10,000 synthetic dyestuffs before the eve of World War I, 2,000 of which were marketed. At the same time they had hit on dyestuffs that wouldn't dye but could cure ills. Many twentieth-century drugs are "failed dyes," Valium being just the most profitable among them. Next to drugs a host of synthetic materials was found "on the way" and gave rise to ever more scrutiny when laboratories were testing newly synthesized chemicals.
>
> Charts of tar-based products show a wide spectrum from explosives to anesthesia, Bakelite, and a number of synthetic dyestuffs and their intermediates. [...] It took the German chemical industry's competitors decades and the scrapping of all property rights in the wake of the wars slowly to erode the position it had built by the turn of the century.

Two of the most important founders of organic chemistry were Friedrich Wöhler and Justus von Liebig, who were friends and research collaborators throughout most of their careers. They also educated and inspired a huge number of younger chemists who went on to make major discoveries themselves.

Friedrich Wöhler (German, 1800–1882), shown in Fig. 3.23, synthesized urea, discovered compound radicals, and made other discoveries that helped to establish the field of organic chemistry. As the years went by, he spent more and more of his time educating and mentoring chemistry students, to whom he was quite devoted and helpful. Oxford University's *Biographical Dictionary of Scientists* summarized some of his research history [Porter 1994, pp. 731–732]:

> In Wöhler's first research in 1827 he isolated metallic aluminium by heating its chloride with potassium; he then prepared many different aluminium salts. In 1828 he used the same procedure to isolate beryllium. Also in 1828 he carried out the reaction for which he is best known. He heated ammonium thiocyanate—a crystalline, inorganic substance—and converted it to urea (carbamide), an organic substance previously obtained only

> from natural sources. Until that time there had been a basic misconception in scientific thinking that the chemical changes undergone by substances in living organisms were not governed by the same laws as were inanimate substances[...]
>
> Wöhler worked with Justus von Liebig on a number of important investigations. In 1830, they proved the polymerism of cyanates and fulminates, and two years later announced a series of studies of benzaldehyde (benzenecarbaldehyde) and the benzoyl (benzenecarboxyl) radical. In 1837, they investigated uric acid and its derivatives. Wöhler also discovered quinone (cyclohexadiene-1,4-dione), hydroquinone or quinol (benzene-1,4-diol) and quinhydrone (a molecular complex composed of equimolar amounts of quinone and hydroquinone).
>
> In the inorganic field Wöhler isolated boron and silicon and prepared silicon nitride and hydride. He prepared phosphorus by the modern method, and discovered calcium carbide and showed that it can be reacted with water to produce acetylene (ethene) [...]

Justus von Liebig (German, 1803–1873) collaborated with Wöhler for much of his career, for example in discovering compound radicals. As illustrated in Fig. 3.24, he taught large number of students in his laboratory, creating generations of later chemists. The *Encyclopedia Britannica* described his research [EB 2010]:

> [T]he radical theory that Liebig did much to develop was the first major attempt at systematization in organic chemistry.
>
> Liebig's studies in organic chemistry were greatly aided by the simple method he developed for the analytical determination of carbon and hydrogen. He also developed a method for the analytical determination of halogens, published important work on polybasic organic acids, and did much to support the hydrogen theory of acids. [...]
>
> After 1838 Liebig's interest shifted from pure organic chemistry to the chemistry of plants and animals. He made a large number of analyses of tissues and body fluids and carried out a study of the nitrogenous products of the animal organism. [...] He [...] showed that plants took carbon dioxide, water, and ammonia from the air and soil.

As shown in Fig. 3.25, Otto Unverdorben (German, 1806–1873), Friedlieb Ferdinand Runge (German, 1795–1867), Carl Fritzsche (German, 1808–1871), and August Wilhelm von Hofmann (German, 1818–1892) synthesized aniline, which can be chemically modified to produce a wide variety of colored dyes, explosives, and drugs. In 1820, Runge was also the first scientist to extract and identify caffeine. Even the American Council of Learned Societies praised von Hofmann's contributions and impact [ACLS 2000, pp. 432–433]:

> He obtained his doctorate in 1841 and taught at the University of Bonn. In 1845, under the sponsorship of Prince Albert, he went to England, where he became director of the Royal College of Chemistry, London. He stayed there until 1865, when he was given the chemistry chair at the University of Berlin. [...]
>
> Hofmann's influence on British and German chemistry was profound. He was responsible for continuing the method of science teaching by laboratory instruction that had been

> established and popularized by Liebig at Giessen and for transporting it to England and Berlin. He created his own school of chemists who were interested primarily in experimental organic chemistry and its industrial applications. Much of his experimentation had to do with coal tar and its derivatives. In 1843 he established that many substances obtainable from coal tar naphtha and its derivatives were all of a single nitrogenous base, aniline. His discoveries—and those of his school—laid the foundation for the coal tar products industries. He also did important work on the chemistry of dyes.

Heinrich Caro (German, 1834–1910), Carl Gräbe (German, 1841–1927), and Carl Theodore Liebermann (German, 1842–1914), shown in Fig. 3.26, synthesized alizarin red dye in 1868.

Adolf von Baeyer (German, 1835–1917), Karl Heumann (German, 1850–1894), Johannes Pfleger (German, 1867–1957), and Rudolf Knietsch (German, 1854–1906) synthesized indigo dye. Adolf von Baeyer won the Nobel Prize in Chemistry in 1905. See Fig. 3.27. Professor A. Lindstedt, President of the Royal Swedish Academy of Sciences, explained the importance of von Baeyer's work [https://www.nobelprize.org/prizes/chemistry/1905/ceremony-speech/]:

> Among the living research workers who have contributed directly or indirectly to the unique development of the tar-dyestuff industry the place of honour goes to the Professor at Munich University, Adolf von Baeyer, for his researches into the composition of indigo as well as into the triphenyl methane dyestuffs.
>
> Indigo, the gorgeous pigment of the indigo plant, has been considered the most important of all organic pigments on account of its beauty and colour fastness, and the annual tribute which the West used to pay India for it amounted to a very considerable sum. To reproduce the pigment by synthetic methods and make it more easily obtainable was therefore an exceptionally inviting task for chemical research.
>
> The complex and unique composition of indigo, however, made this also one of the hardest of tasks. Here there could be no question of one of those casual discoveries, which by happy accident seem to achieve half the work. Years of work were required for even von Baeyer's acumen and experimental skill to achieve the necessary insight into the pigment's chemical composition and to be able to manufacture it from simpler constituents. Even after the purely scientific part of the work had been completed it still took a number of years to make the results obtained from research applicable to technology. [...]
>
> Simultaneously with his analyses within the indigo group, analyses moreover which exerted a far-reaching influence upon the development of organic chemistry and directed research into new channels, von Baeyer was active with no less success in another sphere of the chemistry of organic dyestuffs. The stimulus was given by his discovery of a new group of beautifully coloured compounds, the so-called phthaleins, of which only the eosin pigments, highly important to industry, and the rhodamin dyes derived from them, may have particular mention here. In a series of masterly experiments von Baeyer demonstrated several years ago the chemical nature of the phthaleins and showed that, just like the already known rosaniline dyes, they may be classified as derivatives of the hydrocarbon triphenylmethane. In recent years—more exactly, from 1900 on—von Baeyer has resumed his work on triphenylmethane, and from this a new conception

> of the chemical composition of pigments and in general of the connection between the optical properties of organic substances and their interior atomic structure has been to a high degree prepared.
>
> The dyestuffs studied by von Baeyer belong to the main category of organic substances usually classified under the name of aromatic compounds, which differ decisively from the other organic substances—the so-called aliphatic or fatty acid series—both in their properties and in their behaviour in reaction. In fact this difference has been considered so great that it has caused the division of the whole of organic chemistry into two separate halves: the chemistry of aliphatic, and of aromatic substances. Nevertheless, one of the main tasks of scientific research is to try to bridge the gulfs dividing different sciences, or different branches of the same science. In this respect, too, von Baeyer has carried out notable work in his research, remarkable alike from the experimental as well as from the theoretical point of view, on the so-called hydroaromatic compounds. With these compounds, he has found the transitional form between the two main series just mentioned and by application of the new conception and the new method to the terpenes and the species of camphor occurring in nature and also important for technology, he has opened up fields for synthetic work which were previously inaccessible.

There were many other German-speaking chemists who developed thousands of other artificial dyes. Peter Griess (German, 1829–1888), Otto Nikolaus Witt (German/Swiss, 1853–1915), and Paul Friedländer (German, 1857–1923), depicted in Fig. 3.28, are just a few additional examples of important dye creators.

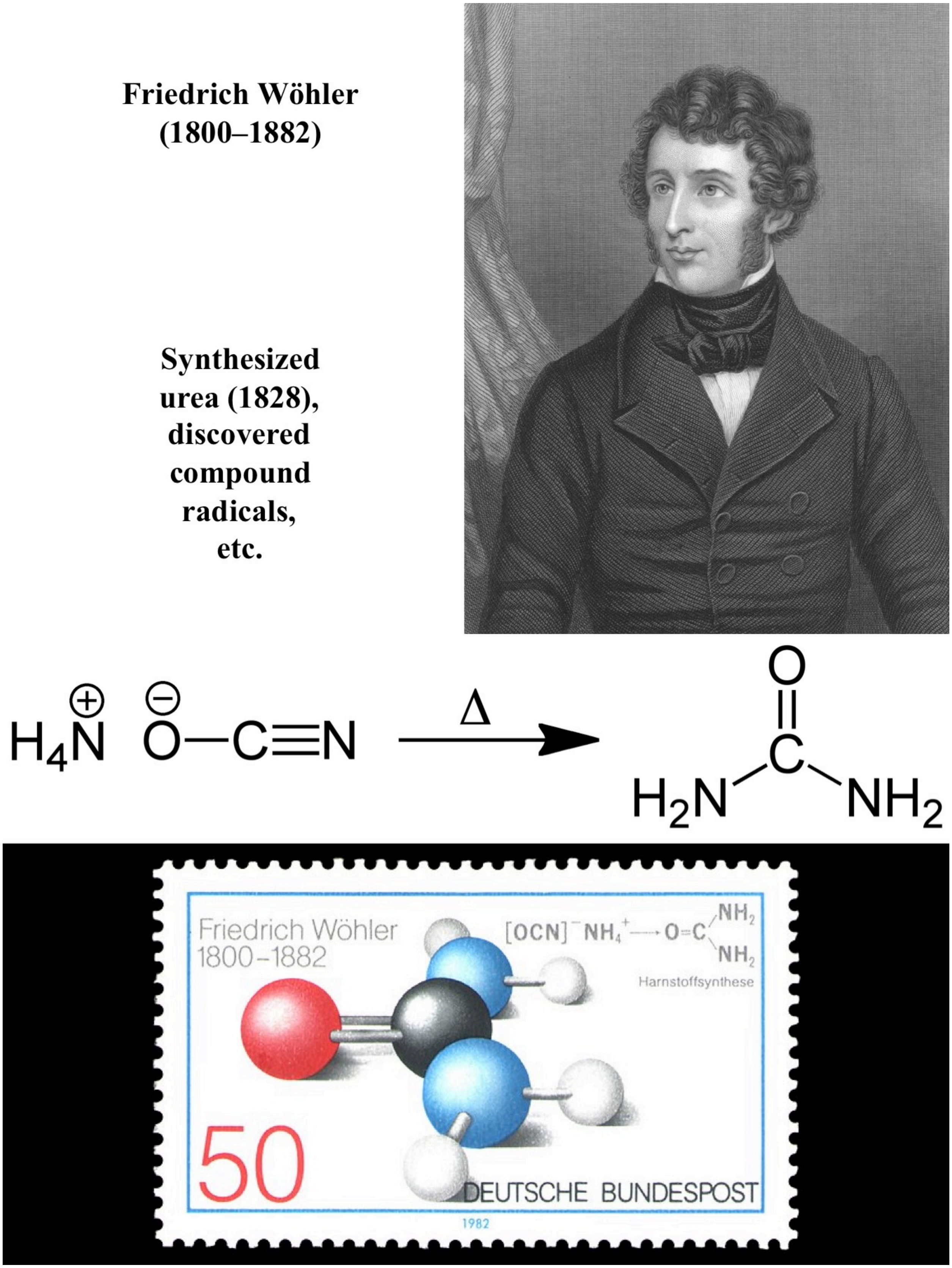
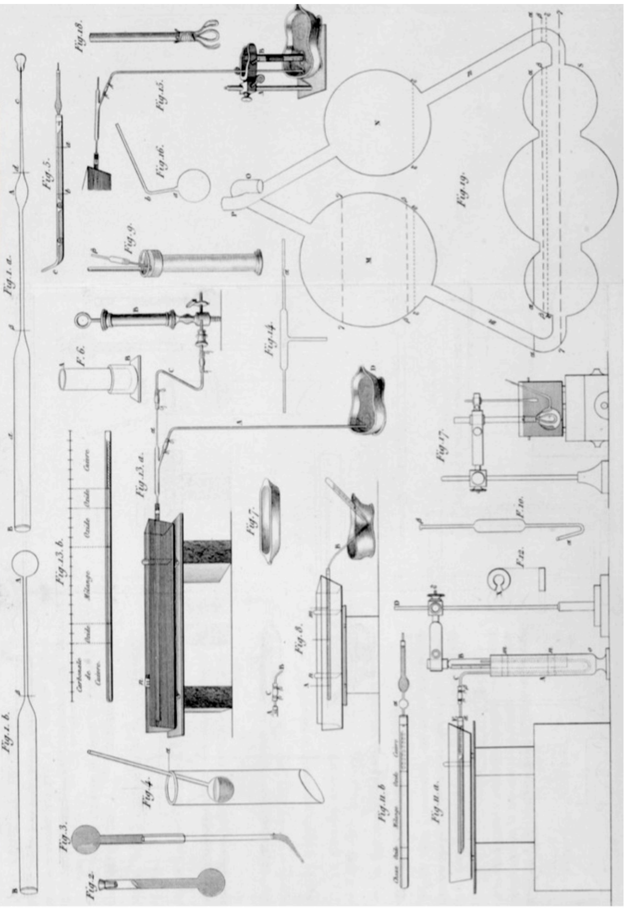


Figure 3.23: Friedrich Wöhler synthesized urea, discovered compound radicals, and made other discoveries that helped to found the field of organic chemistry.

Justus von Liebig (1803–1873)
Compound radicals, etc.



Liebig's laboratory and students in 1840

Figure 3.24: Justus von Liebig collaborated with Wöhler for part of his career, for example in discovering compound radicals. He taught large number of students in his laboratory, creating generations of later chemists.

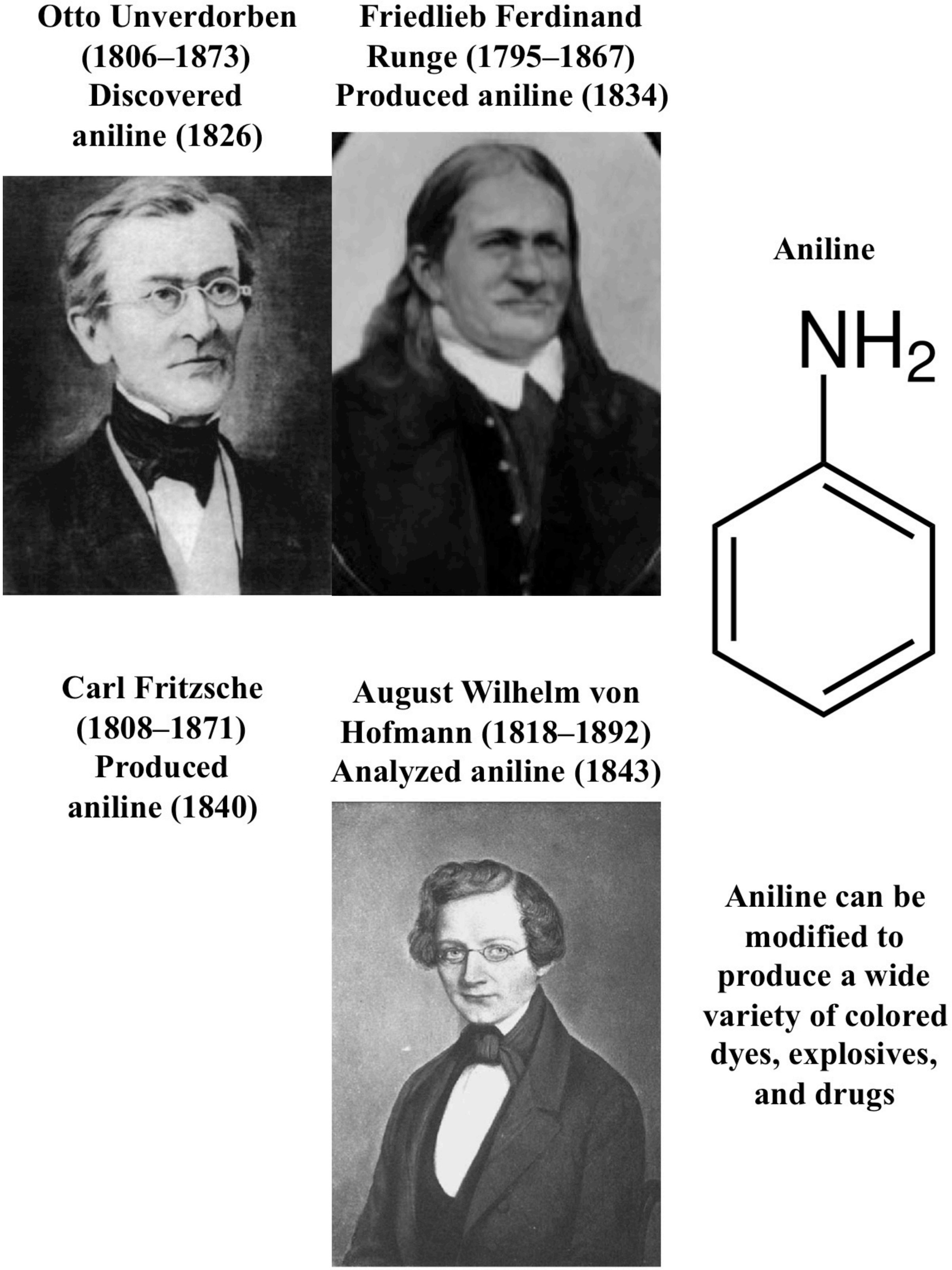


Figure 3.25: Otto Unverdorben, Friedlieb Ferdinand Runge, Carl Fritzsche, and August Wilhelm von Hofmann synthesized aniline, which can be chemically modified to produce a wide variety of colored dyes, explosives, and drugs.

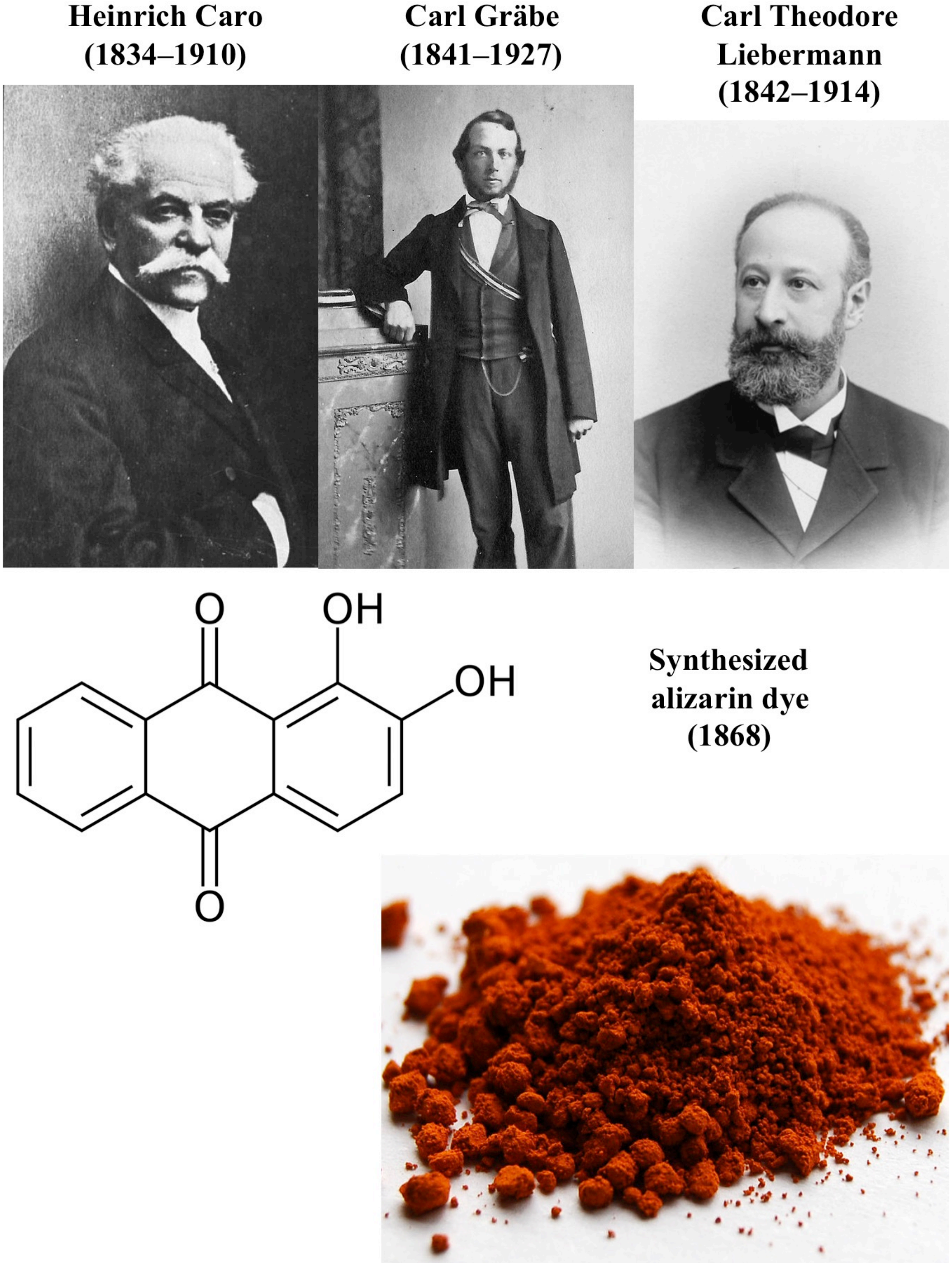


Figure 3.26: Heinrich Caro, Carl Gräbe, and Carl Theodore Liebermann synthesized alizarin red dye in 1868.

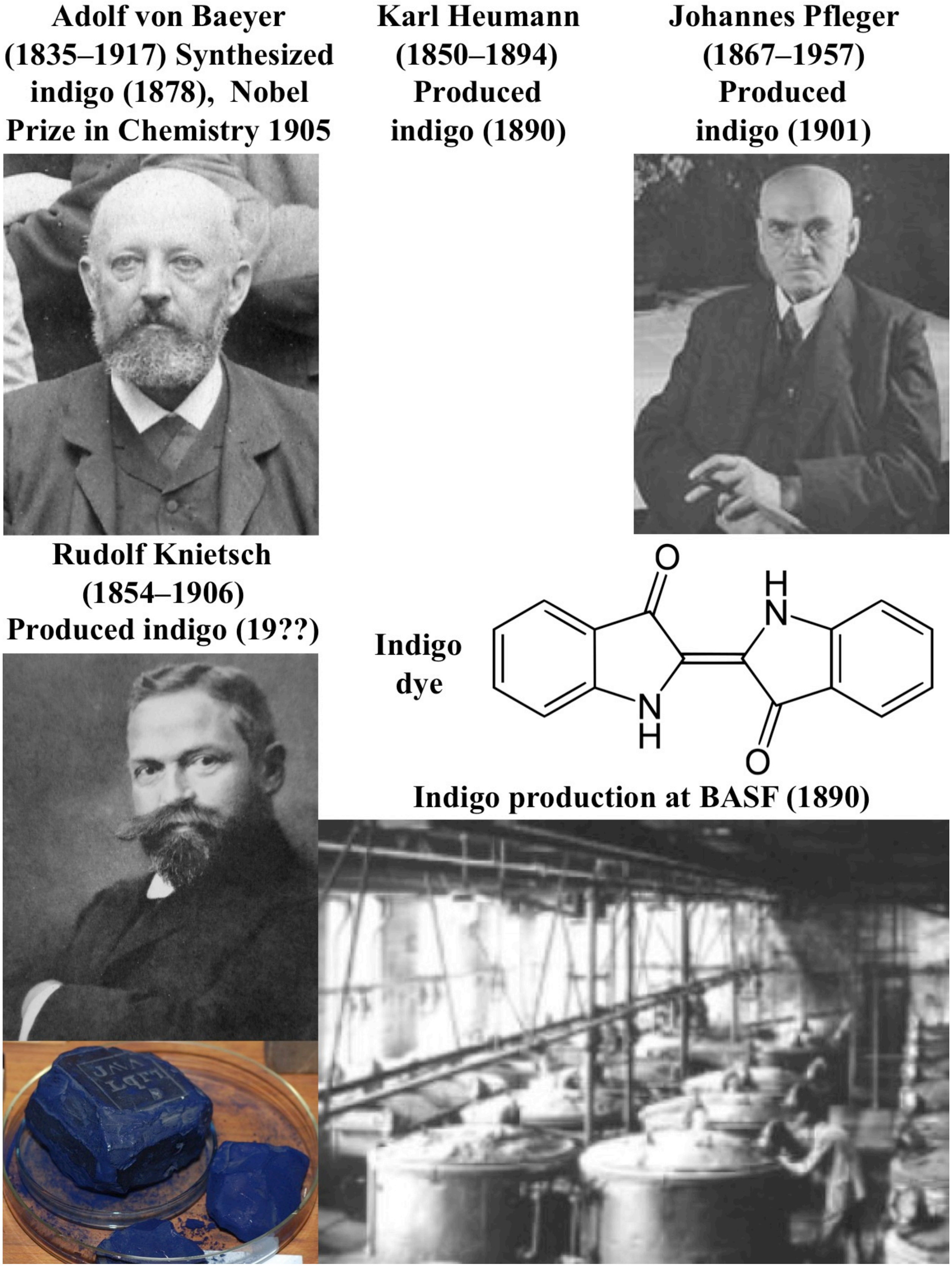
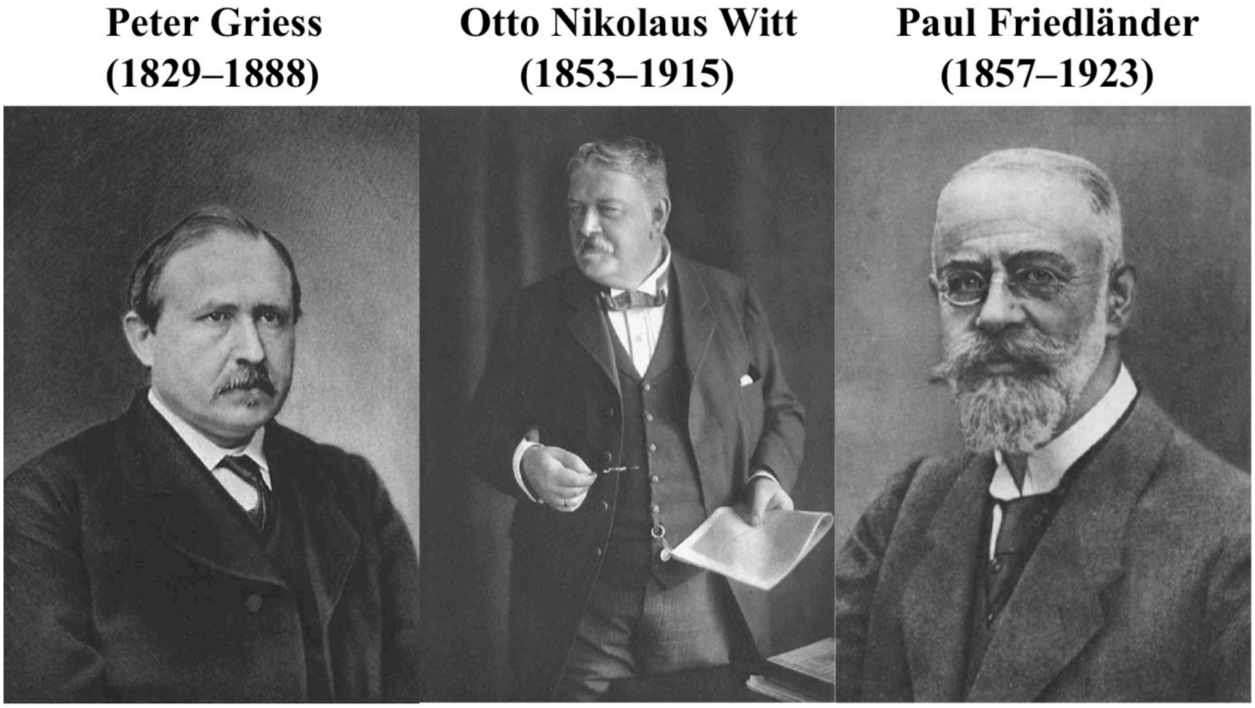


Figure 3.27: Adolf von Baeyer, Karl Heumann, Johannes Pfleger, and Rudolf Knietsch synthesized indigo dye. Adolf von Baeyer won the Nobel Prize in Chemistry in 1905.



Developed other artificial dyes

Figure 3.28: Peter Griess, Otto Nikolaus Witt, and Paul Friedländer developed other artificial dyes.

3.2.2 General Organic Chemistry

An enormous number of German-speaking scientists made important contributions to organic chemistry. This section can only briefly mention some examples (Figs. 3.29–3.47). For simplicity, they are mainly in alphabetical order.

Karl von Auwers (German, 1863–1939, Fig. 3.29) received his Ph.D. under August Wilhelm von Hofmann and in turn was the doctoral adviser of Georg Wittig and Karl Ziegler. He is best remembered for developing Auwers synthesis in 1908.

Eugen Bamberger (German, 1857–1932, Fig. 3.29) also received his Ph.D. under August Wilhelm von Hofmann. He discovered the Bamberger rearrangement in 1894.

Ernst Beckmann (German, 1853–1923) developed the Beckmann rearrangement (1886), shown in Fig. 3.30, which later proved extremely useful for making Nylon and several important drugs. He also invented the Beckmann freezing-point apparatus and thermometer.

Friedrich Beilstein (German, 1838–1906, Fig. 3.30) created the encyclopedic *Beilstein's Handbook of Organic Chemistry* in 1881 and continued to update its collection of organic molecules and information during his lifetime. Other chemists have continued to update and maintain *Beilstein's Handbook* to this day.

Ernst Bergmann (1903–1975, Fig. 3.31) received his Ph.D. under Wilhelm Schlenk at the University of Berlin in 1927 and conducted important research in organic and fluorine chemistry. Soon after the founding of the modern nation of Israel, he became the head scientist of the Israeli program to develop nuclear weapons. (This is another example of German-speaking scientists being responsible for developing nuclear weapons in several different countries.)

Julius von Braun (Polish/German, 1875–1939, Fig. 3.31) was a doctoral student of Otto Wallach and made several discoveries such as the von Braun reaction and the Rosenmund-von Braun reaction.

Julius Bredt (German, 1855–1937, Fig. 3.31) determined the structure of camphor and is also known for Bredt's rule and the Bredt distributor.

Hans Theodor Bucherer (German, 1869–1949, Fig. 3.31) received his Ph.D. under Johannes Wislicenus and went on to discover the Bucherer reaction, Bucherer carbazole synthesis, and the Bucherer-Bergs reaction.

George Büchi (German, 1921–1998, Fig. 3.31) is especially remembered for his studies of photochemical organic reactions.

Ernst Büchner (1850–1924, Fig. 3.31) spent his career working in organic chemistry and developed the Büchner flask and the Büchner funnel, both of which are now widely used for filtration in chemistry and biology experiments.

Robert Bunsen (German, 1811–1899, Fig. 3.32) conducted research in organic chemistry in addition to his well-known work in inorganic chemistry. He worked with organic arsenides, discovered an antidote for arsenic poisoning (iron oxide hydrate) and studied organic photochemistry.

Rainer Ludwig Claisen (German, 1851–1930, Fig. 3.33) developed many incredibly useful experimental methods that have been widely employed in organic chemistry ever since, including Claisen condensation, the Claisen reaction, the Claisen rearrangement, the Claisen flask, etc.

Rudolf Criegee (German, 1902–1975, Fig. 3.32) studied the oxidation of organic molecules and the properties of cyclic reactions. He discovered the Criegee rearrangement and the Criegee intermediate.

Theodor Curtius (German, 1857–1928, Fig. 3.32) discovered the Curtius rearrangement and several novel molecules, including hydrazine, an extremely important rocket fuel.

Walter Dieckmann (German, 1869–1925, Fig. 3.33) is most famous for developing Dieckmann condensation, a step that ever since then has been widely utilized in the synthesis of organic molecules.

Otto Diels (German, 1876–1954) and Kurt Alder (German, 1902–1958) developed Diels-Alder reactions (1928), which are very useful for producing polymers and other complex organic molecules. They both won the Nobel Prize in Chemistry in 1950. See Fig. 3.34. Professor A. Fredga of the Nobel Committee for Chemistry explained the importance of their work [https://www.nobelprize.org/prizes/chemistry/1950/ceremony-speech/]:

> Professor Diels, Professor Alder. More than two decades have passed since the day when you sent in the first paper on “Syntheses in the Hydroaromatic Series” to the Editor of the *Annals*. Much has happened since then—in Science, as well as in the world.
>
> The reciprocal addition of the unsaturated compounds was at that time still somewhat mysterious. The chemistry of the high polymer compounds belonged for the most part to the future. You found it necessary to stress that the new substances which you obtained so easily were not molecular compounds but were really new molecules, stable and firmly bonded. New simple bonds had come into being of the old, well-known kind. This identification has paved the way to a right understanding of the polymerization phenomena of the unsaturated compounds, and through it you have very greatly advanced the development of high polymer chemistry and technics.
>
> In this treatise you have even indicated how highly promising the consequences of the low molecular compounds were for the future of chemistry. In the past years the synthesis of dienes has, to be sure, achieved more than you could either foresee or predict when you wrote your paper. But the general trend, the prophetic leading ideas are already to be found in it.
>
> You mention there the possibilities for discussion of several theoretically interesting questions concerning the forces of attraction in polycyclic systems. You also mention the practical consequences. The possibility of the synthetic production of complicated natural substances or of compounds similar to them is, in your view, immediately in prospect. Finally you indicate the possibility that this astonishingly rapid and smoothly running reaction could also play a significant part in the processes of Nature.
>
> Since 1928 the synthesis of dienes has been developed in various directions by numerous workers, and its significance has become more and more obvious. You have yourselves, partly together, partly independently, worked with great success in the field you have

> opened up. The external circumstances were not always of the best for reasons which we all know. We have been told that you, Professor Diels, were in the past years unable to do any experimental work. And yet your thoughts played keenly upon scientific problems and we hope that you will soon have the opportunity of approaching the problems experimentally as well. You, Professor Alder, in spite of limited facilities for work, are again fully active. During the past year you have, by your splendid work on the steric and energetic conditions in the polycyclic systems, successfully maintained your position as the leading research worker in this field.

André Dreiding (Swiss, 1919–2013, Fig. 3.32) developed Dreiding stereomodel kits for physically building and showing organic molecular structures.

Richard August Carl Emil Erlenmeyer (German, 1825–1909, Fig. 3.32) had a long career working in many different areas of organic chemistry and biochemistry, but he is best remembered for the Erlenmeyer flask and the Erlenmeyer rule.

Hermann von Fehling (1812–1885, Fig. 3.32) is famous for developing Fehling's solution for detecting sugars, which has since been widely used everywhere from public school classrooms to hospital laboratories.

Hermann Emil Fischer (German, 1852–1919, Fig. 3.35) is remembered for many innovations such as Fischer esterification and Fischer projection. He won the Nobel Prize in Chemistry in 1902 for his work on the synthesis of sugars and purines. Professor Hj. Théel, President of the Swedish Royal Academy of Sciences, praised his research [https://www.nobelprize.org/prizes/chemistry/1902/ceremony-speech/]:

> With surprisingly acute judgement and with brilliant discernment in choosing his ways and means Fischer not only reproduced synthetically natural grape- and fruit-sugars, but also some thirty other sugars and an abundance of closely related compounds. Whereas of the naturally occurring, simple sugars only those with 5-6 carbon atoms have been found, Fischer synthesized a continuous series containing from 2 to 9 carbon atoms. Furthermore, by his elegant method of making glucosides artificially, he has also added to the achievements of organic synthesis this group which is so extraordinarily important for vegetable physiology. [...]
>
> Even since 1776 when Scheele found uric acid in urinary calculus, several substances closely related to it such as xanthine, adenine and guanine, etc. have been detected in animal secretions. The same group additionally includes theobromine, theophylline and caffeine which occur in the vegetable kingdom and constitute the stimulants in our staple beverages cocoa, coffee and tea. With the keen perception of the excellent scientist and a masterly technique Professor Fischer brought order and clarity to this field as well. He demonstrated that all those substances are derivatives of the same parent substance, purine, which he had discovered. He successfully prepared them from one another and from simpler constituents in such a way that here, too, the synthesized chain goes back to inorganic carbon, hydrogen and oxygen, and besides these he prepared a large number of new, closely related substances so that the purine derivatives studied by Fischer must now number about 150. The intrinsic composition of each has been fully determined.

Wilhelm Rudolph Fittig (German, 1835–1910, Fig. 3.35) worked in several areas of organic chemistry during his career and discovered several new molecules and new types of organic reactions. His name is most closely associated with the Fittig reaction for the synthesis of alkylbenzene molecules.

Hermann Frasch (1851–1914, Fig. 3.35) spent most of his career using organic chemistry to improve processes in oil refining.

Karl Fries (German, 1875–1962, Fig. 3.35) received his Ph.D. under Theodor Zincke and is best known for discovering the Fries rearrangement of phenolic ester molecules.

Ludwig Gattermann (1860–1920, Fig. 3.35) wrote a widely used textbook of experimental methods in organic synthesis. He also discovered new methods such as the Gattermann reaction.

Carl Glaser (German, 1841–1935, Fig. 3.35) developed Glaser coupling, which was later used to synthesize indigo dye and other important organic molecules.

Irma Goldberg (Russian but educated in Switzerland and worked in Switzerland and Germany, 1871–<1939, Fig. 3.36) worked with and married Fritz Ullmann. She developed several synthetic dye molecules and is remembered for the Goldberg amidation reaction.

Fritz Haber (German, 1868–1934, Fig. 3.36) studied carbon-carbon and carbon-hydrogen bond strengths and other topics in organic chemistry, in addition to his better known work on ammonia synthesis in inorganic chemistry (for which he won the 1918 Nobel Prize in Chemistry—see p. 453).

Arthur Hantzsch (German, 1857–1935, Fig. 3.36) developed Hantzsch pyridine synthesis and Hantzsch pyrrole synthesis.

Kurt Hoesch (German, 1882–1932, Fig. 3.36) focused on the synthesis of phenylketone molecules and developed the Hoesch reaction for that purpose.

Erich Hückel (German, 1896–1980, Fig. 3.36) is famous for the Hückel molecular orbital theory, as well as his contributions to physical chemistry such as the Debye-Hückel theory for electrolysis.

Rolf Huisgen (German, 1920–, Fig. 3.36) studied the reaction mechanisms involved in each step of synthesizing organic molecules, and personally developed the Huisgen reaction.

Claire Hunsdiecker (German, 1903–1995, Fig. 3.37) and Heinz Hunsdiecker (German, 1904–1981, Fig. 3.37) received their Ph.D.s in chemistry, married, and spent their lives conducting research in organic chemistry. They are best known for the Hunsdiecker reaction.

Oskar Georg Friedrich Jacobsen (German, 1840–1889, Fig. 3.37) studied the distillation and components of coal tar, discovered the Jacobsen rearrangement, and pioneered the field of marine chemistry.

Karl Kastner (1783–1857, Fig. 3.37) helped to establish chemistry as a proper academic field of study. He taught Justus von Liebig, who in turn educated a huge number of important chemists.

August Kekulé (German, 1829–1896) figured out the chemical bonds and structure of benzene (1865) and other organic molecules; see Fig. 3.38.

Heinrich Kiliani (German, 1855–1945, Fig. 3.37) studied digitalis and carbohydrate chemistry, and developed (along with Emil Fischer) the Kiliani-Fischer synthesis of sugar molecules.

Emil Knoevenagel (German, 1865–1921, Fig. 3.37) focused on experimental methods of synthesizing organic molecules and is remembered for the Knoevenagel condensation reaction.

Ludwig Knorr (German, 1859–1921, Fig. 3.39) developed processes such as Knorr quinoline synthesis and Knorr pyrrole synthesis, and synthesized phenazone, an aspirin-like drug molecule (p. 270).

Hermann Kolbe (German, 1818–1884, Fig. 3.39) helped to formalize the field of organic chemistry and coined the term "synthesis." His name is associated with Kolbe electrolysis, Kolbe nitrile synthesis, and the Kolbe-Schmitt reaction.

Wilhelm Körner (1839–1925, Fig. 3.39) studied many aromatic compounds as well as biochemical molecules from plants.

Albert Ladenburg (1842–1911, Fig. 3.39) purified scopolamine (which is now used to treat nausea) and synthesized other alkaloid drug molecules.

Carl Mannich (German, 1877–1947, Fig. 3.39) worked in several different areas of organic chemistry, including keto bases and alcohol bases, and remains best known for the Mannich reaction.

Hans Meerwein (German, 1879–1965, Fig. 3.39) developed or determined the mechanisms of several key organic synthesis reactions, leading to his name being associated with methods such as Meerwein arylation, Meerwein's salt, Meerwein-Ponndorf-Verley reduction, and the Wagner-Meerwein rearrangement.

Jakob Meisenheimer (German, 1876–1934, Fig. 3.40) synthesized and determined the structures of a number of organic molecules, most notably the class of molecules that are now known as the Meisenheimer complex.

Julius Lothar Meyer (German, 1830–1895, Fig. 3.40) made his greatest contribution to chemistry by developing the periodic table of the elements (p. 450), but he also did important work in organic chemistry, such as studying the structure of benzene.

Karl Meyer (German, 1899–1990, Fig. 3.40) did fundamental research on polysaccharide molecules such as hyaluronan, a component of many human cells and some bacteria.

Kurt Hans Meyer (German, 1883–1952, Fig. 3.40) received his Ph.D. under Arthur Hantzsch and studied a wide variety of organic reactions over the course of his career.

Viktor Meyer (German, 1848–1897, Fig. 3.40) worked in both organic and inorganic chemistry. Among other accomplishments, he discovered thiophene and developed the Viktor Meyer apparatus for measuring vapor densities.

Eilhard Mitscherlich (German, 1794–1863, Fig. 3.40) did important research in the fields of crystallography, inorganic chemistry, and organic chemistry. In organic chemistry, he is best known for his experiments on benzene derivatives.

Costin D. Nenitzescu (Romanian, educated in Switzerland and Germany, 1902–1970, Fig. 3.41) studied under Hans Fischer and went on to a long career synthesizing and identifying organic molecules. Nenitzescu synthesis is named for him.

George Olah (Oláh György, Hungarian, 1927–2017, Fig. 3.41) won the Nobel Prize in Chemistry in 1994 for his work on carbocations. Professor Salo Gronowitz of the Royal Swedish Academy of Sciences explained his discoveries [https://www.nobelprize.org/prizes/chemistry/1994/ceremony-speech/]:

> Because it was not possible to detect carbocations with spectroscopic methods, different scientists interpreted their experiments differently, and a scientific feud took place in organic chemistry during the 1960s and 1970s.
>
> Through a series of brilliant experiments Professor George Olah solved the problem. He created methods to prepare long-lived carbocations in high concentrations, which made it possible to study their structure, stability and reactions with spectroscopic methods. He achieved this by using special solvents, which did not react with the cations. He observed that in these solvents at low temperatures, carbocations could be prepared with the aid of superacids, acids eighteen powers of ten stronger than concentrated sulfuric acid. Through Olah's pioneering work he and the scientists who followed in his footsteps could obtain detailed knowledge about the structure and reactivity of carbocations. Olah's discovery resulted in a complete revolution for scientific studies of carbocations, and his contributions occupy a prominent place in all modern textbooks of organic chemistry.
>
> Olah found that there are two groups of carbocations, the trivalent ones called carbenium ions, in which the positive carbon atom is surrounded by three atoms, and those in which the positive carbon is surrounded by five atoms, called carbonium ions. The disputed existence of these penta-coordinated carbocations was the reason for the scientific feud. By providing convincing proof that penta-coordinated carbocations exist, Olah demolished the dogma that carbon in organic compounds could at most be tetra-coordinated, or bind a maximum of four atoms. This had been one of the cornerstones of structural organic chemistry since the days of Kekulé in the 1860s.
>
> Olah found that the superacids were so strong that they could donate a proton to simple saturated hydrocarbons, and that these penta-coordinated carbonium ions could undergo further reactions. This fact has contributed to a better understanding of the most important reactions in petrochemistry. His discoveries have led to the development of methods for the isomerization of straight chain alkanes, which have low octane numbers when used in combustion engines, to produce branched alkanes with high octane numbers. Furthermore, these branched alkanes are important as starting materials in industrial syntheses. Olah has also shown that with the aid of superacids it is possible to prepare larger hydrocarbons with methane as the building block. With superacid catalysis it is also possible to crack heavy oils and liquefy coal under surprisingly mild conditions.

Wilhelm Ostwald (1853–1932, Fig. 3.41) made a number of important contributions in organic chemistry, catalytic chemistry, and physical chemistry. He won the Nobel Prize in Chemistry in 1909 (p. 921).

Hans von Pechmann (German, 1850–1902, Fig. 3.41) synthesized or discovered several new organic molecules and is remembered for Pechmann condensation and Pechmann pyrazole synthesis.

Fritz Pregl (Austrian, 1869–1930, Fig. 2.53) developed important methods for quantitative organic microanalysis that have been widely used ever since. For that work, he won the Nobel Prize in Chemistry in 1923. Professor O. Hammarsten, Chairman of the Nobel Committee for Chemistry, announced the award [https://www.nobelprize.org/prizes/chemistry/1923/ceremony-speech/]:

> The improvement consists of the fact that Pregl converted previously used methods for quantitative analysis of relatively large quantities of substances to micro-analytical methods. This has made it possible to carry out these analyses of such small quantities of substances, the analysis of which would previously have been impossible, with exactly the same accuracy, but with great savings in time, labour, and expense. [...]
>
> Pregl's micro-analysis can be equally well applied in all fields of organic chemistry. It has already proved itself in a great number of cases, and has stood the test in this country as well. It opens promising prospects for research in the future, particularly in the vast field of biochemistry. There is every reason to hope that micro-analysis will make possible fruitful study of a great number of substances which so far, in some respects at least, have been practically inaccessible to exact chemical investigation. Such substances, for instance, include enzymes, vitamins and hormones, the extremely great significance of which for the vital processes is well known.

Vladimir Prelog (Austro-Hungarian/Croatian, 1906–1998, Fig. 3.41) made many important discoveries regarding the stereochemistry of organic molecules and the shapes of enzymes, for which he won the Nobel Prize in Chemistry in 1975. Professor Arne Fredga of the Royal Academy of Sciences explained his research [https://www.nobelprize.org/prizes/chemistry/1975/ceremony-speech/]:

> Professor Prelog has worked in many fields of stereochemistry, and often the problems have been connected with the geometrical shapes of the molecules and their influence on the course of the reactions. [...]
>
> Professor Prelog has also made important contributions to enzyme chemistry. He has studied enzymatic reactions on small molecules and in particular oxidation or reduction processes. The experiments may be more or less successful depending on how the enzyme and the other molecule fit together geometrically. By systematic experiments with various small molecules of well-defined shapes, it was possible to construct a "map" of the active part of the enzyme molecule. The results have recently been confirmed in a special case by Swedish scientists using x-ray methods.
>
> Professor Prelog has also with ingenuity and penetration discussed and analysed the fundamental concepts of stereochemistry, not least the conditions for chirality in large and complicated molecules.

Prelog also built up long-lasting research programs in the Kaštel/Pliva pharmaceutical company, leading to work on antibiotics from sulfa drugs to azithromycin.

Robert Pschorr (German, 1868–1930, Fig. 3.42) worked on the synthesis of complex organic molecules and is best known for Pschorr cyclization.

Rudolf Pummerer (Austrian, 1882–1973, Fig. 3.42) focused on the chemistry of sulfoxides and free radicals, and remains known for the Pummerer rearrangement.

Sergey Reformatsky (Russian but educated in Germany, 1860–1934, Fig. 3.42) studied organic synthesis and metal catalysts, and is remembered for the Reformatsky reaction.

Karl Reichenbach (German states, 1788–1869, Fig. 3.42) discovered many useful organic molecules, including phenol and paraffin.

Walter Reppe (German, 1892–1969, Fig. 3.42) was an enormously influential figure in applied organic chemistry, both in Germany and in other countries (through postwar reports on his chemical methods). His work focused on turning Germany's large natural supply of coal into acetylene, and then converting the acetylene into a vast variety of useful chemical molecules, a process that became known as Reppe chemistry.

Karl Wilhelm Rosenmund (German, 1884–1965, Fig. 3.42) received his Ph.D. under Otto Diels. His name is associated with Rosenmund reduction and the Rosenmund-von Braun reaction.

Otto Ruff (German, 1871–1939, Fig. 3.43) conducted important work in high-temperature chemistry, the chemistry of sugars, polymers, and other areas of organic chemistry. He is best known for Ruff degradation.

Traugott Sandmeyer (Swiss, 1854–1922, Fig. 3.43) was an expert at synthesizing complex organic molecules. He is still remembered for the Sandmeyer reaction and Sandmeyer synthesis.

Rudolf Schmitt (German, 1830–1898, Fig. 3.43), along with his Ph.D. advisor Adolph Kolbe, discovered the Kolbe-Schmitt reaction. He also conducted research on salicylic acid and other areas of organic chemistry.

As illustrated in Fig. 3.44, Carl Schotten (German, 1853–1910) and Eugen Baumann (German, 1846–1896) developed Schotten-Baumann reactions (1883), which are used to synthesize a wide variety of useful organic molecules.

Hermann Staudinger (German, 1881–1965, Fig. 3.43) made an enormous number of contributions in the fields of organic chemistry, polymers, and colloids. He discovered ketene molecules and the Staudinger reaction, and won the Nobel Prize in Chemistry in 1953. Professor A. Fredga, a member of the Nobel Committee for Chemistry, praised his work
[https://www.nobelprize.org/prizes/chemistry/1953/ceremony-speech/]:

> Professor Staudinger. More than thirty years ago you expressed the view that a chemical molecule can attain an almost arbitrary size and that such macromolecules are of great importance in our world. Your view was based on logical reasoning. You drew attention to the fact that what are termed high polymers are formed when for some reason or another an anticipated ring closure fails to occur. You thus submitted an argument which an organic chemist cannot ignore. Moreover, in extensive and painstaking series of studies you have provided experimental proof.

Johann Stobbe (German, 1860–1938, Fig. 3.33) is best known for developing Stobbe condensation, a step that ever since then has been widely utilized in the synthesis of organic molecules.

Adolph Strecker (German, 1822–1871), Friedrich Gustav Carl Emil Erlenmeyer, Jr. (German, 1864–1921), Fritz Arndt (German, 1885–1969), and Bernd Eistert (German, 1902–1978) developed methods to artificially synthesize amino acids, the building blocks of proteins. See Fig. 3.45.

Johannes Thiele (German, 1865–1918, Fig. 3.43) synthesized a number of novel types of organic molecules and is still known for the Thiele tube.

Bernhard Tollens (German, 1841–1918, Fig. 3.43) determined the structures of several sugar molecules and developed the Tollens reagent.

Alfred Treibs (German, 1899–1983, Fig. 3.46) founded organic geochemistry. He discovered porphyrin molecules in petroleum, proving that petroleum originated from ancient plants and animals.

Fritz Ullmann (German, 1865–1939, Fig. 3.46) worked with and married Irma Goldberg. He developed several synthetic dye molecules and is remembered for the Ullmann reaction and Ullmann condensation. He also edited the *Enzyklopädie der Technischen Chemie*, which has been updated by others since then and is still in use today.

Jacobus Henricus van 't Hoff (Dutch, 1852–1911, Fig. 3.46) made many important discoveries in the stereochemistry of organic molecules as well as in physical chemistry. He won the Nobel Prize in Chemistry in 1901. C.T. Odhner, President of the Royal Swedish Academy of Sciences, described his research [https://www.nobelprize.org/prizes/chemistry/1901/ceremony-speech/]:

> As a result of his investigations in the fields of atomic and molecular theory van 't Hoff has made the most important discoveries in theoretical chemistry since Dalton's time.
>
> With regard to atomic theory van 't Hoff, following an idea put forward by Pasteur, advanced the hypothesis that the elementary atoms have attachment points geometrically oriented in space—a hypothesis which in so far as carbon compounds are concerned led to the theory of the asymmetry of carbon atoms and to the founding of stereochemistry.
>
> Still more revolutionary were van 't Hoff's discoveries in the field of molecular theory. van 't Hoff's investigations showed that the law, which has been named after the Italian Avogadro, according to which the number of gas molecules in a given volume is the same for all gases at the same pressure and temperature, embraces not only substances in the gaseous phase but also those in solution, provided that their pressure, known as osmotic pressure, is taken into account in the same way as the gas pressure in the case of gases. He proved that gas pressure and osmotic pressure are identical, and thereby that the molecules themselves in the gaseous phase and in solutions are also identical. As a result of this the concept of the molecule in chemistry was found to be definite and universally valid to a degree hitherto undreamed-of. He also discovered how to express the state of chemical equilibrium in reactions and the electromotive force which a reaction can produce; he explained how the transition occurs between the various modifications of the elements, between hydrates of differing water contents, how double salts are formed, etc.
>
> By applying these simple principles, which were originally borrowed from mechanics and thermodynamics, van 't Hoff became one of the founders of chemical dynamics.

Jacob Volhard (1834–1910, Fig. 3.46) and his student Hugo Erdmann discovered the Volhard-Erdmann cyclization reaction. Volhard also trained several other students who went on to make great discoveries, most notably Hermann Staudinger.

Otto Wallach (German, 1847–1931, Fig. 3.46) focused on organic molecules that are alicyclic, or both aliphatic and cyclic. His name is associated with the Wallach rearrangement, Wallach degradation, and Wallach's rule. He won the Nobel Prize in Chemistry 1910, and Professor O. Montelius, President of the Royal Swedish Academy of Sciences, praised his research [https://www.nobelprize.org/prizes/chemistry/1910/ceremony-speech/]:

> Through this pioneering work Wallach opened up a new field for research, which could be investigated further with good hope of success. And it is true that this field was immediately tackled by a great number of research scientists in various countries. Organic chemistry, during the decade that followed, was characterized by the study of the so-called alicyclic compounds, among which the terpenes and the closely related types of camphor with their derivatives played the most important part. Wallach himself, by overcoming considerable difficulties with admirable success and though perseverance, made continuous progress in the field opened up by himself. An extraordinarily large number of compounds were prepared by him and he also determined their structure. Apart from the terpenes proper, he also investigated and scientifically characterized various previously known or newly discovered natural products, such as alcohols, ketones, sesquiterpenes and polyterpenes belonging to the terpene series, which in part are also of great significance in biological and technical respects. For this reason the alicyclic series has, since the middle of the eighties, assumed such size and importance as to make it the equal of the other three main series within organic chemistry. Wallach contributed more towards this than any other research scientist.
>
> Wallach's research activity did not only decisively influence theoretic chemistry, but also chemical industry, namely that branch of the industry which processes essential oils.

Conrad Willgerodt (German, 1841–1930, Fig. 3.46) studied the chemistry of ketones, discovered iodosobenzene, and is still remembered for the Willgerodt reaction.

Johannes Wislicenus (German, 1835–1902, Fig. 3.47) made a number of important discoveries regarding the stereochemistry of organic molecules.

Georg Wittig (German, 1897–1987, Fig. 3.47) is famous for the Wittig reaction and the Wittig rearrangement. He developed a new method to produce alkenes, or hydrocarbon molecules containing double bonds, for which he won the Nobel Prize in Chemistry in 1979. Professor Bengt Lindberg of the Royal Academy of Sciences explained the importance of Wittig's work [https://www.nobelprize.org/prizes/chemistry/1979/ceremony-speech/]:

> Georg Wittig has provided many significant contributions in organic chemistry. The most important of these is the discovery of the synthetic method which bears his name, the Wittig reaction. In this, phosphorus ylides, a type of compound which he discovered, are allowed to react with carbonyl compounds. An exchange of groups takes place and the result is a compound in which two carbon atoms have been joined by a double bond. Since many natural products with biological activity contain such bonds, this elegant

> method has found wide-spread use, for example in the industrial synthesis of vitamin A.

Alfred Wohl (German, 1863–1933, Fig. 3.47) worked in sugar chemistry, developed novel catalysts, and is remembered for Wohl degradation, the Wohl-Aue reaction, and the Wohl-Ziegler reaction.

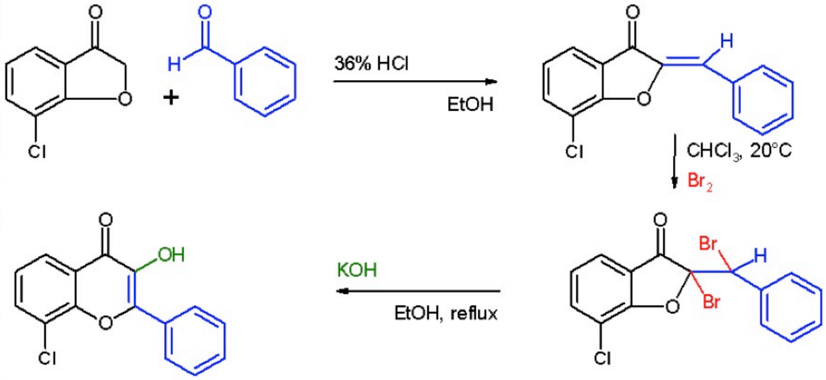
Ludwig Wolff (German, 1857–1919, Fig. 3.47) received his Ph.D. under Rudolph Fittig and conducted important research in organic chemistry; his name is now associated with the Wolff rearrangement and the Wolff reduction.

Charles Adolphe Wurtz (Franco-German, studied in Germany, 1817–1884, Fig. 3.47) discovered the aldol reaction, what is now called the Wurtz reaction, ethylamine, and ethylene glycol.

Ernst Carl Theodor Zincke (German, 1843–1928, Fig. 3.47) received his Ph.D. under Friedrich Wöhler, and in turn was the doctoral advisor of Otto Hahn. He made many organic chemistry discoveries for which he is remembered, such as Zincke reaction, Zincke nitration, Zincke-Suhl reaction, etc.

Karl von Auwers (1863–1939)

Auwers synthesis (1908)



Eugen Bamberger (1857–1932)

Bamberger rearrangement (1894)

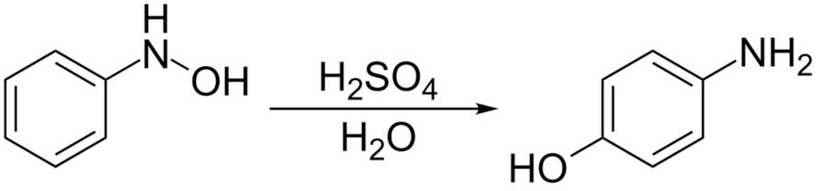
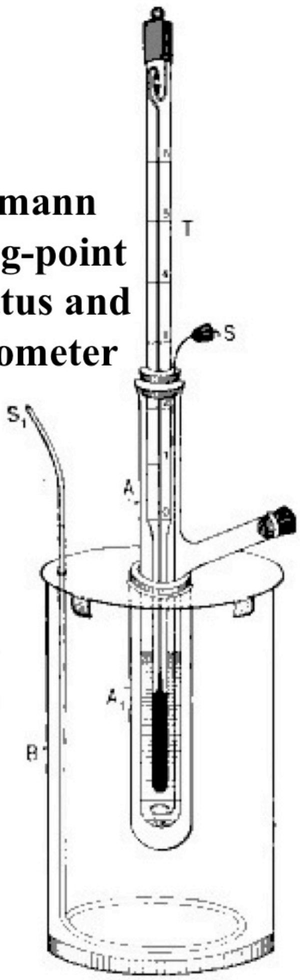


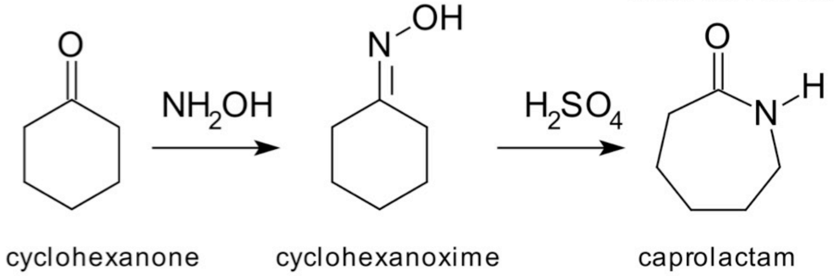
Figure 3.29: Karl von Auwers developed Auwers synthesis in 1908, and Eugen Bamberger discovered the Bamberger rearrangement in 1894.

Ernst Beckmann (1853–1923)

Beckmann freezing-point apparatus and thermometer



Beckmann rearrangement (1886) is useful for making Nylon and several drugs



Friedrich Beilstein (1838–1906)

***Beilstein's Handbook of Organic Chemistry* (1881–)**

BEILSTEINS HANDBUCH
DER ORGANISCHEN CHEMIE

VIERTE AUFLAGE
DIE LITERATUR BIS 1. JANUAR 1910 UMFASSEND

HERAUSGEGEBEN VON DER
DEUTSCHEN CHEMISCHEN GESELLSCHAFT
BEARBEITET VON
BERNHARD PRAGER UND PAUL JACOBSON
UNTER STÄNDIGER MITWIRKUNG VON
PAUL SCHMIDT UND DORA STERN

FÜNFTER BAND
CYCLISCHE KOHLENWASSERSTOFFE

BERLIN
VERLAG VON JULIUS SPRINGER
1922

Figure 3.30: Ernst Beckmann developed the Beckmann rearrangement (1886), which later proved extremely useful for making Nylon and several drugs. He also invented the Beckmann freezing-point apparatus and thermometer. Friedrich Beilstein created the encyclopedic *Beilstein's Handbook of Organic Chemistry*.

Ernst Bergmann (1903–1975) Organic & fluorine chemistry, Israeli nuclear program

Julius von Braun (1875–1939) von Braun reaction, Rosenmund-von Braun reaction

Julius Bredt (1855–1937) Bredt's rule, Bredt distributor, structure of camphor

Hans Theodor Bucherer (1869–1949) Bucherer reaction, Bucherer carbazole synthesis, Bucherer-Bergs reaction

George Büchi (1921–1998) Photochemical organic reactions

Ernst Büchner (1850–1924) Büchner flask, Büchner funnel

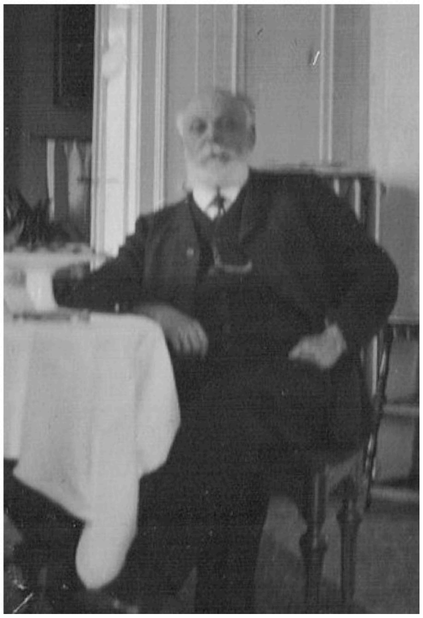


Figure 3.31: Other creators who made important contributions to organic chemistry included Ernst Bergmann, Julius von Braun, Julius Bredt, Hans Theodor Bucherer, George Büchi, and Ernst Büchner.

Robert Bunsen
(1811–1899)
Organic arsenides,
organic photochemistry

Rudolf Criegee
(1902–1975)
Criegee rearrangement,
Criegee intermediate

Theodor Curtius
(1857–1928)
Hydrazine, Curtius
rearrangement

André Dreiding
(1919–2013)
Organic
molecular
structures

Richard August Carl
Emil Erlenmeyer
(1825–1909)
Erlenmeyer rule,
Erlenmeyer flask

Hermann von Fehling
(1812–1885)
Fehling's solution
for detecting
sugars

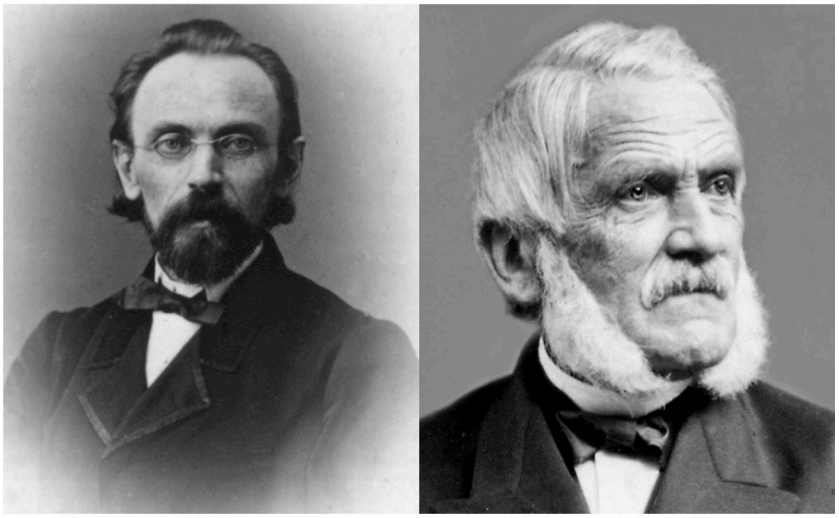


Figure 3.32: Other creators who made important contributions to organic chemistry included Robert Bunsen, Rudolf Criegee, Theodor Curtius, André Dreiding, Richard August Carl Emil Erlenmeyer, and Hermann von Fehling.

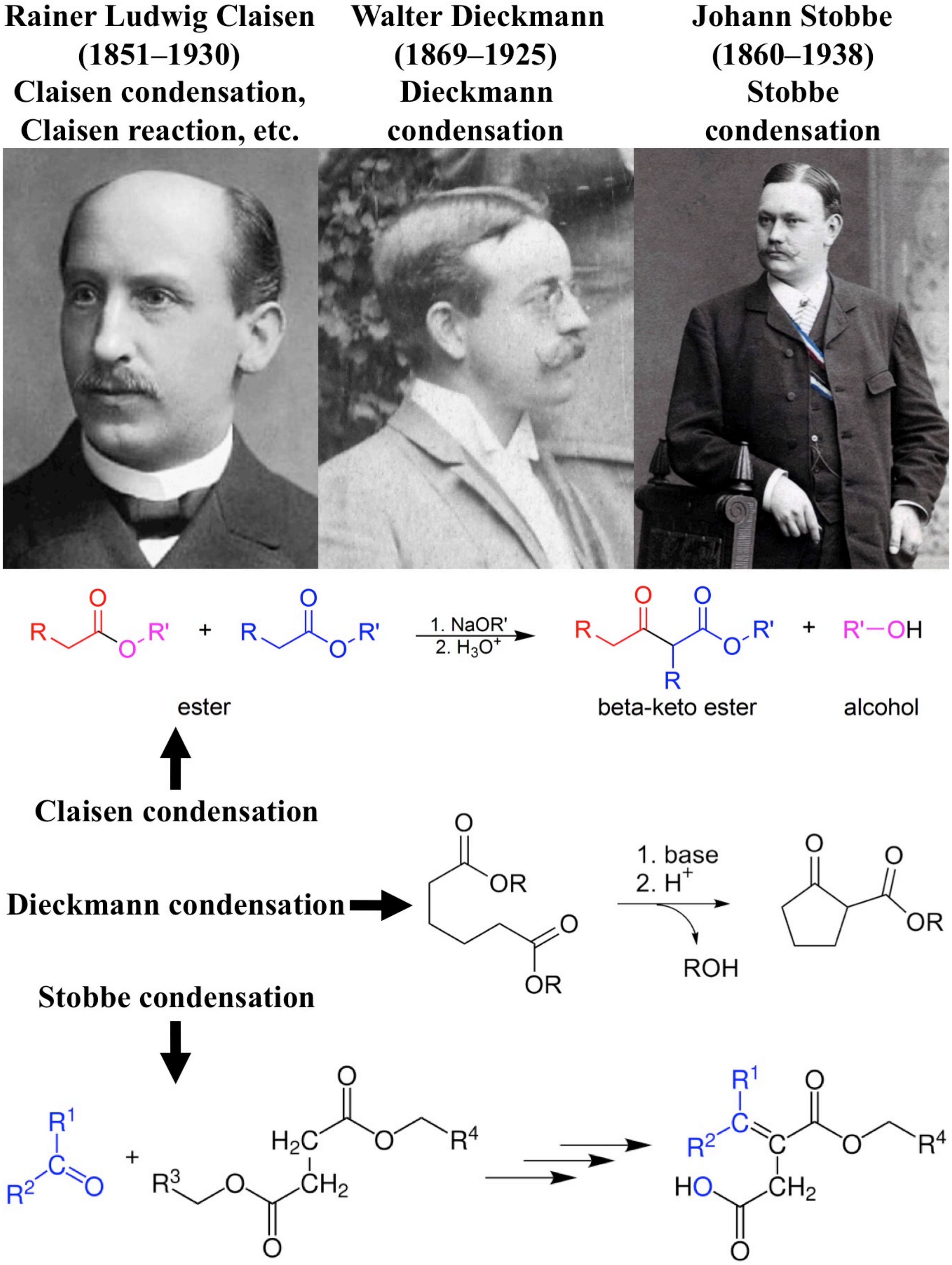


Figure 3.33: Rainer Ludwig Claisen, Walter Dieckmann, and Johann Stobbe developed condensation reactions that have been widely used to synthesize organic molecules ever since.

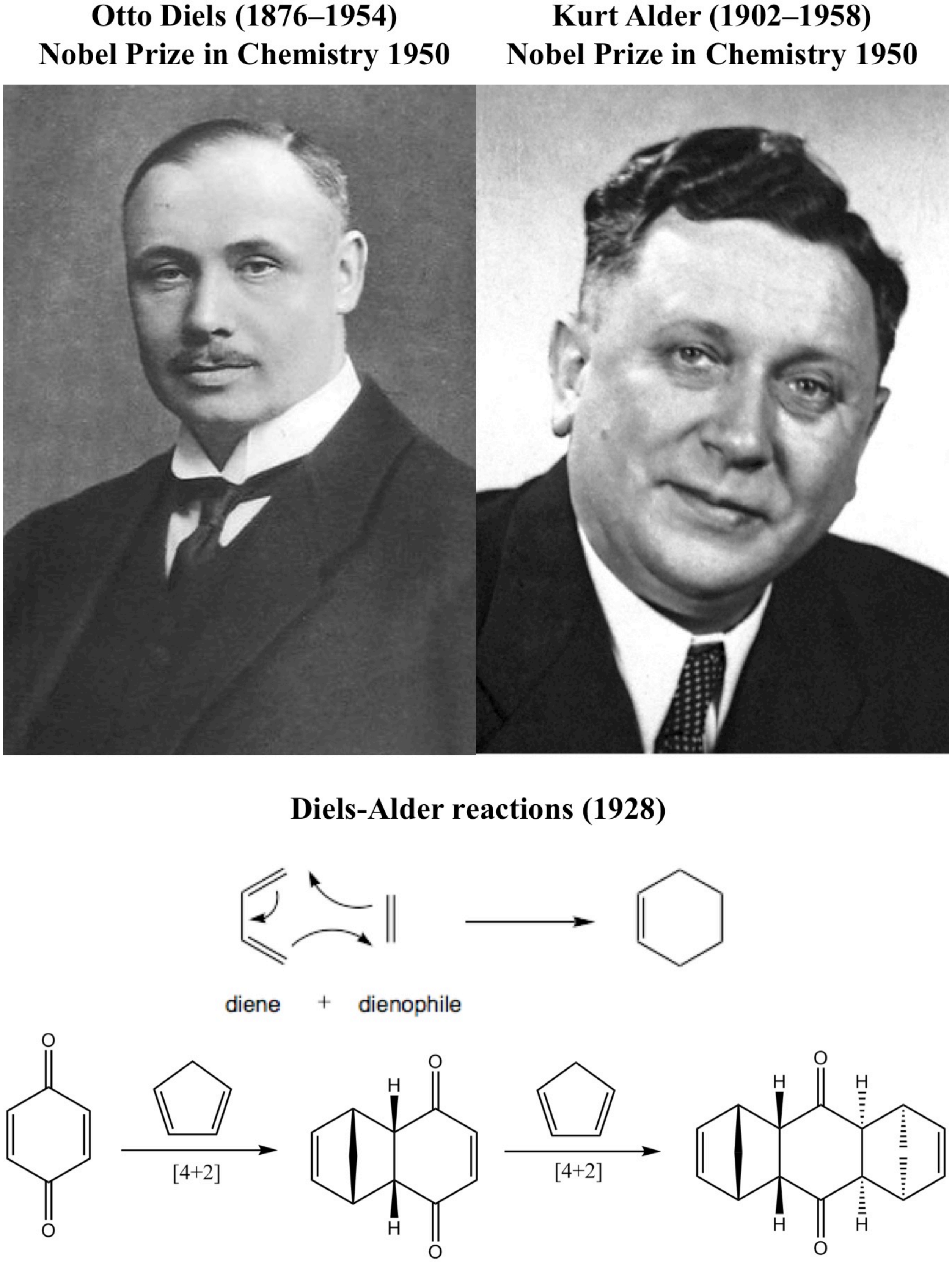
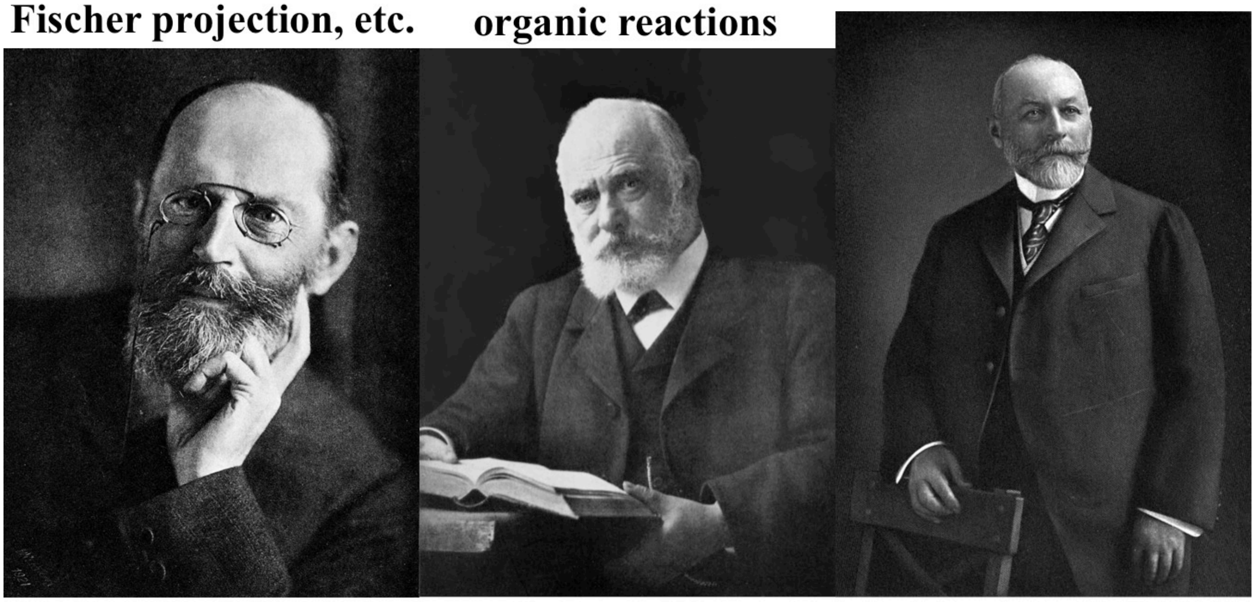


Figure 3.34: Otto Diels and Kurt Alder developed Diels-Alder reactions (1928), which are very useful for producing polymers and other complex organic molecules. They both won the Nobel Prize in Chemistry in 1950.

Hermann Emil Fischer (1852–1919) Fischer esterification, Fischer projection, etc.

Wilhelm Rudolph Fittig (1835–1910) Many types of organic reactions

Hermann Frasch (1851–1914) Oil refining



Karl Fries (1875–1962) Fries rearrangement

Ludwig Gattermann (1860–1920) Gattermann reaction, etc.

Carl Glaser (1841–1935) Glaser coupling

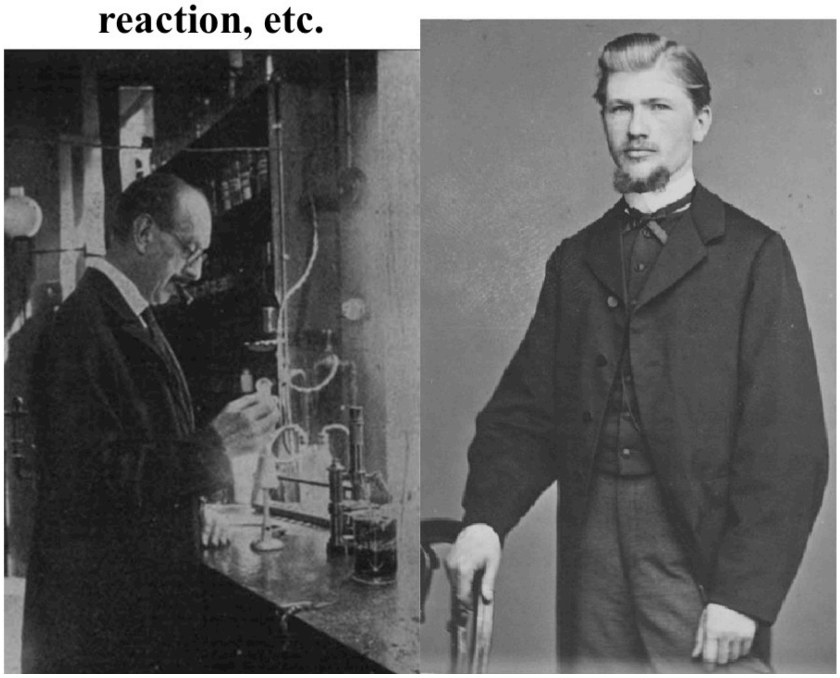
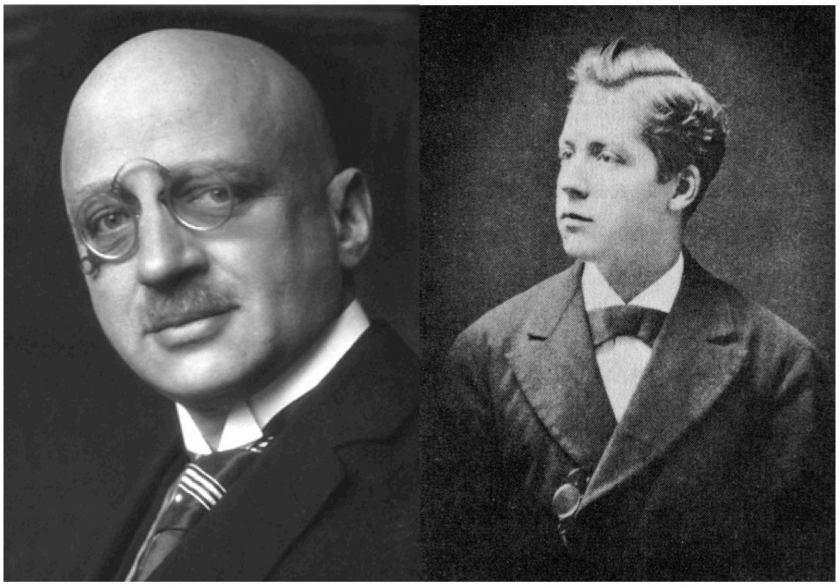


Figure 3.35: Other creators who made important contributions to organic chemistry included Hermann Emil Fischer, Wilhelm Rudolph Fittig, Hermann Frasch, Karl Fries, Ludwig Gattermann, and Carl Glaser.

Irma Goldberg
(1871–<1939)
Goldberg
amidation
reaction

Fritz Haber
(1868–1934)
Carbon-carbon and
carbon-hydrogen
bond strength, etc.

Arthur
Hantzsch
(1857–1935)
Hantzsch
synthesis



Kurt Hoesch
(1882–1932)
Hoesch
reaction

Erich Hückel
(1896–1980)
Hückel Molecular
Orbital Theory, etc.

Rolf Huisgen
(1920–)
Huisgen
reaction

Figure 3.36: Other creators who made important contributions to organic chemistry included Irma Goldberg, Fritz Haber, Arthur Hantzsch, Kurt Hoesch, Erich Hückel, and Rolf Huisgen.

Cläre Hunsdiecker
(1903–1995)
Hunsdiecker
reaction

Heinz Hunsdiecker
(1904–1981)
Hunsdiecker
reaction

Oskar Georg
Friedrich Jacobsen
(1840–1889)
Jacobsen
rearrangement

Karl Kastner
(1783–1857)
Helped establish
academic chemistry,
taught von Liebig

Heinrich Kiliani
(1855–1945)
Kiliani-Fischer
synthesis
of sugars

Emil Knoevenagel
(1865–1921)
Knoevenagel
condensation

Figure 3.37: Other creators who made important contributions to organic chemistry included Cläre Hunsdiecker, Heinz Hunsdiecker, Oskar Georg Friedrich Jacobsen, Karl Kastner, and Heinrich Kiliani, and Emil Knoevenagel.

August Kekulé
(1829–1896)

HISTORISCHE STÄTTE DER CHEMIE

DIESES GEBÄUDE WURDE ZWISCHEN 1864 UND 1868 ALS WELTWEIT GRÖSSTES CHEMISCHES INSTITUT SEINER ZEIT ERRICHTET. HIER LEBTE, FORSCHTE UND LEHRTE VON 1867 AN

FRIEDRICH AUGUST
KEKULÉ VON STRADONITZ
(1829 - 1896)

DURCH IHN STIEG DIESES INSTITUT ZU EINEM CHEMIESTANDORT VON WELTRANG AUF. KEKULÉS FORSCHUNGEN ZUM BENZOLMOLEKÜL SCHUFEN DIE GRUNDLAGEN FÜR DIE MODERNE STRUKTURTHEORIE IN DER ORGANISCHEN CHEMIE SOWIE FÜR DIE ENTWICKLUNG DER CHEMIE DER SO VIELFÄLTIG NUTZBAREN AROMATISCHEN VERBINDUNGEN. HIER ENTDECKTE KEKULÉ DIE AZOKUPPLUNG, DIE MASSGEBLICH ZUR ENTWICKLUNG DER FARBSTOFFINDUSTRIE BEITRUG. ALS BEGNADETER HOCHSCHULLEHRER ZOG ER VIELE JUNGE WISSENSCHAFTLER AN, DARUNTER DIE SPÄTEREN NOBELPREISTRÄGER ADOLF VON BAEYER, OTTO WALLACH UND JACOBUS HENRICUS VAN'T HOFF.

ENTHÜLLT AM 9. MAI 2014
IM 185. GEBURTSJAHR VON FRIEDRICH AUGUST KEKULÉ

GDCh
GESELLSCHAFT DEUTSCHER CHEMIKER

Chemical bonds and structure of
benzene (1865) and other organic molecules

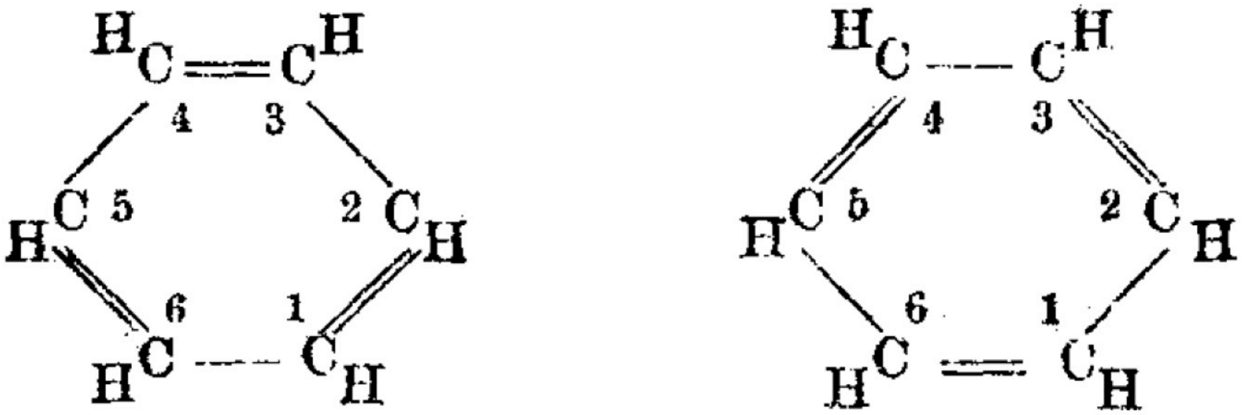
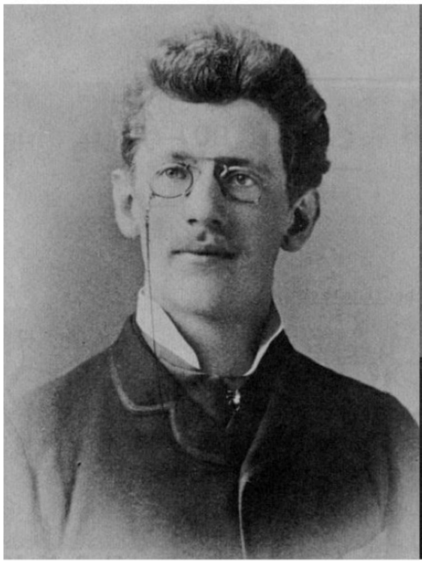


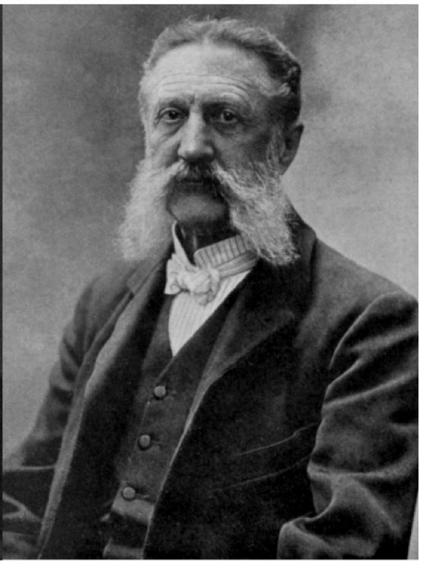
Figure 3.38: August Kekulé figured out the chemical bonds and structure of benzene (1865) and other organic molecules.

Ludwig Knorr
(1859–1921)
Knorr synthesis,
Phenazone



Hermann Kolbe
(1818–1884)
Kolbe electrolysis,
Kolbe nitrile synthesis,
Kolbe-Schmitt reaction

Wilhelm Körner
(1839–1925)
Aromatic
compounds



Albert Ladenburg
(1842–1911)
Synthesized alkaloids,
purified scopolamine

Carl Mannich
(1877–1947)
Mannich reaction

Hans Meerwein
(1879–1965)
Meerwein arylation,
Meerwein's salt, etc.

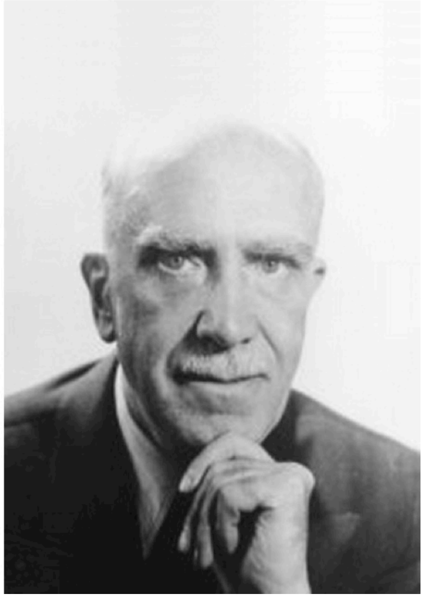


Figure 3.39: Other creators who made important contributions to organic chemistry included Ludwig Knorr, Hermann Kolbe, Wilhelm Körner, Albert Ladenburg, Carl Mannich, and Hans Meerwein.

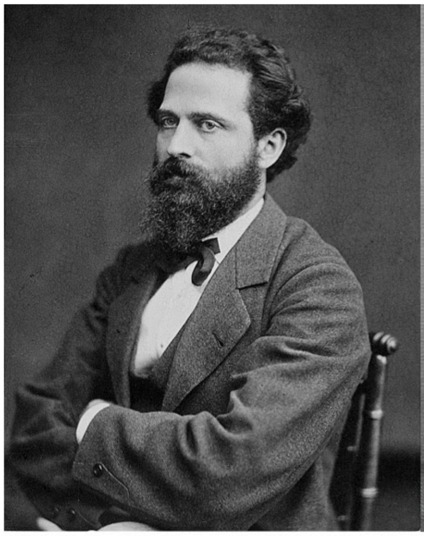
Jakob Meisenheimer
(1876–1934)
Meisenheimer complex

Julius Lothar Meyer
(1830–1895)
Benzene
structure, etc.

Karl Meyer
(1899–1990)
Polysaccharides

Kurt Hans Meyer
(1883–1952)
Organic reactions

Viktor Meyer
(1848–1897)
Thiophene, etc.



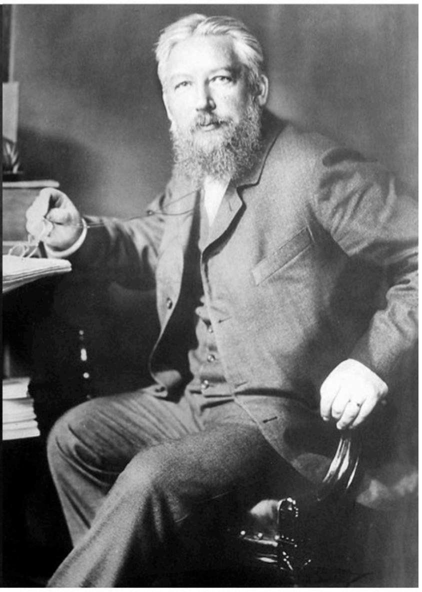
Eilhard Mitscherlich
(1794–1863)
Benzene derivatives

Figure 3.40: Other creators who made important contributions to organic chemistry included Jakob Meisenheimer, Julius Lothar Meyer, Karl Meyer, Kurt Hans Meyer, Viktor Meyer, and Eilhard Mitscherlich.

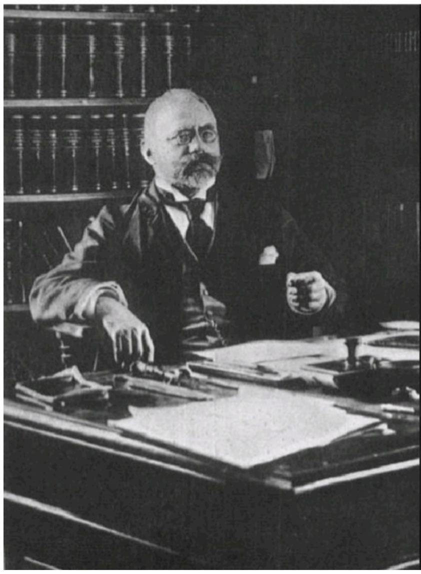
**Costin D.
Nenitzescu
(1902–1970)
Nenitzescu synthesis**

**George Olah
(1927–2017)
Carbocations,
Nobel Prize in
Chemistry 1994**

**Wilhelm Ostwald
(1853–1932)
Physical chemistry,
catalysis, Nobel Prize
in Chemistry 1909**



**Hans von Pechmann
(1850–1902) Pechmann
condensation,
Pechmann pyrazole
synthesis, etc.**



**Fritz Pregl
(1869–1930)
Quantitative organic
microanalysis, Nobel
Prize in Chemistry 1923**

**Vladimir Prelog
(1906–1998)
Stereochemistry,
Nobel Prize in
Chemistry 1975**

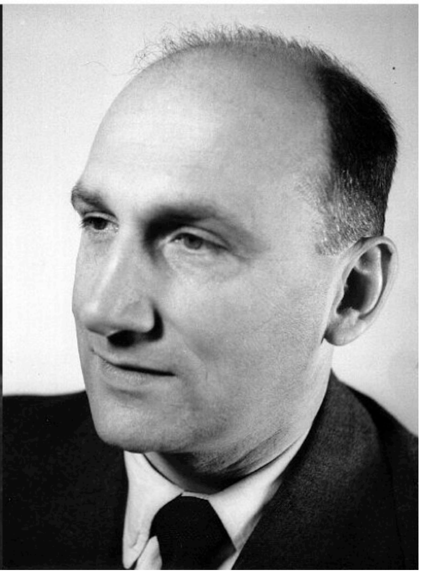


Figure 3.41: Other creators who made important contributions to organic chemistry included Costin D. Nenitzescu, George Olah, Wilhelm Ostwald, Hans von Pechmann, Fritz Pregl, and Vladimir Prelog.

Robert Pschorr
(1868–1930)
Pschorr cyclization

Rudolf
Pummerer
(1882–1973)
Pummerer
rearrangement,
free radicals

Sergey Reformatsky
(Russian but educated
in Germany, 1860–1934)
Reformatsky reaction

Karl Reichenbach
(1788–1869)
Discovered
many useful
organic molecules

Walter Reppe
(1892–1969)
Reppe chemistry
involving acetylene

Karl Wilhelm
Rosenmund
(1884–1965)
Rosenmund reduction,
Rosenmund-von
Braun reaction

Figure 3.42: Other creators who made important contributions to organic chemistry included Robert Pschorr, Rudolf Pummerer, Sergey Reformatsky, Karl Reichenbach, Walter Reppe, and Karl Wilhelm Rosenmund.

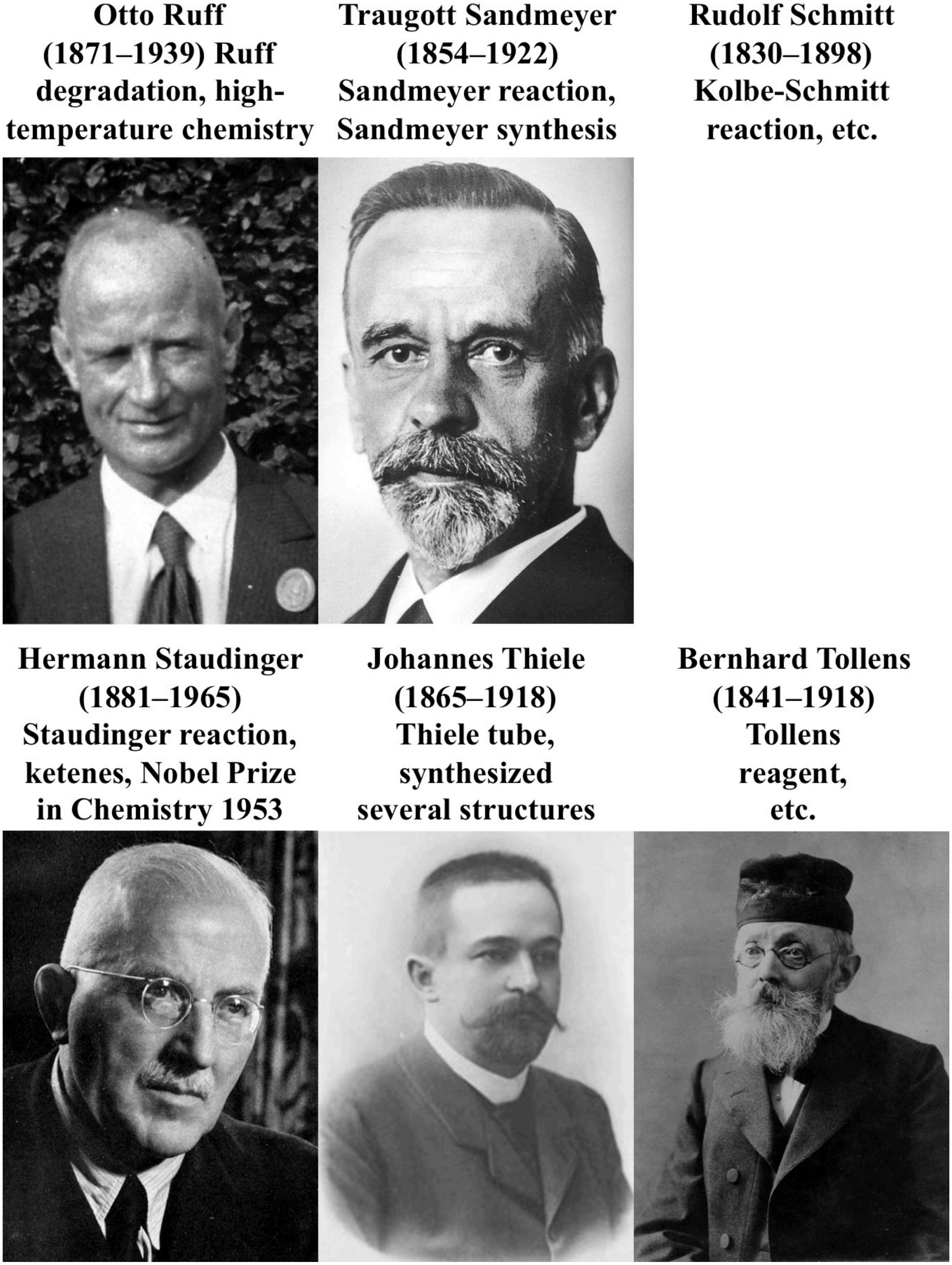


Figure 3.43: Other creators who made important contributions to organic chemistry included Otto Ruff, Traugott Sandmeyer, Rudolf Schmitt, Hermann Staudinger, Johannes Thiele, and Bernhard Tollens.

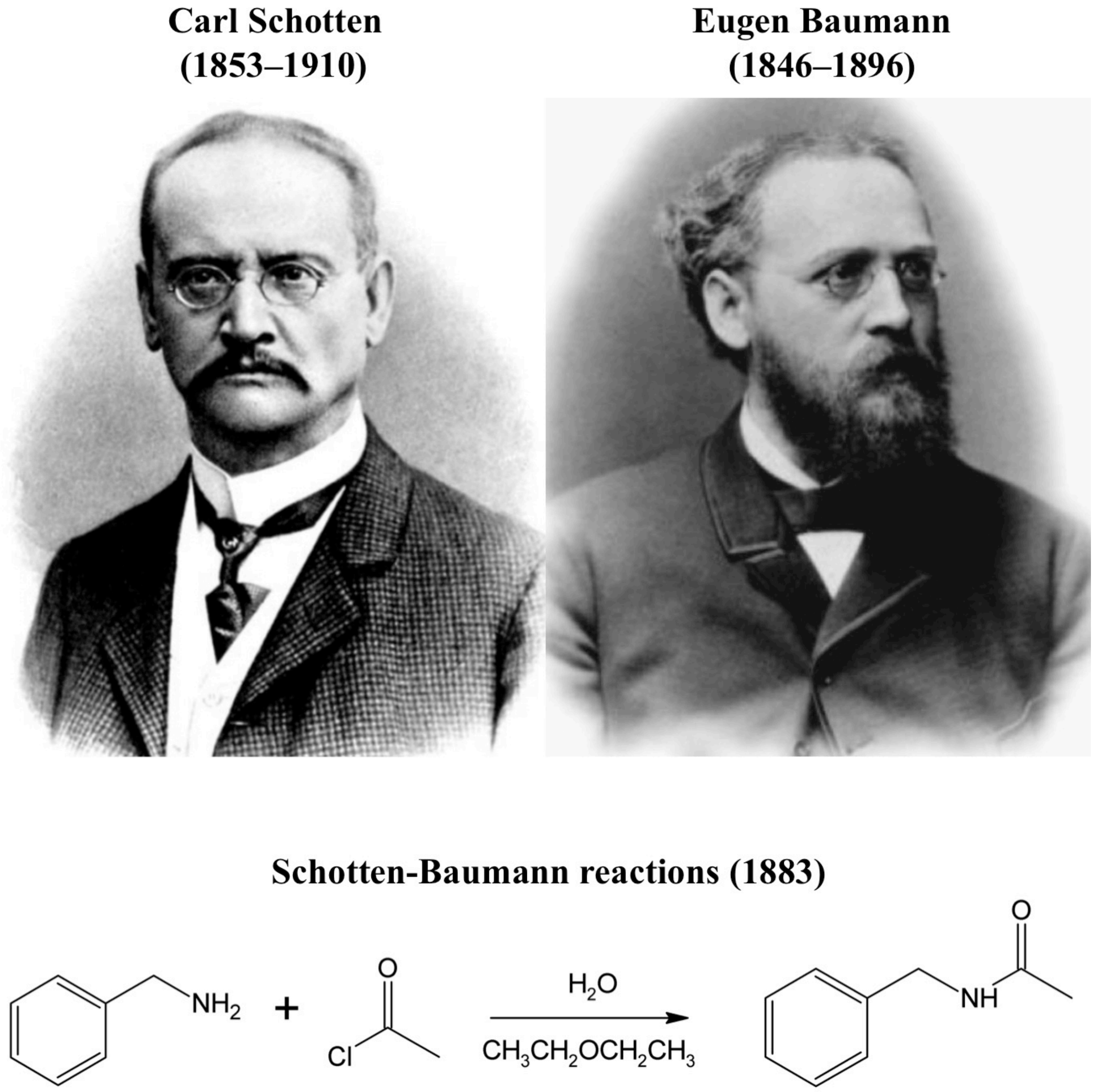


Figure 3.44: Carl Schotten and Eugen Baumann developed Schotten-Baumann reactions (1883), which are used to synthesize a wide variety of useful organic molecules.

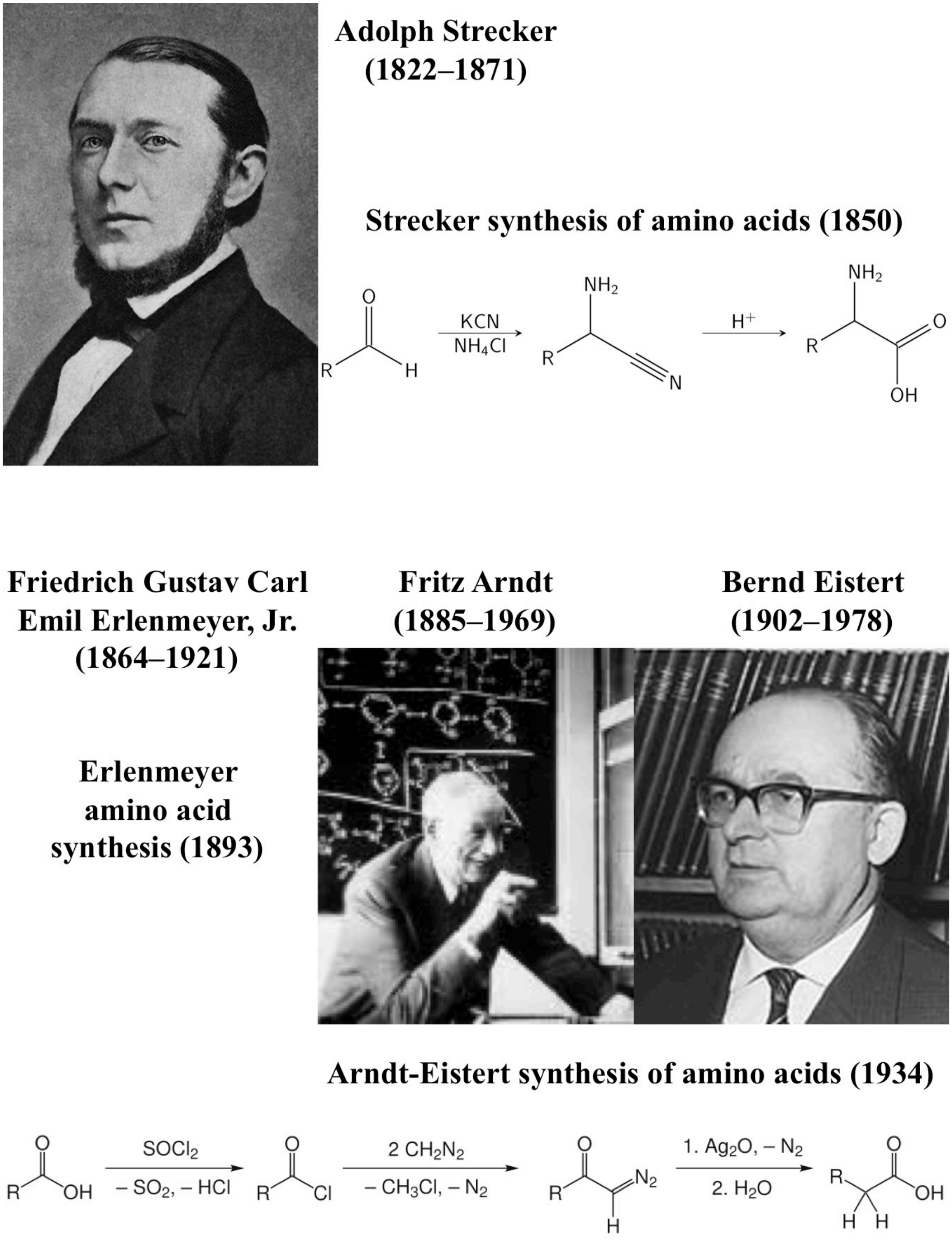
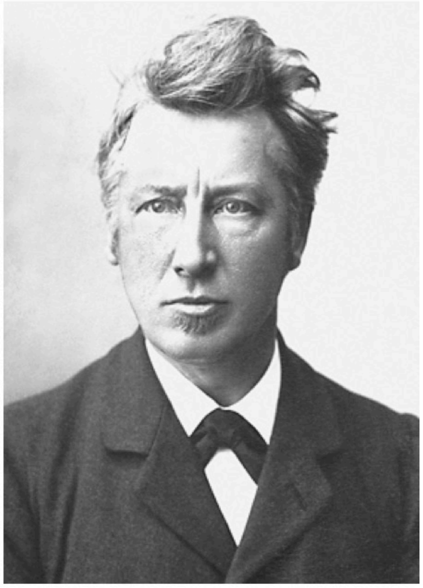


Figure 3.45: Adolph Strecker, Friedrich Gustav Carl Emil Erlenmeyer, Jr., Fritz Arndt, and Bernd Eistert developed methods to artificially synthesize amino acids, the building blocks of proteins.

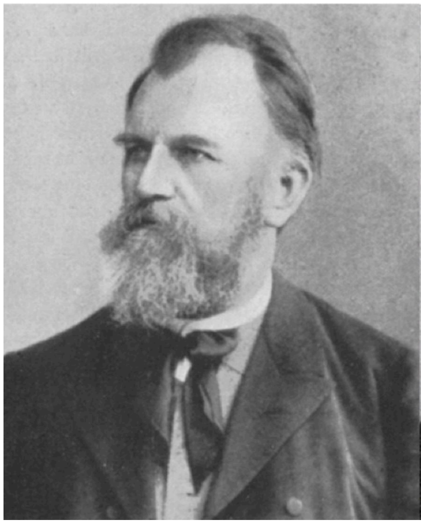
Alfred Treibs
(1899–1983)
Founded
organic
geochemistry

Fritz Ullmann
(1865–1939)
Ullmann reaction,
Ullmann condensation,
Enzyklopädie der
Technischen Chemie

Jacobus Hendricus
van't Hoff (1852–1911)
Physical chemistry,
stereochemistry, Nobel
Prize in Chemistry 1901



Jacob Volhard
(1834–1910)
Volhard-
Erdmann
cyclization
reaction



Otto Wallach
(1847–1931)
Wallach rearrangement,
Wallach degradation,
Wallach's rule, Nobel
Prize in Chemistry 1910

Conrad Willgerodt
(1841–1930)
Willgerodt
reaction

Figure 3.46: Other creators who made important contributions to organic chemistry included Alfred Treibs, Fritz Ullmann, Jacobus Henricus van't Hoff, Jacob Volhard, Otto Wallach, and Conrad Willgerodt.

Johannes Wislicenus (1835–1902)
Stereochemistry of organic molecules

Georg Wittig (1897–1987)
Wittig reaction, Wittig rearrangement, Nobel Prize in Chemistry 1979

Alfred Wohl (1863–1933)
Wohl degradation, Wohl-Aue reaction, Wohl-Ziegler reaction

Ludwig Wolff (1857–1919)
Wolff rearrangement, Wolff reduction

Adolphe Wurtz (1817–1884)
Aldol reaction, Wurtz reaction, ethylamine, ethylene glycol

Ernst Carl Theodor Zincke (1843–1928)
Zincke reaction, Zincke nitration, Zincke-Suhl reaction

Figure 3.47: Other creators who made important contributions to organic chemistry included Johannes Wislicenus, Georg Wittig, Alfred Wohl, Ludwig Wolff, Adolphe Wurtz, and Ernst Carl Theodor Zincke.

3.2.3 Organometallic Chemistry

German-speaking scientists made many important contributions to organometallic chemistry, the study of carbon-rich organic molecules bound to metal atoms.[4] Organometallic compounds are especially useful in catalyzing reactions for the large-scale production of many industrial chemical products. Knowledge about them is also useful for understanding the natural catalytic properties of many enzymes.

Ludwig Mond (German, 1839–1909, Fig. 3.48) founded the field of organometallic chemistry and was one of the pioneers of industrial chemistry. He discovered metal carbonyls such as nickel tetracarbonyl (1890) and used his discovery to make a fortune purifying nickel in the United Kingdom. He also ran an industrial research program that made several other important chemical discoveries. Oxford University's *Biographical Dictionary of Scientists* summarized some of his research history [Porter 1994, pp. 492–493]:

> He studied chemistry at Marburg (under Adolf Wilhelm Hermann Kolbe) and Heidelberg (under Robert Bunsen) [...]
>
> In 1879, Mond became interested in the production of ammonia, an intermediate in the Solvay process which was increasingly being used as an artificial fertilizer. One outcome was the development of the Mond producer gas process, in which carbon monoxide and hydrogen are produced by alternately passing air and steam over heated coal or coke (and the hydrogen used to convert nitrogen into ammonia). [...] An interesting extension of this work was the attempt, with the assistance of K. Langer, to turn the energy of the fuel directly into electrical energy. This early fuel cell, which used porous plates moistened with sulphuric acid, was not developed further at that time. [...]
>
> One unexpected result of the producer gas process came from Mond's observation that nickel is corroded by gases containing carbon monoxide. This led, in 1889, to the discovery of nickel carbonyl, $Ni(CO)_4$, one of the first organometallic compounds. After two years' work, with Langer and Quincke, he had developed a new extraction process for nickel.

Johann (John) Ulric Nef (Swiss, 1862–1915, Fig. 3.48) received his Ph.D. under Adolf von Baeyer at the University of Munich, then spent his career in the United States. He studied carbene molecules, discovered Nef synthesis and the Nef reaction, and applied those methods to organic compounds containing metal ions. The American Council of Learned Societies summarized some of his other contributions to organic chemistry [ACLS 2000, pp. 636–637]:

> A great experimentalist and pioneer in theoretical organic chemistry, whose theoretical work clearly contains the germs of the present concepts of free radicals, transition states, and polymerization. Topics studied included the apparently bivalent carbon compounds and their dissociation, and the action of alkali and alkaline oxidizing agents on the sugars.

---

[4] Abelshauser et al. 2004; Brock 1993; Bugge 1955; Coffey 2008; Deichmann 2001; Drummer and Zwilling 2007; Engels et al. 1989; Farber 1961; Haber 1958, 1971; Ihde 1984; Johnson 1990; Kahlert 2002; Lesch 2000; Maier 2015; Marsch 1994a; Neufeldt 2003; Partington 1935, 1957, 1964; Peppas 2013; Rosner 2004; Sasuly 1947; Schwenk 2000; Soukup 2007; Teltschik 1992; Ungewitter 1938; Welsch 1981; Werner 2017.

Wilhelm Schlenk (German, 1879–1943, Fig. 3.48) discovered organolithium compounds and studied organomagnesium compounds. He remains known for the Schlenk equilibrum, the Schlenk flask, and the Schlenk line.

Franz Hein (German, 1892–1976, Fig. 3.48) focused on organometallic chemistry for his whole career, studying organic compounds containing bismuth, chromium, magnesium, and other metal ions. *ABC Geschichte der Chemie* succinctly listed some of Hein's scientific accomplishments [Engels et al. 1989, p. 204]:

> Umfangreiche Arbeiten auf dem Gebiet der Organometall-Komplexchemie. Entdeckung einer Klasse chromiumorg. Verbindungen (1919); Arbeiten über Metallalkyle (darunter Quecksilberalkyle), Chromium(III)-dihalogen-alkoholate, Organometall-Eisentetracarbonyle, Komplexe des Chromiums mit 2,2'-Dipyridyl; Chromiumphenylverbindungen; Maskierung von Metallionen durch Komplexbildung; Bestimmungsmethode für Wasserstoff mittels $AgMnO_4$.

> Extensive work in the field of organometallic complex chemistry. Discovery of a class of chromium-organic compounds (1919); work on metal alkyls (including mercury alkyls), chromium(III) dihaloalcohols, organometallic iron tetracarbonyls, complexes of chromium with 2,2'-dipyridyl; chromium phenyl compounds; masking of metal ions by complexation; determination method for hydrogen using $AgMnO_4$.

Walter Otto Hieber (German, 1895–1976, Fig. 3.48) made a variety of important discoveries in organometallic chemistry, including organic molecules containing iron, manganese, osmium, rhenium, and other metals. His name remains attached to the Hieber base reaction. He was the doctoral adviser of Ernst Otto Fischer and Erwin Weiss (see below).

Karl Ziegler (German, 1898–1973, Fig. 3.49) won the Nobel Prize in Chemistry in 1963 for his work on organometallic chemistry and its application to polymer production. Professor A. Fredga of the Nobel Committee for Chemistry praised Ziegler's innovations in that area [https://www.nobelprize.org/prizes/chemistry/1963/ceremony-speech/]:

> Professor Ziegler has found entirely new methods of polymerization. Studying organometallic compounds, he discovered that organoaluminium compounds, which are easy to prepare, are particularly suitable for work on the industrial scale. Peculiar electrical forces operate around an aluminium-carbon bond in a hydrocarbon chain: reactive molecules are drawn in and sandwiched between the carbon atom and the aluminium atom, thus increasing the length of the chain. All this happens much more quietly than in free-radical reactions. When the chain is long enough, we detach the aluminium and thus stop the further growth of the molecule. The combination of aluminium compounds with other metallic compounds gives Ziegler catalysts. These can be used to control polymerizations and to obtain molecular chains of the required length. However, many systematic experiments—and indeed some accidental findings—were necessary to reach this stage. Ziegler catalysts, now widely used, have simplified and rationalized polymerization processes, and have given us new and better synthetic materials.

Similarly, Ernst Otto Fischer (German, 1918–2007, Fig. 3.49) won the Nobel Prize in Chemistry in 1973 for his research on organometallic chemistry (along with Geoffrey Wilkinson). Fischer studied ferrocene, created cobaltocene in 1953, and synthesized bis(benzene) chromium together with his student Walter Hafner in 1955. Professor Ingvar Lindqvist of the Royal Academy of Sciences explained Fischer's discoveries [https://www.nobelprize.org/prizes/chemistry/1973/ceremony-speech/]:

> It seems to be appropriate to put forward these views when speaking of this year's Nobel laureates in chemistry, professors Fischer and Wilkinson. The facts were available for all the chemists of the world to see, but the right interpretation was lacking. Once the correct hypothesis was arrived at by fantasy or intuition, it readily lent itself to simple processes of logical deduction. I am of course referring to the way in which they together with the former Nobel laureate Woodward reached the conclusion that certain compounds could not be understood without the introduction of a new concept, namely that of the sandwich compound. This expression applies to the structure of these compounds, which can be thought of as a metal atom—the filling—sandwiched between two flat molecules. Now the science of chemistry involves, of course, more than flashes of visionary inspiration, and both Fischer and Wilkinson did not hesitate to confirm and develop the concept of the sandwich compound by an intensive experimental effort. This they did by the successful synthesis of a large number of compounds which were analogous to the initially discovered ferrocene (named by Woodward in analogy with benzene), but with other metals than iron, and with other flat molecules than the cyclopentadienyl group found in ferrocene. Amongst other things, Fischer managed to surprise chemists by preparing a sandwich of chromium between two benzene molecules. The culinary exploits were pursued further with the progress to open sandwiches, having a flat molecule on one side of the metal atom, and with only small molecules such as carbonyl, methyl or ethyl groups on the other side. [...]
>
> It is a fact that every discovery within the realm of fundamental chemical research has potential applications. The very circumstance of the stability of sandwich compounds has led to involved theoretical discussions, which have also played their part in important advances in theoretical and applied research on catalysis.

Walter Hafner (German, 1927–2004, Fig. 3.49) received his Ph.D. under Ernst Otto Fischer. He and Fischer synthesized bis(benzene) chromium in 1955. Later Hafner harnessed palladium as a catalyst in organometallic reactions for industrial chemical production.

Erwin Weiss (German, 1926–2019, Fig. 3.49) did his Ph.D. studies under Walter Hieber and analyzed the structure of bis(benzene) chromium soon after it was synthesized by Ernst Otto Fischer and Walter Hafner. He spent the rest of his career investigating organic molecules containing lithium, sodium, potassium, rubidium, caesium, magnesium, copper, and other metal ions.

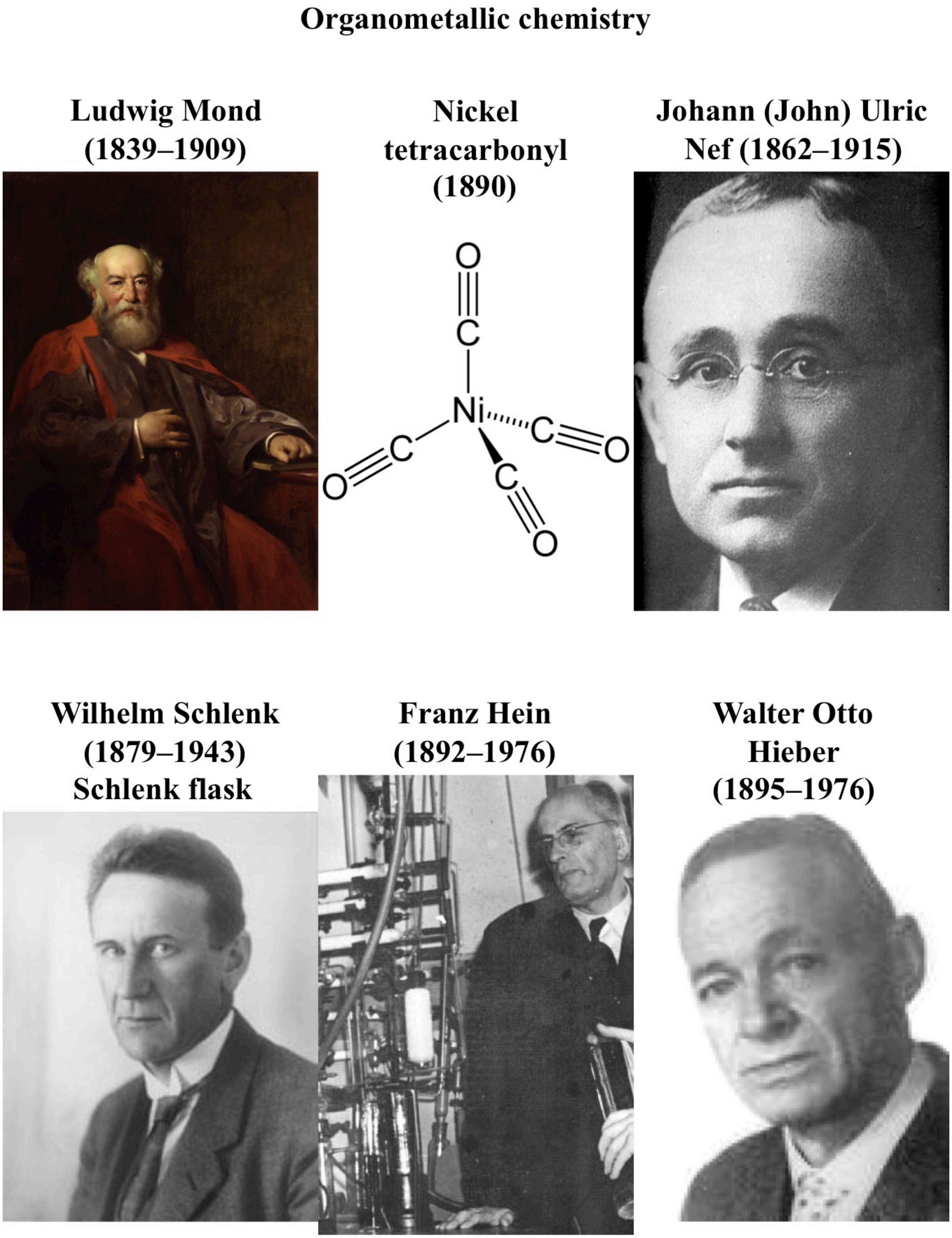


Figure 3.48: Some creators who made important contributions to organometallic chemistry included Ludwig Mond, Johann (John) Ulric Nef, Wilhelm Schlenk, Franz Hein, and Walter Otto Hieber.

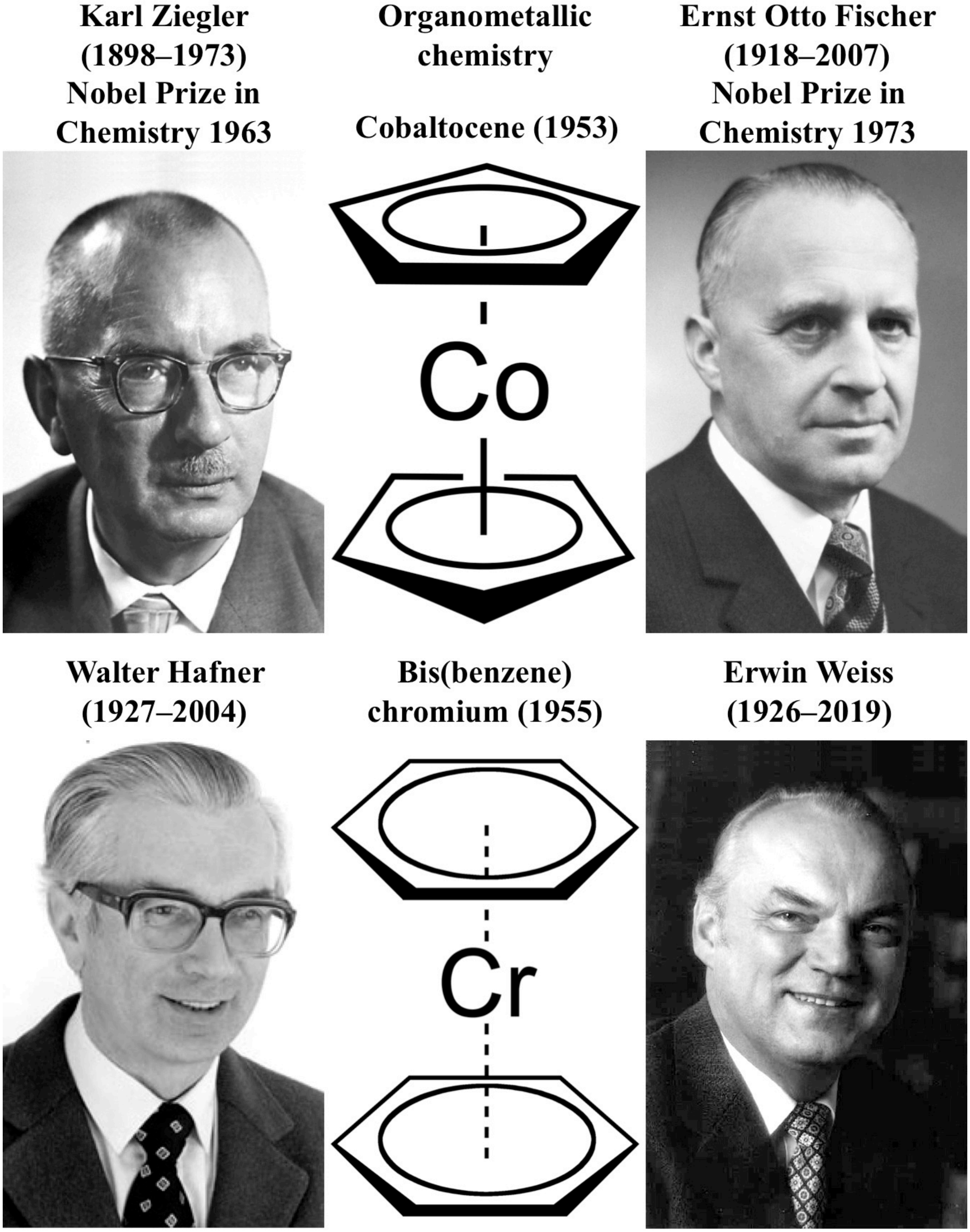


Figure 3.49: Other creators who made important contributions to organometallic chemistry included Karl Ziegler, Ernst Otto Fischer, Walter Hafner, and Erwin Weiss.

3.2.4 Synthetic Fuels

The German-speaking world had large deposits of coal but little oil, natural gas, or most other natural resources. Therefore, especially when imported resources were embargoed or too expensive, there was a strong incentive to harness organic chemistry to convert coal into synthetic liquid fuels, synthetic gaseous fuels, synthetic motor oil, and a variety of other synthetic hydrocarbon products.[5]

In 1913, Friedrich Bergius (German, 1884–1949) created and Carl Bosch (German, 1874–1940) scaled up the Bergius high-pressure process for producing synthetic liquid fuels from coal, for which they both won the Nobel Prize in Chemistry 1931. See Fig. 3.50. Professor W. Palmær, Member of the Nobel Committee for Chemistry, announced the award [https://www.nobelprize.org/prizes/chemistry/1931/ceremony-speech/]:

> You, Professor Bosch, were the first to enrich the chemical industry with this powerful tool, for the production of ammonia from the elements. Between the presentation of the scientific bases of this synthesis and its industrial exploitation lay a mighty chasm, which you bridged, inter alia, by the brilliant invention and construction of the high-pressure apparatus. By doing so, you made it possible for nitrogen to be made available to mankind in inexhaustible quantities, in a form suitable for agriculture, and even at lower prices than hitherto. Furthermore, you developed high-pressure methods for the production of other important substances. By virtue of this, the Academy wishes to thank you and congratulate you, and requests you to receive the distinction from the hands of His Majesty the King.
>
> General Director Bergius. You undertook to tackle a problem which, in its importance for humanity, can be compared with the solution of the nitrogen question. You have shown how, by the injection of hydrogen under pressure, pit coal, brown coal, and other carbon-bearing materials can be processed to liquid fuels which are considered indispensable in modern life for the propulsion of ships and vehicles. You have thereby obviated the danger which threatened of exhaustion of petroleum deposits, an event which must have happened sooner or later. In your work, you arrived at the high-pressure method quite independently. On the basis of your work, a powerful industry has already been formed.

Similarly, in 1925, Franz Fischer (German, 1877–1947) and Hans Tropsch (Austrian, 1889–1935) created the Fischer-Tropsch process for synthesizing fuels and other hydrocarbons, as shown in Fig. 3.51. The chemist and chemical historian Aaron Ihde explained [Ihde 1984, p. 683]:

> Perhaps of even greater interest in this connection is the Fischer-Tropsch process developed in the twenties by the Germans Franz Fischer (1877–1947) and Hans Tropsch (1889–1935). Water gas [$CO + H_2$] passed over suitable metal oxide catalysts at about 200^o C. and moderate pressure is converted into hydrocarbons suitable for motor fuels. The process was ready for commercial production of hydrocarbons after 1935 and was an important factor in the German war effort, as evidenced by the attention given to synthetic oil plants by Allied bombers. The hydrocarbons thus produced also were oxidized to fatty acids to help Germany overcome a shortage of food fats.

At the end of World War II, Allied countries seized all information on German synthetic fuel production processes. Due to limited worldwide resources and concerns about global warming and pollution, such synthetic fuels or related approaches may have a renewed importance in the future.

---

[5] See for example: Becker 1981; Gimbel 1990a; Hasche 1945; Kastens et al. 1952; Krammer 1978, 1981; Lampe 1977; Albert Miller 1945; Schroeder 1945; Sheldon 1945; Stranges 1984; Vieter 1980.

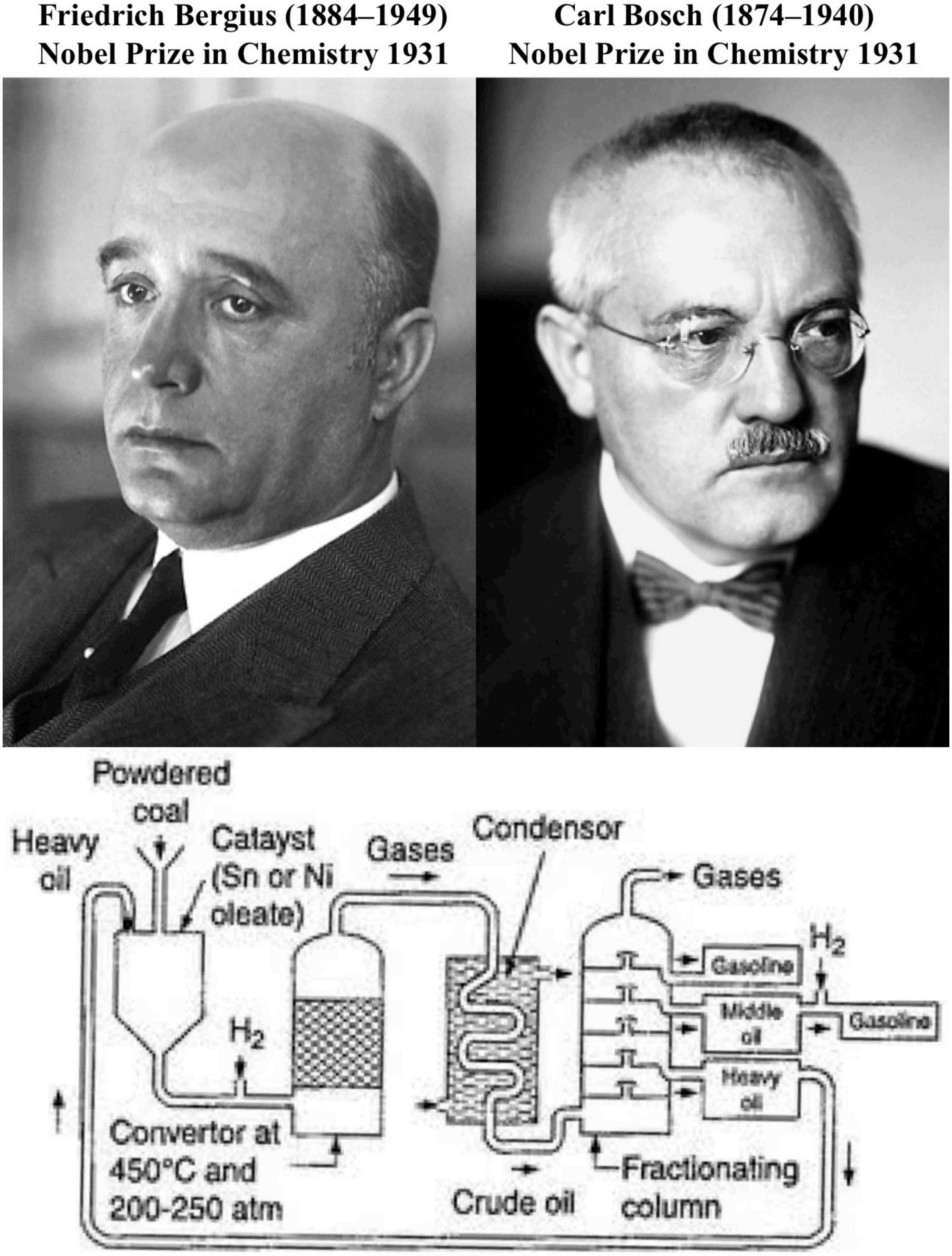
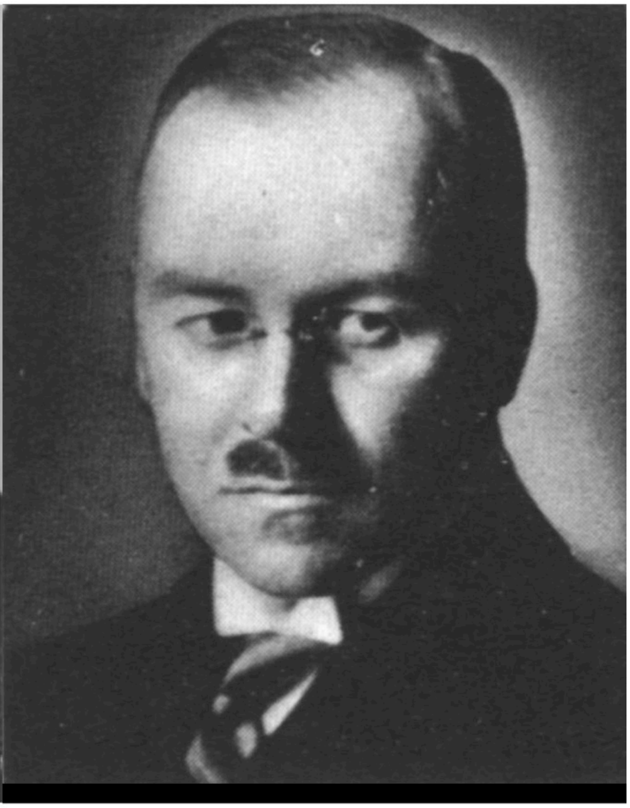


Figure 3.50: Friedrich Bergius created and Carl Bosch scaled up the Bergius process for producing synthetic fuels (1913), for which they both won the Nobel Prize in Chemistry 1931.

Franz Fischer (1877–1947)

Hans Tropsch (1889–1935)



Fischer-Tropsch process for hydrocarbon synthesis (1925)

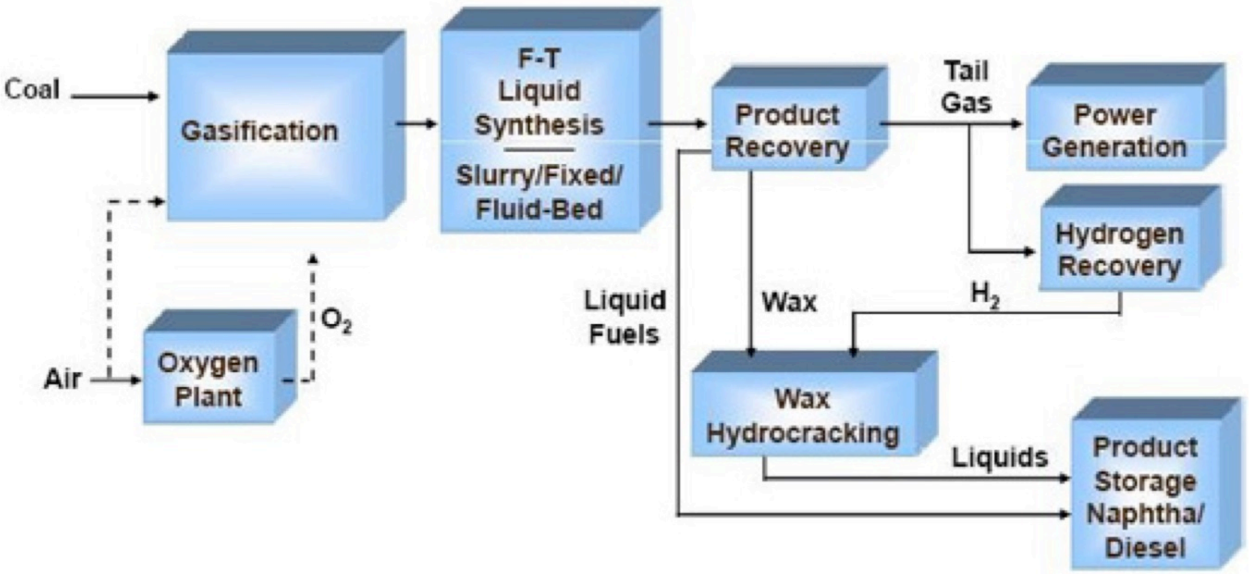


Figure 3.51: In 1925, Franz Fischer and Hans Tropsch created the Fischer-Tropsch process for producing synthetic fuels and other hydrocarbons.

3.2.5 Liquid Crystals

Scientists from the German-speaking world discovered and developed liquid crystals, which can respond to changing temperatures, voltages, pressure, or other conditions by changing their optical properties.[6] One simple application of liquid crystals is to create materials that change colors over a custom-designed range of temperatures. More importantly, electrically controlled liquid crystals are now widely used in electronic display panels from watches to television screens (Fig. 3.52).

Friedrich Reinitzer (Austrian, 1857–1927), a biochemist, discovered liquid crystals in 1888. He noticed the liquid crystal properties of cholesteryl benzoate that he had purified from plants, and he continued to study those properties for several years.

After first discovering liquid crystals, in 1888 Reinitzer enlisted the assistance of Otto Lehmann (German, 1855–1922) in further analyzing and experimenting with them. Lehmann was a physicist and already an expert on the optical properties of materials that could rotate the polarization of light or bend light differently depending on its direction of polarization. Lehmann spent the rest of his life studying the optical properties of liquid crystals in conjunction with polarizers, the temperature-sensitive phase transitions of liquid crystals, and the microscopic and chemical properties of liquid crystals. He was the one who named them "liquid crystals," and he produced a string of publications that firmly established this field, explored its applications, and promoted it to other scientists. For all of his research on liquid crystals, Lehmann was repeatedly nominated for a Nobel Prize, but unfortunately he never won.

Inspired by the pioneering work of Reinitzer and Lehmann, Daniel Vorländer (German, 1867–1941) spent his career synthesizing and analyzing hundreds of different liquid crystal compounds. He also trained a number of students in this field.

Based on the decades of work by Reinitzer, Lehmann, Vorländer, and other scientists that they inspired and/or trained,[7] by the end of World War II, there was a large body of research on the synthesis, properties, and applications of liquid crystals. After the war, all of that information and many of the relevant researchers were seized and harnessed by Allied countries. For example, liquid crystals and some of their applications were described in BIOS 1688, *Radiological Activities in Germany*, p. 12:

> 6. Thermo-Colour Methods
> Berthold attempted to apply Thermo-Colour materials, developed by Dr. Penzig of I.G. Farben in 1939, to non-destructive methods of testing. With these materials it is possible to detect small changes of temperature of the order of a few degrees in temperature ranges up to 360^{o}C. It was Berthold's intention to apply the method to inspect the fit or surface contact of cast inserts, duplex bearings, etc.

As a result of that technology transfer, in the decades after World War II, liquid crystals slowly began appearing in commercial products in Allied countries—first novelty mood rings, then small liquid crystal displays for watches and calculators, and finally larger liquid crystal displays for everything from smart phones to computers to wall-sized television screens. Much more archival research should be conducted to elucidate the full history of liquid crystal research in the German-speaking world, as well as the transfer and influence of that research in other countries.

---

[6] Bruce et al. 1997; Dunmur and Sluckin 2011; Kelker 1973; Kelker 1988; Kelker and Scheurle 1969; Lehmann 1889; Lehmann 1904; Lehmann 1911; Mitov 2014; Reinitzer 1888; Sluckin et al. 2004; Stegemeyer 1994; Weygand 1943.

[7] For example, Hans Kelker (German, 19??–??), Horst Sackmann (German, 1921–1993), Horst Stegemeyer (German, 1931–), and others.

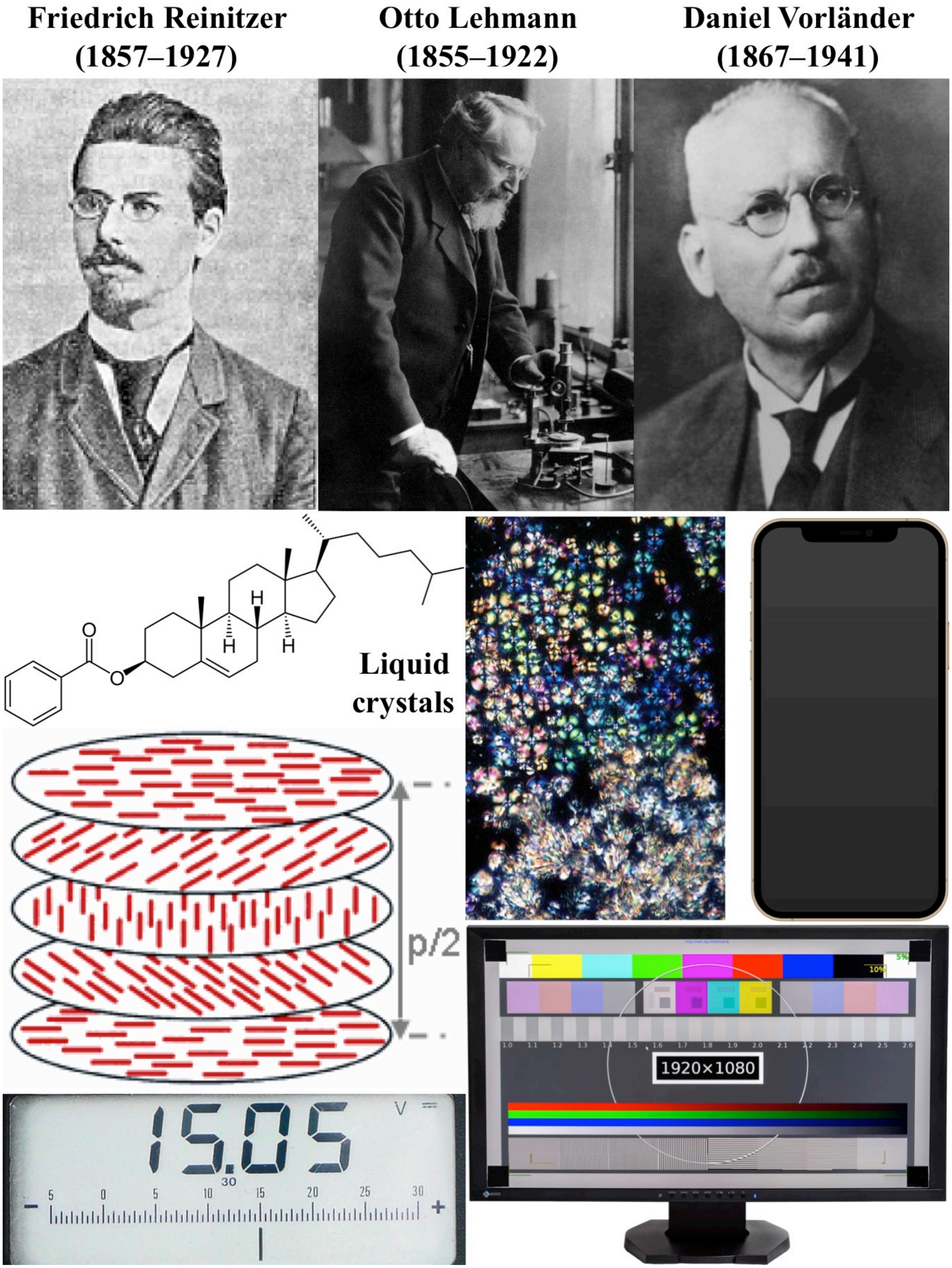


Figure 3.52: Friedrich Reinitzer, Otto Lehmann, and Daniel Vorländer discovered and developed liquid crystals, which are now widely used in electronic display panels from watches and phones to television sets and computer screens.

3.2.6 Technology Transfer out of the German-Speaking World

Many chemical innovations were transferred from the German-speaking world to other countries before World War II, in the form of published papers and patents, commercial transactions, foreign students who visited the German-speaking world, German and Austrian assets seized by other countries during World War I, and chemists who left the German-speaking world to seek careers elsewhere and/or to flee the rising tide of antisemitism and National Socialism.

All remaining chemical innovations, of which there were still a huge number, were seized by Allied countries at the end of World War II. For some examples, see pp. 427–429, as well as the large number of chemistry-related BIOS ER, BIOS, BIOS Misc., BIOS Overall, CIOS ER, CIOS, FIAT, *FIAT Review*, JIOA, NavTecMisEu LR, and NavTecMisEu reports in the Bibliography.

In September 1945, R. P. Linstead and T. J. Betts, the British and American chairs of the Combined Intelligence Objectives Subcommittee (CIOS), gave a very incomplete yet still highly impressive list of important German innovations in synthetic chemistry that had been found by U.S. and U.K. investigators [AFHRA A5186 electronic version pp. 904–1026, Ch. 4, pp. 54–56]:

> The German war time economy was based on its abundant supplies of coal and therefore coke; water gas; on calcium carbide from coke and lime, leading to acetylene; on nitrogen and hydrogen, leading to ammonia; and on salt, leading to chlorine and caustic soda. From these basic products the entire German chemical industry was erected by the following catalytic processes:
>
> 1. Hydrogenation of coal, tar, and oils, and their subsequent conversion into motor fuels, and diesel oils with its long line of by-products such as lubricants, lower aliphatic hydrocarbons and olefines and compounds containing oxygen, like phenol and its homologues.
> 2. The variety of processes of catalytic conversion of CO and H_2 in different proportions leading to methanol, ethanol and their homologues up to long chain fatty alcohols.
>   (a) The synthesis of isobutanol and its conversion to isobutylene and isooctane.
>   (b) The production of hydrocarbons according to the Fischer-Tropsch synthesis leading to aliphatics and olefines from low to very high chain length. Further conversion of the olefines so obtained by addition of CO and H_2 of the type of the oxo reactions or with CO and water according to the fatty acid synthesis of Reppe.
> 3. The reactions of acetylene and ethylene and their many derivatives leading to solvents, plastics, rubber and synthetic fibres.
> 4. The latest types of aliphatic reactions of acetylene and olefine with CO.
>
> Of particular significance is the manufacture of synthetic rubber (BUNA) by the Reppe process, which uses only 1/3 of the quantity of carbide and acetylene required in the conventional process. The discovery of the "Koresine" tacking process is regarded as being of primary importance. The application of this process to the synthetic rubber industry in the U.S. resulted in increased production, and did much to eliminate the threat of a cut in tire production during the critical phase of combat operations.

> The development of plastics covered a very large number of polymer products, among which the polyisocyanates and polyurethanes (Demodurs), the superpolyamides of the Igamid and Perlon types (German nylon) consisting of dibasic acids, diamides, the polyethylenes (Lupolenes), the vinylchloride polymers (Igelites), the vinylacetate polymers (Nowiliths), as well as their derivatives, represent outstanding achievements.

Similarly, Linstead and Betts listed a number of important German innovations for synthetic fuels and oils that had been found by U.S. and U.K. investigators [AFHRA A5186 electronic version pp. 904–1026, Ch. 4, pp. 59–60]:

> The two principal features of the German synthetic fuels and lubricants industry consisted of the hydrogenation of coal, coal tar, and coal tar products; and the Fischer-Tropsch process for the production of fuel from water gas.
>
> The acquisition of a vast amount of specific German data has been one of the significant accomplishments resulting from exploitation of intelligence in this field. Should the U.S. or Great Britain be faced with another national emergency, adequate supplies of fuels and lubricants will be much more assured as the result of this information.
>
> The DHD process for obtaining aviation fuels by hydrogenation and conversion to aromatics is a development hitherto unknown in this detail.
>
> The Germans were discovered to have adopted new methods which permitted the successful hydrogenation of brown coal from Rhineland reserves. They had also perfected a novel process for producing water gas from brown coal.
>
> Interrogation of German authorities and examination of documents and plants revealed that the Fischer-Tropsch process could not be expected to yield more than 15 to 20% of fuel and oil requirements of the German economy. However, the Fischer-Tropsch process has a certain advantage of yielding crude chemicals which possess a considerable potential for further refining.
>
> The Germans have recently developed a new iron catalyst which could be used to supplant catalysts of conventional cobalt type.
>
> The following additional discoveries resulting from investigation of the German fuel and oil industry are worthy of mention:
>
> 1. New high grade aviation lubricants obtained by polymerization of ethylene.
> 2. New methods of testing fuels and lubricants.
> 3. Fairly complete specifications for German fuels and lubricating oils.
> 4. Details of German shale oil distillations and the refining of these distillates.
>
> Many laboratory improvements were encountered which had not been applied to industrial use, but which will prove of value in U.S. and British development work.

The organic chemistry methods, discoveries, and expertise that were transferred out of the German-speaking world created our modern world of consumer products from colored fabrics and plastic materials to pharmaceuticals and liquid crystal display screens.

3.3 Chemistry of Foods and Drinks

In food and drink production, as in many other areas, the German-speaking world possessed very limited natural resources. When key food and drink ingredients from foreign sources became too expensive during peacetime, and especially when key ingredients were embargoed and unavailable during World Wars I and II, German-speaking scientists developed a number of highly innovative food substitutes and related synthetic products and preservatives. This is a large field, and only a few examples are briefly discussed in this section, including:

3.3.1. Synthetic flavors

3.3.2. Synthetic drinks

3.3.3. Synthetic fats

3.3.4. Synthetic protein products

3.3.5. Preservatives

Several of the above innovations, those related to biotechnology, are covered in more detail in Appendix A.

Even after the wars, several of these innovative food and drink products continued to be used both in German-speaking countries and in other countries around the world that adopted the innovations, especially in cases where the innovative product was cheaper or better than the original food, drink, or ingredient. The strong interest by other countries in these innovations is demonstrated by the large number of BIOS, CIOS, and FIAT reports that Allied countries wrote about them.

3.3.1 Synthetic Flavors

Karl Reimer (German, 1845–1883), Wilhelm Haarmann (German, 1847–1931), and Ferdinand Tiemann (German, 1848–1899) found the molecular structure of natural vanillin flavor from vanilla beans, and developed purely chemical methods of synthesizing it in 1874, as illustrated in Fig. 3.53. In the modern world, most vanillin flavor is chemically synthesized using these same or similar methods, since chemical synthesis is less expensive than growing and processing vanilla beans.

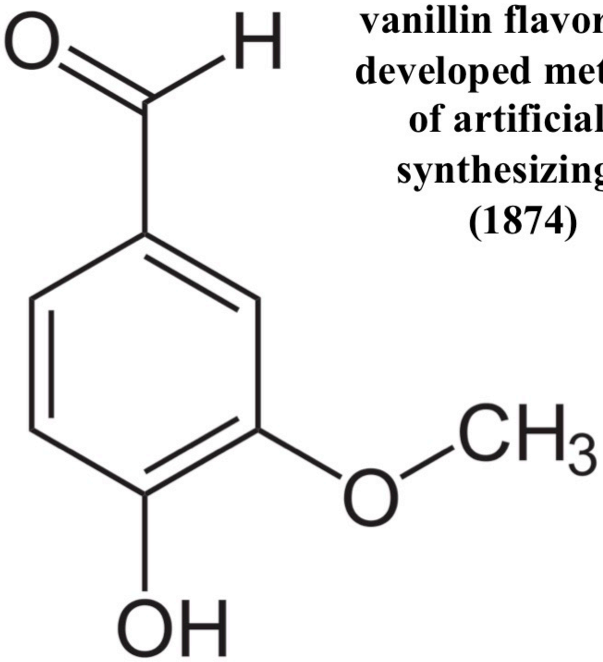
In 1879, Constantin Fahlberg (Russian but studied and worked in Germany, 1850–1910) discovered the artificial sweetener saccharin. By the 1880s, saccharin was synthesized on a large scale in Germany (Fig. 3.54), and it has been sold around the world ever since [BIOS 1576].

During World War I, Hermann Staudinger (German, 1881–1965) and Paul Immerwahr (German, 1886–1926) developed an artificial substitute for scarce black pepper: ground nutshells soaked in chemically synthesized piperine or piperine derivatives (the key ingredient of real black pepper) [Vaupel 2010, 2011]. See Fig. 3.55.

By World War II, the German-speaking world had developed a number of other artificial spices, such as synthetic allspice, cinnamon, cloves, cardamom, and nutmeg [Vaupel 2011; CIOS XXXII-47; FIAT 244].

Artificial vanillin

Karl Reimer (1845–1883) **Wilhelm Haarmann (1847–1931)**



Found molecular structure of natural vanillin flavor and developed methods of artificially synthesizing it (1874)

Ferdinand Tiemann (1848–1899)

Figure 3.53: Karl Reimer, Wilhelm Haarmann, and Ferdinand Tiemann found the molecular structure of natural vanillin flavor and developed methods of artificially synthesizing it in 1874.

Artificial sweetener

Constantin Fahlberg
(Russian but studied and worked
in Germany, 1850–1910)

Saccharin

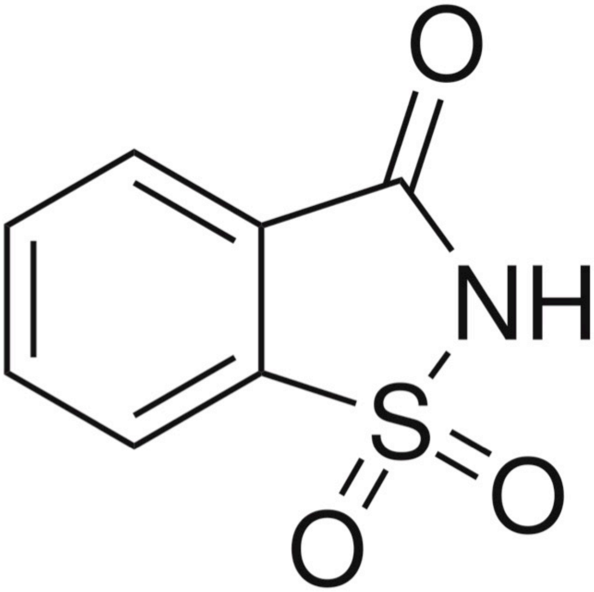
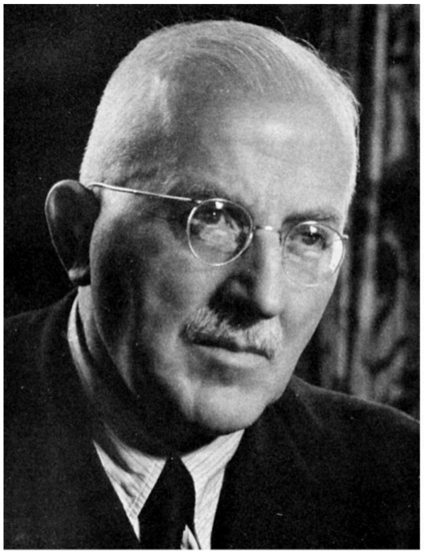
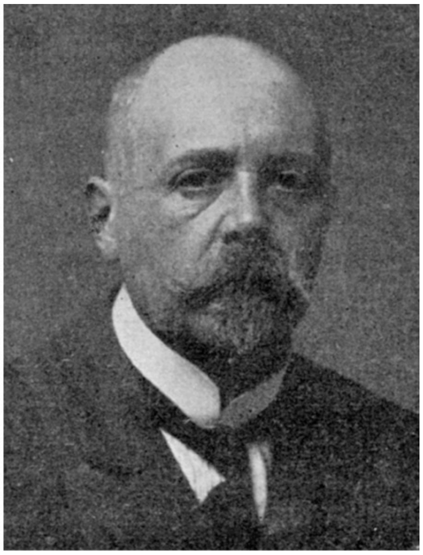


Figure 3.54: Constantin Fahlberg discovered the artificial sweetener saccharin in 1879. By the 1880s, saccharin was synthesized on a large scale in Germany.

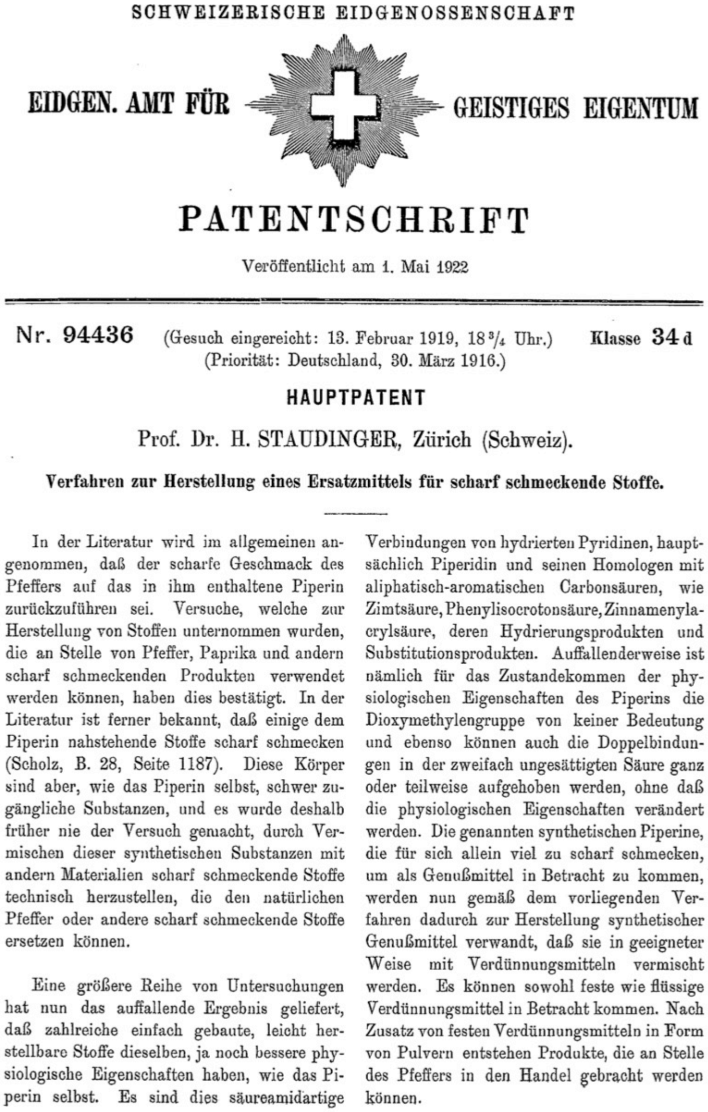
Artificial black pepper



Hermann Staudinger (1881–1965)



Paul Immerwahr (1886–1926)



SCHWEIZERISCHE EIDGENOSSENSCHAFT

EIDGEN. AMT FÜR GEISTIGES EIGENTUM

PATENTSCHRIFT

Veröffentlicht am 1. Mai 1922

Nr. 94436 (Gesuch eingereicht: 13. Februar 1919, 18 $^{3}/_{4}$ Uhr.) Klasse 34 d
(Priorität: Deutschland, 30. März 1916.)

HAUPTPATENT

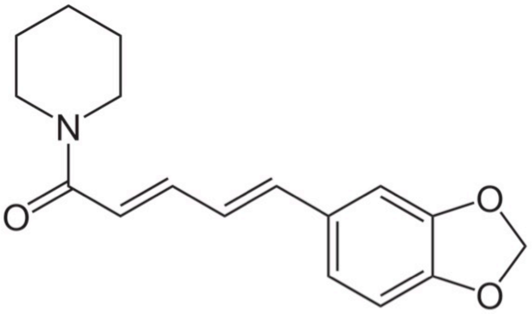
Prof. Dr. H. STAUDINGER, Zürich (Schweiz).

Verfahren zur Herstellung eines Ersatzmittels für scharf schmeckende Stoffe.

In der Literatur wird im allgemeinen angenommen, daß der scharfe Geschmack des Pfeffers auf das in ihm enthaltene Piperin zurückzuführen sei. Versuche, welche zur Herstellung von Stoffen unternommen wurden, die an Stelle von Pfeffer, Paprika und andern scharf schmeckenden Produkten verwendet werden können, haben dies bestätigt. In der Literatur ist ferner bekannt, daß einige dem Piperin nahstehende Stoffe scharf schmecken (Scholz, B. 28, Seite 1187). Diese Körper sind aber, wie das Piperin selbst, schwer zugängliche Substanzen, und es wurde deshalb früher nie der Versuch gemacht, durch Vermischen dieser synthetischen Substanzen mit andern Materialien scharf schmeckende Stoffe technisch herzustellen, die den natürlichen Pfeffer oder andere scharf schmeckende Stoffe ersetzen können.

Eine größere Reihe von Untersuchungen hat nun das auffallende Ergebnis geliefert, daß zahlreiche einfach gebaute, leicht herstellbare Stoffe dieselben, ja noch bessere physiologische Eigenschaften haben, wie das Piperin selbst. Es sind dies säureamidartige Verbindungen von hydrierten Pyridinen, hauptsächlich Piperidin und seinen Homologen mit aliphatisch-aromatischen Carbonsäuren, wie Zimtsäure, Phenylisocrotonsäure, Zinnamenylacrylsäure, deren Hydrierungsprodukten und Substitutionsprodukten. Auffallenderweise ist nämlich für das Zustandekommen der physiologischen Eigenschaften des Piperins die Dioxymethylengruppe von keiner Bedeutung und ebenso können auch die Doppelbindungen in der zweifach ungesättigten Säure ganz oder teilweise aufgehoben werden, ohne daß die physiologischen Eigenschaften verändert werden. Die genannten synthetischen Piperine, die für sich allein viel zu scharf schmecken, um als Genußmittel in Betracht zu kommen, werden nun gemäß dem vorliegenden Verfahren dadurch zur Herstellung synthetischer Genußmittel verwandt, daß sie in geeigneter Weise mit Verdünnungsmitteln vermischt werden. Es können sowohl feste wie flüssige Verdünnungsmittel in Betracht kommen. Nach Zusatz von festen Verdünnungsmitteln in Form von Pulvern entstehen Produkte, die an Stelle des Pfeffers in den Handel gebracht werden können.

Piperine



Dem fehlenden Naturprodukt vollkommen ebenbürtig iſt unſer künſtlicher

Pfeffer

auf rein chemiſchem Wege erzeugt aus inländiſchen Rohſtoffen. G4572

Chemiſche Fabrik Dr. Höhn & Cie.

Neuß am Rhein.

Figure 3.55: During World War I, Hermann Staudinger and Paul Immerwahr developed an artificial substitute for scarce black pepper: ground nutshells soaked in chemically synthesized piperine or piperine derivatives (the key ingredient of real black pepper).

3.3.2 Synthetic Drinks

During wartime, caffeine was an important stimulant, yet its natural sources—tea leaves and coffee beans—were difficult to obtain due to embargoes. Therefore, many German-speaking chemists developed artificial methods of producing caffeine (Fig. 3.56). Most of those methods involved direct chemical synthesis of caffeine by a long series of reactions [BIOS 306; BIOS 449; BIOS 1404; CIOS XXVI-9; FIAT 71; FIAT 885]. However, some especially ingenious (or desperate) scientists also developed and demonstrated methods to farm large quantities of snake urine, which contains an especially high concentration of uric acid, and then convert that uric acid to caffeine [BIOS 449; see p. 2366].

Amalie Melitta Bentz (German, 1873–1950) invented paper coffee filters and the corresponding brewing system in 1908 (Fig. 3.57). She founded the Melitta coffee company.

In the 1930s, Hermann Staudinger (German, 1881–1965), Tadeusz Reichstein (Polish, educated and worked in Switzerland, 1897–1996), Max Kerschbaum (German?, 18??–10??), Eligius Freudl (Austrian, 1875–1951), and other chemists developed Coffarom and other instant coffee mixes derived from synthetic ingredients [Priesner 2014, 2016; FIAT 244; FIAT 407]. See Fig. 3.58.

In parallel during the 1930s, Max Rudolf Morgenthaler (Swiss, 1901–1980) and other chemists developed Nescafé, an instant coffee mix derived from coffee bean extracts and other natural ingredients [Priesner 2014, 2016]. See Fig. 3.59.

During World War II, German-speaking scientists also made a number of improvements to the processing and sterilization of fruit juices that were adopted by other countries after the war [e.g., Kertesz 1946; FIAT 50].

3.3.3 Synthetic Fats

In the 1930s and early 1940s, many German-speaking scientists developed artificial methods to produce lipids or fats for foods, soaps, fuels, and other products.

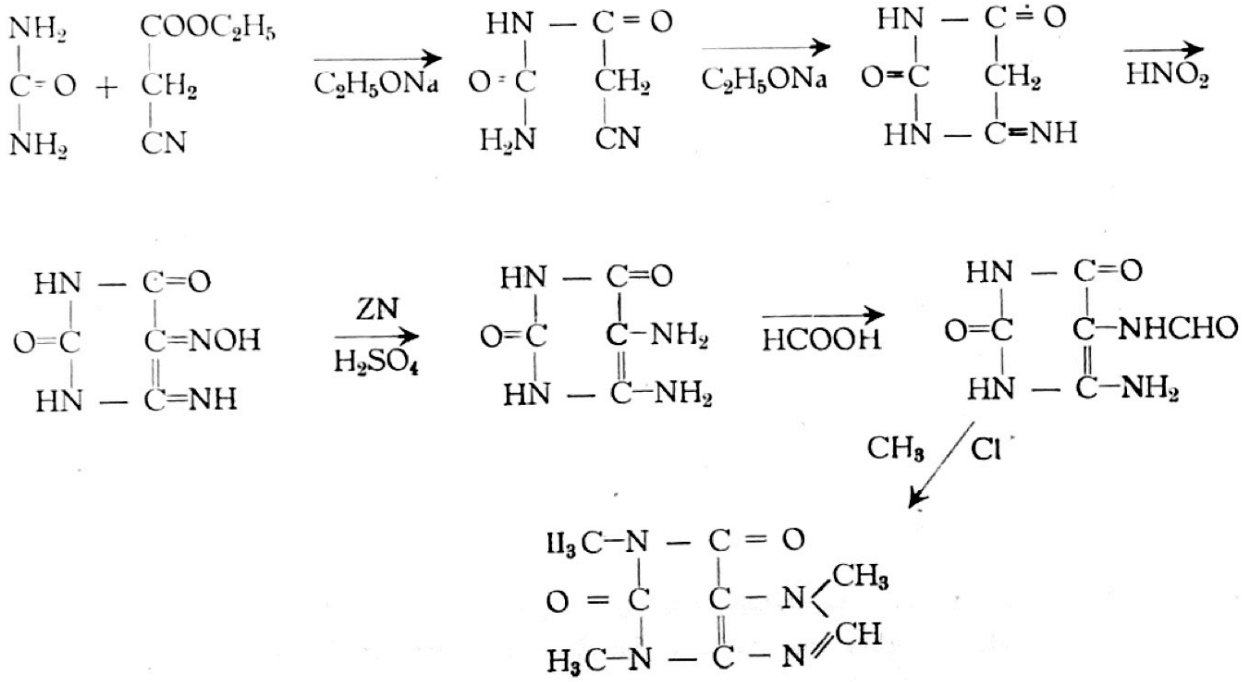
Glycerin, sterols, fatty acids, and triglycerides were produced from chemical synthesis on an industrial scale and sold for food products and other applications [BIOS 86; BIOS 805; FIAT 213; FIAT 407]. See Fig. 3.60.

Fats were produced and purified from various strains of cultured algae and fungi using biotechnology methods [BIOS 236; BIOS 691; FIAT 371]. In addition to the food applications, this appears to have been the origin of algal and other microbial biofuel technologies. See Fig. 3.61.

Artificially produced fats were used to make a variety of food products, including cooking oil, cooking fat (shortening), margarine, creamer, salad oil, chocolate [Clarke 1946], synthetic human milk (infant formula) [FIAT 107], etc. [See also Gemmill 1946 for examples of other innovations in butter production.]

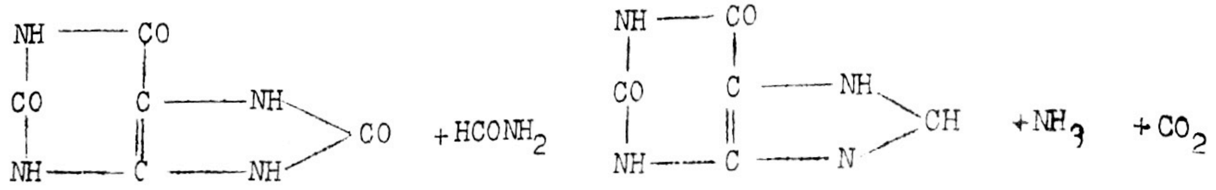
Artificial caffeine

From chemical synthesis [FIAT 885]



From conversion of uric acid from snake urine [BIOS 449]

Together with Prof. Bredereck we elaborate a procedure for the manufacture of caffeine from uric acid. The uric acid is to be added in a formamide-melt of about 200° and so transformed to xanthine, which is easily converted to caffeine by methylating with dimethylsulphate:



Bredereck further found that the degree of methylating depands on the pH, so that also theophylline and theobromine can be obtained from xanthine. We could confirm these statements with very small experiments only, whereas with larger charges caffeine was always the main product. The greatest obstacle in this process is to procure a sufficiently pure and cheap uric acid.

The process with serpents' excrement which contains more than 80% of uric acid, is very easy and needs no further purification.

Figure 3.56: German-speaking chemists developed artificial methods of producing caffeine, including from direct chemical synthesis [FIAT 885] and from the conversion of uric acid harvested from snake urine [BIOS 449].

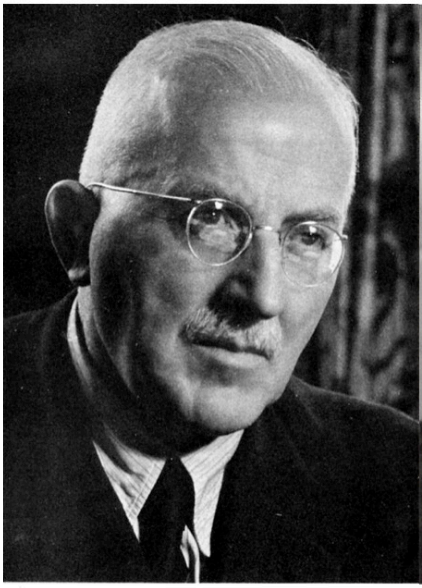
Figure 3.57: Amalie Melitta Bentz invented paper coffee filters and the corresponding brewing system in 1908.

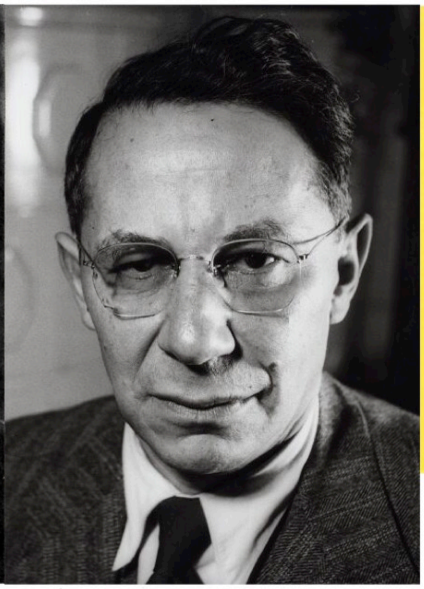
Instant coffee: Coffarom

Hermann Staudinger (1881–1965)

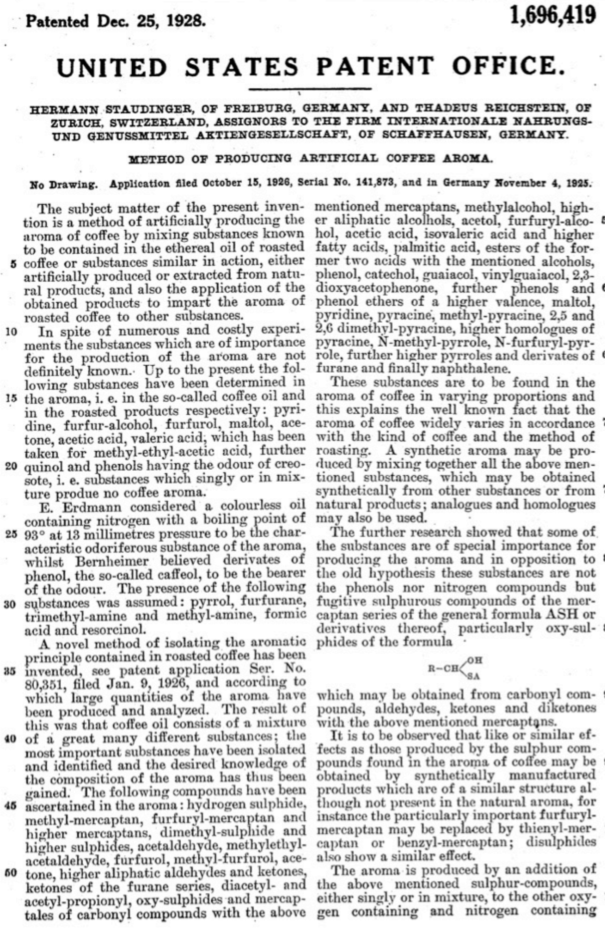
Tadeusz Reichstein (1897–1996)

Max Kerschbaum (18??–19??)





Eligius Freudl (1875–1951)



Patented Dec. 25, 1928. **1,696,419**

UNITED STATES PATENT OFFICE.

HERMANN STAUDINGER, OF FREIBURG, GERMANY, AND THADEUS REICHSTEIN, OF ZURICH, SWITZERLAND, ASSIGNORS TO THE FIRM INTERNATIONALE NAHRUNGS- UND GENUSSMITTEL AKTIENGESELLSCHAFT, OF SCHAFFHAUSEN, GERMANY.

METHOD OF PRODUCING ARTIFICIAL COFFEE AROMA.

No Drawing. Application filed October 15, 1926, Serial No. 141,873, and in Germany November 4, 1925.

The subject matter of the present invention is a method of artificially producing the aroma of coffee by mixing substances known to be contained in the ethereal oil of roasted coffee or substances similar in action, either artificially produced or extracted from natural products, and also the application of the obtained products to impart the aroma of roasted coffee to other substances.

In spite of numerous and costly experiments the substances which are of importance for the production of the aroma are not definitely known. Up to the present the following substances have been determined in the aroma, i. e. in the so-called coffee oil and in the roasted products respectively: pyridine, furfur-alcohol, furfurol, maltol, acetone, acetic acid, valeric acid, which has been taken for methyl-ethyl-acetic acid, further quinol and phenols having the odour of creosote, i. e. substances which singly or in mixture produe no coffee aroma.

E. Erdmann considered a colourless oil containing nitrogen with a boiling point of 93° at 13 millimetres pressure to be the characteristic odoriferous substance of the aroma, whilst Bernheimer believed derivates of phenol, the so-called caffeol, to be the bearer of the odour. The presence of the following substances was assumed: pyrrol, furfurane, trimethyl-amine and methyl-amine, formic acid and resorcinol.

A novel method of isolating the aromatic principle contained in roasted coffee has been invented, see patent application Ser. No. 80,351, filed Jan. 9, 1926, and according to which large quantities of the aroma have been produced and analyzed. The result of this was that coffee oil consists of a mixture of a great many different substances; the most important substances have been isolated and identified and the desired knowledge of the composition of the aroma has thus been gained. The following compounds have been ascertained in the aroma: hydrogen sulphide, methyl-mercaptan, furfuryl-mercaptan and higher mercaptans, dimethyl-sulphide and higher sulphides, acetaldehyde, methylethyl-acetaldehyde, furfurol, methyl-furfurol, acetone, higher aliphatic aldehydes and ketones, ketones of the furane series, diacetyl- and acetyl-propionyl, oxy-sulphides and mercaptales of carbonyl compounds with the above mentioned mercaptans, methylalcohol, higher aliphatic alcolhols, acetol, furfuryl-alcohol, acetic acid, isovaleric acid and higher fatty acids, palmitic acid, esters of the former two acids with the mentioned alcohols, phenol, catechol, guaiacol, vinylguaiacol, 2,3-dioxyacetophenone, further phenols and phenol ethers of a higher valence, maltol, pyridine, pyracine, methyl-pyracine, 2,5 and 2,6 dimethyl-pyracine, higher homologues of pyracine, N-methyl-pyrrole, N-furfuryl-pyrrole, further higher pyrroles and derivates of furane and finally naphthalene.

These substances are to be found in the aroma of coffee in varying proportions and this explains the well known fact that the aroma of coffee widely varies in accordance with the kind of coffee and the method of roasting. A synthetic aroma may be produced by mixing together all the above mentioned substances, which may be obtained synthetically from other substances or from natural products; analogues and homologues may also be used.

The further research showed that some of the substances are of special importance for producing the aroma and in opposition to the old hypothesis these substances are not the phenols nor nitrogen compounds but fugitive sulphurous compounds of the mercaptan series of the general formula ASH or derivatives thereof, particularly oxy-sulphides of the formula

$$\mathrm{R{-}CH}\begin{matrix}\diagup \mathrm{OH}\\ \diagdown \mathrm{SA}\end{matrix}$$

which may be obtained from carbonyl compounds, aldehydes, ketones and diketones with the above mentioned mercaptans.

It is to be observed that like or similar effects as those produced by the sulphur compounds found in the aroma of coffee may be obtained by synthetically manufactured products which are of a similar structure although not present in the natural aroma, for instance the particularly important furfuryl-mercaptan may be replaced by thienyl-mercaptan or benzyl-mercaptan; disulphides also show a similar effect.

The aroma is produced by an addition of the above mentioned sulphur-compounds, either singly or in mixture, to the other oxygen containing and nitrogen containing

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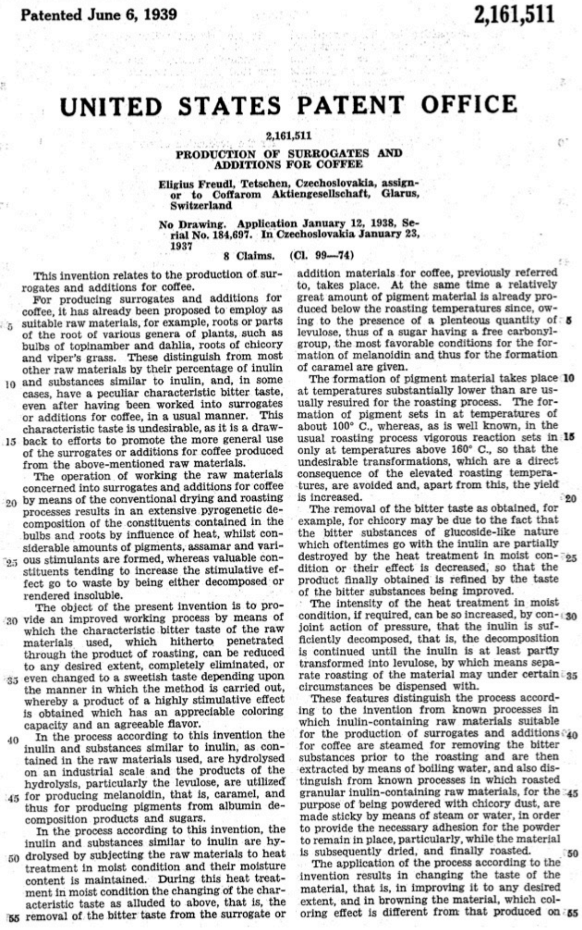


Patented June 6, 1939 **2,161,511**

UNITED STATES PATENT OFFICE

2,161,511

PRODUCTION OF SURROGATES AND ADDITIONS FOR COFFEE

Eligius Freudl, Tetschen, Czechoslovakia, assignor to Coffarom Aktiengesellschaft, Glarus, Switzerland

No Drawing. Application January 12, 1938, Serial No. 184,697. In Czechoslovakia January 23, 1937

8 Claims. (Cl. 99—74)

This invention relates to the production of surrogates and additions for coffee.

For producing surrogates and additions for coffee, it has already been proposed to employ as suitable raw materials, for example, roots or parts of the root of various genera of plants, such as bulbs of topinamber and dahlia, roots of chicory and viper's grass. These distinguish from most other raw materials by their percentage of inulin and substances similar to inulin, and, in some cases, have a peculiar characteristic bitter taste, even after having been worked into surrogates or additions for coffee, in a usual manner. This characteristic taste is undesirable, as it is a drawback to efforts to promote the more general use of the surrogates or additions for coffee produced from the above-mentioned raw materials.

The operation of working the raw materials concerned into surrogates and additions for coffee by means of the conventional drying and roasting processes results in an extensive pyrogenetic decomposition of the constituents contained in the bulbs and roots by influence of heat, whilst considerable amounts of pigments, assamar and various stimulants are formed, whereas valuable constituents tending to increase the stimulative effect go to waste by being either decomposed or rendered insoluble.

The object of the present invention is to provide an improved working process by means of which the characteristic bitter taste of the raw materials used, which hitherto penetrated through the product of roasting, can be reduced to any desired extent, completely eliminated, or even changed to a sweetish taste depending upon the manner in which the method is carried out, whereby a product of a highly stimulative effect is obtained which has an appreciable coloring capacity and an agreeable flavor.

In the process according to this invention the inulin and substances similar to inulin, as contained in the raw materials used, are hydrolysed on an industrial scale and the products of the hydrolysis, particularly the levulose, are utilized for producing melanoidin, that is, caramel, and thus for producing pigments from albumin decomposition products and sugars.

In the process according to this invention, the inulin and substances similar to inulin are hydrolysed by subjecting the raw materials to heat treatment in moist condition and their moisture content is maintained. During this heat treatment in moist condition the changing of the characteristic taste as alluded to above, that is, the removal of the bitter taste from the surrogate or addition materials for coffee, previously referred to, takes place. At the same time a relatively great amount of pigment material is already produced below the roasting temperatures since, owing to the presence of a plenteous quantity of levulose, thus of a sugar having a free carbonyl-group, the most favorable conditions for the formation of melanoidin and thus for the formation of caramel are given.

The formation of pigment material takes place at temperatures substantially lower than are usually resuired for the roasting process. The formation of pigment sets in at temperatures of about 100° C., whereas, as is well known, in the usual roasting process vigorous reaction sets in only at temperatures above 160° C., so that the undesirable transformations, which are a direct consequence of the elevated roasting temperatures, are avoided and, apart from this, the yield is increased.

The removal of the bitter taste as obtained, for example, for chicory may be due to the fact that the bitter substances of glucoside-like nature which oftentimes go with the inulin are partially destroyed by the heat treatment in moist condition or their effect is decreased, so that the product finally obtained is refined by the taste of the bitter substances being improved.

The intensity of the heat treatment in moist condition, if required, can be so increased, by conjoint action of pressure, that the inulin is sufficiently decomposed, that is, the decomposition is continued until the inulin is at least partly transformed into levulose, by which means separate roasting of the material may under certain circumstances be dispensed with.

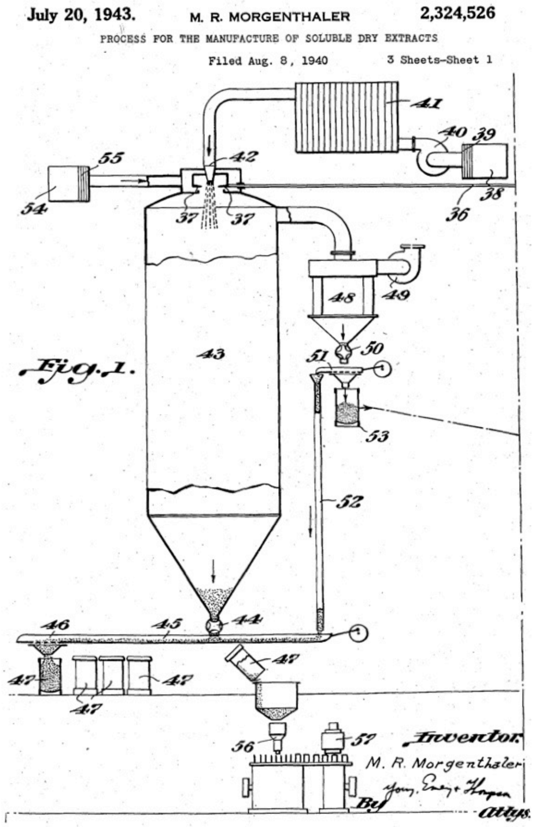
These features distinguish the process according to the invention from known processes in which inulin-containing raw materials suitable for the production of surrogates and additions for coffee are steamed for removing the bitter substances prior to the roasting and are then extracted by means of boiling water, and also distinguish from known processes in which roasted granular inulin-containing raw materials, for the purpose of being powdered with chicory dust, are made sticky by means of steam or water, in order to provide the necessary adhesion for the powder to remain in place, particularly, while the material is subsequently dried, and finally roasted.

The application of the process according to the invention results in changing the taste of the material, that is, in improving it to any desired extent, and in browning the material, which coloring effect is different from that produced on

Figure 3.58: In the 1930s, Hermann Staudinger, Tadeusz Reichstein, Max Kerschbaum, Eligius Freudl, and other chemists developed Coffarom, an instant coffee derived from synthetic ingredients.

Instant coffee: Nescafé

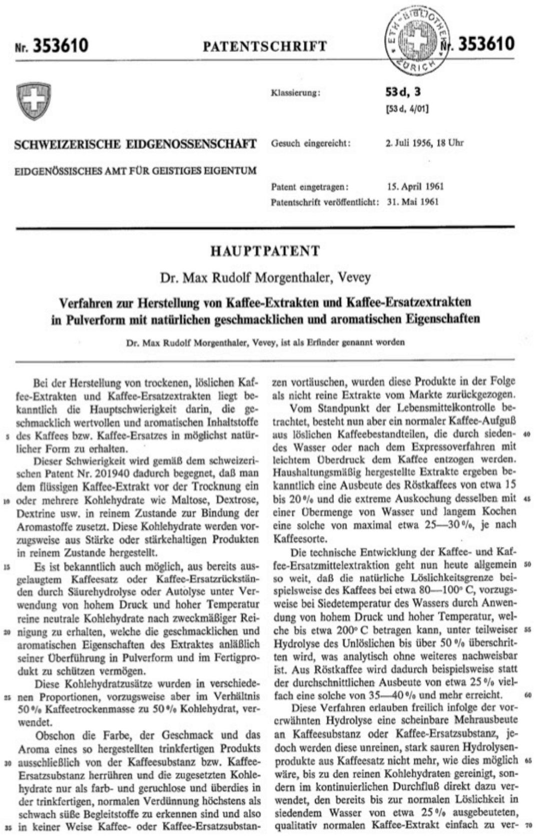
Max Rudolf Morgenthaler (1901–1980)



July 20, 1943. M. R. MORGENTHALER **2,324,526**

PROCESS FOR THE MANUFACTURE OF SOLUBLE DRY EXTRACTS

Filed Aug. 8, 1940 3 Sheets-Sheet 1



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HAUPTPATENT

Dr. Max Rudolf Morgenthaler, Vevey

Verfahren zur Herstellung von Kaffee-Extrakten und Kaffee-Ersatzextrakten in Pulverform mit natürlichen geschmacklichen und aromatischen Eigenschaften

Dr. Max Rudolf Morgenthaler, Vevey, ist als Erfinder genannt worden

Bei der Herstellung von trockenen, löslichen Kaffee-Extrakten und Kaffee-Ersatzextrakten liegt bekanntlich die Hauptschwierigkeit darin, die geschmacklich wertvollen und aromatischen Inhaltstoffe des Kaffees bzw. Kaffee-Ersatzes in möglichst natürlicher Form zu erhalten.

Dieser Schwierigkeit wird gemäß dem schweizerischen Patent Nr. 201940 dadurch begegnet, daß man dem flüssigen Kaffee-Extrakt vor der Trocknung ein oder mehrere Kohlehydrate wie Maltose, Dextrose, Dextrine usw. in reinem Zustande zur Bindung der Aromastoffe zusetzt. Diese Kohlehydrate werden vorzugsweise aus Stärke oder stärkehaltigen Produkten in reinem Zustande hergestellt.

Es ist bekanntlich auch möglich, aus bereits ausgelaugtem Kaffeesatz oder Kaffee-Ersatzrückständen durch Säurehydrolyse oder Autolyse unter Verwendung von hohem Druck und hoher Temperatur reine neutrale Kohlehydrate nach zweckmäßiger Reinigung zu erhalten, welche die geschmacklichen und aromatischen Eigenschaften des Extraktes anläßlich seiner Überführung in Pulverform und im Fertigprodukt zu schützen vermögen.

Diese Kohlehydratzusätze wurden in verschiedenen Proportionen, vorzugsweise aber im Verhältnis 50 % Kaffeetrockenmasse zu 50 % Kohlehydrat, verwendet.

Obschon die Farbe, der Geschmack und das Aroma eines so hergestellten trinkfertigen Produkts ausschließlich von der Kaffeesubstanz bzw. Kaffee-Ersatzsubstanz herrühren und die zugesetzten Kohlehydrate nur als farb- und geruchlose und überdies in der trinkfertigen, normalen Verdünnung höchstens als schwach süße Begleitstoffe zu erkennen sind und also in keiner Weise Kaffee- oder Kaffee-Ersatzsubstanzen vortäuschen, wurden diese Produkte in der Folge als nicht reine Extrakte vom Markte zurückgezogen.

Vom Standpunkt der Lebensmittelkontrolle betrachtet, besteht nun aber ein normaler Kaffee-Aufguß aus löslichen Kaffeebestandteilen, die durch siedendes Wasser oder nach dem Expressoverfahren mit leichtem Überdruck dem Kaffee entzogen werden. Haushaltungsmäßig hergestellte Extrakte ergeben bekanntlich eine Ausbeute des Röstkaffees von etwa 15 bis 20 % und die extreme Auskochung desselben mit einer Übermenge von Wasser und langem Kochen eine solche von maximal etwa 25—30 %, je nach Kaffeesorte.

Die technische Entwicklung der Kaffee- und Kaffee-Ersatzmittelextraktion geht nun heute allgemein so weit, daß die natürliche Löslichkeitsgrenze beispielsweise des Kaffees bei etwa 80—100° C, vorzugsweise bei Siedetemperatur des Wassers durch Anwendung von hohem Druck und hoher Temperatur, welche bis etwa 200° C betragen kann, unter teilweiser Hydrolyse des Unlöslichen bis über 50 % überschritten wird, was analytisch ohne weiteres nachweisbar ist. Aus Röstkaffee wird dadurch beispielsweise statt der durchschnittlichen Ausbeute von etwa 25 % vielfach eine solche von 35—40 % und mehr erreicht.

Diese Verfahren erlauben freilich infolge der vorerwähnten Hydrolyse eine scheinbare Mehrausbeute an Kaffeesubstanz oder Kaffee-Ersatzsubstanz, jedoch werden diese unreinen, stark sauren Hydrolysenprodukte aus Kaffeesatz nicht mehr, wie dies möglich wäre, bis zu den reinen Kohlehydraten gereinigt, sondern im kontinuierlichen Durchfluß direkt dazu verwendet, den bereits bis zur normalen Löslichkeit in siedendem Wasser von etwa 25 % ausgebeuteten, qualitativ normalen Kaffee-Extrakt einfach zu ver-

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1

Bei der Herstellung von trockenen, löslichen Kaffee-Extrakten liegt bekanntlich die Hauptschwierigkeit darin, die geschmacklich wertvollen und aromatischen Inhaltstoffe des Kaffees in möglichst natürlicher Form zu erhalten.

Zu Anfang versuchte man dieser Schwierigkeit dadurch zu begegnen, daß man dem flüssigen Kaffee-Extrakt vor der Trocknung ein oder mehrere Kohlehydrate, z. B. Maltose, Dextrose, Dextrine in reinem Zustand, zur Bindung der Aromastoffe zusetzte. Diese Kohlehydrate wurden vorzugsweise aus Stärke oder stärkehaltigen Produkten in reinem Zustande hergestellt.

Es ist bekanntlich auch möglich, aus bereits ausgelaugtem Kaffeesatz durch Säurehydrolyse oder Autolyse unter Verwendung von hohem Druck und hoher Temperatur reine neutrale Kohlehydrate nach zweckmäßiger Reinigung zu erhalten, welche die geschmacklichen und aromatischen Eigenschaften des Kaffee-Extraktes bei dessen Überführung in Pulverform und im Fertigprodukt zu schützen vermögen.

Diese Kohlehydratzusätze wurden in verschiedenen Verhältnissen, vorzugsweise 50 % Kaffeetrockenmasse zu 50 % Kohlehydrat verwendet.

Obwohl in einer solchen Konserve die farblichen, geschmacklichen und aromatischen Eigenschaften des trinkfertigen Produktes ausschließlich von der reinen Kaffeesubstanz herrühren und die Kohlehydrate nur als farb- und geruchlose und überdies in der trinkfertigen, normalen Verdünnung höchstens als schwach süße Begleitstoffe zu erkennen sind und also in keiner Weise Kaffeesubstanz vortäuschen, wurden diese Produkte in der Folge als nicht reine Kaffee-Extrakte vom Markte zurückgezogen.

Vom Standpunkt der Lebensmittelkontrolle betrachtet, besteht ein normaler Kaffee-Aufguß aus löslichen Kaffeebestandteilen, die durch siedendes Wasser oder nach dem Expressoverfahren unter leichtem Überdruck dem Kaffee entzogen werden. Haushaltungsgemäß hergestellte Extrakte ergeben bekanntlich eine Ausbeute des Röstkaffees von z. B. 15 bis 20 % und die extreme Auskochung mit einer Übermenge von Wasser und langem Kochen von höchstens etwa 25 bis 30 % je nach Kaffeesorte.

Die technische Entwicklung der Kaffee-Extraktion geht nun heute allgemein so weit, daß die natürliche Löslichkeitsgrenze des Kaffees bei etwa 90 bis 110° C durch Einwirkung von hohem Druck und hoher Temperatur durch Hydrolyse bis über 50 % überschritten wird, was analytisch ohne weiteres nachweisbar ist. Aus Röstkaffee wird dadurch statt der durchschnittlichen Ausbeute von etwa 25 % vielfach eine solche von 35 bis 40 % und mehr erreicht.

Verfahren zur Herstellung eines trockenen, löslichen vollaromatischen Kaffee-Extraktes

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Beanspruchte Priorität:
Schweiz vom 2. Juli 1956 (Nr. 34 954)

Dr. Max Rudolf Morgenthaler, Vevey (Schweiz),
ist als Erfinder genannt worden

2

Diese Verfahren erlauben also infolge der Hydrolyse eine scheinbare Mehrausbeute an Kaffeesubstanz, jedoch werden diese unreinen, stark sauren Hydrolysenprodukte aus Kaffeesatz nicht mehr, wie dies möglich wäre, bis zu den reinen Kohlehydraten gereinigt, sondern im kontinuierlichen Durchfluß direkt dazu verwendet, den bereits bis zur normalen Löslichkeit in siedendem Wasser von etwa 25 % ausgebeuteten, qualitativ normalen Kaffee-Extrakt einfach zu verdünnen. Damit wird erreicht, daß das Trocken-Extraktgewicht pro Tasse unnatürlich erhöht wird.

Diese, für sich allein betrachtet, nachweisbar geschmacklich minderwertigen, stark sauren Hydrolysate von Kaffeesatz, die ein p_H von 3 bis 4 aufweisen können, sind normalerweise in einem reinen, trinkfertigen Kaffee von etwa 25%iger Löslichkeit nicht vorhanden, und es kann somit von einem 100%ig natürlichen, löslichen Kaffee-Extrakt nicht mehr gesprochen werden (Gordian, Kaffee- u. Tee-Markt, 4. Januar 1955, Wurziger »Zur Untersuchung von Röstkaffe und Kaffee-Extrakt«).

Die ungereinigten sauren Hydrolysenprodukte mindern die Kaffeequalität so stark, daß auch ein Zusatz von Kohlehydraten die Qualität des Extraktes nicht zu verbessern vermag. Die auf dem Markt befindlichen Produkte distanzieren sich somit ganz wesentlich von einem normalen Kaffee-Trockenextrakt bzw. von einer normalen Kaffeeinfusion.

Figure 3.59: In the 1930s, Max Rudolf Morgenthaler and other chemists developed Nescafé, an instant coffee derived from natural ingredients.

Production of fats via industrial chemical synthesis

[BIOS 805]

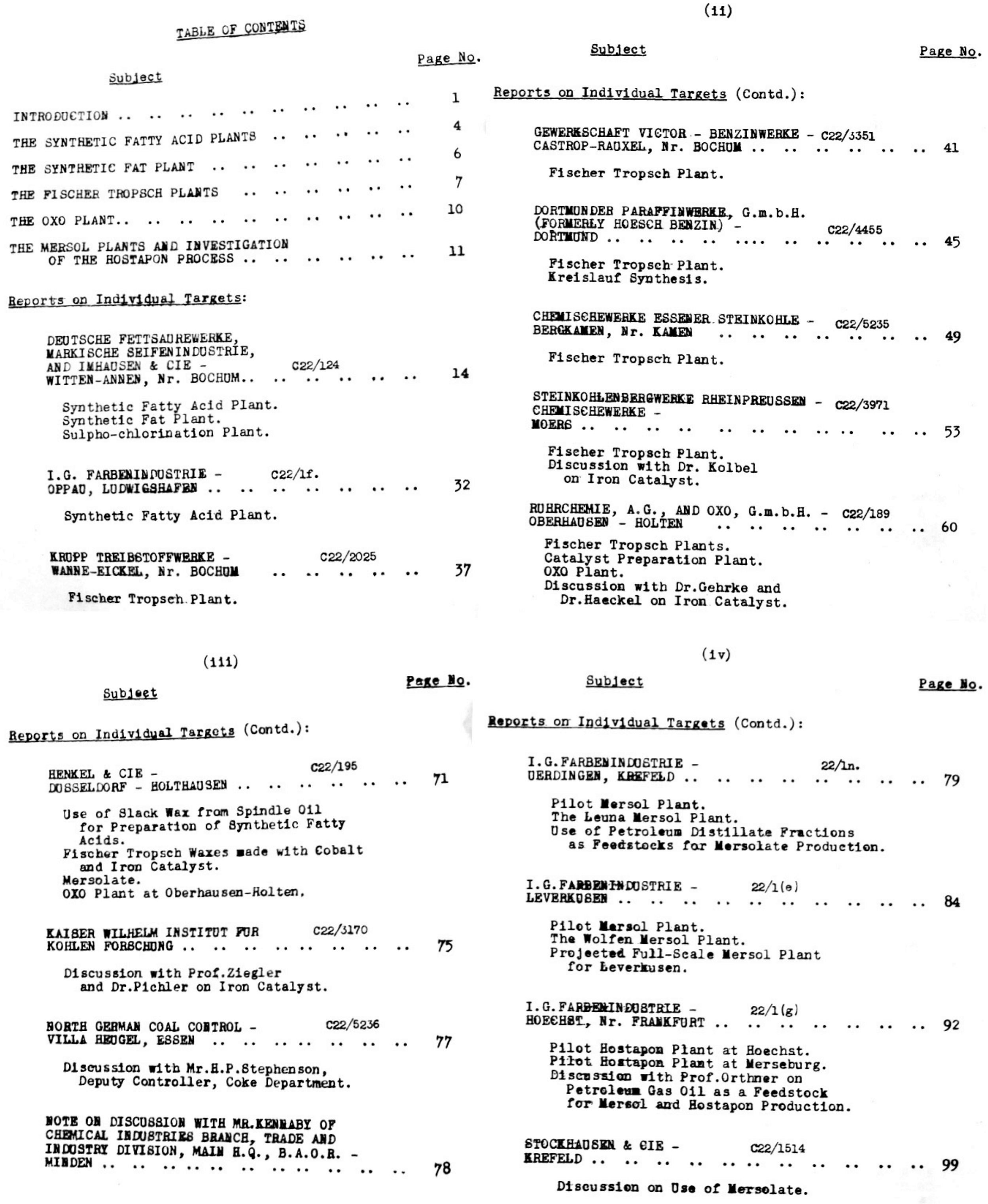

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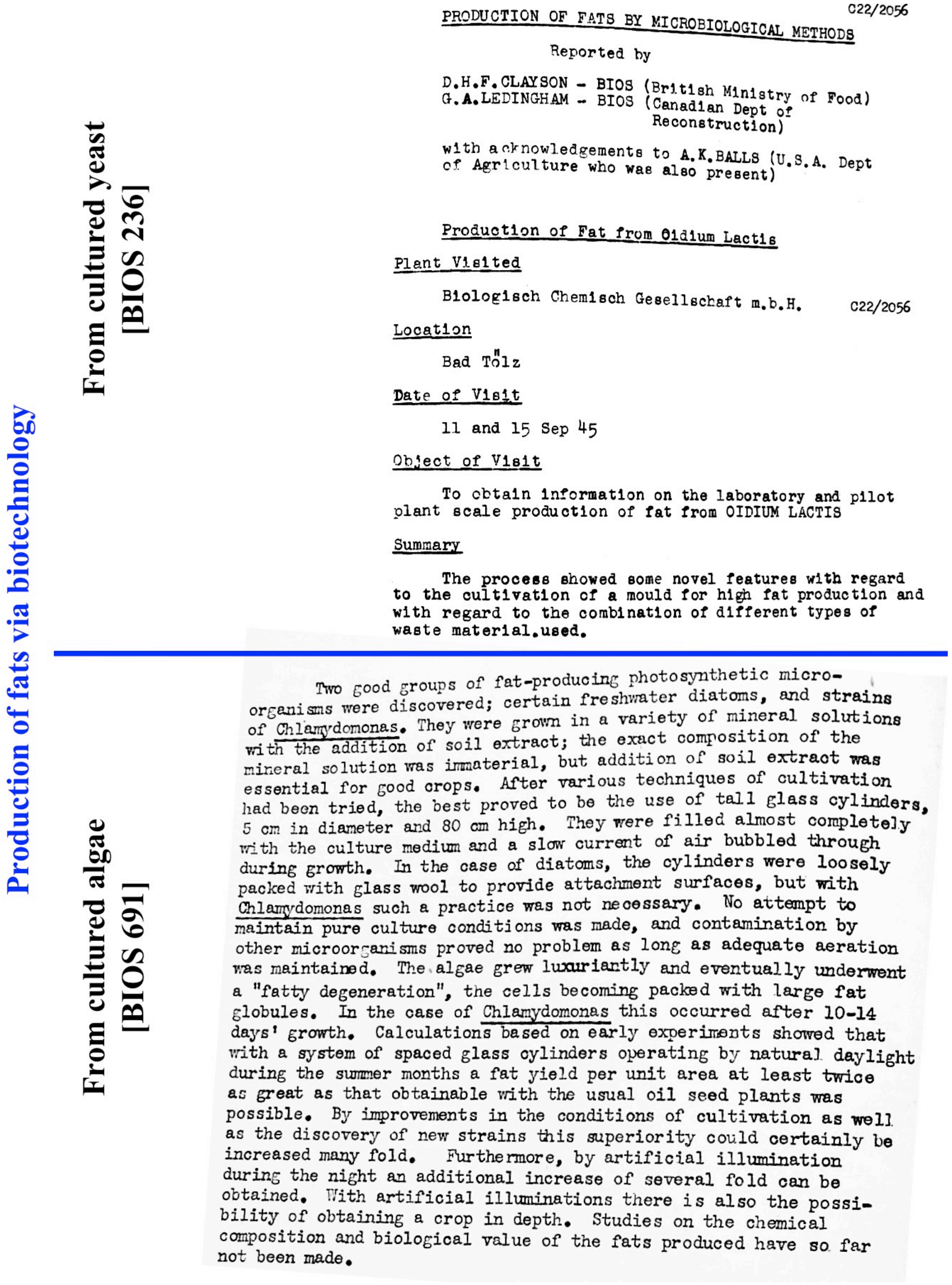
Figure 3.60: In the 1930s and early 1940s, German-speaking scientists developed methods to produce fats via industrial chemical synthesis [BIOS 805].



C22/2056

PRODUCTION OF FATS BY MICROBIOLOGICAL METHODS

Reported by

D.H.F.CLAYSON - BIOS (British Ministry of Food)
G.A.LEDINGHAM - BIOS (Canadian Dept of Reconstruction)

with acknowledgements to A.K.BALLS (U.S.A. Dept of Agriculture who was also present)

Production of Fat from Oidium Lactis

Plant Visited

Biologisch Chemisch Gesellschaft m.b.H. C22/2056

Location

Bad Tölz

Date of Visit

11 and 15 Sep 45

Object of Visit

To obtain information on the laboratory and pilot plant scale production of fat from OIDIUM LACTIS

Summary

The process showed some novel features with regard to the cultivation of a mould for high fat production and with regard to the combination of different types of waste material.used.

Two good groups of fat-producing photosynthetic micro-organisms were discovered; certain freshwater diatoms, and strains of Chlamydomonas. They were grown in a variety of mineral solutions with the addition of soil extract; the exact composition of the mineral solution was immaterial, but addition of soil extract was essential for good crops. After various techniques of cultivation had been tried, the best proved to be the use of tall glass cylinders, 5 cm in diameter and 80 cm high. They were filled almost completely with the culture medium and a slow current of air bubbled through during growth. In the case of diatoms, the cylinders were loosely packed with glass wool to provide attachment surfaces, but with Chlamydomonas such a practice was not necessary. No attempt to maintain pure culture conditions was made, and contamination by other microorganisms proved no problem as long as adequate aeration was maintained. The algae grew luxuriantly and eventually underwent a "fatty degeneration", the cells becoming packed with large fat globules. In the case of Chlamydomonas this occurred after 10-14 days' growth. Calculations based on early experiments showed that with a system of spaced glass cylinders operating by natural daylight during the summer months a fat yield per unit area at least twice as great as that obtainable with the usual oil seed plants was possible. By improvements in the conditions of cultivation as well as the discovery of new strains this superiority could certainly be increased many fold. Furthermore, by artificial illumination during the night an additional increase of several fold can be obtained. With artificial illuminations there is also the possibility of obtaining a crop in depth. Studies on the chemical composition and biological value of the fats produced have so far not been made.

Figure 3.61: In the 1930s and early 1940s, German-speaking scientists developed methods to produce fats via biotechnology using cultured yeast or algae cells [BIOS 236; BIOS 691].

3.3.4 Synthetic Protein Products

Likewise in the 1930s and early 1940s, German-speaking scientists developed several egg protein substitutes that consisted of protein extracted and processed on an industrial scale from (Fig. 3.62):

- Cultured strains of yeast that produced the variety of amino acids needed by humans, as developed by Andreas Lembke (German, 1911–2002) and other scientists [BIOS 236; BIOS 691; FIAT 491].

- Animal blood plasma (a final product called Plenora), as developed by scientists at the Rugamer & Co. Plenora-Werke in Hamburg [BIOS 1417; FIAT 491].

- Fish (a final product called Eiweiss), as developed by Peter Paul Hiltner (German, 19??–19??) and other scientists [BIOS 1481; FIAT 491].

- Milk (a final product called Milei), as developed by Georg Demmler (German, 19??–19??) and other scientists [BIOS 32; BIOS 275; BIOS 1513; BIOS 1782; FIAT 491].

3.3.5 Preservatives

In order to preserve valuable food stocks for storage and transport during both peacetime and wartime, German-speaking scientists developed many important food preservatives that work by chelating (trapping) metal ions that are needed by degradative enzymes and bacteria. These preservatives have been widely used ever since, and include for example:

- Ascorbic acid (vitamin C), which was identified in 1930 by Albert Szent-Györgyi (Hungarian, 1893–1986) and mass-produced via chemical synthesis in 1933 by Tadeusz Reichstein (Polish, educated and worked in Switzerland, 1897–1996, Fig. 3.63).

- Benzoic acid, which was first analyzed in 1832 by Friedrich Wöhler (German, 1800–1882) and Justus von Liebig (German, 1803–1873, Fig. 3.63).

- Citric acid, which was first produced from fermentation in fungi in 1890 by Carl Wehmer (German, 1858–1935, Fig. 3.63) [Benninga 1990, p. 140].

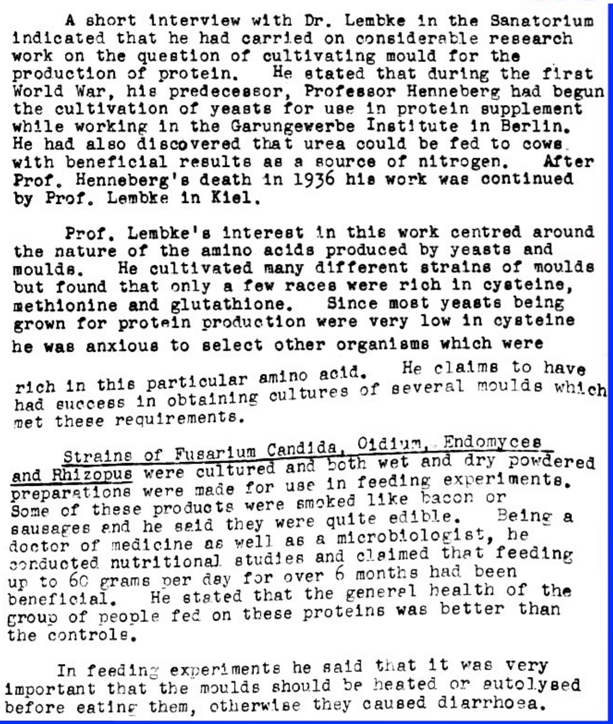
- Sorbic acid, which was discovered in 1859 by August Wilhelm von Hofmann (German, 1818–1892, Fig. 3.63).

- Ethylenediaminetetraacetic acid (EDTA), an extremely effective chelator, which was synthesized and demonstrated in 1935 by Ferdinand Münz (Austrian, 1888–1969, Fig. 3.64) Schahinian 2018.

In 1940, German-speaking scientists also developed and successfully implemented the use of ultraviolet light to sterilize drinks so that they could be packaged for safe long-term storage without requiring refrigeration [BIOS 770; FIAT 50; FIAT 107; FIAT 257]. Some of the most important scientists in the project were Andreas Lembke (German, 1911–2002), Hellmuth Bayha (German?, 19??–19??), Karl Krammer (German?, 19??–19??), and Eugen Sauter (German?, 19??–19??). For more information, see pp. 2379–2385.

Artificial egg protein

Protein derived from cultured yeast [BIOS 236]



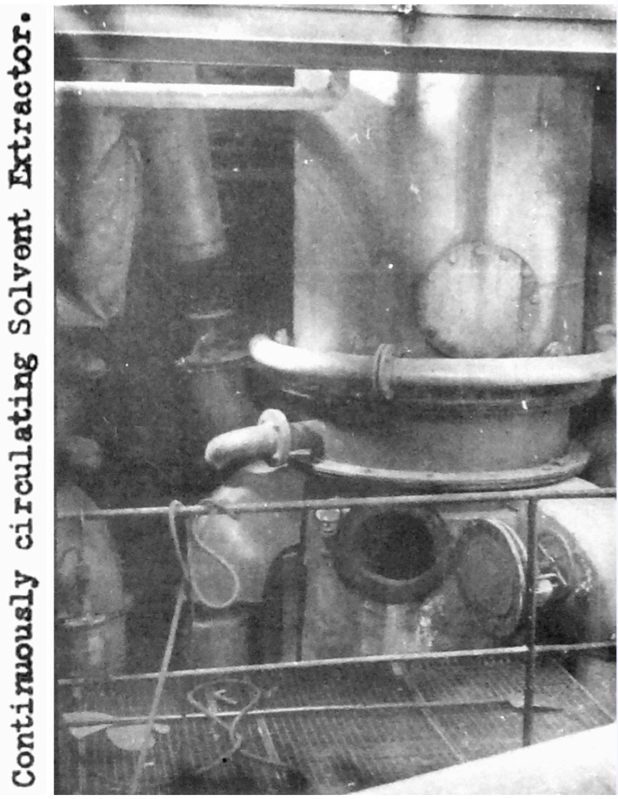
A short interview with Dr. Lembke in the Sanatorium indicated that he had carried on considerable research work on the question of cultivating mould for the production of protein. He stated that during the first World War, his predecessor, Professor Henneberg had begun the cultivation of yeasts for use in protein supplement while working in the Garungewerbe Institute in Berlin. He had also discovered that urea could be fed to cows with beneficial results as a source of nitrogen. After Prof. Henneberg's death in 1936 his work was continued by Prof. Lembke in Kiel.

Prof. Lembke's interest in this work centred around the nature of the amino acids produced by yeasts and moulds. He cultivated many different strains of moulds but found that only a few races were rich in cysteine, methionine and glutathione. Since most yeasts being grown for protein production were very low in cysteine he was anxious to select other organisms which were rich in this particular amino acid. He claims to have had success in obtaining cultures of several moulds which met these requirements.

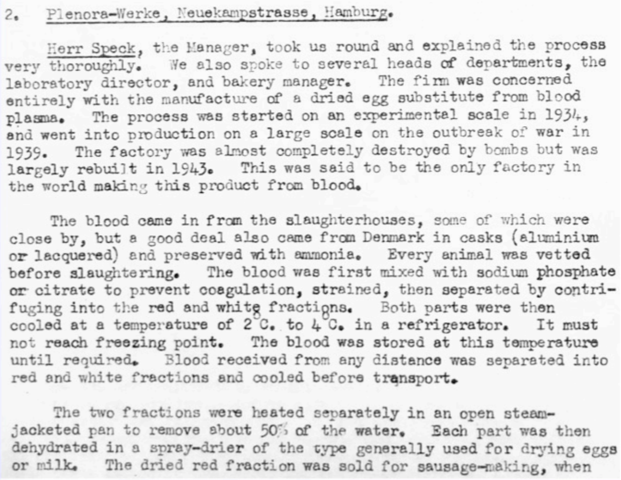
Strains of Fusarium Candida, Oidium, Endomyces and Rhizopus were cultured and both wet and dry powdered preparations were made for use in feeding experiments. Some of these products were smoked like bacon or sausages and he said they were quite edible. Being a doctor of medicine as well as a microbiologist, he conducted nutritional studies and claimed that feeding up to 60 grams per day for over 6 months had been beneficial. He stated that the general health of the group of people fed on these proteins was better than the controls.

In feeding experiments he said that it was very important that the moulds should be heated or autolysed before eating them, otherwise they caused diarrhoea.

Eiweiss derived from fish [BIOS 1481]



Plenora derived from animal blood plasma [BIOS 1417]



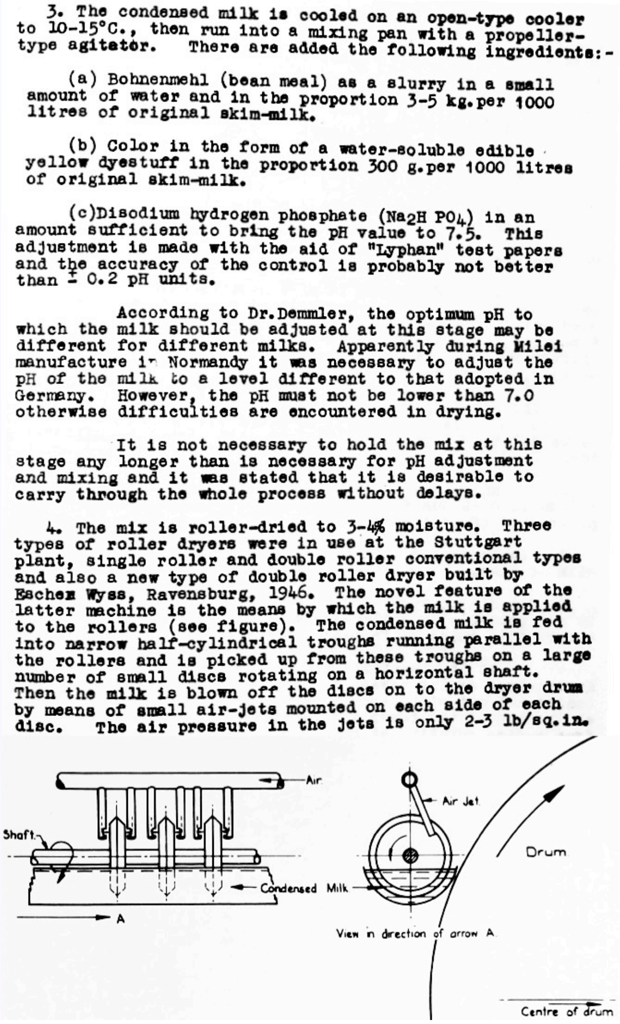
2. Plenora-Werke, Neuekampstrasse, Hamburg.

Herr Speck, the Manager, took us round and explained the process very thoroughly. We also spoke to several heads of departments, the laboratory director, and bakery manager. The firm was concerned entirely with the manufacture of a dried egg substitute from blood plasma. The process was started on an experimental scale in 1934, and went into production on a large scale on the outbreak of war in 1939. The factory was almost completely destroyed by bombs but was largely rebuilt in 1943. This was said to be the only factory in the world making this product from blood.

The blood came in from the slaughterhouses, some of which were close by, but a good deal also came from Denmark in casks (aluminium or lacquered) and preserved with ammonia. Every animal was vetted before slaughtering. The blood was first mixed with sodium phosphate or citrate to prevent coagulation, strained, then separated by contrifuging into the red and white fractions. Both parts were then cooled at a temperature of 2°C. to 4°C. in a refrigerator. It must not reach freezing point. The blood was stored at this temperature until required. Blood received from any distance was separated into red and white fractions and cooled before transport.

The two fractions were heated separately in an open steam-jacketed pan to remove about 50% of the water. Each part was then dehydrated in a spray-drier of the type generally used for drying eggs or milk. The dried red fraction was sold for sausage-making, when

Milei derived from milk [BIOS 1513]



3. The condensed milk is cooled on an open-type cooler to 10-15°C., then run into a mixing pan with a propeller-type agitator. There are added the following ingredients:-

(a) Bohnenmehl (bean meal) as a slurry in a small amount of water and in the proportion 3-5 kg.per 1000 litres of original skim-milk.

(b) Color in the form of a water-soluble edible yellow dyestuff in the proportion 300 g.per 1000 litres of original skim-milk.

(c)Disodium hydrogen phosphate ($Na_2H\ PO_4$) in an amount sufficient to bring the pH value to 7.5. This adjustment is made with the aid of "Lyphan" test papers and the accuracy of the control is probably not better than ± 0.2 pH units.

According to Dr.Demmler, the optimum pH to which the milk should be adjusted at this stage may be different for different milks. Apparently during Milei manufacture in Normandy it was necessary to adjust the pH of the milk to a level different to that adopted in Germany. However, the pH must not be lower than 7.0 otherwise difficulties are encountered in drying.

It is not necessary to hold the mix at this stage any longer than is necessary for pH adjustment and mixing and it was stated that it is desirable to carry through the whole process without delays.

4. The mix is roller-dried to 3-4% moisture. Three types of roller dryers were in use at the Stuttgart plant, single roller and double roller conventional types and also a new type of double roller dryer built by Eschez Wyss, Ravensburg, 1946. The novel feature of the latter machine is the means by which the milk is applied to the rollers (see figure). The condensed milk is fed into narrow half-cylindrical troughs running parallel with the rollers and is picked up from these troughs on a large number of small discs rotating on a horizontal shaft. Then the milk is blown off the discs on to the dryer drum by means of small air-jets mounted on each side of each disc. The air pressure in the jets is only 2-3 lb/sq.in.

Figure 3.62: In the 1930s and early 1940s, German-speaking scientists developed several egg protein substitutes that consisted of protein extracted and processed on an industrial scale from cultured yeast, animal blood plasma (Plenora), fish (Eiweiss), and milk (Milei) [BIOS 236; BIOS 1417; BIOS 1481; BIOS 1513].

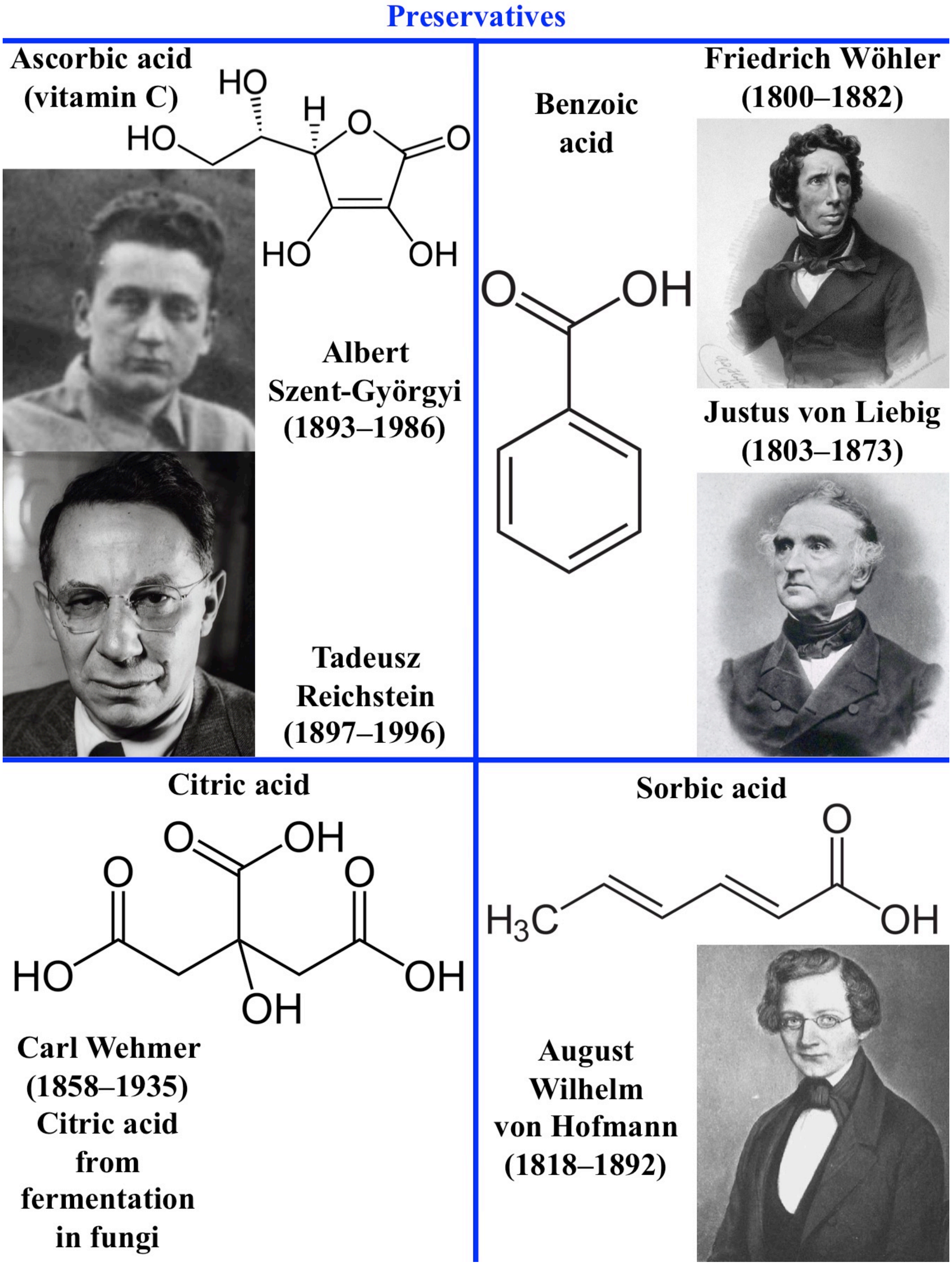


Figure 3.63: German-speaking scientists developed many important food preservatives, including ascorbic acid (vitamin C, identified by Albert Szent-Györgyi and mass-produced by Tadeusz Reichstein), benzoic acid (first analyzed by Friedrich Wöhler and Justus von Liebig), citric acid (first produced from fermentation in fungi by Carl Wehmer), and sorbic acid (discovered by August Wilhelm von Hofmann).

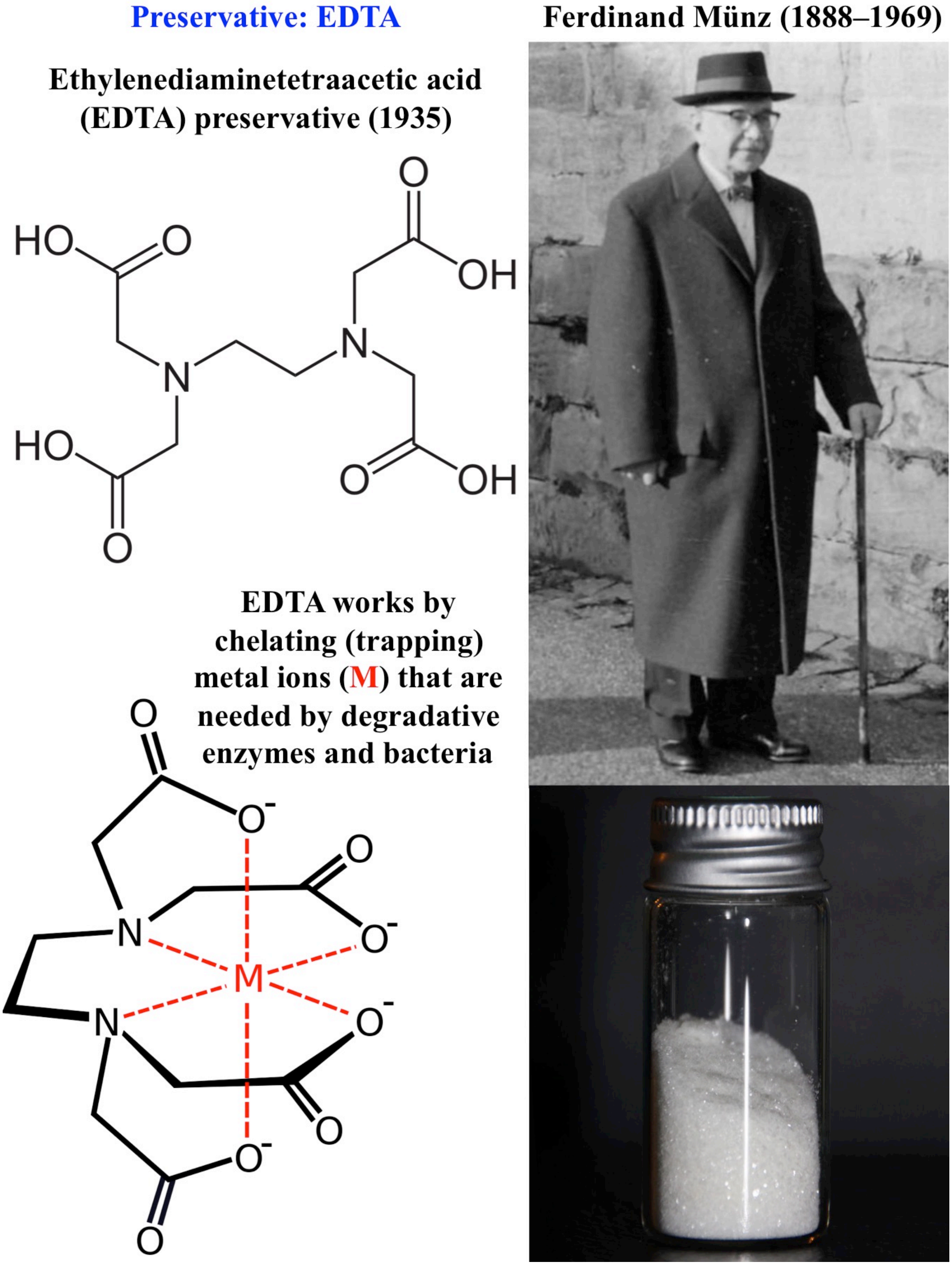


Figure 3.64: In 1935, Ferdinand Münz created the synthetic preservative ethylenediaminetetraacetic acid (EDTA), which works by chelating (trapping) metal ions that are needed by degradative enzymes and bacteria.

3.4 Explosives

Scientists from the German-speaking world were responsible for most of the major innovations in modern explosives, including:[8]

3.4.1. Explosive chemical compounds

3.4.2. Fuel-air explosives

3.4.3. Shaped explosive charges

3.4.4. Radio control and electric timers for explosives

3.4.1 Explosive Chemical Compounds

German-speaking chemists developed most of the major modern explosive chemical compounds.

The first known high explosive was fulminating gold, a complex mixture of compounds containing gold, ammonia, and chlorine. Fulminating gold was produced and demonstrated by Sebalt Schwertzer (German states, 1552–1598) and Johann Thölde/Thölden (German states, 1565–1614). Historical portraits of Schwertzer and Thölde(n) do not appear to exist, but Fig. 3.65 shows illustrations of typical alchemists from that time and place.

As illustrated in Fig. 3.66, Christian Schönbein (German states, 1799–1868), Rudolf Christian Böttger (German, 1806–1881), Friedrich Julius Otto (German, 1809–1870), and Wilhelm Lenk von Wolfsberg (Austrian, 1809–1894) developed nitrocellulose or guncotton explosive.

Johann F. E. Schultze (German?, 18??–19??), Max Duttenhofer (German, 1843–1903), and Frederick Volkmann (German?, 18??–19??) developed smokeless powder, shown in Fig. 3.67. Smokeless powder is essentially an improved nitrocellulose material in flake or powder form, and has been widely used as propellant for small solid rockets.

Johann Rudolf Glauber (German states, 1604–1670) discovered picric acid around 1648, and Hermann Sprengel (German states, 1834–1906) produced large quantities of picric acid as an explosive in 1871 (Fig. 3.68). Sprengel also produced safety explosives (binary explosives that can be safely stored as separate components, then mixed shortly before use) and other explosive-related products.

As shown in Fig. 3.69, Julius Wilbrand (German, 1839–1906) first synthesized trinitrotoluene (TNT) in 1863, Paul Hepp (German, 18??–19??) improved the synthesis in 1880, and Karl Häussermann (German, 1853–1918) used TNT as an explosive in 1889. Science historian Peter Krehl described their contributions [Krehl 2009, p. 404]:

---

[8] George Brown 1998; Field 2017; Kennedy 1990; Krehl 2009; Walters and Zukas 1989.

> 1891: Karl Häussermann, a German chemist, discovers the explosive properties of trinitrotoluene [...], later known as TNT. The substance was first crudely synthesized by the German chemist Julius Wilbrand [...]; pure TNT was first prepared by the German chemist Paul Hepp in 1880. Häussermann, who undertook the manufacture of TNT on an industrial scale, was also the first to suggest its military use: pressed into shells, it can withstand the shock developed by the propellant when a shell is fired from a gun barrel. In 1902, TNT was adopted for use by the German army.

The chemist and chemical historian Aaron Ihde added [Ihde 1984, p. 706]:

> During World War I TNT and picric acid explosives were brought into large-scale use. The Germans, with their flourishing coal tar chemicals industry, were prepared for the production of high explosives. The French and British were not nearly as well prepared.

Wilhelm Michler (German, 1846–1889), Carl Meyer (German, 18??–19??), Karel Hendrik Mertens (Dutch, 18??–19??), and Pieter van Romburgh (Dutch, 1855–1945) developed tetryl explosive beginning in 1877 (Fig. 3.70). The chemist Simon Field summarized the story [Field 2017, pp. 81–82]:

> In 1877, German chemists Wilhelm Michler and Carl Meyer invented the compound tetryl, or 2,4,6-trinitrophenylmethylnitramine. It took until 1886 before its structure was established by Dutch chemist Karel Hendrik Mertens. Another Dutch chemist, Pieter van Romburgh later (in 1889) proved the structure by synthesizing it from picryl chloride and potassium methylnitramine.
>
> Tetryl was the first of the nitramine class of high explosives, which includes many of the most explosive compounds currently in use. [...] Nitramines are characterized by the two nitrogen atoms connected together, with one of them then connected to two oxygen atoms.
>
> Tetryl was used in both World Wars as a booster, and by itself in some of the smaller caliber shells.

As illustrated in Fig. 3.71, Georg Friedrich Henning (German, 1863–1945) first synthesized hexogen in 1898, and Edmund von Herz (German, 18??–19??) patented hexogen as an explosive in 1919. Hexogen was named for its six-sided central ring, surrounded by three symmetrical nitro groups. Later it became much more widely known as “Research Department Explosive” or RDX in the United Kingdom and United States. During the Third Reich, German chemists extended the approach of hexogen to create octogen, an eight-sided central ring with four symmetrical nitro groups. Octogen later became better known as HMX.

Figure 3.72 shows that nitroglycerin and dynamite were also closely connected to the German-speaking research world. Ascanio Sobrero (Italian but studied under Justus Liebig, 1812–1888) developed nitroglycerin explosive in 1847. Nitroglycerin is extremely powerful but quite sensitive to physical shock. In 1867, Alfred Nobel (Swedish but worked in Germany, 1833–1996) developed dynamite, which is clay soaked with nitroglycerin, in order to make the nitroglycerin less sensitive to shock and therefore much easier to transport and use.

Bernhard Tollens (German, 1841–1918) and Peter Wigand (German, 18??–19??), shown in Fig. 3.73, developed pentaerythritol tetranitrate (PETN) explosive in 1891. The general public nowadays is more familiar with Semtex plastic explosive, which is a mixture of PETN and RDX with a small amount of plasticizer and binder. PETN is also used as a blood pressure medication.

Figure 3.74 presents examples of German-speaking scientists who made important contributions to the mathematical theory of explosions. Walther Nernst (German, 1864–1941) and Max Bodenstein (German, 1871–1942) worked out the theory of explosive chain reactions; Nernst won the Nobel Prize in Chemistry in 1920 (p. 921). Heinrich Mache (Austrian, 1876–1954) and Ludwig Flamm (Austrian, 1885–1964) developed the theory of explosive gas mixtures.

Over two years after World War II ended in Europe, the U.S. War Department General Staff (WDGS) Intelligence Division wrote a report summarizing what they had learned about “New Explosives Developed by the Germans” during the war. Even after so many decades, that report remains classified and unavailable to the public. Why? What new explosive compounds or methods were described in that report, or in others like it that may still be buried in classified archives? See Fig. 3.75.

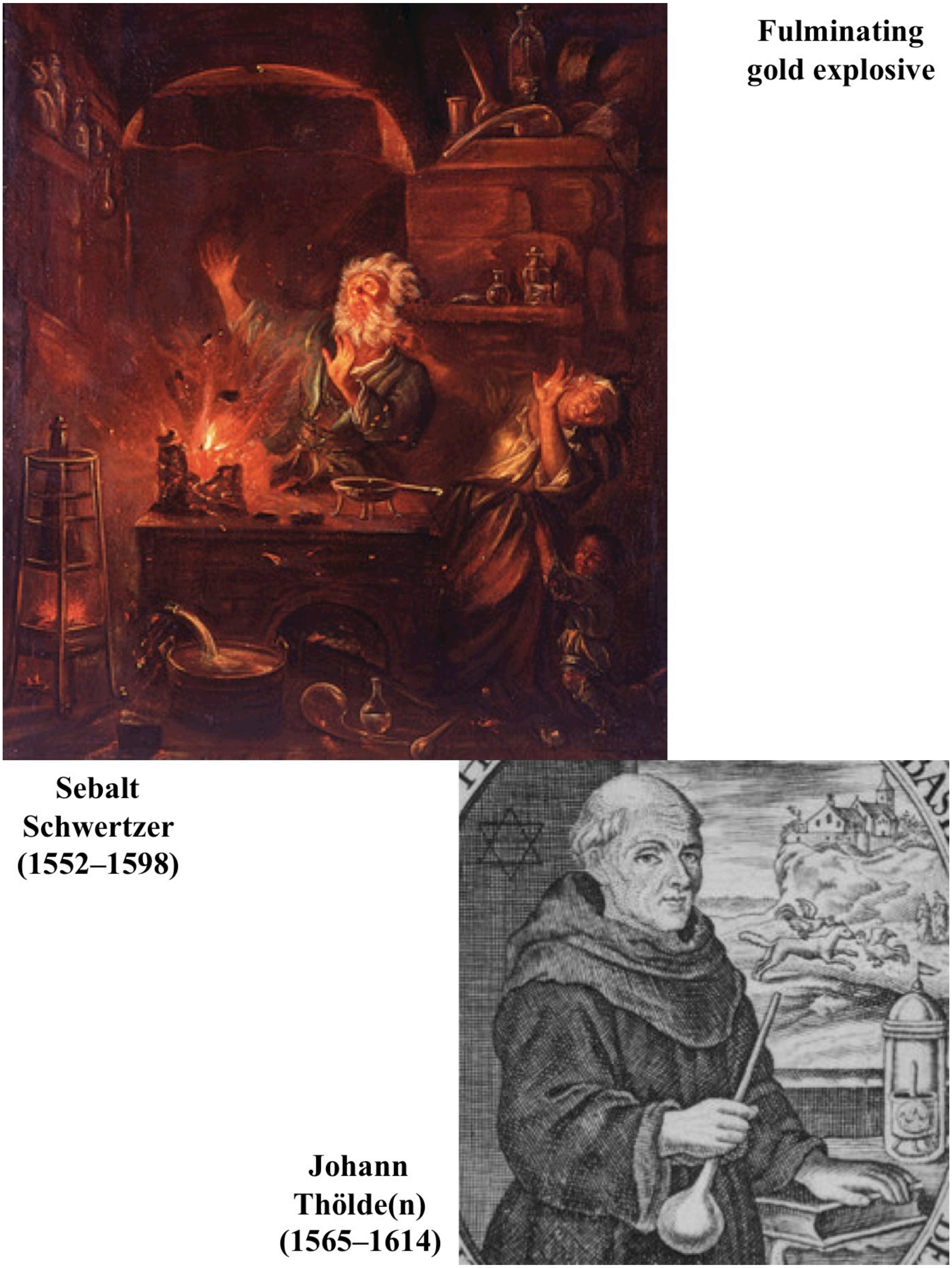


Figure 3.65: Sebalt Schwertzer and Johann Thölde(n) developed and demonstrated fulminating gold explosive.

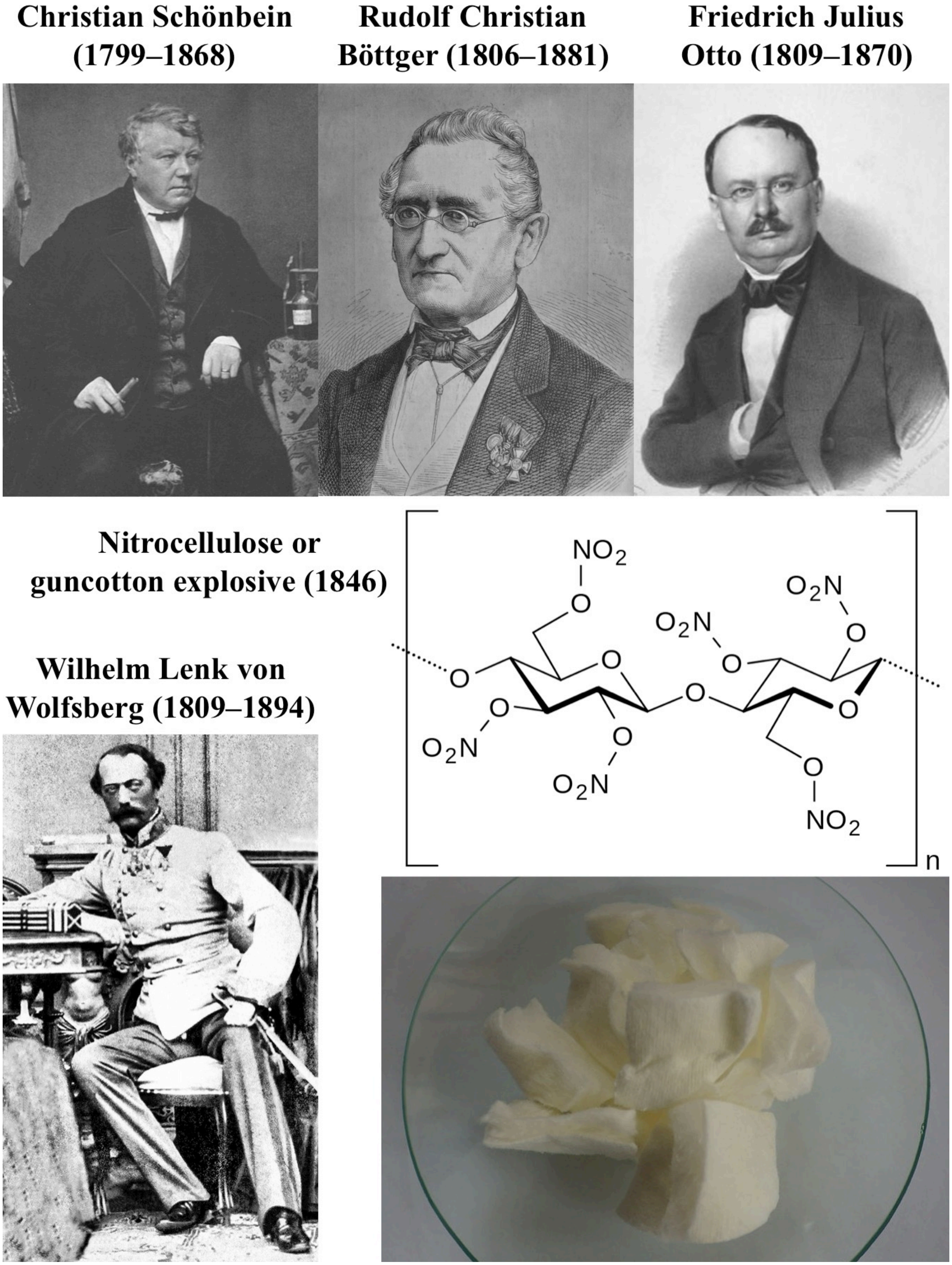


Figure 3.66: Christian Schönbein, Rudolf Christian Böttger, Friedrich Julius Otto, and Wilhelm Lenk von Wolfsberg developed nitrocellulose or guncotton explosive.

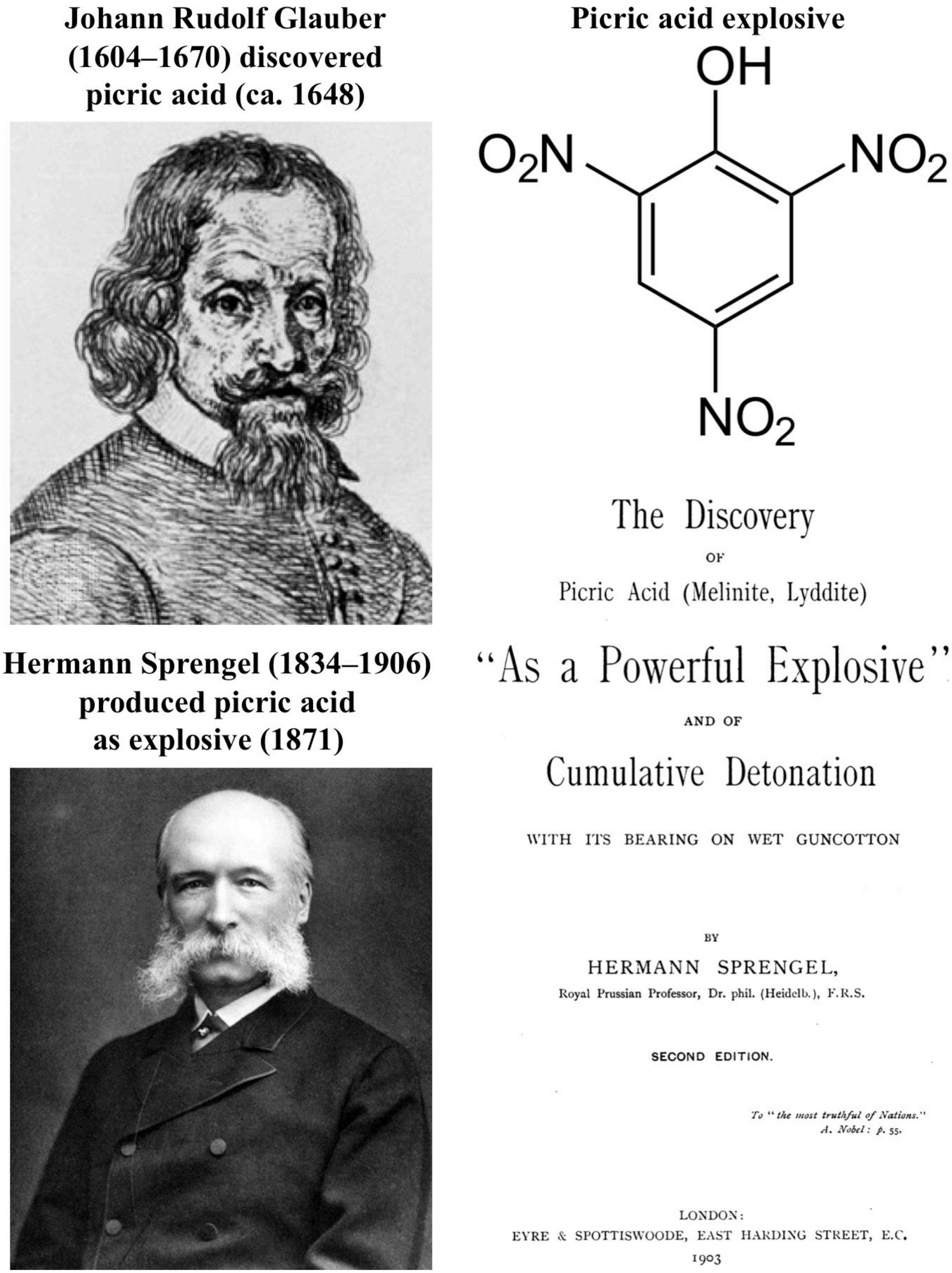
Johann F. E. Schultze
(18??–18??)

Max Duttenhofer
(1843–1903)

Frederick Volkmann
(18??–19??)

Smokeless powder

Figure 3.67: Johann F. E. Schultze, Max Duttenhofer, and Frederick Volkmann developed smokeless powder.



The Discovery
OF
Picric Acid (Melinite, Lyddite)

"As a Powerful Explosive"
AND OF
Cumulative Detonation

WITH ITS BEARING ON WET GUNCOTTON

BY
HERMANN SPRENGEL,
Royal Prussian Professor, Dr. phil. (Heidelb.), F.R.S.

SECOND EDITION.

To "the most truthful of Nations."
A. Nobel: p. 55.

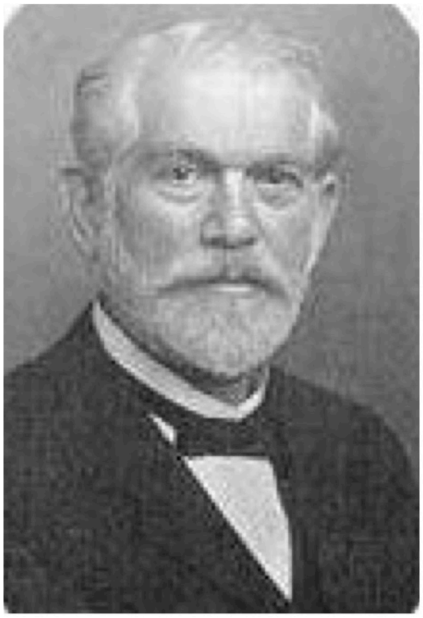
LONDON:
EYRE & SPOTTISWOODE, EAST HARDING STREET, E.C.
1903

Figure 3.68: Johann Rudolf Glauber discovered picric acid around 1648, and Hermann Sprengel produced large quantities of picric acid as an explosive in 1871.

Julius Wilbrand
(1839–1906)
synthesized
TNT (1863)

Paul Hepp
(18??–19??)
improved TNT
synthesis (1880)

Karl Häussermann
(1853–1918)
used TNT as
explosive (1889)



Trinitrotoluene (TNT) explosive

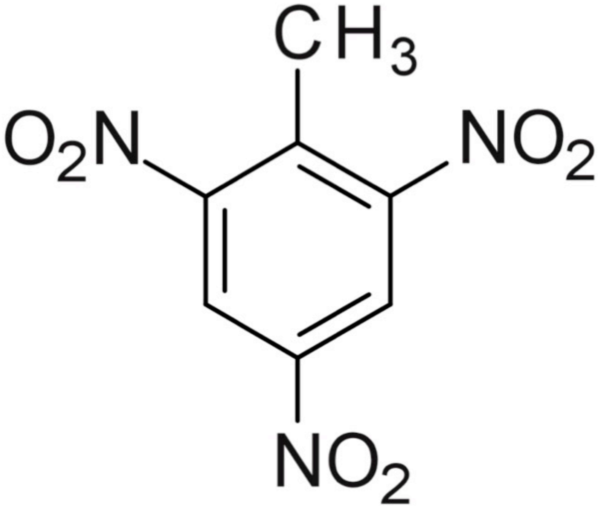
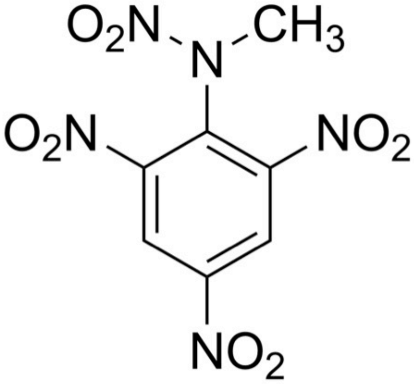


Figure 3.69: Julius Wilbrand synthesized trinitrotoluene (TNT) in 1863, Paul Hepp improved the synthesis in 1880, and Karl Häussermann used TNT as an explosive in 1889.

Wilhelm Michler
(1846–1889)

Carl Meyer
(18??–19??)

Tetryl explosive (1877)



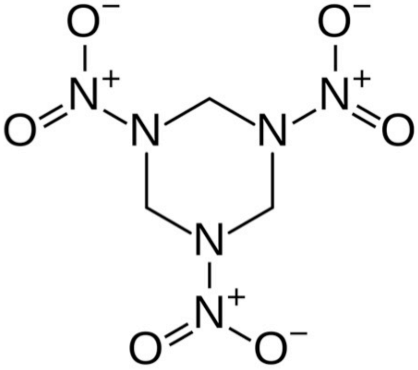
Karel Hendrik Mertens
(18??–19??)

Pieter van Romburgh
(1855–1945)

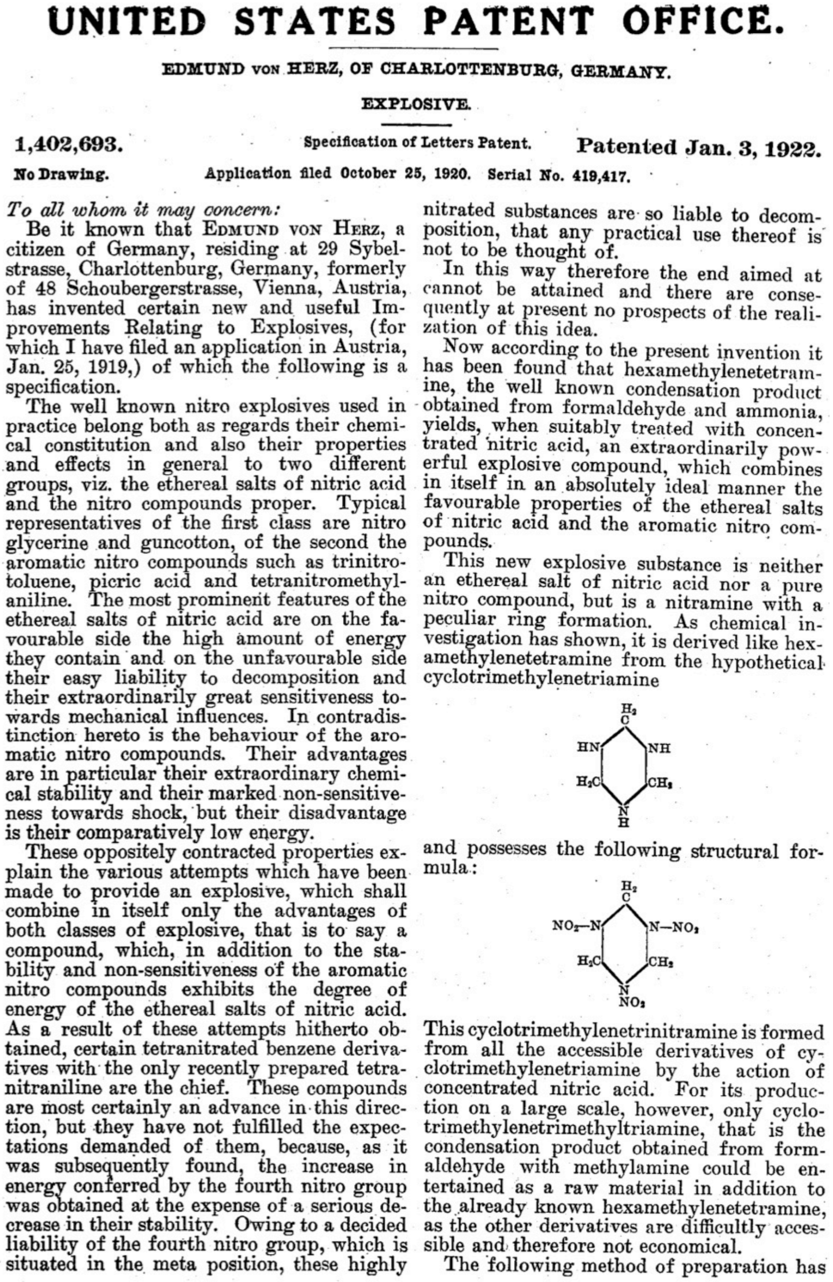
Figure 3.70: Wilhelm Michler, Carl Meyer, Karel Hendrik Mertens, and Pieter van Romburgh developed tetryl explosive beginning in 1877.

Georg Friedrich Henning (1863–1945) synthesized RDX (1898)

Hexogen (RDX) explosive



Edmund von Herz (18??–19??) patented RDX as explosive (1919)



UNITED STATES PATENT OFFICE.

EDMUND VON HERZ, OF CHARLOTTENBURG, GERMANY.

EXPLOSIVE.

1,402,693. Specification of Letters Patent. **Patented Jan. 3, 1922.**

No Drawing. Application filed October 25, 1920. Serial No. 419,417.

To all whom it may concern:

Be it known that Edmund von Herz, a citizen of Germany, residing at 29 Sybelstrasse, Charlottenburg, Germany, formerly of 48 Schoubergerstrasse, Vienna, Austria, has invented certain new and useful Improvements Relating to Explosives, (for which I have filed an application in Austria, Jan. 25, 1919,) of which the following is a specification.

The well known nitro explosives used in practice belong both as regards their chemical constitution and also their properties and effects in general to two different groups, viz. the ethereal salts of nitric acid and the nitro compounds proper. Typical representatives of the first class are nitro glycerine and guncotton, of the second the aromatic nitro compounds such as trinitrotoluene, picric acid and tetranitromethylaniline. The most prominent features of the ethereal salts of nitric acid are on the favourable side the high amount of energy they contain and on the unfavourable side their easy liability to decomposition and their extraordinarily great sensitiveness towards mechanical influences. In contradistinction hereto is the behaviour of the aromatic nitro compounds. Their advantages are in particular their extraordinary chemical stability and their marked non-sensitiveness towards shock, but their disadvantage is their comparatively low energy.

These oppositely contracted properties explain the various attempts which have been made to provide an explosive, which shall combine in itself only the advantages of both classes of explosive, that is to say a compound, which, in addition to the stability and non-sensitiveness of the aromatic nitro compounds exhibits the degree of energy of the ethereal salts of nitric acid. As a result of these attempts hitherto obtained, certain tetranitrated benzene derivatives with the only recently prepared tetranitraniline are the chief. These compounds are most certainly an advance in this direction, but they have not fulfilled the expectations demanded of them, because, as it was subsequently found, the increase in energy conferred by the fourth nitro group was obtained at the expense of a serious decrease in their stability. Owing to a decided liability of the fourth nitro group, which is situated in the meta position, these highly nitrated substances are so liable to decomposition, that any practical use thereof is not to be thought of.

In this way therefore the end aimed at cannot be attained and there are consequently at present no prospects of the realization of this idea.

Now according to the present invention it has been found that hexamethylenetetramine, the well known condensation product obtained from formaldehyde and ammonia, yields, when suitably treated with concentrated nitric acid, an extraordinarily powerful explosive compound, which combines in itself in an absolutely ideal manner the favourable properties of the ethereal salts of nitric acid and the aromatic nitro compounds.

This new explosive substance is neither an ethereal salt of nitric acid nor a pure nitro compound, but is a nitramine with a peculiar ring formation. As chemical investigation has shown, it is derived like hexamethylenetetramine from the hypothetical cyclotrimethylenetriamine

and possesses the following structural formula:

This cyclotrimethylenetrinitramine is formed from all the accessible derivatives of cyclotrimethylenetriamine by the action of concentrated nitric acid. For its production on a large scale, however, only cyclotrimethylenetrimethyltriamine, that is the condensation product obtained from formaldehyde with methylamine could be entertained as a raw material in addition to the already known hexamethylenetetramine, as the other derivatives are difficultly accessible and therefore not economical.

The following method of preparation has

Figure 3.71: Georg Friedrich Henning synthesized hexogen or RDX in 1898, and Edmund von Herz patented RDX as an explosive in 1919.

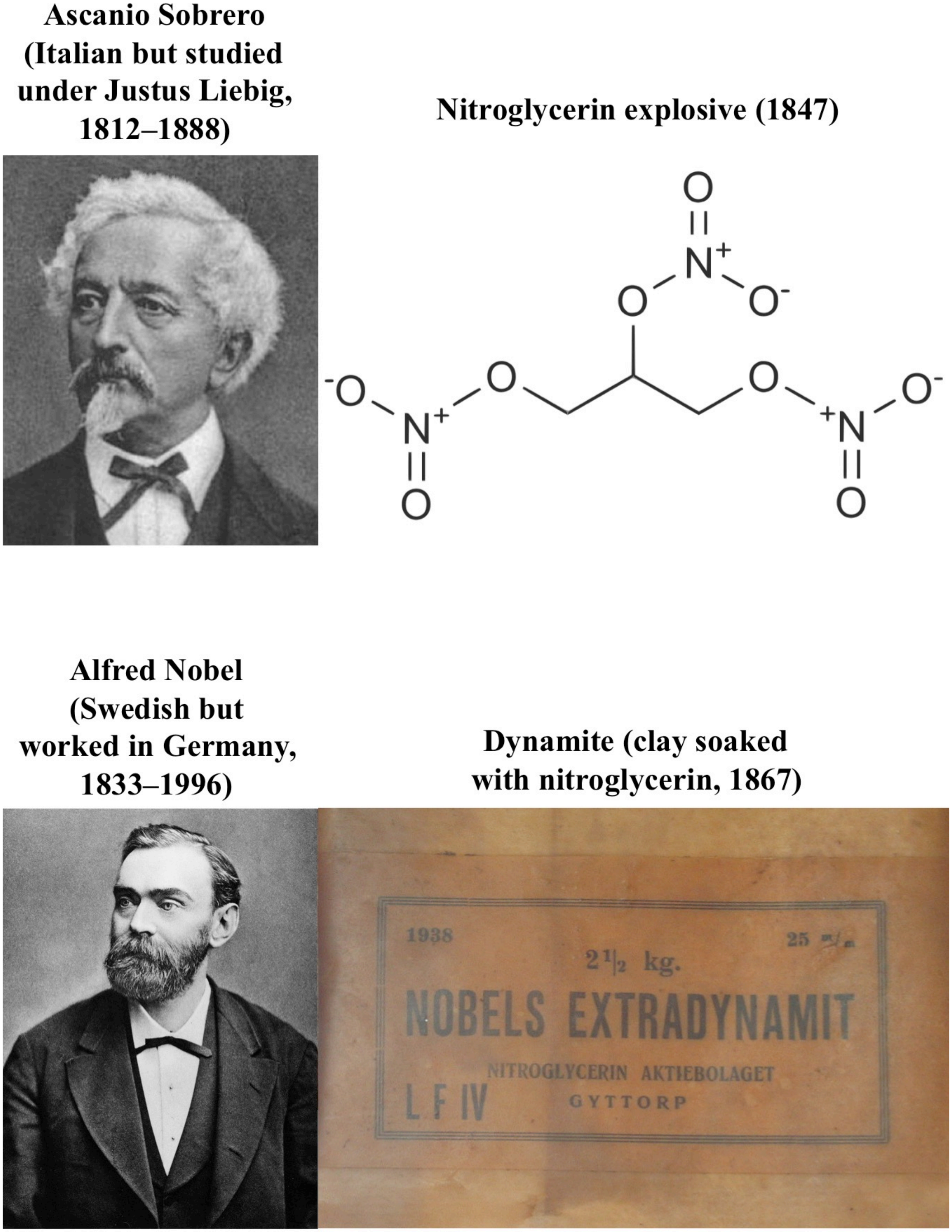


Figure 3.72: Ascanio Sobrero, who studied under Justus Liebig, developed nitroglycerin explosive in 1847. Alfred Nobel developed dynamite (clay soaked with nitroglycerin) in 1867.

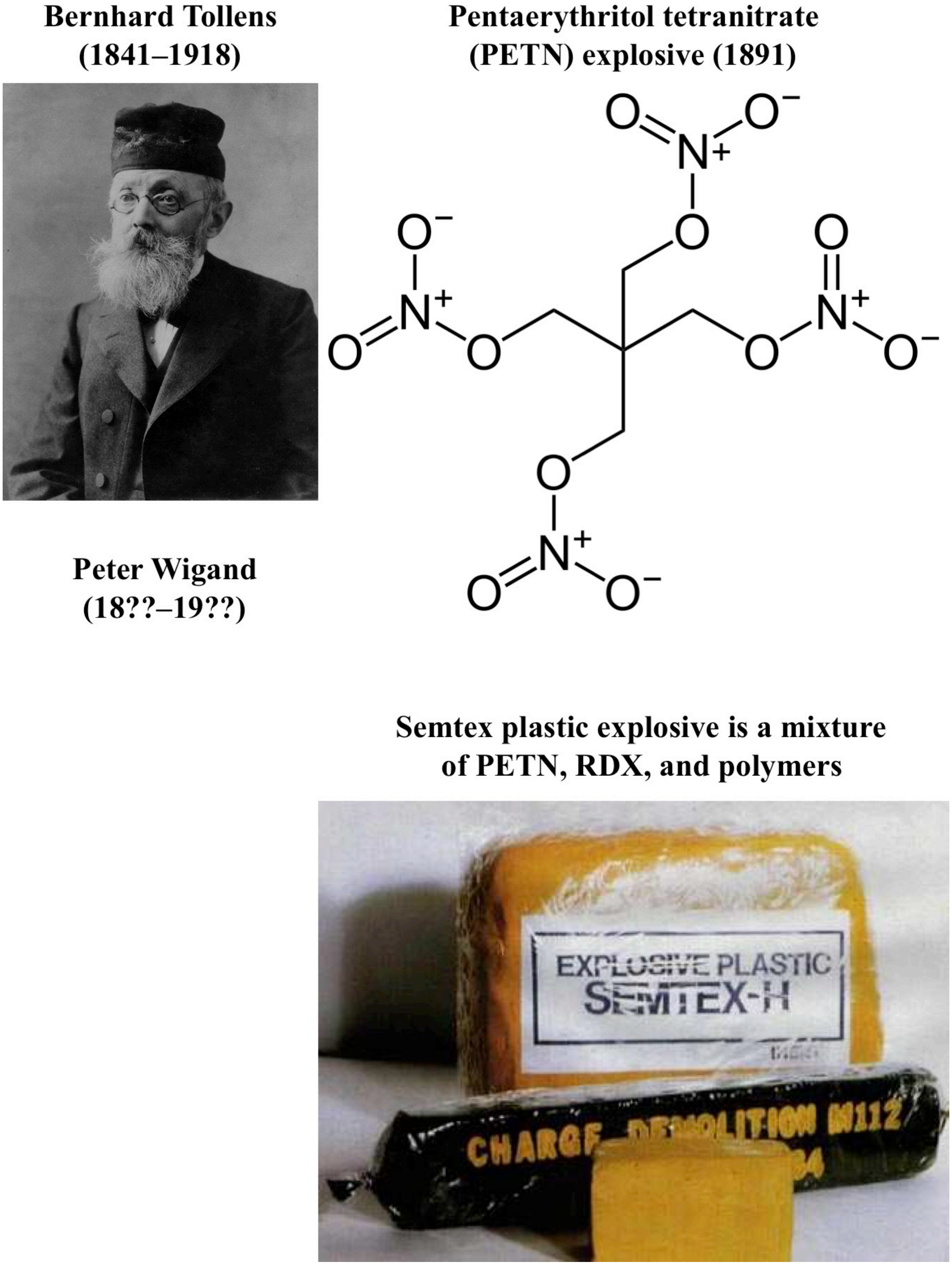
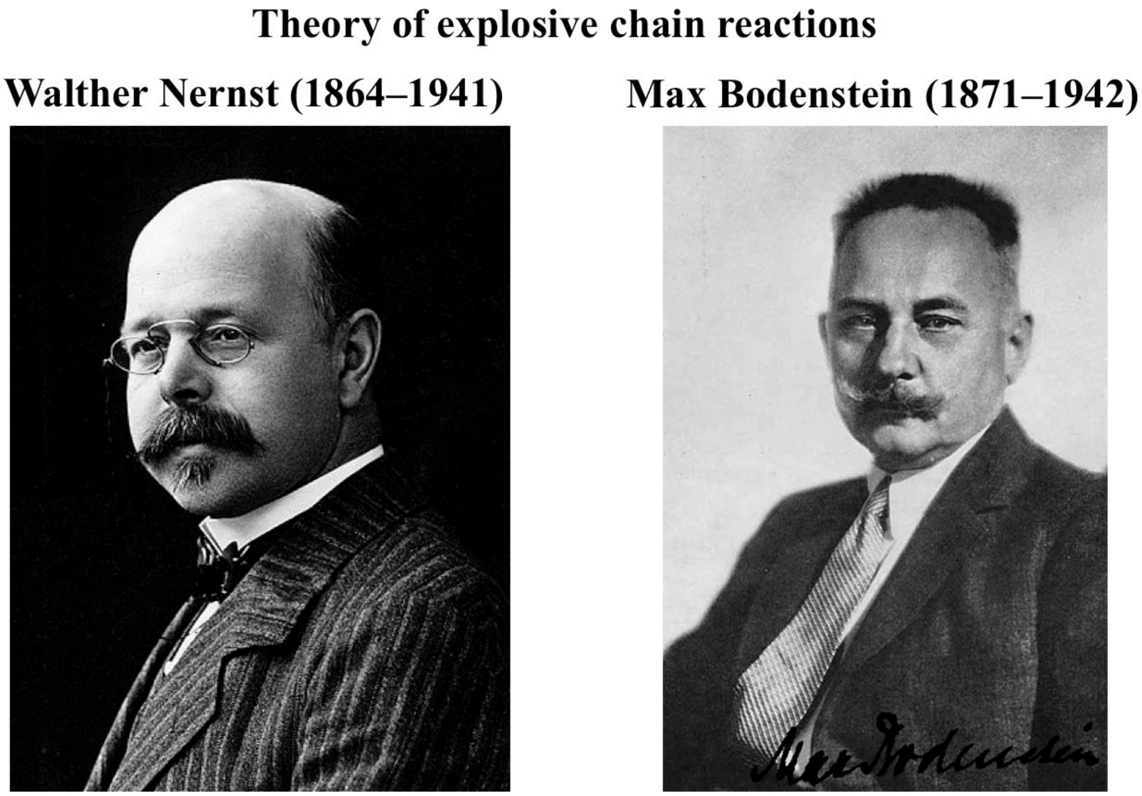


Figure 3.73: Bernhard Tollens and Peter Wigand developed pentaerythritol tetranitrate (PETN) explosive in 1891. Semtex plastic explosive is a mixture of PETN, RDX, and polymers. PETN is also used as a blood pressure medication.



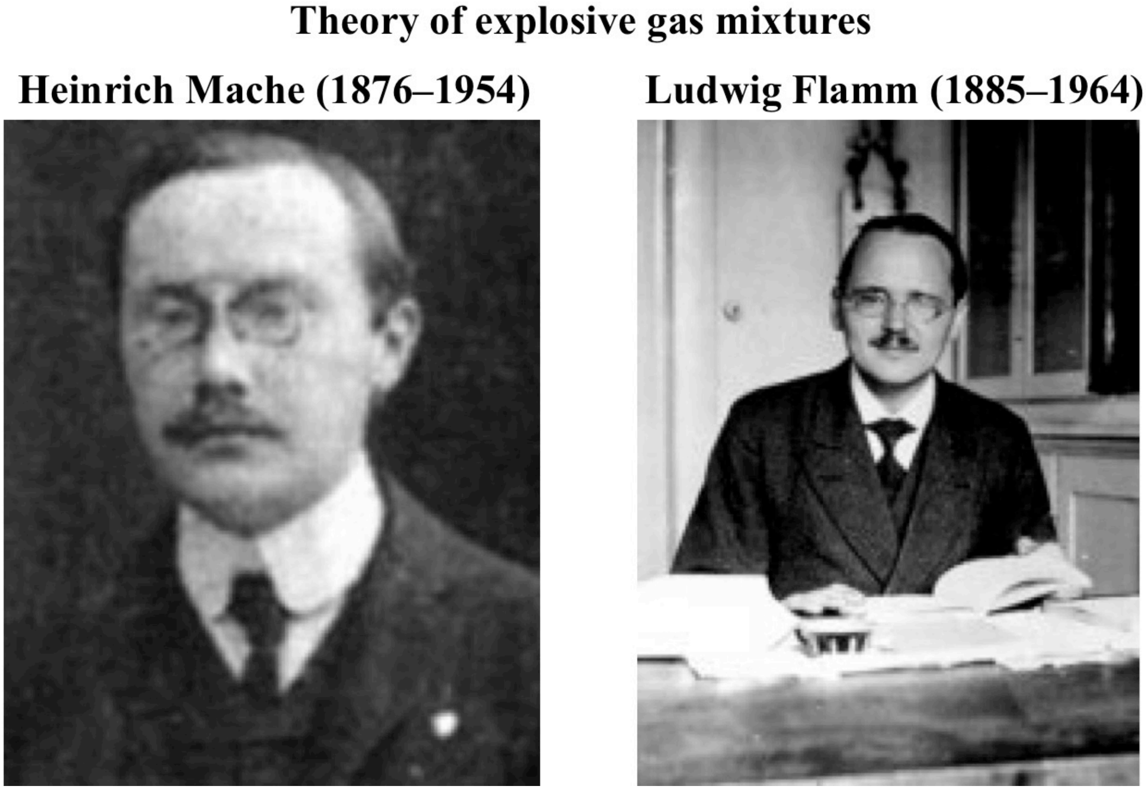


Figure 3.74: Walther Nernst and Max Bodenstein worked out the theory of explosive chain reactions. Heinrich Mache and Ludwig Flamm developed the theory of explosive gas mixtures.

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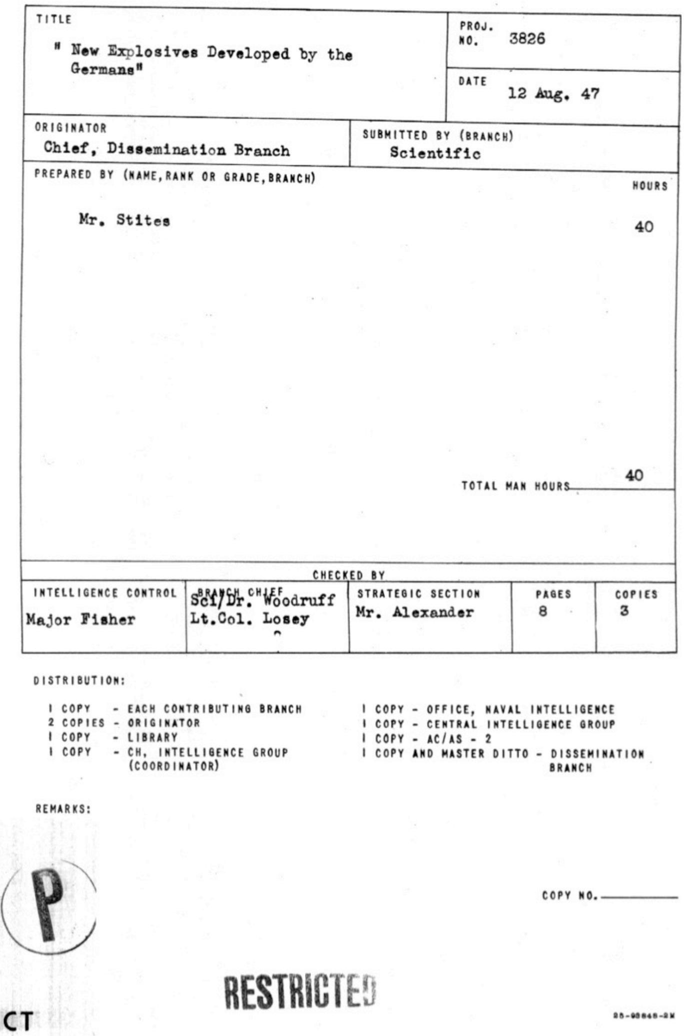

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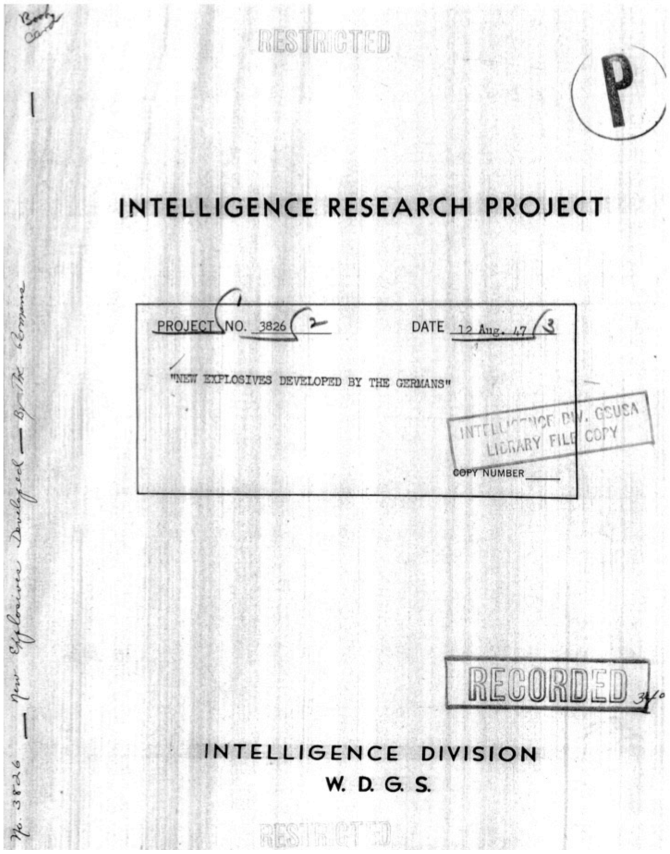

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No. 3826 — New Explosives Developed — By The Germans

Figure 3.75: Over two years after World War II ended in Europe, the U.S. War Department General Staff (WDGS) Intelligence Division wrote a report summarizing what they had learned about "New Explosives Developed by the Germans" during the war. Even after so many decades, that report remains classified and unavailable to the public. Why? What information is in the report? [NARA RG 319, Entry NM3-82, Box 2899, Folder Project 3826]

3.4.2 Fuel-Air Explosives

German-speaking scientists also invented and developed fuel-air explosives [von Haken 1933; Karlsch 2007b; Stevens 2007, pp. 103–111; CIOS ER 201]. While fuel-air explosives use conventional chemical explosive compounds, they disperse those explosive compounds widely before the detonation, and allow the compounds to combust with oxygen in the air. Therefore, fuel-air explosives can cause damage to a much larger area than would be possible with normally packaged bombs of the same explosive compounds.

The earliest known description of a fuel-air explosive bomb is a patent application filed on 6 April 1933 by Kurd von Haken (German?, 18??–19??), DE680483, Fliegerbombe für Kohlenstaubexplosionen [Airborne Bombs for Coal Dust Explosions] (Fig. 3.76):

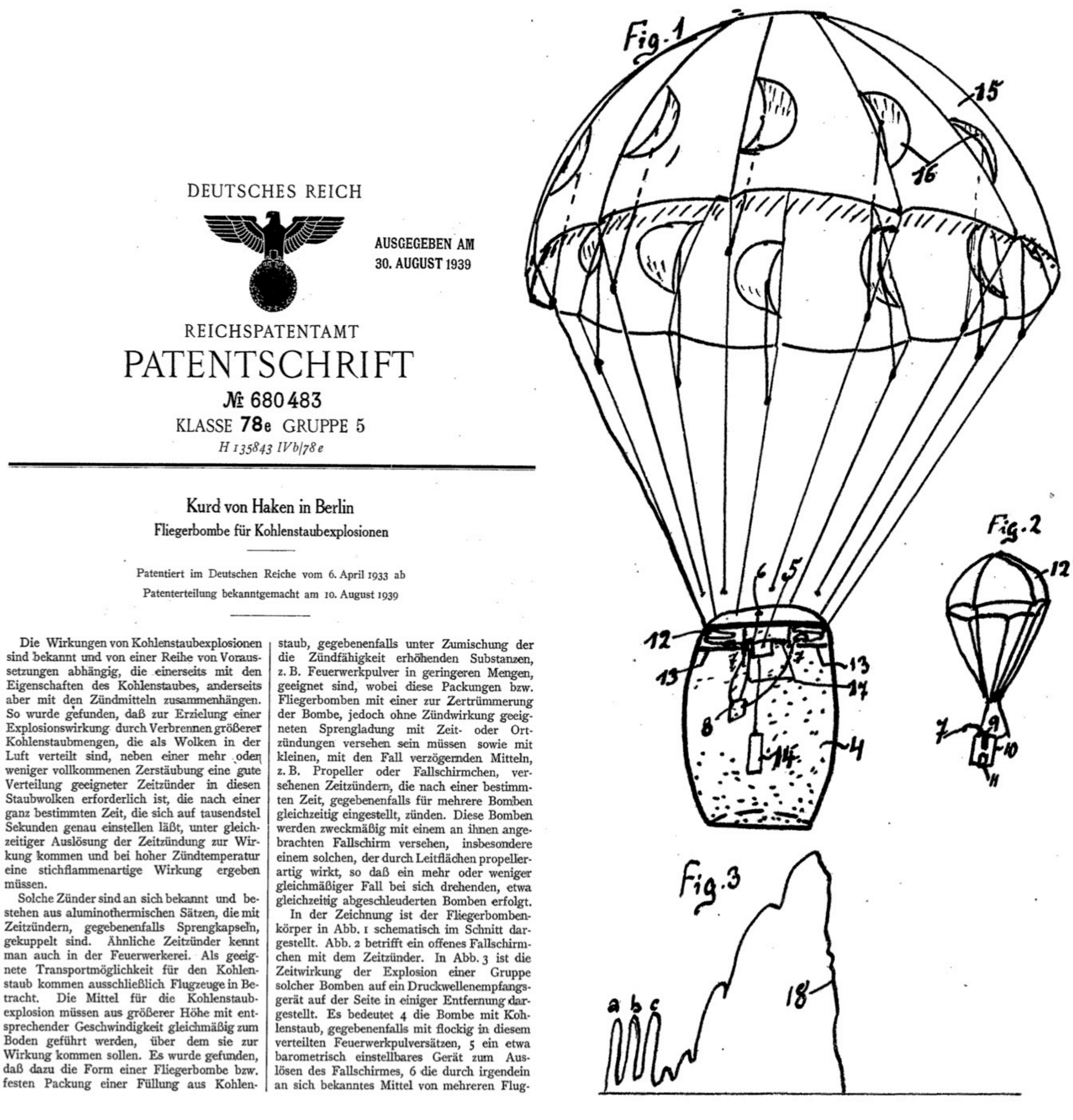
> In der Zeichnung ist der Fliegerbombenkörper in Abb. 1 schematisch im Schnitt dargestellt. Abb. 2 betrifft ein offenes Fallschirmchen mit dem Zeitzünder. In Abb. 3 ist die Zeitwirkung der Explosion einer Gruppe solcher Bomben auf ein Druckwellenempfangsgerät auf der Seite in einiger Entfernung dargestellt. Es bedeutet 4 die Bombe mit Kohlenstaub, gegebenenfalls mit flockig in diesem verteilten Feuerwerkpulversätzen, 5 ein etwa barometrisch einstellbares Gerät zum Auslösen des Fallschirmes, 6 die durch irgendein an sich bekanntes Mittel von mehreren Flugzeugen aus für alle Bomben gleichzeitig einzustellende Zündvorrichtung, die zu den einzelnen Zündern 7 führt, die mit etwa mittels einer Taschenlampenbatterie 8 auszulösende Zeitzünderchen 9 versehen sind. Die Zeitzünderchen 9 sind von den von ihnen zu zündenden Zündsätzen für den Kohlenstaub 10 umgeben, an die ein sie zerstäubender Sprengstoffkörper 11 sich anschließt. 12 ist das Fallschirmchen für diese Zeitzünder, die in zusammengelegtern Zustande in besonderen Kammern 13 der leicht zu zerteilenden Bombe angeordnet sind. 14 ist der Initialsprengkörper zum Zerstäuben der ganzen Bombe. 15 ist ein Fallschirm, gegebenenfalls mit propellerförmig angeordneten Öffnungen 16 versehen, damit die Bombe in Drehung gerät und so in begrenztem Maße durch die Schwingungen der Fallschirme gehemmt wird. 12' ist das Fallschirmchen mit dem Zeitzünder in geöffnetem Zustande.

> In the drawing, the aerial bomb is shown schematically in section in Fig. 1. Fig. 2 concerns an open parachute with the time fuse. Figure 3 shows the time effect of the explosion of a group of such bombs on a pressure wave receiving device on the side at some distance. 4 means the bomb with pulverized coal dust, possibly with a flare in the distributed fireworks powder etching, 5 an approximately barometrically adjustable device for triggering the parachute, 6 which, by means of a means known per se from a plurality of airplanes, which are provided with timers 7 to be triggered by means of a torch battery 8, for example. The timers 9 are of the ignitions to be lit by them. For the carbon dust 10, to which an explosive body, which atomizes them, follows. 12 is the parachute for these time igniters, which are arranged in a combined state in particular chambers 13 of the easy-to-split bomb. 14 is the atomic bubble for atomizing the whole bomb. 15 is a parachute, provided if necessary with propeller-shaped openings 16, so that the bomb is turned and thus limited to a certain degree by the vibrations of the parachutes. 12' is the parachute with the time fuse in the opened state.

Beim etwa gleichzeitigen Abwurf einer Reihe von Bomben öffnen sich nicht alle Bombenfallschirme gleichzeitig, so daß die Bomben in verschiedener Höhe und in verschiedener Zeit über einer mehr oder weniger großen Zielfläche, z.B. 1 qkm, verteilt sind, im Gesamtgewicht von etwa 10 t. Bei der Primärzerstäubungdurch Zünden der Sprengkörper 14 bilden sich um die Bomben eine Reihe Staubwolken, die in langsamem Falle weiter sinken. Die kleinen Fallschirmchen mit den kleinen Zeitzündern öffnen sich gleichzeitig oder früher durch Auslösung einex Hilfsvorrichtung 17 vom Manometer aus und verteilen sich in gleichmäßigem Falle in diesen Staubwolken, so daß sie auch annähernd gleichzeitig zur Explosion kommen. Auf dem Zeitmeßgerät zeichnen sich dann, je nach der Entfernung der Bomben 1, 2, 3 und der Zündkörperchen 1 bis 10, drei Wellen *a, b, c* für die Zerstäubung und etwa fünf kleine Wellen, von der Explosion der Zündkörperchen herrührend, ab. Um die detonierenden Zündkörperchen herum wirkt sich progressiv steigernd eine große Druckwelle 18 aus, die im Zusammenhang mit der Großluftbewegung mit Überschallgeschwindigkeit auf große Entfernung zur Wirkung gelangt.	When a series of bombs are dropped at the same time, not all of the bombshells open at the same time, so that the bombs are at different heights and at different times over a more or less large target area, for example, 1 square kilometer, with a total weight of approximately 10 t. In primary sputtering by igniting the explosive bodies 14, a series of dust clouds form around the bombs, which sink further in a slow case. The little parachutes with the small time fuses open at the same time or earlier by triggering an auxiliary device from the manometer and distributing themselves in this case evenly in the dust clouds, so that they also almost explode at the same time. According to the distance of the bombs 1, 2, 3 and the ignition body 1 to 10, three waves *a, b, c* for the atomization and about five small waves, which originate from the explosion of the ignition cores, are then distinguished on the time-measuring device. Around the detonating detonators, a large pressure wave 18 acts progressively increasing, which in conjunction with the shock wave arrives at a great distance with a supersonic velocity.

Currently it is not clear what role (if any) Kurd von Haken played in the subsequent development and testing of his ideas for fuel-air explosives.

Kurd von Haken (18??–19??) invented fuel-air explosives



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30. AUGUST 1939

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H 135843 IVb/78e

Kurd von Haken in Berlin

Fliegerbombe für Kohlenstaubexplosionen

Patentiert im Deutschen Reiche vom 6. April 1933 ab
Patenterteilung bekanntgemacht am 10. August 1939

Die Wirkungen von Kohlenstaubexplosionen sind bekannt und von einer Reihe von Voraussetzungen abhängig, die einerseits mit den Eigenschaften des Kohlenstaubes, anderseits aber mit den Zündmitteln zusammenhängen. So wurde gefunden, daß zur Erzielung einer Explosionswirkung durch Verbrennen größerer Kohlenstaubmengen, die als Wolken in der Luft verteilt sind, neben einer mehr oder weniger vollkommenen Zerstäubung eine gute Verteilung geeigneter Zeitzünder in diesen Staubwolken erforderlich ist, die nach einer ganz bestimmten Zeit, die sich auf tausendstel Sekunden genau einstellen läßt, unter gleichzeitiger Auslösung der Zeitzündung zur Wirkung kommen und bei hoher Zündtemperatur eine stichflammenartige Wirkung ergeben müssen.

Solche Zünder sind an sich bekannt und bestehen aus aluminothermischen Sätzen, die mit Zeitzündern, gegebenenfalls Sprengkapseln, gekuppelt sind. Ähnliche Zeitzünder kennt man auch in der Feuerwerkerei. Als geeignete Transportmöglichkeit für den Kohlenstaub kommen ausschließlich Flugzeuge in Betracht. Die Mittel für die Kohlenstaubexplosion müssen aus größerer Höhe mit entsprechender Geschwindigkeit gleichmäßig zum Boden geführt werden, über dem sie zur Wirkung kommen sollen. Es wurde gefunden, daß dazu die Form einer Fliegerbombe bzw. festen Packung einer Füllung aus Kohlenstaub, gegebenenfalls unter Zumischung der die Zündfähigkeit erhöhenden Substanzen, z. B. Feuerwerkpulver in geringeren Mengen, geeignet sind, wobei diese Packungen bzw. Fliegerbomben mit einer zur Zertrümmerung der Bombe, jedoch ohne Zündwirkung geeigneten Sprengladung mit Zeit- oder Ortzündungen versehen sein müssen sowie mit kleinen, mit den Fall verzögernden Mitteln, z. B. Propeller oder Fallschirmchen, versehenen Zeitzündern, die nach einer bestimmten Zeit, gegebenenfalls für mehrere Bomben gleichzeitig eingestellt, zünden. Diese Bomben werden zweckmäßig mit einem an ihnen angebrachten Fallschirm versehen, insbesondere einem solchen, der durch Leitflächen propellerartig wirkt, so daß ein mehr oder weniger gleichmäßiger Fall bei sich drehenden, etwa gleichzeitig abgeschleuderten Bomben erfolgt.

In der Zeichnung ist der Fliegerbombenkörper in Abb. 1 schematisch im Schnitt dargestellt. Abb. 2 betrifft ein offenes Fallschirmchen mit dem Zeitzünder. In Abb. 3 ist die Zeitwirkung der Explosion einer Gruppe solcher Bomben auf ein Druckwellenempfangsgerät auf der Seite in einiger Entfernung dargestellt. Es bedeutet 4 die Bombe mit Kohlenstaub, gegebenenfalls mit flockig in diesem verteilten Feuerwerkpulversätzen, 5 ein etwa barometrisch einstellbares Gerät zum Auslösen des Fallschirmes, 6 die durch irgendein an sich bekanntes Mittel von mehreren Flug-

Figure 3.76: Kurd von Haken filed a patent application on fuel-air explosives in 1933.

Using von Haken's patent, Mario Zippermayr (Austrian, 1899–1979) and other scientists developed and tested fuel-air explosives during World War II, as shown in Figs. 3.77–3.90 [CIOS ER 201, NavTecMisEu 548-45]. Historian Rainer Karlsch explained the development program [Karlsch 2007b]:

> During the war a group of scientists under the direction of the Austrian physicist Mario Zippermayr made use of the patent belonging to Kurd von Haken. They improved the concept of the coal dust bomb. [...]
>
> Zippermayr's activities for the Air Force and the establishment of his research institute probably did not begin until 1942. The swift progress of the group is therefore even more astounding. Zippermayr was not, however, the scientific "brain" of the group, but rather its loyal Nazi manager.
>
> According to reports by the US Forces Austria Counter-Intelligence Corps, his group had 35 individuals employed in locations in Vienna and in Lofer, Tyrol. The most important research project was the development of a highly explosive warhead with which the anti-aircraft missiles 'Enzian' (Gentian) and 'Schmetterling' (Butterfly) were to be fitted.
>
> The project work was accelerated in the second half of 1944, after the landing of the Allies at Normandy and the assassination attempt on Hitler. At that point the SS took over the most modern weapons development projects, and tried to bring these weapons to a usable stage of development. Among the many exotic ideas there were also some technically very demanding projects such as the development of nerve gases, missiles and nuclear explosives.
>
> Himmler's organization also had an influence on the project of SS officer Mario Zippermayr, and in this case the cooperation between researchers and the SS was probably especially close. The researchers were on a promising path, as Zippermayr reported in October 1944 in a report for the Reichsforschungsrat (Research Advisory Council) labeled "Geheime Kommandosache" (Secret Commando Matter). He referred to experiments that took place in the spring of 1943 with 60 kilograms of a mixture of coal dust and liquid oxygen in the vicinity of the air base Zwölfaxing near Vienna. The explosions broke windows up to 1.5 kilometers away. As far as 3.5 kilometers away, windows and doors that had been pulled to were pushed open by the explosions.
>
> The project was given the code name "Witches Cauldron" [Hexenkessel]. Contributors to the project were scientists from Dynamit Nobel Corporation, Rheinmetall-Borsig, the Ballistic Institute in Gatow, as well as specialists from the brown coal industry and from the Zippermayr group. Probably there was at least one more SS research group that conducted similar experiments in Silesia and in other locations.
>
> According to information that reached British intelligence early in 1945, a test north of Berlin achieved a destructive radius of approximately 600 meters. The heat and pressure wave ignited trees in the target area and knocked them over. The air force could have made good use of such a weapon. The plan was to target these at aircraft formations via anti-aircraft missiles. As far as we know, these missiles were never used, however.

> But the new bomb could have been used against large surface target areas. This was a very real danger. According to American secret service reports, the German military possessed at war's end 5-ton "liquid air bombs," as the thermobaric bombs were called then. In the National Archive in Washington, there is a document naming a plant in Nordhausen, in the Harz region, where the V-2 missiles were produced, as the location for the production of even larger "oxygen bombs" (yet another name for these same bombs). [See pp. 562–563.] An actual use of the bombs never occurred.
>
> Even as late as the capitulation, the victors possessed only vague secret service information about the super bomb. Nevertheless, there was an interest in the immediate study and development of this technology, of course under conditions of utmost secrecy. For this reason, Zippermayr was repeatedly questioned by the Chemical Warfare Service, beginning on 3 August 1945. During a later interrogation in 1949, he told the Americans that with his bomb—whether with pulverized coal dust or with gas or other liquids—he could achieve the area destruction of a small atomic bomb. Furthermore, the production of such a bomb would be much cheaper.
>
> In contrast to other prominent German weapons industry researchers, there was reluctance to transport the SS man Zippermayr to the United States. However, several of his colleagues were offered the opportunity to continue their research in America in the context of "Operation Paperclip." Apparently the Soviets also benefited from the knowledge produced by the Zippermayr group. According to an American report, Heinrich Mache, a professor at the Technical University in Vienna, was forced to conduct experiments with coal dust explosives in October 1945 under Soviet supervision.
>
> The terrible fruits of the Zippermayr group did not just remain in the arsenals. They were used as "enhanced blast weapons" in the Vietnam War and in 1969 in Soviet-Chinese border conflicts at the Ussuri River. This name comes from the fact that the temperatures achieved by these bombs were not extreme. This changed in the late 1980s when the reaction temperature was raised substantially through added metallic particles, primarily aluminum, but also through other metals, as well as through oxygen. The principle of the thermobaric bomb, however, remained the same and is one example for the fact that it was not just in the case of missiles and jet planes that the victors in the Second World War made use of the knowledge of the defeated powers. That the technology behind the "father of all bombs" is old hat should not obscure the fact that this is a weapon of mass destruction that should be forbidden.

Note that the use of powdered aluminum in explosives to enhance the temperature and blast (as described above) was also developed in wartime Germany; see pp. 5790–5793 [BIOS 27; BIOS 100; BIOS 1261]. Thus the "thermobaric" and "enhanced blast weapons" built by the United States and other countries after the war were entirely derived from technologies that had previously been designed and demonstrated in Germany and Austria, based on information and materials obtained from German-speaking scientists, as well as the direct assistance of many of those scientists themselves (as shown below).

An August 1949 JIOA document, Immigration of Austrian Scientists to Soviet Zone, listed several key members of Zippermayr's team [NARA RG 319, Entry A1-134A, Box 31, Folder 02/006 430]:

> FRITSCHE, Doz. Dr. Ing. Volker, Technische Hochschule, Vienna. Formerly with the Zippermayr Laboratory engaged in research in use of coal dust as antiaircraft explosive. Member of the Electro-technical Institute, Technische Hochschule. Reportedly making survey for Russians on high frequency prospecting for oil.
>
> HOENIG, Dr Alfred, Scheffsnoth 8, Zell am See, Austria. Formerly worked at Zippermayr Institute engaged in research on coal dust explosives. Chemical Corps and Air Corps interestd. Chemical expert interviewed subject and ZIPPERMAYER, and agreed that their theories were basically sound and could not be permitted to reach potential U.S. enemies. It will be recommended that these two with KILLIAN be employed in U. S. HOENIG fears that he might be kidnapp[blacked out]
>
> KILLIAN, Karl, Hattlegasse 40, Hitzing, Vienna XIII, Austria. Mathematician and aerodynamics expert who formerly worked with ZIPPERMAYER and HOENIG on Pfeil aircraft, torpedoes designed to be released from great heights and torpedoes with luminous underwater trails. Being considered along with HOENIG and ZIPPERMAYER for employment in U. S. by Chemical Corps.
>
> MACHE, Prof. Dr. Heinrich, Pokenvgasse 25, Vienna XIX/117. Professor at Technische Hochschule, Vienna and regular member of Austrian Academy of Science. In October 1945, conducted experiments with coal dust explosives under Soviet orders. Specialist on discharge of electric energy in gases.
>
> ZIPPERMAYR, Prof. Dr. Mario, Lofer Au 3, Zell am See, Austria. Stateless. Chemist. NSDAP member and SD from 1937 to 1945. Headed Zippermayr [blacked out] in coal dust explosives. [blacked out]. See HOENIG and KILLIAN.
>
> BE[ETZ?], Dr.—Halle, Germany. Formerly with Zippermayr Institute engaged in research on methods of transmitting course of enemy bombers to night fighters and on dust explosions.
>
> MELDAU, Dr. Ing—Last reported at Spremberg, Germany. Formerly with Zippermayr Institute engaged in research on coal dust explosives.

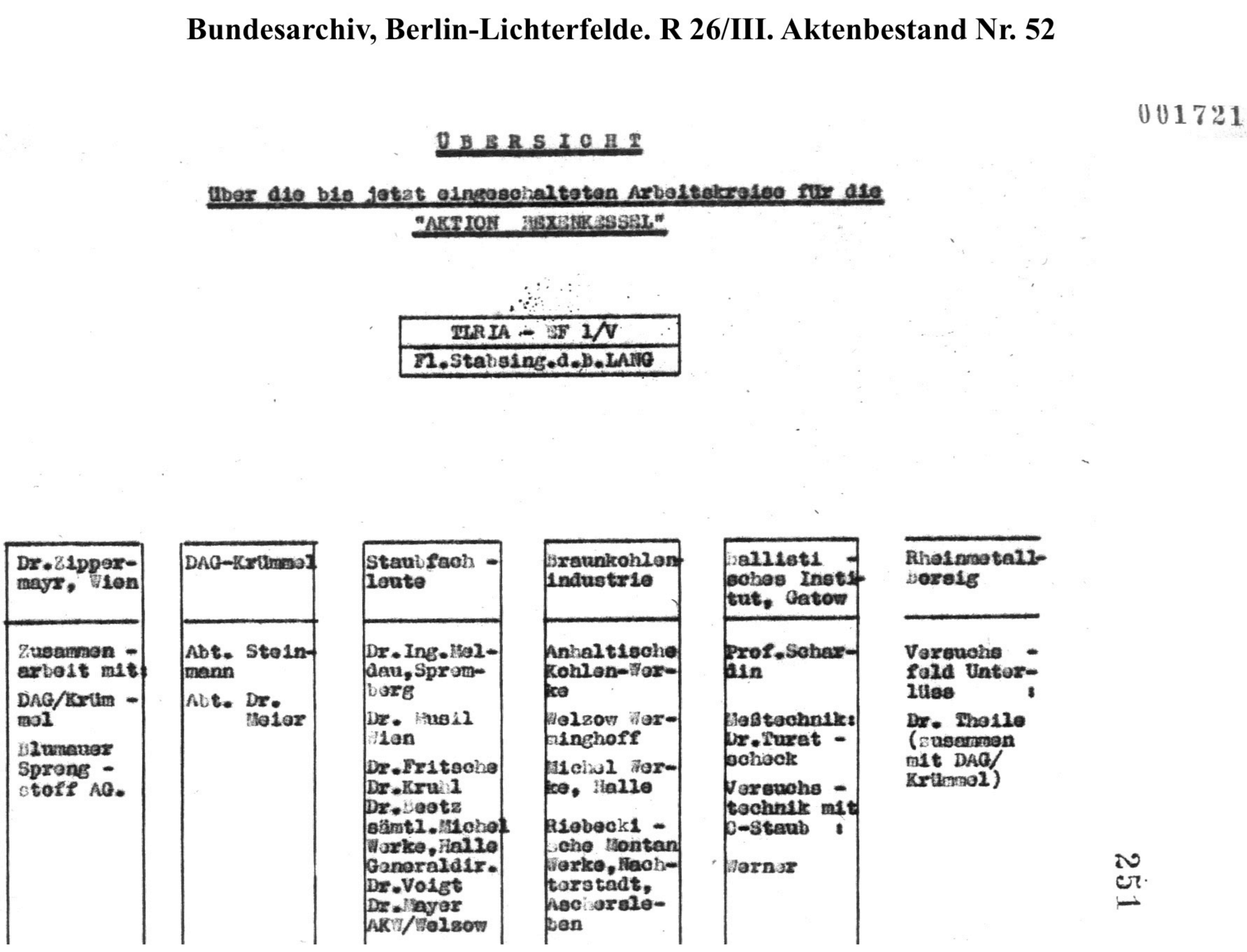
Zippermayr and some of the other scientists were extensively interrogated after the war, and some were taken to work for the United States, Russia, or other countries.

Zippermayr's Austrian group was part of a much larger wartime program to develop, test, and mass-produce fuel-air explosives (pp. 550–551).

There were several reports of successful tests of fuel-air explosives during the war. Some archival documents even mentioned fuel-air explosives actually being used on the Eastern front during the war. See pp. 552–561, 2627–2635, 4434–4435.

By the end of the war, at least 7000 workers had mass-produced 5-ton fuel-air explosive bombs and stockpiled them (pp. 562–563). There were also stockpiles of fuel-air explosives in an assortment of smaller sizes. Those stockpiled bombs were probably taken by Allied countries after the war.

Much more historical research on this topic could be quite enlightening.



Bundesarchiv, Berlin-Lichterfelde. R 26/III. Aktenbestand Nr. 52

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251

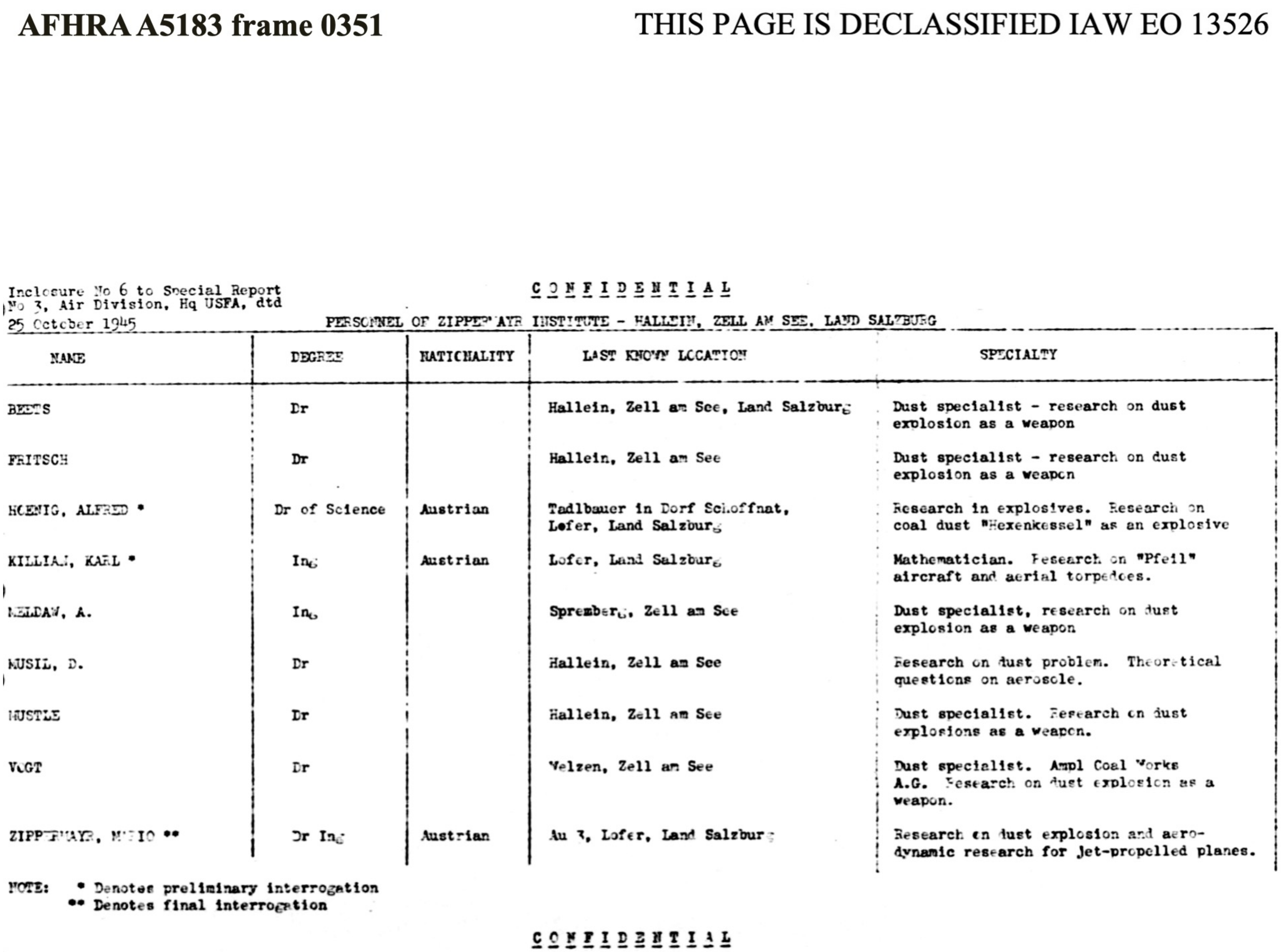
ÜBERSICHT

über die bis jetzt eingeschalteten Arbeitskreise für die
"AKTION HEXENKESSEL"

TLR IA - EF 1/V
Fl.Stabsing.d.B.LANG

Dr.Zippermayr, Wien	DAG-Krümmel	Staubfach-leute	Braunkohlen-industrie	ballistisches Institut, Gatow	Rheinmetall-Borsig
Zusammen-arbeit mit: DAG/Krümmel Blumauer Sprengstoff AG.	Abt. Steinmann Abt. Dr. Meier	Dr.Ing.Meldau, Spremberg Dr. Musil Wien Dr.Fritsche Dr.Kruhl Dr.Beetz sämtl.Michel Werke, Halle Generaldir. Dr.Voigt Dr.Mayer AKW/Welsow	Anhaltische Kohlen-Werke Welzow Werminghoff Michel Werke, Halle Riebecki-sche Montan Werke, Nachterstadt, Aschersleben	Prof.Schardin Meßtechnik: Dr.Turatschek Versuchstechnik mit C-Staub: Werner	Versuchsfeld Unterlüss: Dr. Theile (zusammen mit DAG/Krümmel)

Figure 3.77: A large program, including a group led by Mario Zippermayr, developed and tested fuel-air explosives during the war [Bundesarchiv, Berlin-Lichterfelde, R 26/III, Aktenbestand Nr. 52].



AFHRA A5183 frame 0351

THIS PAGE IS DECLASSIFIED IAW EO 13526

Inclosure No 6 to Special Report
No 3, Air Division, Hq USFA, dtd
25 October 1945

C O N F I D E N T I A L

PERSONNEL OF ZIPPERMAYR INSTITUTE - HALLEIN, ZELL AM SEE, LAND SALZBURG

NAME	DEGREE	NATIONALITY	LAST KNOWN LOCATION	SPECIALTY
BEETS	Dr		Hallein, Zell am See, Land Salzburg	Dust specialist - research on dust explosion as a weapon
FRITSCH	Dr		Hallein, Zell am See	Dust specialist - research on dust explosion as a weapon
HOENIG, ALFRED *	Dr of Science	Austrian	Tadlbauer in Dorf Schoffnat, Lofer, Land Salzburg	Research in explosives. Research on coal dust "Hexenkessel" as an explosive
KILLIAN, KARL *	Ing	Austrian	Lofer, Land Salzburg	Mathematician. Research on "Pfeil" aircraft and aerial torpedoes.
MELDAW, A.	Ing		Spremberg, Zell am See	Dust specialist, research on dust explosion as a weapon
MUSIL, D.	Dr		Hallein, Zell am See	Research on dust problem. Theoretical questions on aerosole.
HUSTLE	Dr		Hallein, Zell am See	Dust specialist. Research on dust explosions as a weapon.
VOGT	Dr		Velzen, Zell am See	Dust specialist. Ampl Coal Works A.G. Research on dust explosion as a weapon.
ZIPPERMAYR, MARIO **	Dr Ing	Austrian	Au 3, Lofer, Land Salzburg	Research on dust explosion and aero-dynamic research for Jet-propelled planes.

NOTE: * Denotes preliminary interrogation
** Denotes final interrogation

C O N F I D E N T I A L

Figure 3.78: A large program, including a group led by Mario Zippermayr, developed and tested fuel-air explosives during the war [AFHRA A5183 frame 0351].

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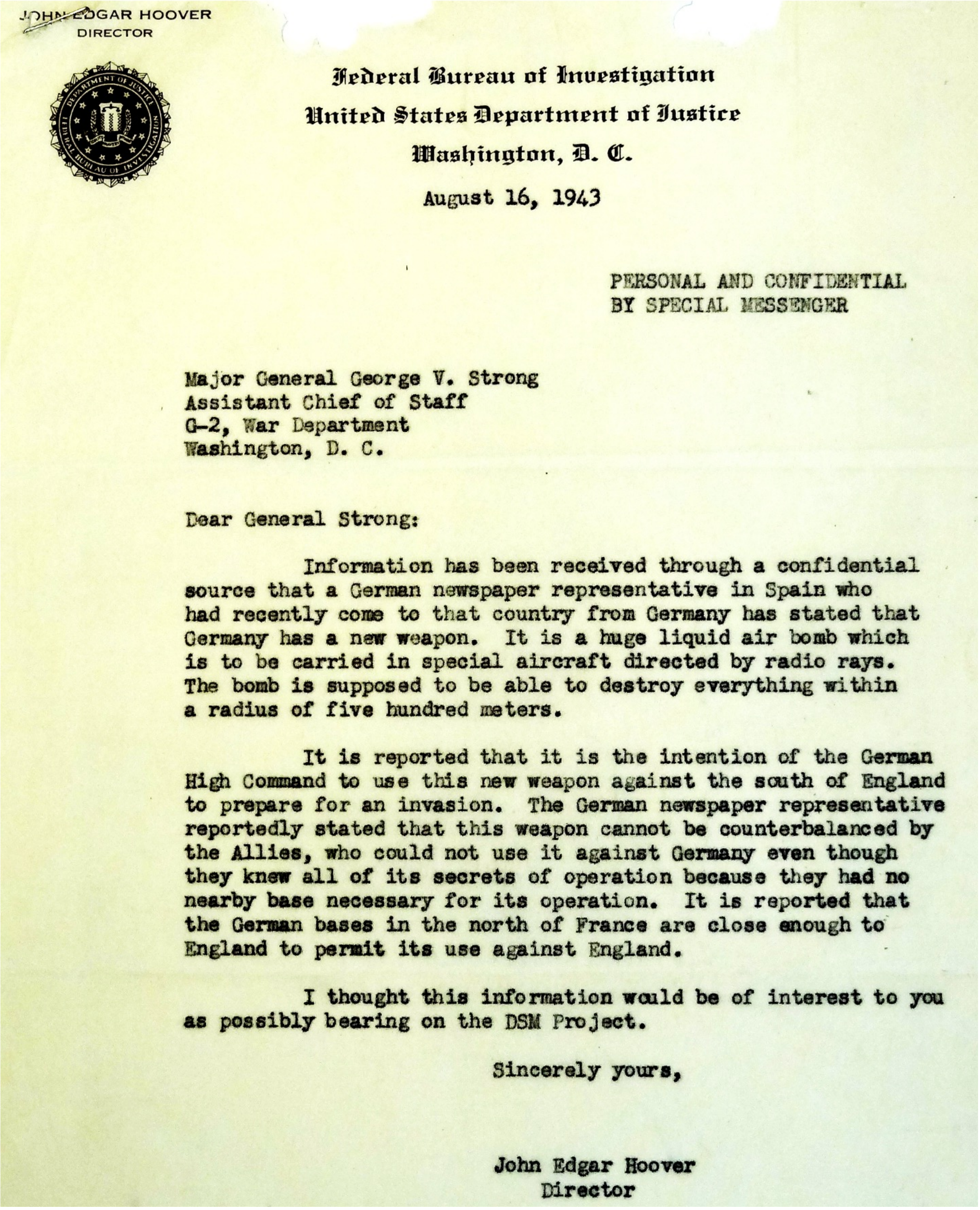
Authority NND 917017

NARA RG 77, Entry UD-22A,
Box 163, Folder Australia



JOHN EDGAR HOOVER
DIRECTOR

Federal Bureau of Investigation
United States Department of Justice
Washington, D. C.

August 16, 1943

PERSONAL AND CONFIDENTIAL
BY SPECIAL MESSENGER

Major General George V. Strong
Assistant Chief of Staff
G-2, War Department
Washington, D. C.

Dear General Strong:

Information has been received through a confidential source that a German newspaper representative in Spain who had recently come to that country from Germany has stated that Germany has a new weapon. It is a huge liquid air bomb which is to be carried in special aircraft directed by radio rays. The bomb is supposed to be able to destroy everything within a radius of five hundred meters.

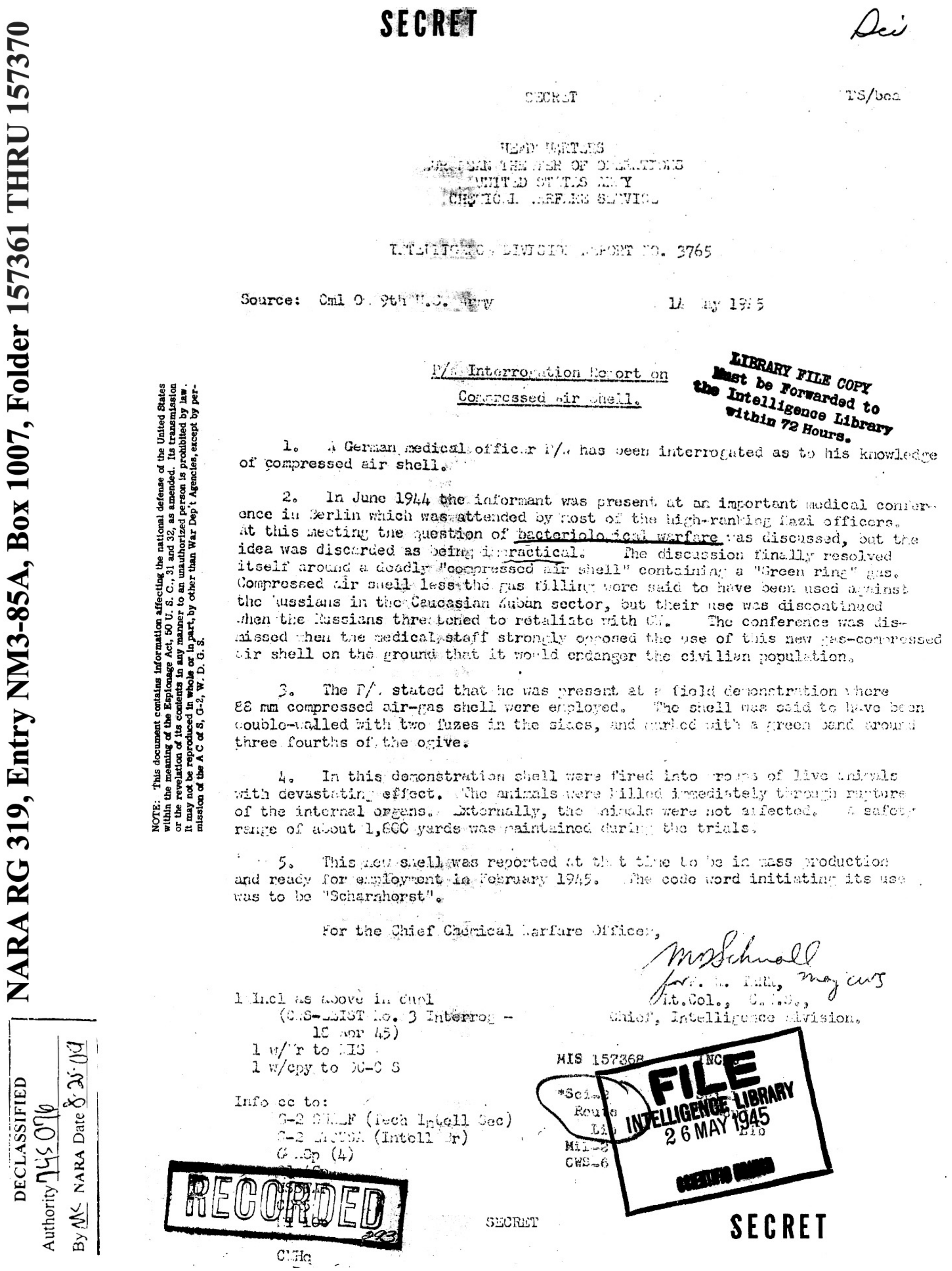
It is reported that it is the intention of the German High Command to use this new weapon against the south of England to prepare for an invasion. The German newspaper representative reportedly stated that this weapon cannot be counterbalanced by the Allies, who could not use it against Germany even though they knew all of its secrets of operation because they had no nearby base necessary for its operation. It is reported that the German bases in the north of France are close enough to England to permit its use against England.

I thought this information would be of interest to you as possibly bearing on the DSM Project.

Sincerely yours,

John Edgar Hoover
Director

Figure 3.79: J. Edgar Hoover. 16 August 1943 [NARA RG 77, Entry UD-22A, Box 163, Folder Australia].



NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370

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Authority 745096
By NK NARA Date 8-25-09

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HEADQUARTERS
EUROPEAN THEATER OF OPERATIONS
UNITED STATES ARMY
CHEMICAL WARFARE SERVICE

INTELLIGENCE DIVISION REPORT NO. 3765

Source: Cml O. 9th U.S. Army 14 May 1945

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the Intelligence Library
within 72 Hours.

P/W Interrogation Report on
Compressed air Shell.

1. A German medical officer P/W has been interrogated as to his knowledge of compressed air shell.

2. In June 1944 the informant was present at an important medical conference in Berlin which was attended by most of the high-ranking Nazi officers. At this meeting the question of bacteriological warfare was discussed, but the idea was discarded as being impractical. The discussion finally resolved itself around a deadly "compressed air shell" containing a "Green ring" gas. Compressed air shell less the gas filling were said to have been used against the Russians in the Caucasian Kuban sector, but their use was discontinued when the Russians threatened to retaliate with CW. The conference was dismissed when the medical staff strongly opposed the use of this new gas-compressed air shell on the ground that it would endanger the civilian population.

3. The P/W stated that he was present at a field demonstration where 88 mm compressed air-gas shell were employed. The shell was said to have been double-walled with two fuzes in the sides, and marked with a green band around three fourths of the ogive.

4. In this demonstration shell were fired into groups of live animals with devastating effect. The animals were killed immediately through rupture of the internal organs. Externally, the animals were not affected. A safety range of about 1,800 yards was maintained during the trials.

5. This new shell was reported at that time to be in mass production and ready for employment in February 1945. The code word initiating its use was to be "Scharnhorst".

For the Chief Chemical Warfare Officer,

M. D. Schnall
for [illegible], Maj CWS
Lt.Col., C.W.S.,
Chief, Intelligence Division.

1 Incl as above in dupl
(CWS-LSIST No. 3 Interrog -
18 Apr 45)
1 w/Tr to MIS
1 w/cpy to OC-CS

Info cc to:
G-2 SHAEF (Tech Intell Sec)
G-2 ETOUSA (Intell Br)
G A Gp (4)

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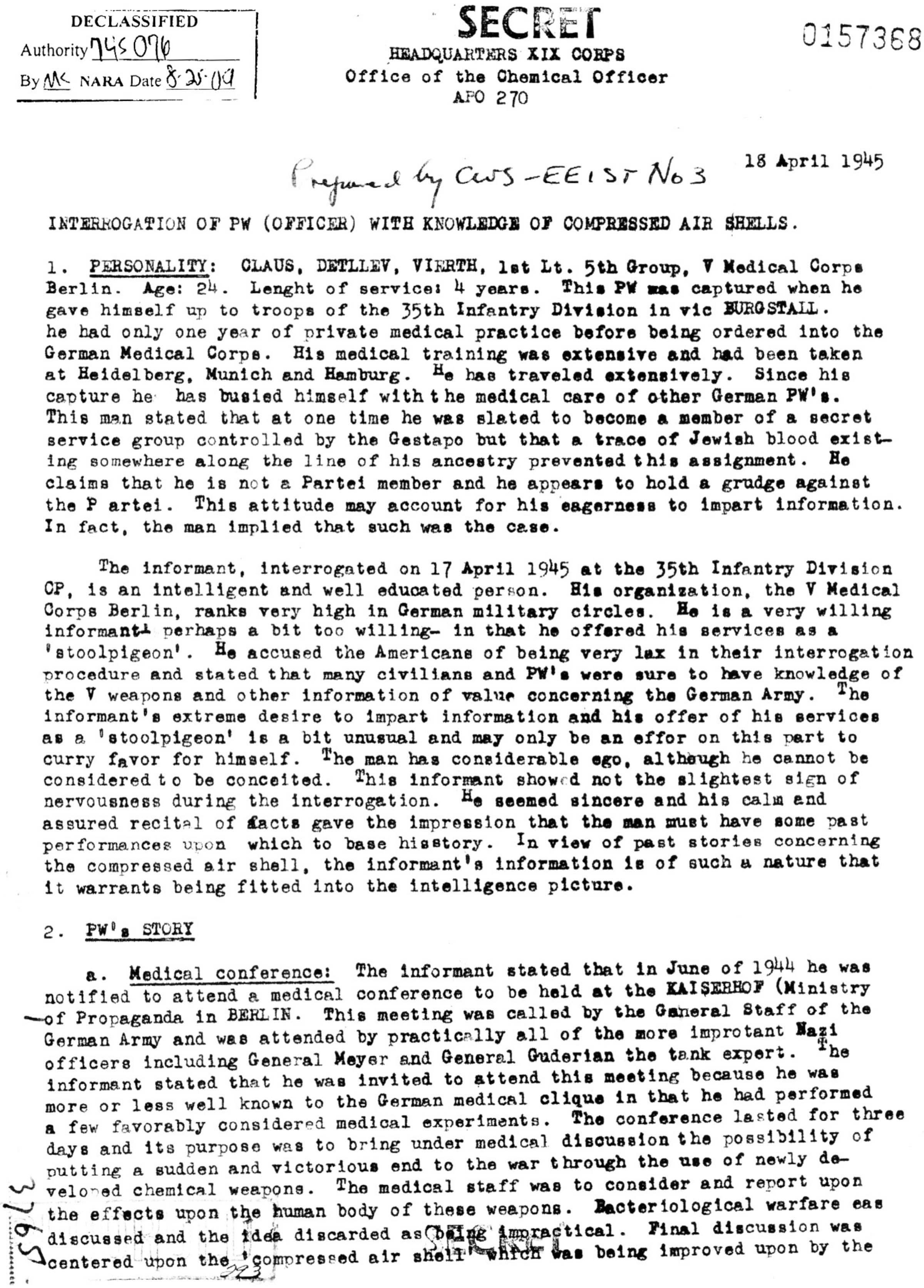
Figure 3.80: A reported test of a fuel-air explosive (or possibly a chemical agent) [NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370].

NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370



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Authority 745076
By NK NARA Date 8-25-09

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HEADQUARTERS XIX CORPS
Office of the Chemical Officer
APO 270

0157368

Prepared by CWS-EEIST No 3

18 April 1945

INTERROGATION OF PW (OFFICER) WITH KNOWLEDGE OF COMPRESSED AIR SHELLS.

1. PERSONALITY: CLAUS, DETLLEV, VIERTH, 1st Lt. 5th Group, V Medical Corps Berlin. Age: 24. Lenght of service: 4 years. This PW was captured when he gave himself up to troops of the 35th Infantry Division in vic EUROSTALL. he had only one year of private medical practice before being ordered into the German Medical Corps. His medical training was extensive and had been taken at Heidelberg, Munich and Hamburg. He has traveled extensively. Since his capture he has busied himself with the medical care of other German PW's. This man stated that at one time he was slated to become a member of a secret service group controlled by the Gestapo but that a trace of Jewish blood existing somewhere along the line of his ancestry prevented this assignment. He claims that he is not a Partei member and he appears to hold a grudge against the Partei. This attitude may account for his eagerness to impart information. In fact, the man implied that such was the case.

The informant, interrogated on 17 April 1945 at the 35th Infantry Division CP, is an intelligent and well educated person. His organization, the V Medical Corps Berlin, ranks very high in German military circles. He is a very willing informant- perhaps a bit too willing- in that he offered his services as a 'stoolpigeon'. He accused the Americans of being very lax in their interrogation procedure and stated that many civilians and PW's were sure to have knowledge of the V weapons and other information of value concerning the German Army. The informant's extreme desire to impart information and his offer of his services as a 'stoolpigeon' is a bit unusual and may only be an effor on this part to curry favor for himself. The man has considerable ego, although he cannot be considered to be conceited. This informant showd not the slightest sign of nervousness during the interrogation. He seemed sincere and his calm and assured recital of facts gave the impression that the man must have some past performances upon which to base hisstory. In view of past stories concerning the compressed air shell, the informant's information is of such a nature that it warrants being fitted into the intelligence picture.

2. PW's STORY

a. Medical conference: The informant stated that in June of 1944 he was notified to attend a medical conference to be held at the KAISERHOF (Ministry of Propaganda in BERLIN. This meeting was called by the General Staff of the German Army and was attended by practically all of the more improtant Nazi officers including General Meyer and General Guderian the tank expert. The informant stated that he was invited to attend this meeting because he was more or less well known to the German medical clique in that he had performed a few favorably considered medical experiments. The conference lasted for three days and its purpose was to bring under medical discussion the possibility of putting a sudden and victorious end to the war through the use of newly developed chemical weapons. The medical staff was to consider and report upon the effects upon the human body of these weapons. Bacteriological warfare eas discussed and the idea discarded as being impractical. Final discussion was centered upon the 'compressed air shell' which was being improved upon by the

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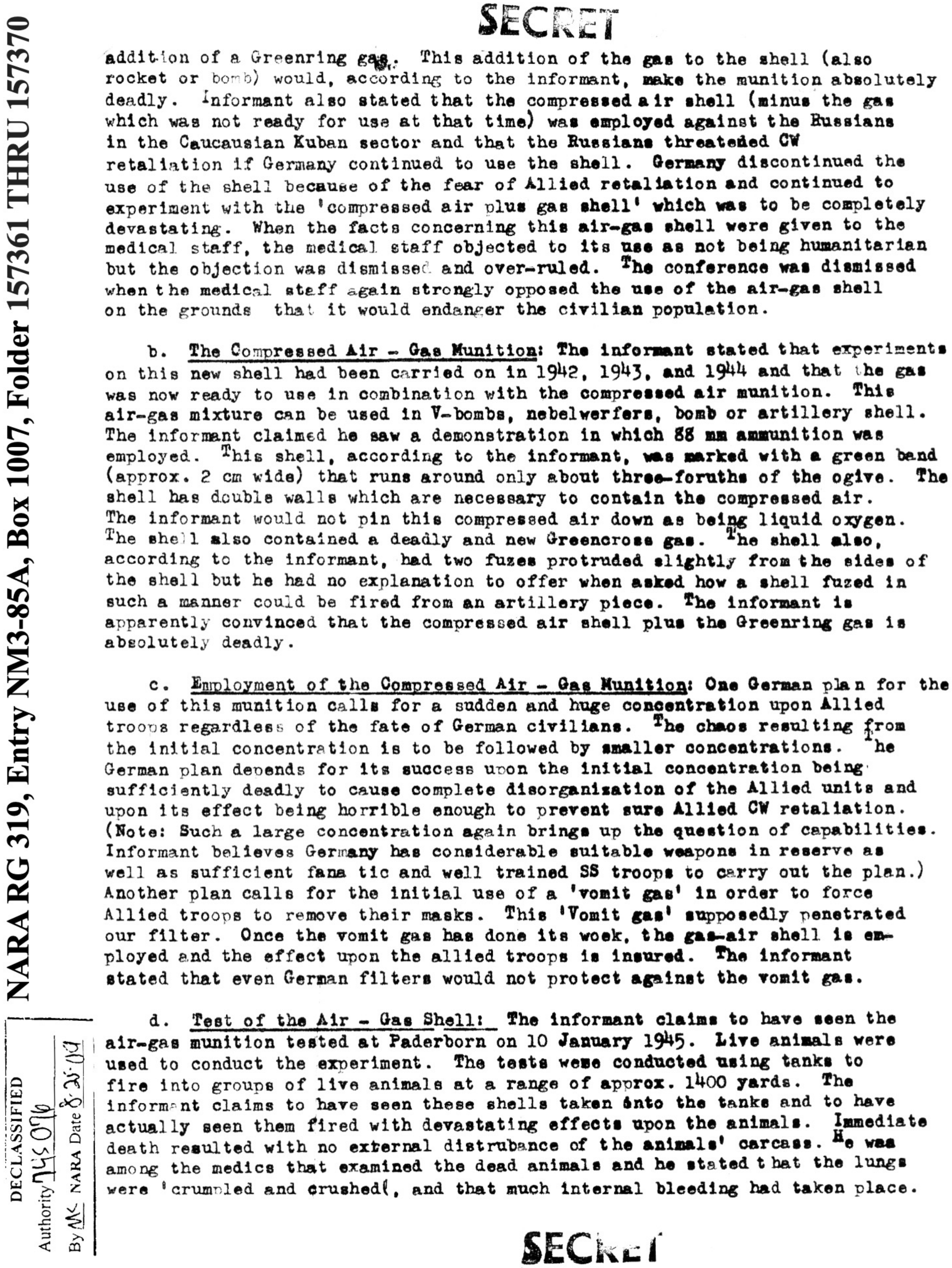
Figure 3.81: A reported test of a fuel-air explosive (or possibly a chemical agent) [NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370].



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addition of a Greenring gas. This addition of the gas to the shell (also rocket or bomb) would, according to the informant, make the munition absolutely deadly. Informant also stated that the compressed air shell (minus the gas which was not ready for use at that time) was employed against the Russians in the Caucausian Kuban sector and that the Russians threatened CW retaliation if Germany continued to use the shell. Germany discontinued the use of the shell because of the fear of Allied retaliation and continued to experiment with the 'compressed air plus gas shell' which was to be completely devastating. When the facts concerning this air-gas shell were given to the medical staff, the medical staff objected to its use as not being humanitarian but the objection was dismissed and over-ruled. The conference was dismissed when the medical staff again strongly opposed the use of the air-gas shell on the grounds that it would endanger the civilian population.

b. <u>The Compressed Air - Gas Munition</u>: The informant stated that experiments on this new shell had been carried on in 1942, 1943, and 1944 and that the gas was now ready to use in combination with the compressed air munition. This air-gas mixture can be used in V-bombs, nebelwerfers, bomb or artillery shell. The informant claimed he saw a demonstration in which 88 mm ammunition was employed. This shell, according to the informant, was marked with a green band (approx. 2 cm wide) that runs around only about three-foruths of the ogive. The shell has double walls which are necessary to contain the compressed air. The informant would not pin this compressed air down as being liquid oxygen. The shell also contained a deadly and new Greencross gas. The shell also, according to the informant, had two fuzes protruded slightly from the sides of the shell but he had no explanation to offer when asked how a shell fuzed in such a manner could be fired from an artillery piece. The informant is apparently convinced that the compressed air shell plus the Greenring gas is absolutely deadly.

c. <u>Employment of the Compressed Air - Gas Munition</u>: One German plan for the use of this munition calls for a sudden and huge concentration upon Allied troops regardless of the fate of German civilians. The chaos resulting from the initial concentration is to be followed by smaller concentrations. The German plan depends for its success upon the initial concentration being sufficiently deadly to cause complete disorganization of the Allied units and upon its effect being horrible enough to prevent sure Allied CW retaliation. (Note: Such a large concentration again brings up the question of capabilities. Informant believes Germany has considerable suitable weapons in reserve as well as sufficient fanatic and well trained SS troops to carry out the plan.) Another plan calls for the initial use of a 'vomit gas' in order to force Allied troops to remove their masks. This 'Vomit gas' supposedly penetrated our filter. Once the vomit gas has done its woek, the gas-air shell is employed and the effect upon the allied troops is insured. The informant stated that even German filters would not protect against the vomit gas.

d. <u>Test of the Air - Gas Shell</u>: The informant claims to have seen the air-gas munition tested at Paderborn on 10 January 1945. Live animals were used to conduct the experiment. The tests wese conducted using tanks to fire into groups of live animals at a range of approx. 1400 yards. The informant claims to have seen these shells taken onto the tanks and to have actually seen them fired with devastating effects upon the animals. Immediate death resulted with no external distrubance of the animals' carcass. He was among the medics that examined the dead animals and he stated that the lungs were 'crumpled and crushed', and that much internal bleeding had taken place.

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NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370

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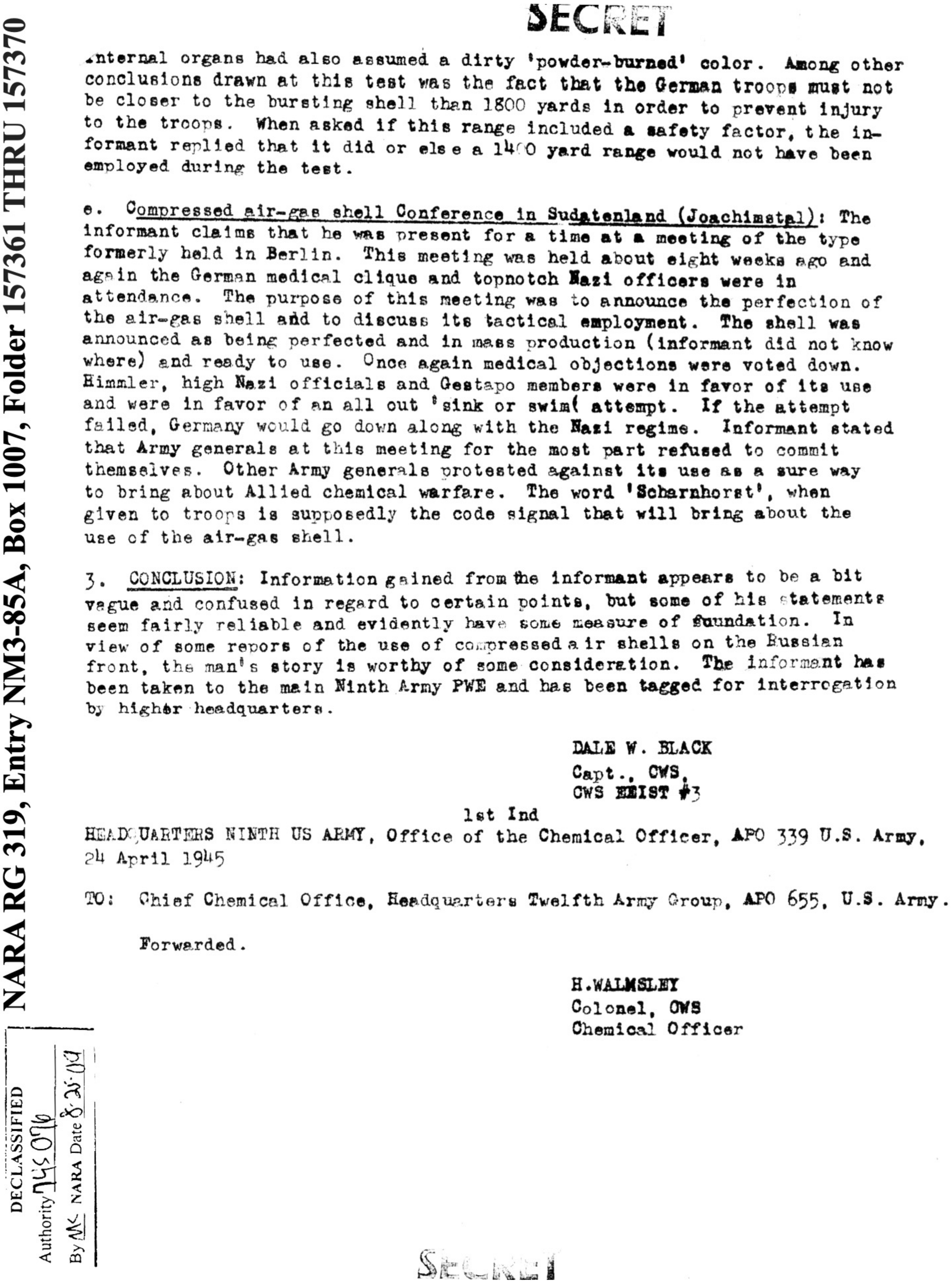
By AK NARA Date 8-25-03

Figure 3.82: A reported test of a fuel-air explosive (or possibly a chemical agent) [NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370].



NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370

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internal organs had also assumed a dirty 'powder-burned' color. Among other conclusions drawn at this test was the fact that the German troops must not be closer to the bursting shell than 1800 yards in order to prevent injury to the troops. When asked if this range included a safety factor, the informant replied that it did or else a 1400 yard range would not have been employed during the test.

e. Compressed air-gas shell Conference in Sudatenland (Joachimstal): The informant claims that he was present for a time at a meeting of the type formerly held in Berlin. This meeting was held about eight weeks ago and again the German medical clique and topnotch Nazi officers were in attendance. The purpose of this meeting was to announce the perfection of the air-gas shell and to discuss its tactical employment. The shell was announced as being perfected and in mass production (informant did not know where) and ready to use. Once again medical objections were voted down. Himmler, high Nazi officials and Gestapo members were in favor of its use and were in favor of an all out 'sink or swim(attempt. If the attempt failed, Germany would go down along with the Nazi regime. Informant stated that Army generals at this meeting for the most part refused to commit themselves. Other Army generals protested against its use as a sure way to bring about Allied chemical warfare. The word 'Scharnhorst', when given to troops is supposedly the code signal that will bring about the use of the air-gas shell.

3. CONCLUSION: Information gained from the informant appears to be a bit vague and confused in regard to certain points, but some of his statements seem fairly reliable and evidently have some measure of foundation. In view of some repors of the use of compressed air shells on the Russian front, the man's story is worthy of some consideration. The informant has been taken to the main Ninth Army PWE and has been tagged for interrogation by higher headquarters.

DALE W. BLACK
Capt., CWS,
CWS EEIST #3

1st Ind

HEADQUARTERS NINTH US ARMY, Office of the Chemical Officer, APO 339 U.S. Army, 24 April 1945

TO: Chief Chemical Office, Headquarters Twelfth Army Group, APO 655, U.S. Army.

Forwarded.

H.WALMSLEY
Colonel, CWS
Chemical Officer

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By NC NARA Date 8-25-09

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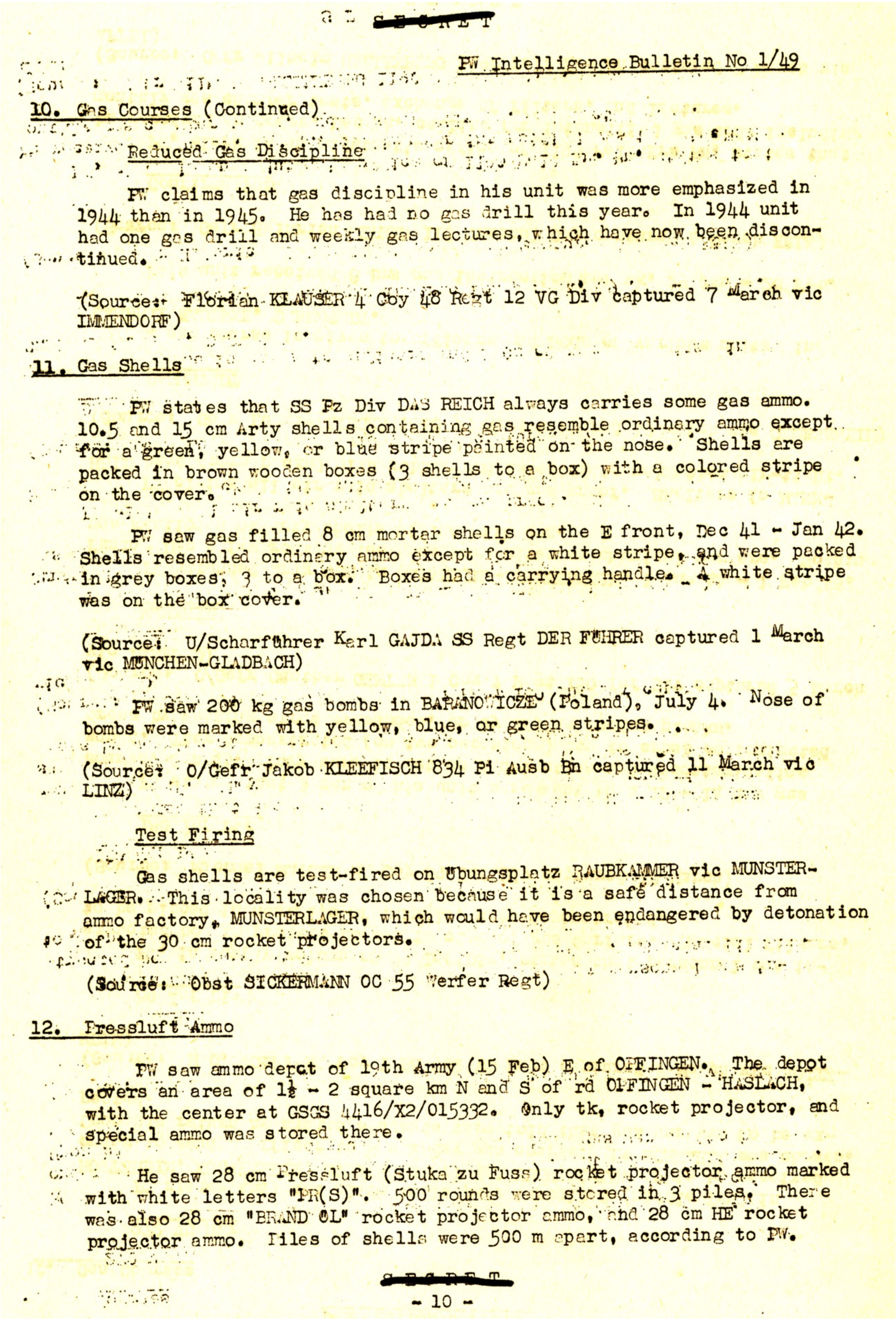
Figure 3.83: A reported test of a fuel-air explosive (or possibly a chemical agent) [NARA RG 319, Entry NM3-85A, Box 1007, Folder 157361 THRU 157370].

PW Intelligence Bulletin No 1/49, AFHRA folder THIS PAGE IS DECLASSIFIED IAW EO 13526
506.61951 Nos. 1/47--1/56 13 Mar--9 Apr 1945, IRIS 207526



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PW Intelligence Bulletin No 1/49

10. Gas Courses (Continued)

Reduced Gas Discipline

PW claims that gas discipline in his unit was more emphasized in 1944 than in 1945. He has had no gas drill this year. In 1944 unit had one gas drill and weekly gas lectures, which have now been discontinued.

(Source: Florian KLAUSER 4 Coy 48 Regt 12 VG Div captured 7 March vic IMMENDORF)

11. Gas Shells

PW states that SS Pz Div DAS REICH always carries some gas ammo. 10.5 and 15 cm Arty shells containing gas resemble ordinary ammo except for a green, yellow, or blue stripe painted on the nose. Shells are packed in brown wooden boxes (3 shells to a box) with a colored stripe on the cover.

PW saw gas filled 8 cm mortar shells on the E front, Dec 41 - Jan 42. Shells resembled ordinary ammo except for a white stripe, and were packed in grey boxes, 3 to a box. Boxes had a carrying handle. A white stripe was on the box cover.

(Source: U/Scharführer Karl GAJDA SS Regt DER FÜHRER captured 1 March vic MÜNCHEN-GLADBACH)

PW saw 200 kg gas bombs in BARANOWICZE (Poland), July 4. Nose of bombs were marked with yellow, blue, or green stripes.

(Source: O/Gefr Jakob KLEEFISCH 834 Pi Ausb Bn captured 11 March vic LINZ)

Test Firing

Gas shells are test-fired on Übungsplatz RAUBKAMMER vic MUNSTERLAGER. This locality was chosen because it is a safe distance from ammo factory, MUNSTERLAGER, which would have been endangered by detonation of the 30 cm rocket projectors.

(Source: Obst SICKERMANN OC 55 Werfer Regt)

12. Pressluft Ammo

PW saw ammo depot of 19th Army (15 Feb) E of OFFINGEN. The depot covers an area of 1½ - 2 square km N and S of rd OFFINGEN - HASLACH, with the center at GSGS 4416/X2/015332. Only tk, rocket projector, and special ammo was stored there.

He saw 28 cm Pressluft (Stuka zu Fuss) rocket projector ammo marked with white letters "PR(S)". 500 rounds were stored in 3 piles. There was also 28 cm "BRAND ÖL" rocket projector ammo, and 28 cm HE rocket projector ammo. Piles of shells were 500 m apart, according to PW.

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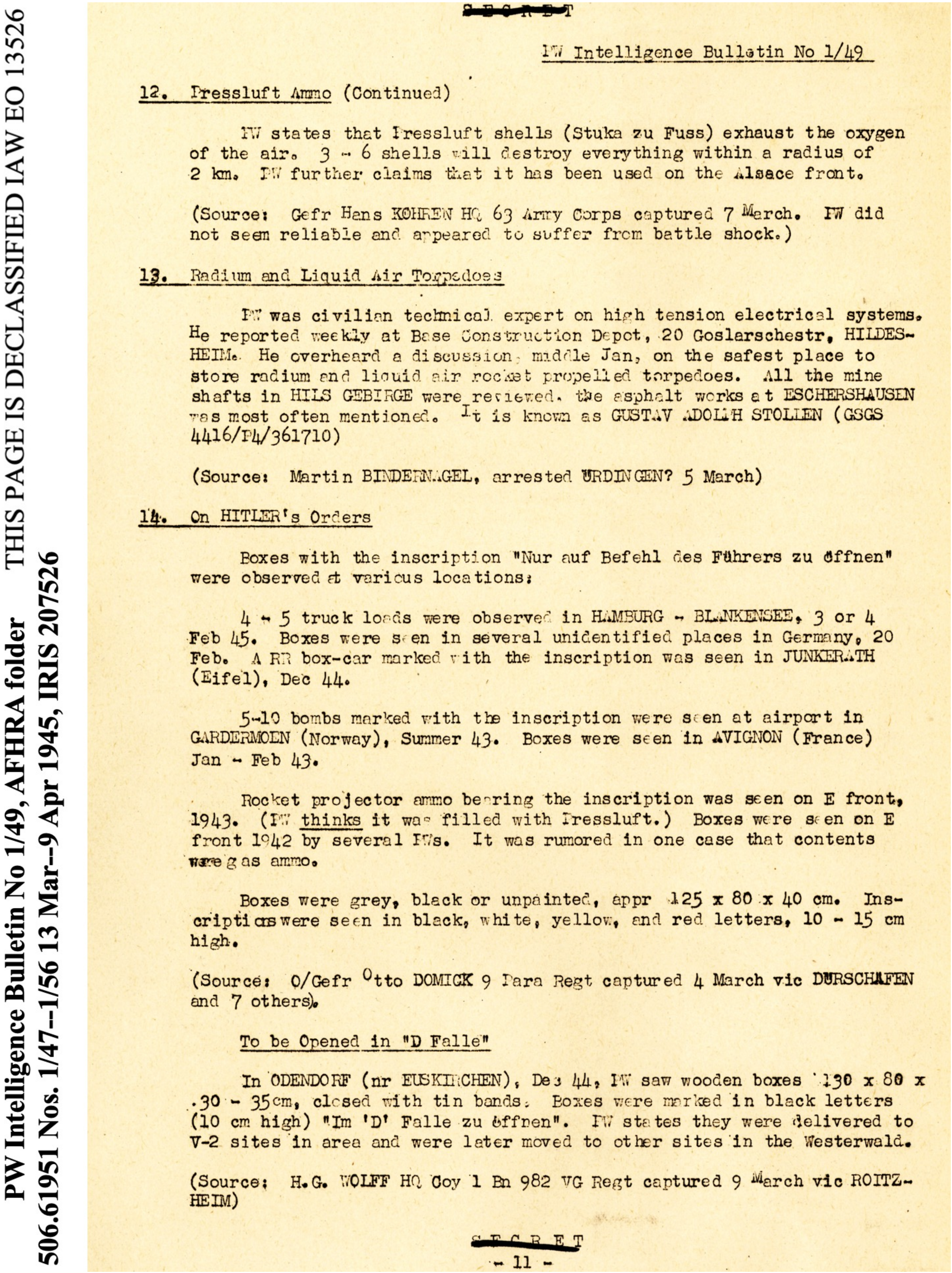
- 10 -

Figure 3.84: Reports of stockpiled fuel-air explosives and other weapons. PW Intelligence Bulletin No 1/49 [AFHRA folder 506.61951 Nos. 1/47–1/56 13 Mar–9 Apr 1945, IRIS 207526; AFHRA A5185 frames 840–841].



PW Intelligence Bulletin No 1/49, AFHRA folder 506.61951 Nos. 1/47--1/56 13 Mar--9 Apr 1945, IRIS 207526

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PW Intelligence Bulletin No 1/49

12. Pressluft Ammo (Continued)

PW states that Pressluft shells (Stuka zu Fuss) exhaust the oxygen of the air. 3 - 6 shells will destroy everything within a radius of 2 km. PW further claims that it has been used on the Alsace front.

(Source: Gefr Hans KOHREN HQ 63 Army Corps captured 7 March. PW did not seem reliable and appeared to suffer from battle shock.)

13. Radium and Liquid Air Torpedoes

PW was civilian technical expert on high tension electrical systems. He reported weekly at Base Construction Depot, 20 Goslarschestr, HILDESHEIM. He overheard a discussion, middle Jan, on the safest place to store radium and liquid air rocket propelled torpedoes. All the mine shafts in HILS GEBIRGE were reviewed. the asphalt works at ESCHERSHAUSEN was most often mentioned. It is known as GUSTAV ADOLPH STOLLEN (GSGS 4416/P4/361710)

(Source: Martin BINDERNAGEL, arrested URDINGEN? 5 March)

14. On HITLER's Orders

Boxes with the inscription "Nur auf Befehl des Führers zu öffnen" were observed at various locations:

4 - 5 truck loads were observed in HAMBURG - BLANKENSEE, 3 or 4 Feb 45. Boxes were seen in several unidentified places in Germany, 20 Feb. A RR box-car marked with the inscription was seen in JUNKERATH (Eifel), Dec 44.

5-10 bombs marked with the inscription were seen at airport in GARDERMOEN (Norway), Summer 43. Boxes were seen in AVIGNON (France) Jan - Feb 43.

Rocket projector ammo bearing the inscription was seen on E front, 1943. (PW thinks it was filled with Pressluft.) Boxes were seen on E front 1942 by several PWs. It was rumored in one case that contents were gas ammo.

Boxes were grey, black or unpainted, appr 125 x 80 x 40 cm. Inscriptions were seen in black, white, yellow, and red letters, 10 - 15 cm high.

(Source: O/Gefr Otto DOMICK 9 Para Regt captured 4 March vic DURSCHAFEN and 7 others).

To be Opened in "D Falle"

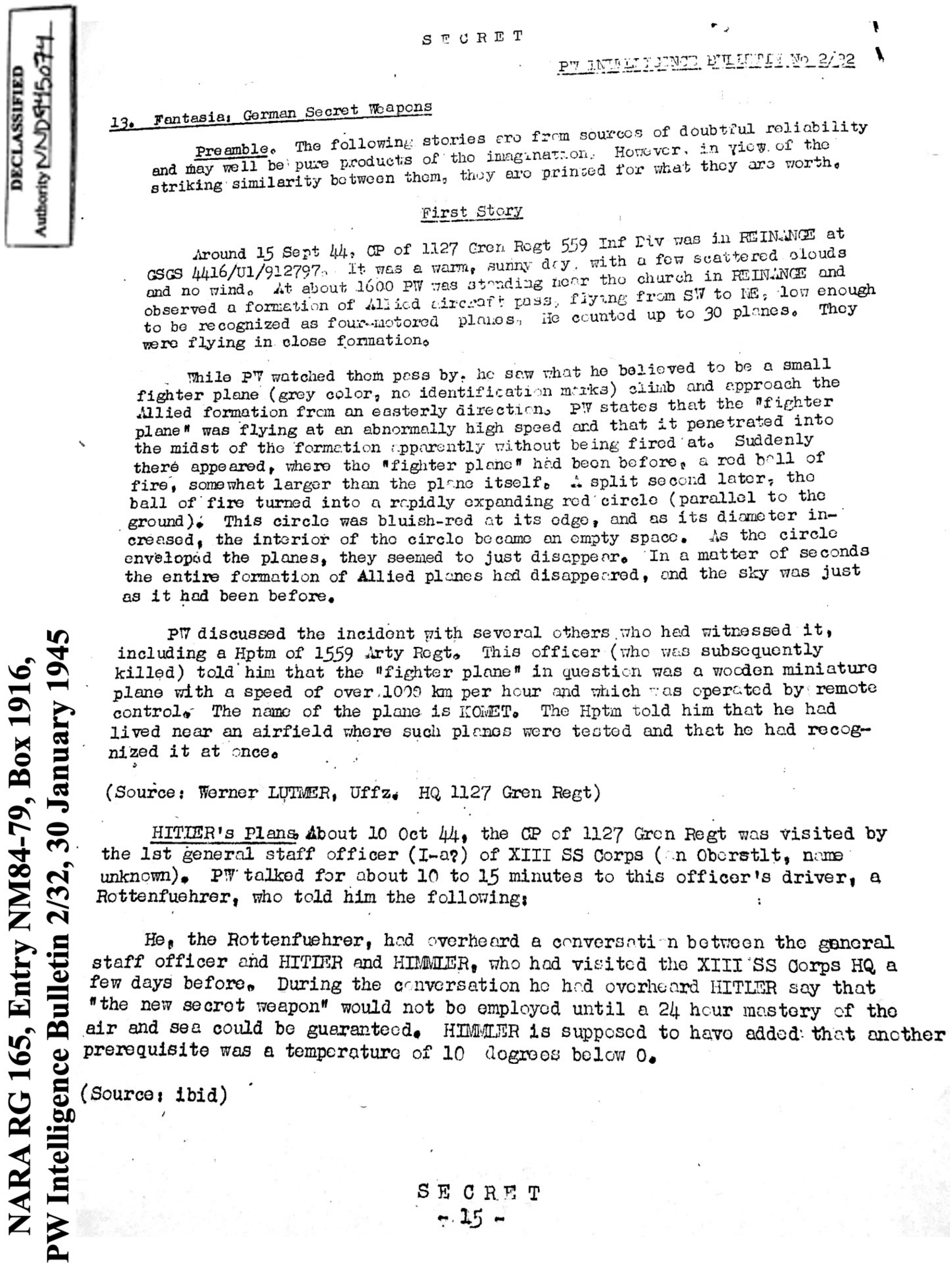
In ODENDORF (nr EUSKIRCHEN), Dec 44, PW saw wooden boxes 130 x 80 x 30 - 35cm, closed with tin bands. Boxes were marked in black letters (10 cm high) "Im 'D' Falle zu öffnen". PW states they were delivered to V-2 sites in area and were later moved to other sites in the Westerwald.

(Source: H.G. WOLFF HQ Coy 1 Bn 982 VG Regt captured 9 March vic ROITZHEIM)

~~SECRET~~

- 11 -

Figure 3.85: Reports of stockpiled fuel-air explosives and other weapons. PW Intelligence Bulletin No 1/49 [AFHRA folder 506.61951 Nos. 1/47–1/56 13 Mar–9 Apr 1945, IRIS 207526; AFHRA A5185 frames 840–841].



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Authority NND945074

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PW INTELLIGENCE BULLETIN No 2/32

13. Fantasia: German Secret Weapons

Preamble. The following stories are from sources of doubtful reliability and may well be pure products of the imagination. However, in view of the striking similarity between them, they are printed for what they are worth.

First Story

Around 15 Sept 44, CP of 1127 Gren Regt 559 Inf Div was in REINANGE at GSGS 4416/U1/912797. It was a warm, sunny day, with a few scattered clouds and no wind. At about 1600 PW was standing near the church in REINANGE and observed a formation of Allied aircraft pass, flying from SW to NE, low enough to be recognized as four-motored planes. He counted up to 30 planes. They were flying in close formation.

While PW watched them pass by, he saw what he believed to be a small fighter plane (grey color, no identification marks) climb and approach the Allied formation from an easterly direction. PW states that the "fighter plane" was flying at an abnormally high speed and that it penetrated into the midst of the formation apparently without being fired at. Suddenly there appeared, where the "fighter plane" had been before, a red ball of fire, somewhat larger than the plane itself. A split second later, the ball of fire turned into a rapidly expanding red circle (parallel to the ground). This circle was bluish-red at its edge, and as its diameter increased, the interior of the circle became an empty space. As the circle enveloped the planes, they seemed to just disappear. In a matter of seconds the entire formation of Allied planes had disappeared, and the sky was just as it had been before.

PW discussed the incident with several others who had witnessed it, including a Hptm of 1559 Arty Regt. This officer (who was subsequently killed) told him that the "fighter plane" in question was a wooden miniature plane with a speed of over 1000 km per hour and which was operated by remote control. The name of the plane is KOMET. The Hptm told him that he had lived near an airfield where such planes were tested and that he had recognized it at once.

(Source: Werner LUTMER, Uffz. HQ 1127 Gren Regt)

HITLER's Plans. About 10 Oct 44, the CP of 1127 Gren Regt was visited by the 1st general staff officer (I-a?) of XIII SS Corps (an Oberstlt, name unknown). PW talked for about 10 to 15 minutes to this officer's driver, a Rottenfuehrer, who told him the following:

He, the Rottenfuehrer, had overheard a conversation between the general staff officer and HITLER and HIMMLER, who had visited the XIII SS Corps HQ a few days before. During the conversation he had overheard HITLER say that "the new secret weapon" would not be employed until a 24 hour mastery of the air and sea could be guaranteed. HIMMLER is supposed to have added that another prerequisite was a temperature of 10 degrees below 0.

(Source: ibid)

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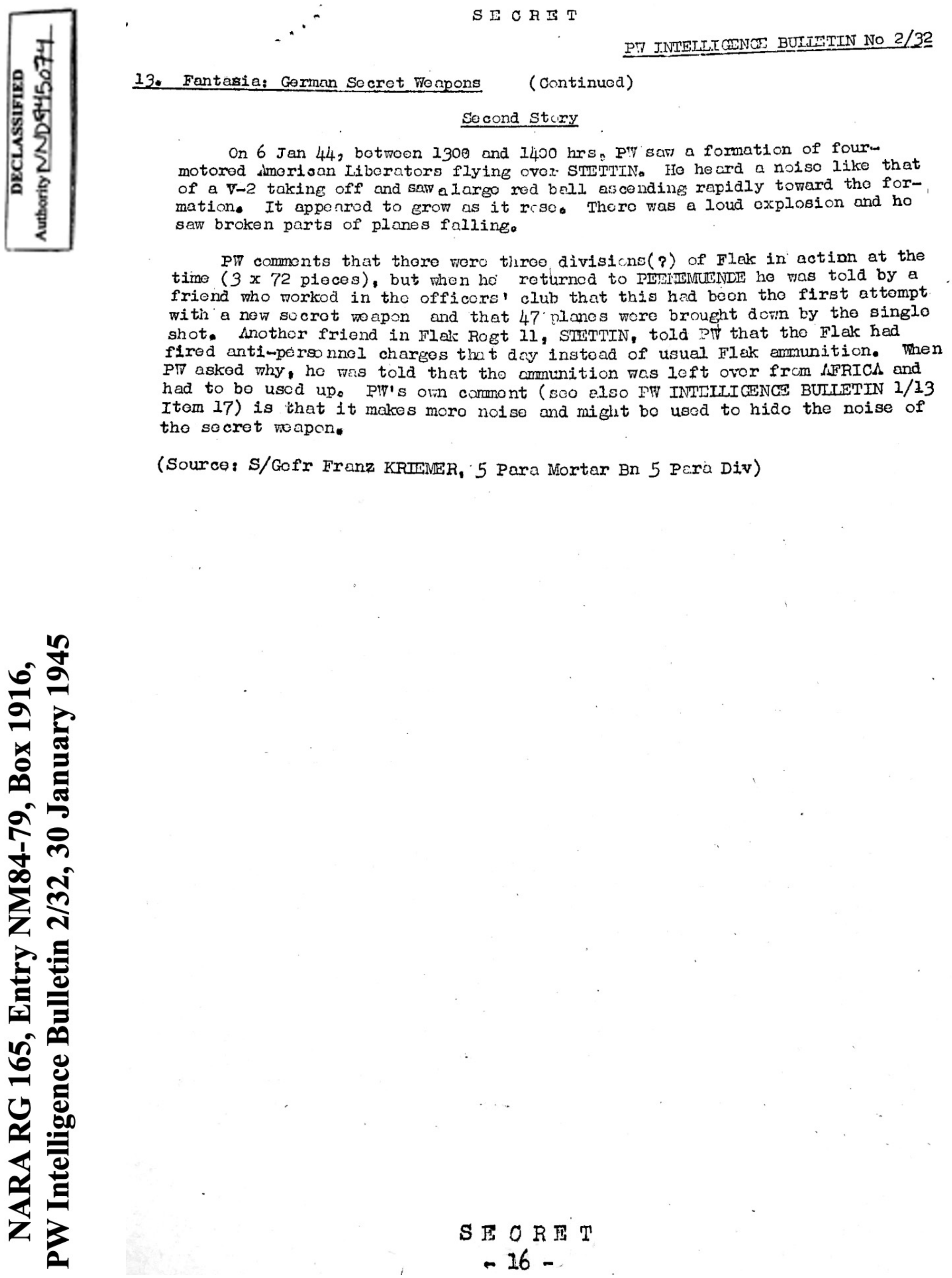
NARA RG 165, Entry NM84-79, Box 1916,
PW Intelligence Bulletin 2/32, 30 January 1945

Figure 3.86: A reported test of a fuel-air explosive. PW Intelligence Bulletin 2/32, 30 January 1945. [NARA RG 165, Entry NM84-79, Box 1916].



DECLASSIFIED
Authority NND945074

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PW INTELLIGENCE BULLETIN No 2/32

13. Fantasia: German Secret Weapons (Continued)

Second Story

On 6 Jan 44, between 1300 and 1400 hrs, PW saw a formation of four-motored American Liberators flying over STETTIN. He heard a noise like that of a V-2 taking off and saw a large red ball ascending rapidly toward the formation. It appeared to grow as it rose. There was a loud explosion and he saw broken parts of planes falling.

PW comments that there were three divisions(?) of Flak in action at the time (3 x 72 pieces), but when he returned to PEENEMUENDE he was told by a friend who worked in the officers' club that this had been the first attempt with a new secret weapon and that 47 planes were brought down by the single shot. Another friend in Flak Regt 11, STETTIN, told PW that the Flak had fired anti-personnel charges that day instead of usual Flak ammunition. When PW asked why, he was told that the ammunition was left over from AFRICA and had to be used up. PW's own comment (see also PW INTELLIGENCE BULLETIN 1/13 Item 17) is that it makes more noise and might be used to hide the noise of the secret weapon.

(Source: S/Gefr Franz KRIEMER, 5 Para Mortar Bn 5 Para Div)

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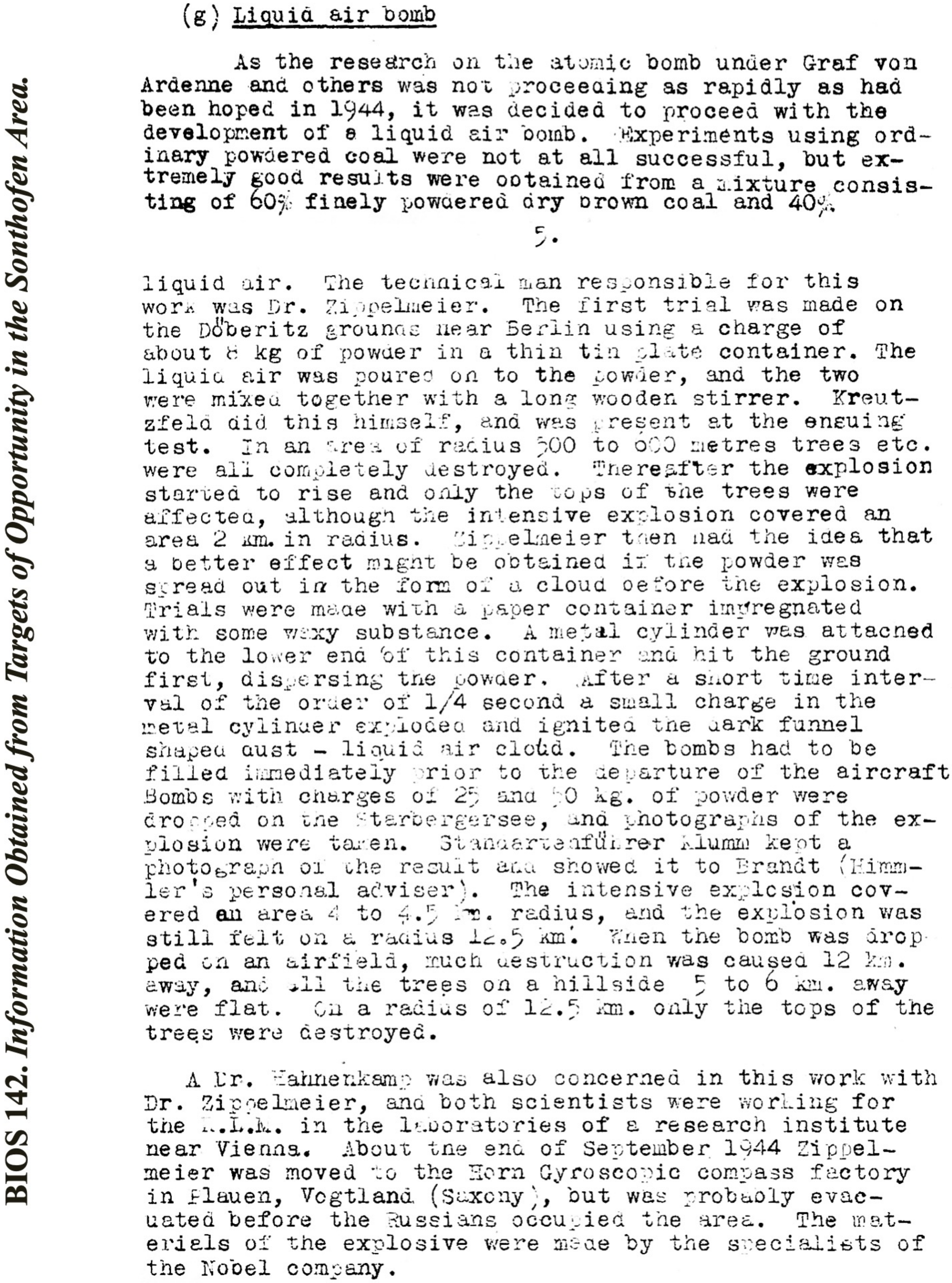
NARA RG 165, Entry NM84-79, Box 1916,
PW Intelligence Bulletin 2/32, 30 January 1945

Figure 3.87: A reported test of a fuel-air explosive. PW Intelligence Bulletin 2/32, 30 January 1945. [NARA RG 165, Entry NM84-79, Box 1916].



BIOS 142. Information Obtained from Targets of Opportunity in the Sonthofen Area.

(g) Liquid air bomb

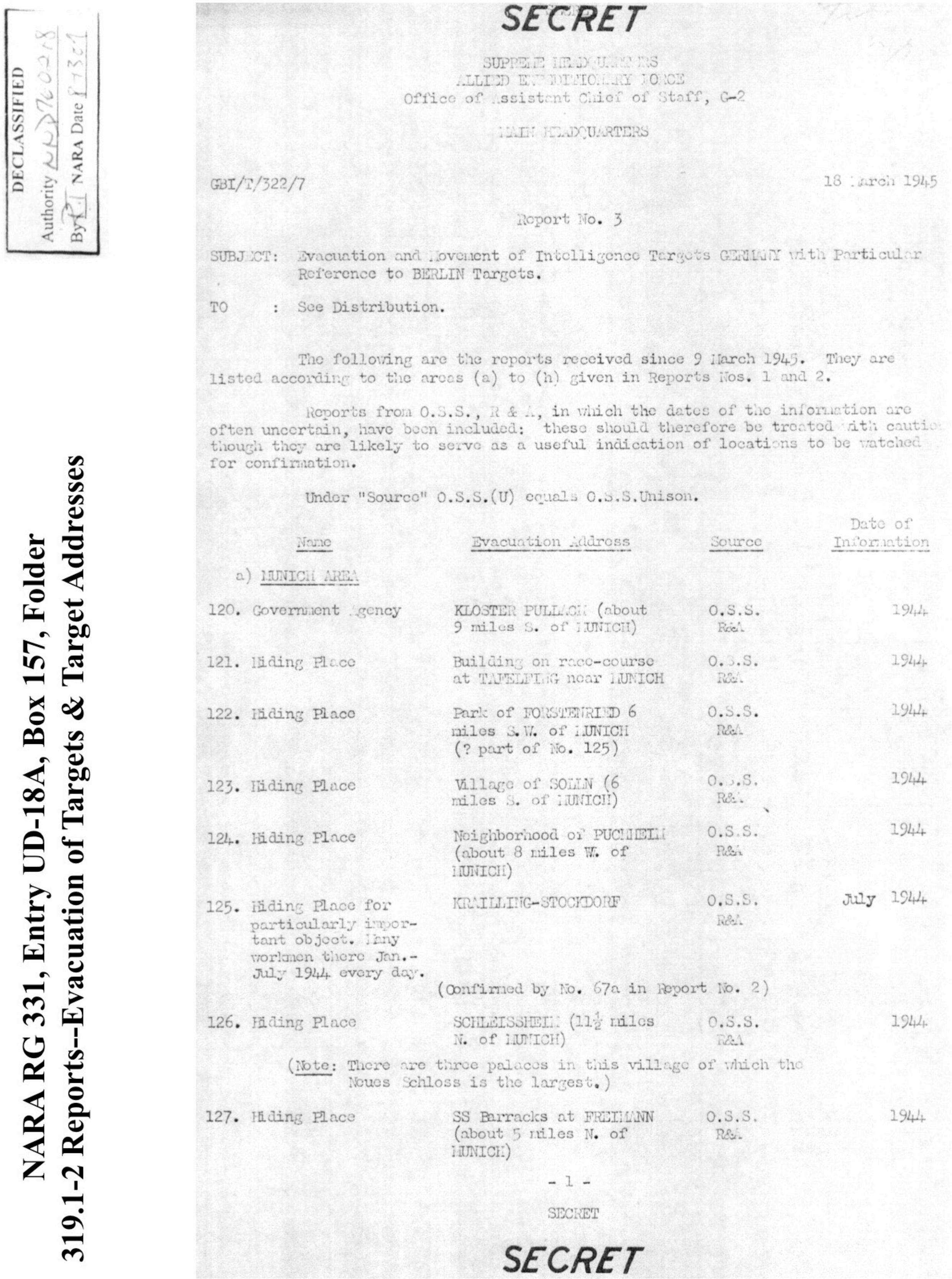
As the research on the atomic bomb under Graf von Ardenne and others was not proceeding as rapidly as had been hoped in 1944, it was decided to proceed with the development of a liquid air bomb. Experiments using ordinary powdered coal were not at all successful, but extremely good results were obtained from a mixture consisting of 60% finely powdered dry brown coal and 40%

5.

liquid air. The technical man responsible for this work was Dr. Zippelmeier. The first trial was made on the Döberitz grounds near Berlin using a charge of about 8 kg of powder in a thin tin plate container. The liquid air was poured on to the powder, and the two were mixed together with a long wooden stirrer. Kreutzfeld did this himself, and was present at the ensuing test. In an area of radius 500 to 600 metres trees etc. were all completely destroyed. Thereafter the explosion started to rise and only the tops of the trees were affected, although the intensive explosion covered an area 2 km. in radius. Zippelmeier then had the idea that a better effect might be obtained if the powder was spread out in the form of a cloud before the explosion. Trials were made with a paper container impregnated with some waxy substance. A metal cylinder was attached to the lower end of this container and hit the ground first, dispersing the powder. After a short time interval of the order of 1/4 second a small charge in the metal cylinder exploded and ignited the dark funnel shaped dust - liquid air cloud. The bombs had to be filled immediately prior to the departure of the aircraft. Bombs with charges of 25 and 50 kg. of powder were dropped on the Starbergersee, and photographs of the explosion were taken. Standartenführer Klumm kept a photograph of the result and showed it to Brandt (Himmler's personal adviser). The intensive explosion covered an area 4 to 4.5 km. radius, and the explosion was still felt on a radius 12.5 km. When the bomb was dropped on an airfield, much destruction was caused 12 km. away, and all the trees on a hillside 5 to 6 km. away were flat. On a radius of 12.5 km. only the tops of the trees were destroyed.

A Dr. Hahnenkamp was also concerned in this work with Dr. Zippelmeier, and both scientists were working for the R.L.M. in the laboratories of a research institute near Vienna. About the end of September 1944 Zippelmeier was moved to the Horn Gyroscopic compass factory in Plauen, Vogtland (Saxony), but was probably evacuated before the Russians occupied the area. The materials of the explosive were made by the specialists of the Nobel company.

Figure 3.88: Reported tests of fuel-air explosives [BIOS 142, pp. 4–5]. The tests sound real although the blast radii (reported secondhand and from memory) seem exaggerated for the amounts of explosives and dispersal methods described. The “waxy substance” coating the container was probably to keep the coal dust from sticking to the container.



DECLASSIFIED
Authority NND760218
By RT NARA Date 8/13/01

NARA RG 331, Entry UD-18A, Box 157, Folder 319.1-2 Reports--Evacuation of Targets & Target Addresses

SECRET

SUPREME HEADQUARTERS
ALLIED EXPEDITIONARY FORCE
Office of Assistant Chief of Staff, G-2

MAIN HEADQUARTERS

GBI/T/322/7 18 March 1945

Report No. 3

SUBJECT: Evacuation and Movement of Intelligence Targets GERMANY with Particular Reference to BERLIN Targets.

TO : See Distribution.

The following are the reports received since 9 March 1945. They are listed according to the areas (a) to (h) given in Reports Nos. 1 and 2.

Reports from O.S.S., R & A, in which the dates of the information are often uncertain, have been included: these should therefore be treated with caution though they are likely to serve as a useful indication of locations to be watched for confirmation.

Under "Source" O.S.S.(U) equals O.S.S.Unison.

Name	Evacuation Address	Source	Date of Information
a) MUNICH AREA			
120. Government Agency	KLOSTER PULLACH (about 9 miles S. of MUNICH)	O.S.S. R&A	1944
121. Hiding Place	Building on race-course at TAFELFING near MUNICH	O.S.S. R&A	1944
122. Hiding Place	Park of FORSTENRIED 6 miles S.W. of MUNICH (? part of No. 125)	O.S.S. R&A	1944
123. Hiding Place	Village of SOLLN (6 miles S. of MUNICH)	O.S.S. R&A	1944
124. Hiding Place	Neighborhood of PUCHHEIM (about 8 miles W. of MUNICH)	O.S.S. R&A	1944
125. Hiding Place for particularly important object. Many workmen there Jan.-July 1944 every day.	KRAILLING-STOCKDORF	O.S.S. R&A	July 1944
	(Confirmed by No. 67a in Report No. 2)		
126. Hiding Place	SCHLEISSHEIM ($11\frac{1}{2}$ miles N. of MUNICH)	O.S.S. R&A	1944
	(Note: There are three palaces in this village of which the Neues Schloss is the largest.)		
127. Hiding Place	SS Barracks at FREIMANN (about 5 miles N. of MUNICH)	O.S.S. R&A	1944

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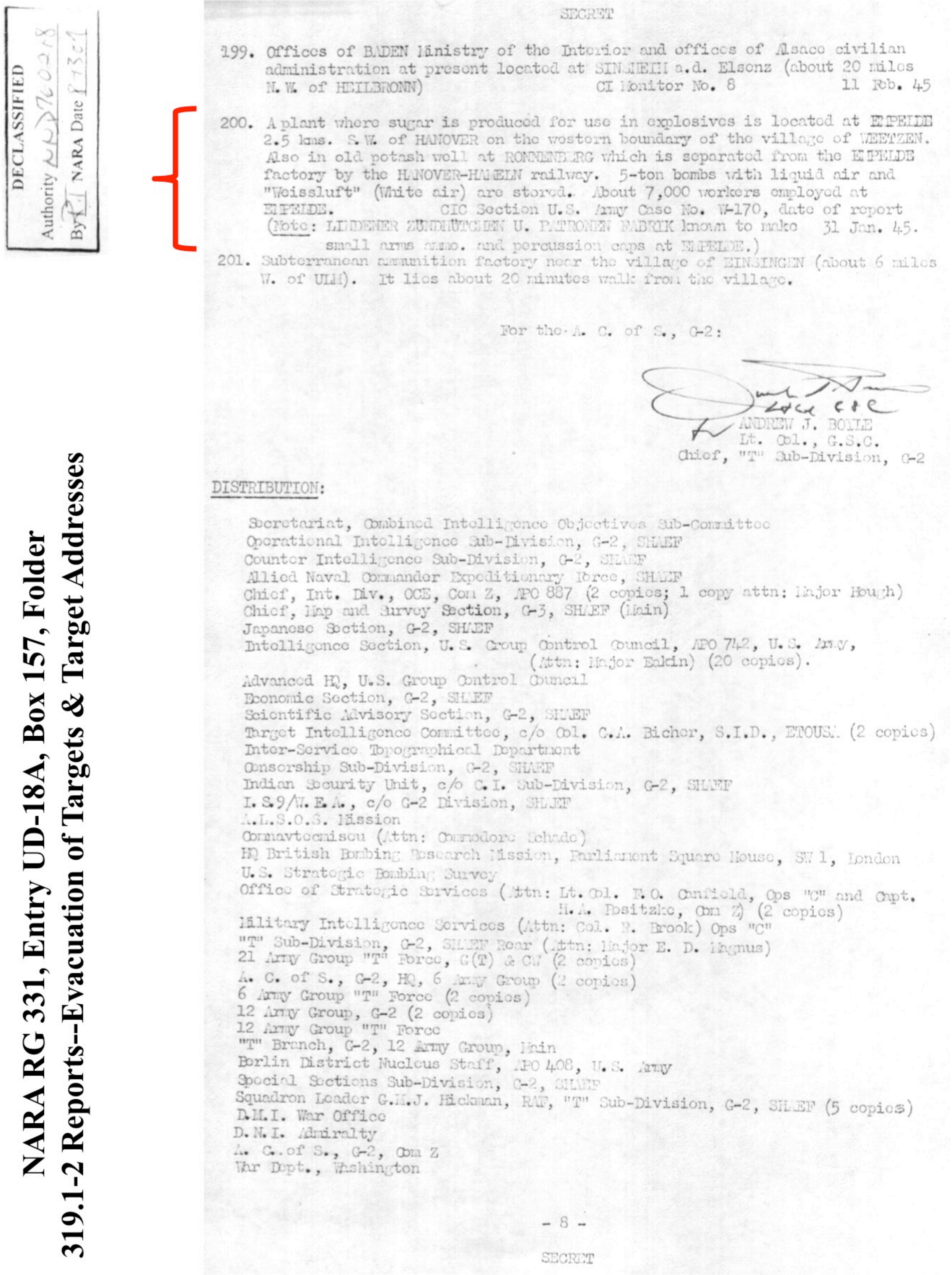
Figure 3.89: By the end of the war, at least 7000 workers had mass-produced 5-ton fuel-air explosive bombs and stockpiled them [NARA RG 331, Entry UD-18A, Box 157, Folder 319.1-2 Reports—Evacuation of Targets & Target Addresses].



DECLASSIFIED
Authority NND760218
By RI NARA Date 8/13/01

NARA RG 331, Entry UD-18A, Box 157, Folder 319.1-2 Reports--Evacuation of Targets & Target Addresses

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199. Offices of BADEN Ministry of the Interior and offices of Alsace civilian administration at present located at SINSHEIM a.d. Elsenz (about 20 miles N.W. of HEILBRONN) CI Monitor No. 8 11 Feb. 45

200. A plant where sugar is produced for use in explosives is located at EMPELDE 2.5 kms. S.W. of HANOVER on the western boundary of the village of WEETZEN. Also in old potash well at RONNENBERG which is separated from the EMPELDE factory by the HANOVER-HAMELN railway. 5-ton bombs with liquid air and "Weissluft" (White air) are stored. About 7,000 workers employed at EMPELDE. CIC Section U.S. Army Case No. W-170, date of report 31 Jan. 45. (Note: LINDENER ZÜNDHÜTCHEN U. PATRONEN FABRIK known to make small arms ammo. and percussion caps at EMPELDE.)

201. Subterranean ammunition factory near the village of EINSINGEN (about 6 miles W. of ULM). It lies about 20 minutes walk from the village.

For the A. C. of S., G-2:

ANDREW J. BOYLE
Lt. Col., G.S.C.
Chief, "T" Sub-Division, G-2

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I.S.9/W.E.A., c/o G-2 Division, SHAEF
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Comnavtecmiseu (Attn: Commodore Schade)
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D.N.I. Admiralty
A. C. of S., G-2, Com Z
War Dept., Washington

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Figure 3.90: By the end of the war, at least 7000 workers had mass-produced 5-ton fuel-air explosive bombs and stockpiled them [NARA RG 331, Entry UD-18A, Box 157, Folder 319.1-2 Reports—Evacuation of Targets & Target Addresses].

3.4.3 Shaped Explosive Charges

Similarly, German-speaking scientists led the development of shaped (or hollow) explosive charges, which concentrate the force of an explosion in a particular direction—for example in the forward direction to penetrate tank armor upon impact (Fig. 3.91), or radially inward in an implosion bomb to compress nuclear fuel (Sections D.8–D.9).[9]

Franz von Baader (German states, 1765–1841, Fig. 3.92) designed and utilized shaped charges for mining.

Gustav Bloem (German?, 18??–19??, Fig. 3.92) invented metal-lined shaped charges as detonator caps.

Carl Julius Cranz (German, 1858–1945, Fig. 3.92) worked on many aspects of ballistics and supported Franz Rudolf Thomanek and others in developing militarily useful shaped charges.

Rolf Engel (German, 1912–1993, Fig. 3.92) was an expert on rockets, explosives, shaped charges, and implosion designs. He worked on secretive weapons projects for the German military during World War II and for the French military after the war.

Ernst Richard Escales (German, 1863–1924, Fig. 3.92) published handbooks and journals about a wide variety of explosives and explosive techniques, including shaped charges.

Max von Förster (German, 1845–1905, Fig. 3.92) designed, tested, and published descriptions of shaped explosive charges.

Hellmuth von Huttern (German?, 19??–19??, Fig. 3.93) worked with Franz Rudolf Thomanek in developing the first prototypes for military shaped charge weapons.

Heinrich Langweiler (German?, 19??–19??, Fig. 3.93) led the team that developed the Faustpatrone and Panzerfaust anti-tank weapons [BIOS 99; BIOS 100]. See also p. 2143.

Hans Mohaupt (Swiss, 1915–2001, Fig. 3.93) brought the concept of shaped explosive charges to the United States, leading to the design of the bazooka.

Egon Neumann (German, 18??–19??, Fig. 3.93) developed sophisticated shaped charge explosives in 1910 and helped to publicize the general concept [George Brown 1998, p. 166; Walters and Zukas 1989, pp. 12–13].

Hubert Schardin (German, 1902–1965, Fig. 3.93) worked for the Luftwaffe as an expert on the design and experimental measurement of shaped explosive charges and implosion bombs [Krehl 2009, pp. 1160–1162; Nagel 2012a, p. 149 ff.]. After the war, he worked for the French military.

Erich Schumann (German, 1898–1985, Fig. 3.93) ran a Heereswaffenamt (Army Ordnance Office) program to design and conduct experimental measurements of shaped explosive charges and implosion bombs [Karlsch 2005; Nagel 2012a].

---

[9] George Brown 1998; DOD 1953; DOW 1945a; Field 2017; Karlsch 2005; Kennedy 1990; Krehl 2009; Mrazek 1970; Nagel 2012a; Simon 1947a; Walters and Zukas 1989; BIOS 99; BIOS 100.

Alfred Stettbacher (Swiss, 1888–1961, Fig. 3.94) designed and tested shaped charges.

Franz Rudolf Thomanek (Austrian, 1913–1990, Fig. 3.94) began designing and developing hollow-charge antitank weapons in 1932 and worked on them until 1945.

Walter Trinks (German, 1910–1995, Fig. 3.94) worked closely with Erich Schumann as part of the Heereswaffenamt (Army Ordnance Office) program to design and conduct experimental measurements of shaped explosive charges and implosion bombs [Karlsch 2005; Nagel 2012a].

The chemist Simon Field [Field 2017, pp. 131–132, 136] emphasized the contributions of many of the above scientists to the development of shaped explosive charges:

> In 1792 the twenty-six-year-old German Catholic philospher, theologist, and mining engineer Franz Xaver von Baader came up with a way of saving gunpowder in mines. The idea was to make a conical of mushroom-shaped hollow in the front of the gunpowder charge. His reasoning was not recorded, and it is not clear what effect it had, if any, but it was used in Norway and later in the mines of the Harz Mountains in Germany[...]
>
> Things were a little different ninety-one years later, in 1883. The chief company engineer of the nitrocellulose factor of Wolff and Co. in Walsrode, Germany, was a man named Max von Förster. Von Förster tested a hypothesis “to give the detonating gases of guncotton a certain direction aiming toward the target” through a series of experiments with hollowed-out charges. “Estimated on the whole, it appears that the effect of the hollow cartridge of the same size and less weight is superior to the full one of more weight.” [...]
>
> In 1883 Gustav Bloem patented a metal detonator cap with a hollow in it, to get a “concentration of the effect of the explosion in an axial direction.” This was the first lined cavity shaped charge.
>
> [...] Dr. Franz Rudolph Thomanek, on February 4, 1938, discovered the importance of the metal lining. [...] Between then and 1943, Thomanek experimented with different hollow shapes and different liner thicknesses, including tapering the thickness.
>
> In Zurich in 1937 a Swiss engineer, Dr. Henry Hans Mohaupt, also came up with a metal-lined hollow cavity shaped charge, and tried to get the British government to pay him for the expense of developing it. [...]
>
> Mohaupt brought his idea to the United States on October 18, 1940. First developed as a rifle grenade, the idea morphed into a rocket-propelled munition with a shaped charge armor-piercing warhead that became known as the “bazooka” [...]

A small group of German soldiers successfully used two innovations, troop gliders (p. 1701) and shaped explosive charges, to land at and penetrate through the thick reinforced concrete walls of Fort Eben-Emael in Belgium in May 1940 [Mrazek 1970].

For more information on the use of shaped charges and implosion for German nuclear weapons during World War II, see Section D.8.

Shaped explosive charges

Erteilt auf Grund des Ersten Überleitungsgesetzes vom 8. Juli 1949
(WiGBl. S. 175)

BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM
2. AUGUST 1956

DEUTSCHES PATENTAMT

PATENTSCHRIFT

№ 946 689
KLASSE 72i GRUPPE 3 01
INTERNAT. KLASSE F 07 l ———
S 33412 XI/72i

Henri Hans Mohaupt, Brunswick, Me. (V. St. A.)
ist als Erfinder genannt worden

SAGEB, Société Anonyme de Gestion et d'Exploitation de Brevets,
Freiburg (Schweiz)

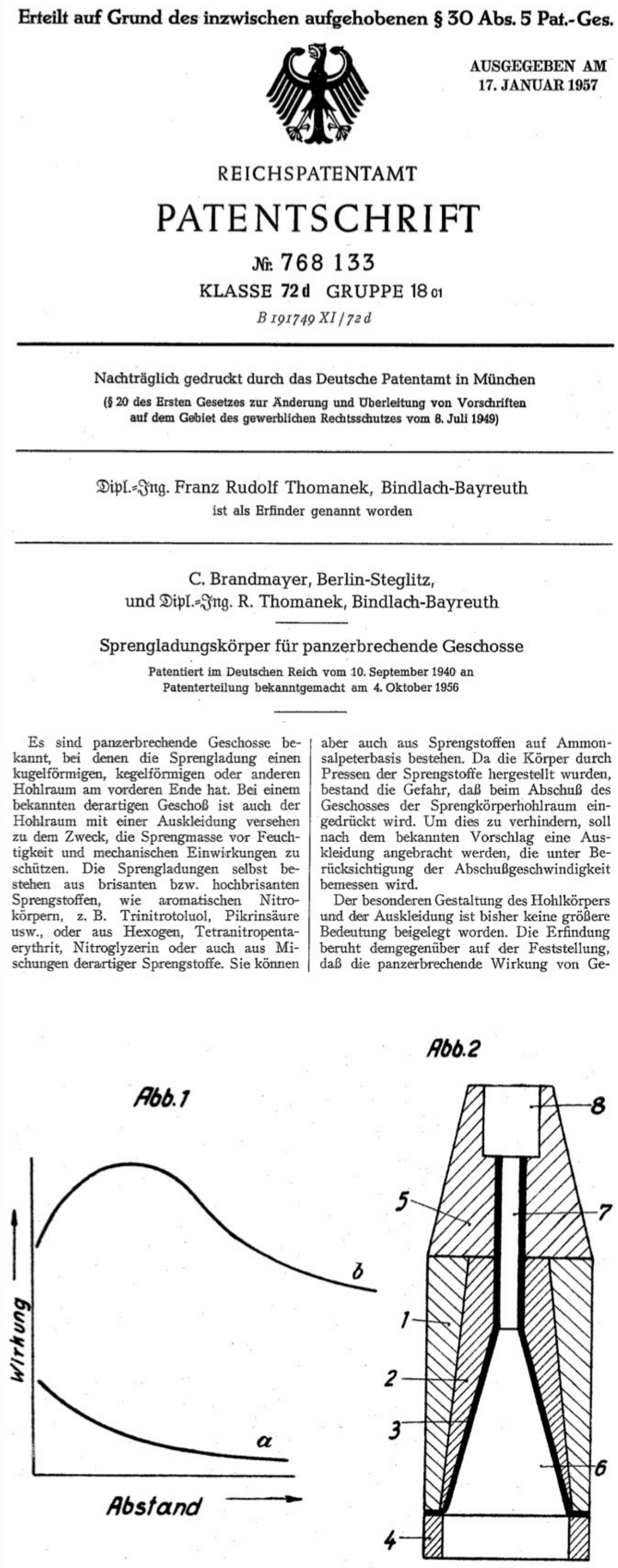
Zündung eines Sprenggeschosses, dessen Hohlraum-Sprengladung vorn eine vorzugsweise kegelförmige Metallauskleidung aufweist

Patentiert im Gebiet der Bundesrepublik Deutschland vom 9. November 1940 an
Patentanmeldung bekanntgemacht am 9. September 1954
Patenterteilung bekanntgemacht am 12. Juli 1956
Die Priorität der Anmeldung in Frankreich vom 9. November 1939 ist in Anspruch genommen

Die Erfindung bezieht sich auf die Zündung eines Sprenggeschosses, bei dem in der Hohlraum-Sprengladung mindestens eine vorzugsweise kegelförmige Auskleidung angeordnet ist, deren Spitze dem Geschoßboden und deren Basis einem Hohlraum im Kopf des Geschosses zugekehrt ist.

Es ist bekannt, daß Sprengkörper, die mit einem gegen den zu sprengenden Gegenstand, z. B. eine Panzerplatte, gerichteten Hohlraum versehen sind, ein größeres Durchschlagsvermögen erzielen als ein volles Sprenggeschoß von gleichen äußeren Abmessungen. Diese Steigerung der Durchschlagskraft ist unter dem Namen Neumanneffekt bekannt. Die hohlen Sprengkörper werden in Bergwerken und Steinbrüchen viel verwendet, denn man erzielt damit eine beträchtliche Sprengstoffersparnis.

Bei einer früher vorgeschlagenen Anwendung des Neumanneffektes auf Geschosse hat das Geschoß einen dünnwandigen Spitzbogenkopf, der sich beim Aufschlag breit drücken soll. Die Sprengladung enthält vorn einen kegelförmigen Hohlraum, der mit einer kegeligen Metallauskleidung versehen ist, um eine Verlagerung des Sprengstoffes in den Hohlraum beim Abschuß zu verhindern. Man nahm an, daß sich beim Aufschlag nach Zertrümmerung des dünnwandigen Geschoßkopfes der Neumanneffekt in gleicher Weise aus-



Erteilt auf Grund des inzwischen aufgehobenen § 30 Abs. 5 Pat.-Ges.

AUSGEGEBEN AM
17. JANUAR 1957

REICHSPATENTAMT

PATENTSCHRIFT

№ 768 133
KLASSE 72d GRUPPE 18 01
B 191749 XI/72d

Nachträglich gedruckt durch das Deutsche Patentamt in München
(§ 20 des Ersten Gesetzes zur Änderung und Überleitung von Vorschriften auf dem Gebiet des gewerblichen Rechtsschutzes vom 8. Juli 1949)

Dipl.-Ing. Franz Rudolf Thomanek, Bindlach-Bayreuth
ist als Erfinder genannt worden

C. Brandmayer, Berlin-Steglitz,
und Dipl.-Ing. R. Thomanek, Bindlach-Bayreuth

Sprengladungskörper für panzerbrechende Geschosse

Patentiert im Deutschen Reich vom 10. September 1940 an
Patenterteilung bekanntgemacht am 4. Oktober 1956

Es sind panzerbrechende Geschosse bekannt, bei denen die Sprengladung einen kugelförmigen, kegelförmigen oder anderen Hohlraum am vorderen Ende hat. Bei einem bekannten derartigen Geschoß ist auch der Hohlraum mit einer Auskleidung versehen zu dem Zweck, die Sprengmasse vor Feuchtigkeit und mechanischen Einwirkungen zu schützen. Die Sprengladungen selbst bestehen aus brisanten bzw. hochbrisanten Sprengstoffen, wie aromatischen Nitrokörpern, z. B. Trinitrotoluol, Pikrinsäure usw., oder aus Hexogen, Tetranitropentaerythrit, Nitroglyzerin oder auch aus Mischungen derartiger Sprengstoffe. Sie können aber auch aus Sprengstoffen auf Ammonsalpeterbasis bestehen. Da die Körper durch Pressen der Sprengstoffe hergestellt wurden, bestand die Gefahr, daß beim Abschuß des Geschosses der Sprengkörperhohlraum eingedrückt wird. Um dies zu verhindern, soll nach dem bekannten Vorschlag eine Auskleidung angebracht werden, die unter Berücksichtigung der Abschußgeschwindigkeit bemessen wird.

Der besonderen Gestaltung des Hohlkörpers und der Auskleidung ist bisher keine größere Bedeutung beigelegt worden. Die Erfindung beruht demgegenüber auf der Feststellung, daß die panzerbrechende Wirkung von Ge-

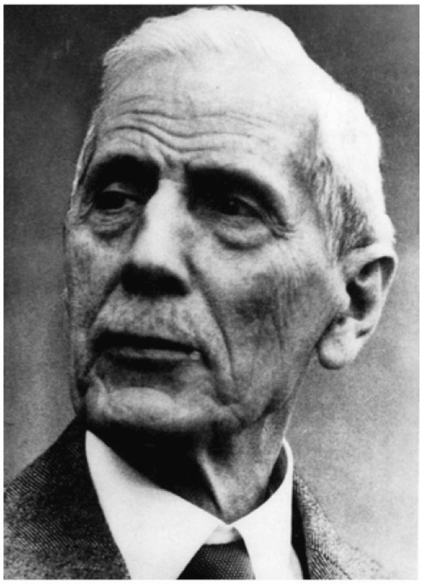
Figure 3.91: German-speaking scientists led the development of shaped explosive charges, as illustrated by these examples of patents from Hans Mohaupt and Franz Rudolf Thomanek.

Shaped explosive charges

Franz von Baader
(1765–1841)

Gustav Bloem
(18??–19??)

Carl Julius Cranz
(1858–1945)



Rolf Engel
(1912–1993)

Ernst Richard Escales
(1863–1924)

Max von Förster
(1845–1905)

Figure 3.92: German-speaking scientists who were responsible for the development of shaped explosive charges included Franz von Baader, Gustav Bloem, Carl Julius Cranz, Rolf Engel, Ernst Richard Escales, and Max von Förster.

Shaped explosive charges

Hellmuth von Huttern (19??–19??)

Heinrich Langweiler (19??–19??)

Hans Mohaupt (1915–2001)

Egon Neumann (18??–19??)

Hubert Schardin (1902–1965)

Erich Schumann (1898–1985)

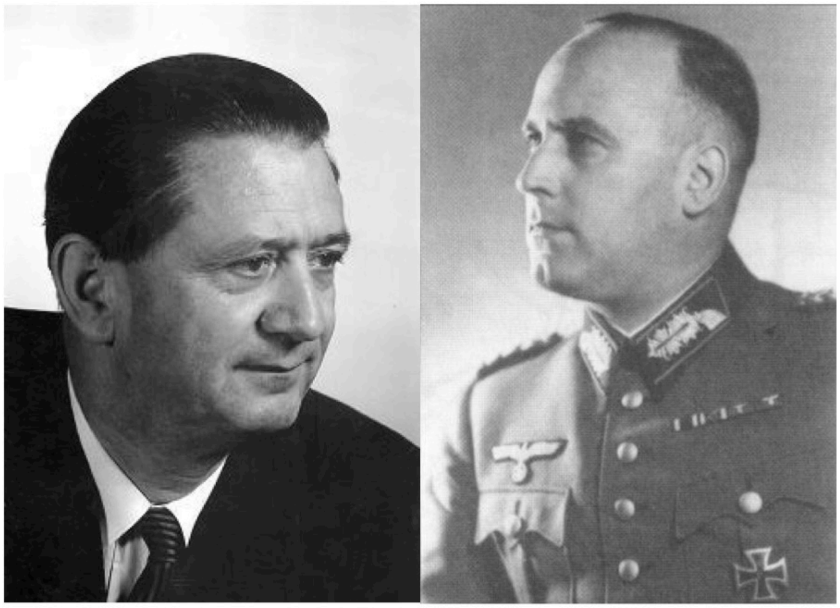


Figure 3.93: Other German-speaking scientists who were responsible for the development of shaped explosive charges included Hellmuth von Huttern, Heinrich Langweiler, Hans Mohaupt, Egon Neumann, Hubert Schardin, and Erich Schumann.

Shaped explosive charges

Alfred Stettbacher (1888–1961)

Franz Rudolf Thomanek (1913–1990)

Walter Trinks (1910–1995)

Figure 3.94: Other German-speaking scientists who were responsible for the development of shaped explosive charges included Alfred Stettbacher, Franz Rudolf Thomanek, and Walter Trinks.

3.4.4 Radio Control and Electric Timers for Explosives

In addition to developing explosives, German-speaking creators invented precise electrical means of detonating the explosives, including radio control and electric timers.

Ferdinand Schneider (German, 1866–1955) invented radio-controlled mines in 1904 and patented them in many countries, directly inspiring subsequent copies and implementations. See Fig. 3.95. Schneider also created many other electrical inventions, including radio systems, radio-synchronized clocks, depth charges, audiovisual equipment, and wind turbines.

As shown in Fig. 3.96, Herbert Rühlemann (German, 1902–19??) invented time-delay electric bomb fuses in the 1920s. Ernst Marquard (German, 1897–1980) helped to further develop them during World War II.

Bombs equipped with such time-delay fuses can be set to detonate hours, days, or even longer after they are dropped. Because people in the targeted region do not know what times the fuses are programmed for, they do not know if it is safe to begin clearing and repairing the damage from the attack. Thus time-delay bombs can cause much more chaos and institutional paralysis than bombs that detonate immediately upon impact, especially when bombs with many different time settings are dropped at once.

Both Rühlemann and Marquard aided ordnance development in the United States after the war.

Ferdinand Schneider (1866–1955)

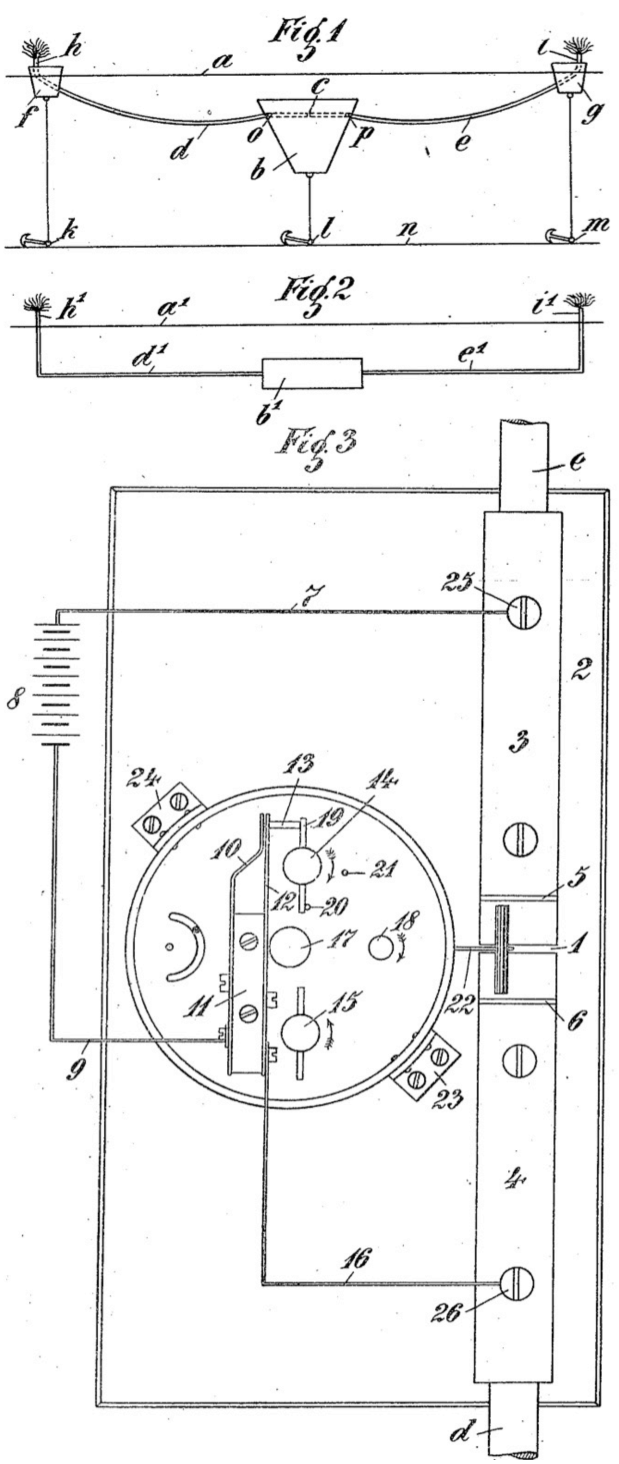
Radio-controlled mines (1904) + many other electrical inventions

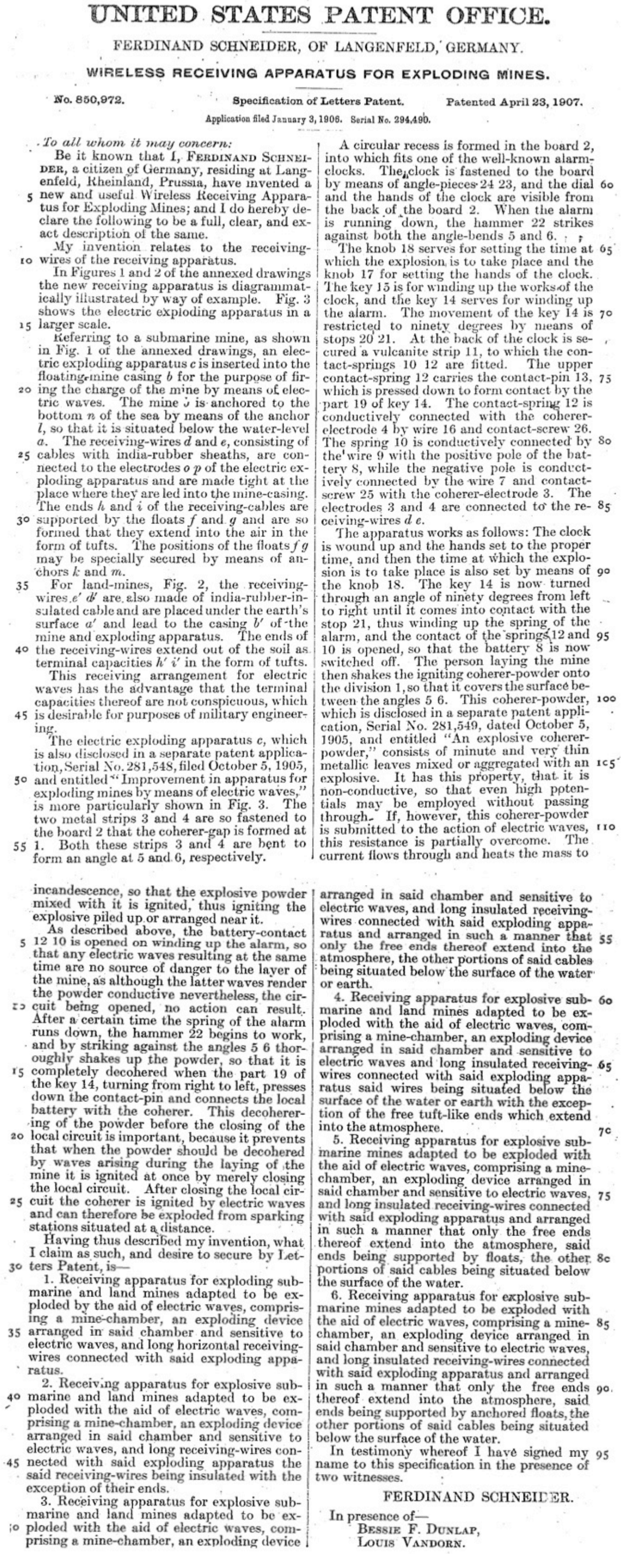
No. 850,972. PATENTED APR. 23, 1907.

F. SCHNEIDER.

WIRELESS RECEIVING APPARATUS FOR EXPLODING MINES.

APPLICATION FILED JAN. 3, 1906.





UNITED STATES PATENT OFFICE.

FERDINAND SCHNEIDER, OF LANGENFELD, GERMANY.

WIRELESS RECEIVING APPARATUS FOR EXPLODING MINES.

No. 850,972. Specification of Letters Patent. Patented April 23, 1907.

Application filed January 3, 1906. Serial No. 294,490.

To all whom it may concern:

Be it known that I, FERDINAND SCHNEIDER, a citizen of Germany, residing at Langenfeld, Rheinland, Prussia, have invented a new and useful Wireless Receiving Apparatus for Exploding Mines; and I do hereby declare the following to be a full, clear, and exact description of the same.

My invention relates to the receiving-wires of the receiving apparatus.

In Figures 1 and 2 of the annexed drawings the new receiving apparatus is diagrammatically illustrated by way of example. Fig. 3 shows the electric exploding apparatus in a larger scale.

Referring to a submarine mine, as shown in Fig. 1 of the annexed drawings, an electric exploding apparatus *c* is inserted into the floating-mine casing *b* for the purpose of firing the charge of the mine by means of electric waves. The mine *b* is anchored to the bottom *n* of the sea by means of the anchor *l*, so that it is situated below the water-level *a*. The receiving-wires *d* and *e*, consisting of cables with india-rubber sheaths, are connected to the electrodes *o p* of the electric exploding apparatus and are made tight at the place where they are led into the mine-casing. The ends *h* and *i* of the receiving-cables are supported by the floats *f* and *g* and are so formed that they extend into the air in the form of tufts. The positions of the floats *f g* may be specially secured by means of anchors *k* and *m*.

For land-mines, Fig. 2, the receiving-wires *e′ d′* are also made of india-rubber-insulated cable and are placed under the earth's surface *a′* and lead to the casing *b′* of the mine and exploding apparatus. The ends of the receiving-wires extend out of the soil as terminal capacities *h′ i′* in the form of tufts.

This receiving arrangement for electric waves has the advantage that the terminal capacities thereof are not conspicuous, which is desirable for purposes of military engineering.

The electric exploding apparatus *c*, which is also disclosed in a separate patent application, Serial No. 281,548, filed October 5, 1905, and entitled "Improvement in apparatus for exploding mines by means of electric waves," is more particularly shown in Fig. 3. The two metal strips 3 and 4 are so fastened to the board 2 that the coherer-gap is formed at 1. Both these strips 3 and 4 are bent to form an angle at 5 and 6, respectively.

A circular recess is formed in the board 2, into which fits one of the well-known alarm-clocks. The clock is fastened to the board by means of angle-pieces 24 23, and the dial and the hands of the clock are visible from the back of the board 2. When the alarm is running down, the hammer 22 strikes against both the angle-bends 5 and 6.

The knob 18 serves for setting the time at which the explosion is to take place and the knob 17 for setting the hands of the clock. The key 15 is for winding up the works of the clock, and the key 14 serves for winding up the alarm. The movement of the key 14 is restricted to ninety degrees by means of stops 20 21. At the back of the clock is secured a vulcanite strip 11, to which the contact-springs 10 12 are fitted. The upper contact-spring 12 carries the contact-pin 13, which is pressed down to form contact by the part 19 of key 14. The contact-spring 12 is conductively connected with the coherer-electrode 4 by wire 16 and contact-screw 26. The spring 10 is conductively connected by the wire 9 with the positive pole of the battery 8, while the negative pole is conductively connected by the wire 7 and contact-screw 25 with the coherer-electrode 3. The electrodes 3 and 4 are connected to the receiving-wires *d e*.

The apparatus works as follows: The clock is wound up and the hands set to the proper time, and then the time at which the explosion is to take place is also set by means of the knob 18. The key 14 is now turned through an angle of ninety degrees from left to right until it comes into contact with the stop 21, thus winding up the spring of the alarm, and the contact of the springs 12 and 10 is opened, so that the battery 8 is now switched off. The person laying the mine then shakes the igniting coherer-powder onto the division 1, so that it covers the surface between the angles 5 6. This coherer-powder, which is disclosed in a separate patent application, Serial No. 281,549, dated October 5, 1905, and entitled "An explosive coherer-powder," consists of minute and very thin metallic leaves mixed or aggregated with an explosive. It has this property, that it is non-conductive, so that even high potentials may be employed without passing through. If, however, this coherer-powder is submitted to the action of electric waves, this resistance is partially overcome. The current flows through and heats the mass to incandescence, so that the explosive powder mixed with it is ignited, thus igniting the explosive piled up or arranged near it.

As described above, the battery-contact 12 10 is opened on winding up the alarm, so that any electric waves resulting at the same time are no source of danger to the layer of the mine, as although the latter waves render the powder conductive nevertheless, the circuit being opened, no action can result. After a certain time the spring of the alarm runs down, the hammer 22 begins to work, and by striking against the angles 5 6 thoroughly shakes up the powder, so that it is completely decohered when the part 19 of the key 14, turning from right to left, presses down the contact-pin and connects the local battery with the coherer. This decoherering of the powder before the closing of the local circuit is important, because it prevents that when the powder should be decohered by waves arising during the laying of the mine it is ignited at once by merely closing the local circuit. After closing the local circuit the coherer is ignited by electric waves and can therefore be exploded from sparking stations situated at a distance.

Having thus described my invention, what I claim as such, and desire to secure by Letters Patent, is—

1. Receiving apparatus for exploding submarine and land mines adapted to be exploded by the aid of electric waves, comprising a mine-chamber, an exploding device arranged in said chamber and sensitive to electric waves, and long horizontal receiving-wires connected with said exploding apparatus.

2. Receiving apparatus for explosive submarine and land mines adapted to be exploded with the aid of electric waves, comprising a mine-chamber, an exploding device arranged in said chamber and sensitive to electric waves, and long receiving-wires connected with said exploding apparatus the said receiving-wires being insulated with the exception of their ends.

3. Receiving apparatus for explosive submarine and land mines adapted to be exploded with the aid of electric waves, comprising a mine-chamber, an exploding device arranged in said chamber and sensitive to electric waves, and long insulated receiving-wires connected with said exploding apparatus and arranged in such a manner that only the free ends thereof extend into the atmosphere, the other portions of said cables being situated below the surface of the water or earth.

4. Receiving apparatus for explosive submarine and land mines adapted to be exploded with the aid of electric waves, comprising a mine-chamber, an exploding device arranged in said chamber and sensitive to electric waves and long insulated receiving-wires connected with said exploding apparatus said wires being situated below the surface of the water or earth with the exception of the free tuft-like ends which extend into the atmosphere.

5. Receiving apparatus for explosive submarine mines adapted to be exploded with the aid of electric waves, comprising a mine-chamber, an exploding device arranged in said chamber and sensitive to electric waves, and long insulated receiving-wires connected with said exploding apparatus and arranged in such a manner that only the free ends thereof extend into the atmosphere, said ends being supported by floats, the other portions of said cables being situated below the surface of the water.

6. Receiving apparatus for explosive submarine mines adapted to be exploded with the aid of electric waves, comprising a mine-chamber, an exploding device arranged in said chamber and sensitive to electric waves, and long insulated receiving-wires connected with said exploding apparatus and arranged in such a manner that only the free ends thereof extend into the atmosphere, said ends being supported by anchored floats, the other portions of said cables being situated below the surface of the water.

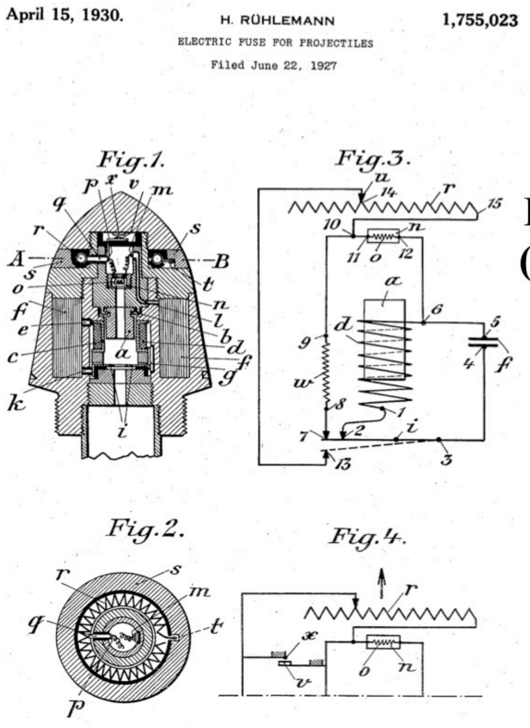
In testimony whereof I have signed my name to this specification in the presence of two witnesses.

FERDINAND SCHNEIDER.

In presence of—
BESSIE F. DUNLAP,
LOUIS VANDORN.

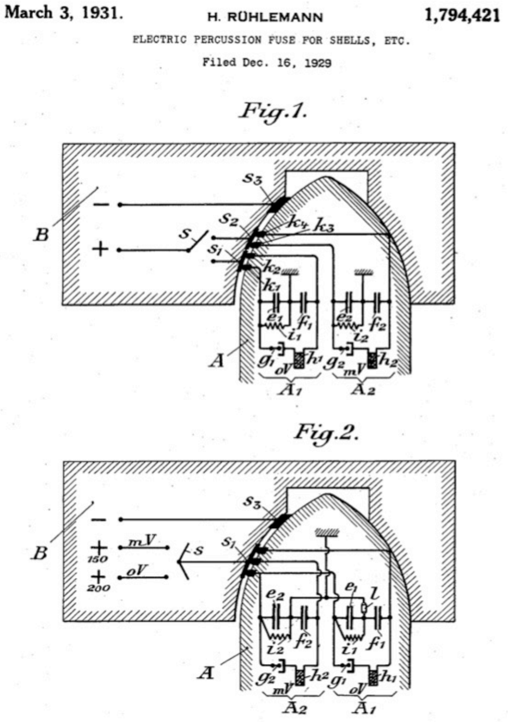
Figure 3.95: Ferdinand Schneider invented radio-controlled mines in 1904; he also created many other electrical inventions.

Time-delay electric bomb fuses

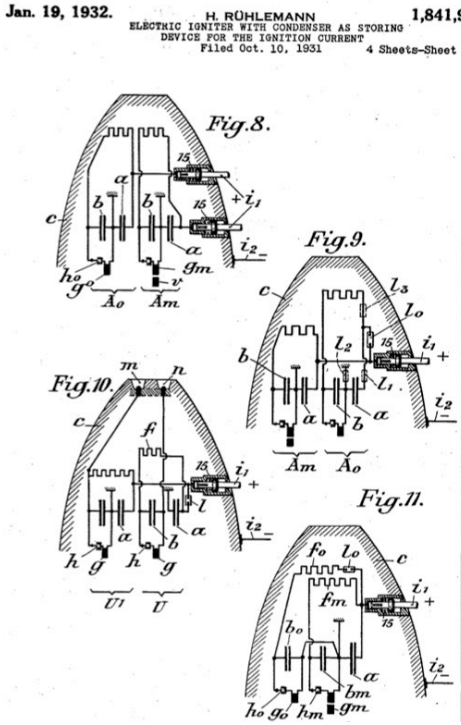


April 15, 1930. H. RÜHLEMANN 1,755,023
ELECTRIC FUSE FOR PROJECTILES
Filed June 22, 1927

Herbert Rühlemann (1902–19??)

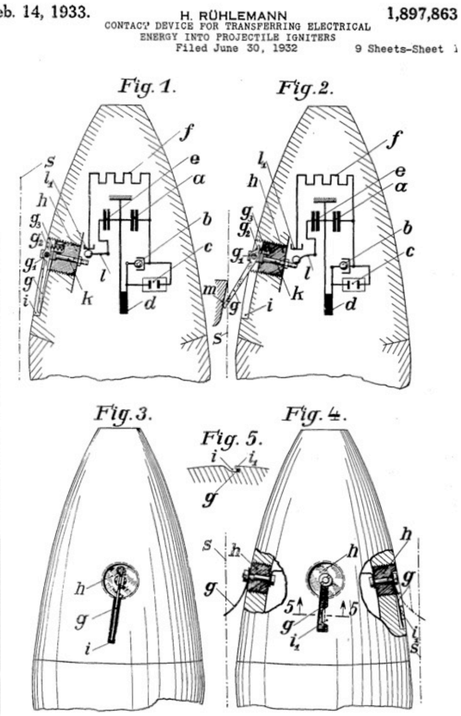


March 3, 1931. H. RÜHLEMANN 1,794,421
ELECTRIC PERCUSSION FUSE FOR SHELLS, ETC.
Filed Dec. 16, 1929



Jan. 19, 1932. H. RÜHLEMANN 1,841,983
ELECTRIC IGNITER WITH CONDENSER AS STORING DEVICE FOR THE IGNITION CURRENT
Filed Oct. 10, 1931 4 Sheets-Sheet 3

Ernst Marquard (1897–1980)



Feb. 14, 1933. H. RÜHLEMANN 1,897,863
CONTACT DEVICE FOR TRANSFERRING ELECTRICAL ENERGY INTO PROJECTILE IGNITERS
Filed June 30, 1932 9 Sheets-Sheet 1

Figure 3.96: Herbert Rühlemann invented time-delay electric bomb fuses in the 1920s, Ernst Marquard helped to further develop them during World War II, and both aided ordnance development in the United States after the war.

3.5 Chemical Warfare Agents and Pesticides

German-speaking scientists dominated the development of chemical warfare agents and pesticides, including:[10]

3.5.1. First-generation chemical weapons

3.5.2. Insecticides

3.5.3. G-series nerve agents

3.5.4. V-series nerve agents

3.5.5. Other chemical weapons

Figure 3.97 illustrates the chemical structures of some major chemical warfare agents and pesticides.

Figures 3.98–3.110 show some of the German-speaking scientists who were involved in developing and testing chemical warfare agents and pesticides.

3.5.1 First-Generation Chemical Weapons

Several compounds became famous or infamous after their first use in World War I (Fig. 3.97). They were developed by German-speaking scientists, but then later copied and used by other countries.

The cyanide-containing Prussian blue pigment was developed in the German-speaking world around 1700. Hydrogen cyanide gas derived from the Prussian blue pigment was called Prussic acid. It was deployed to some extent on WWI battlefields, but was also used as an insecticide. In World War II, it was called Zyklon B and used in the gas chambers of the Holocaust, yet even long after the wars, it was still used for government executions in the United States.

Chlorine gas, two chlorine atoms bonded together, was used on World War I battlefields, and is caustic to lungs, eyes, and other sensitive tissues with which it comes into contact.

In phosgene gas, the two chlorine atoms were coupled to a carbon atom and an oxygen atom, making the molecule more readily absorbed by tissues and hence even more toxic.

In mustard agent, the two chlorine atoms were linked to a hydrocarbon chain. This hydrocarbon chain gave mustard agent an oily feel, made it persist on surfaces for long periods of time instead of rapidly dispersing like a gas, and allowed it to penetrate through skin so that it could attack even people wearing gas masks.

---

[10] Friedrich et al. 2017; Gellermann 1986; Gröhler 1989; Hager 2008; Harris and Paxman 2002; Hein Hofmann 2008; Kaszeta 2020; Pfingsten 2003; Stoltzenberg 1994, 2005; Szöllösi-Janze 2015; Tucker 2006; Zecha 2000; BIOS 110; BIOS 542; BIOS 714; BIOS 760; BIOS 761; BIOS 782; CIOS ER 33; CIOS II-1; CIOS IX-4; CIOS XI-12; CIOS XXI-4; CIOS XXIV-19; CIOS XXVI-49; CIOS XXVII-34; CIOS XXVIII-59; CIOS XXX-19; CIOS XXXI-86; CIOS XXXII-13.

The U.S. chemical weapons expert Jonathan Tucker described how Fritz Haber (German, 1868–1934) and other German scientists developed the first generation of chemical warfare agents [Tucker 2006, pp. 10–12, 18–19]:

> Because Germany possessed the world's most advanced chemical industry, it enjoyed an inherent advantage in this type of warfare. [...]
>
> The individual who became responsible for developing chemical weapons for the German War Office was Professor Fritz Haber, a brilliant young chemist and ardent Prussian nationalist who directed the Kaiser Wilhelm Institute for Physical Chemistry in Berlin. [...]
>
> In late 1914, Haber had the idea of loading artillery shells with chlorine, which the German chemical industry produced in large quantities for the production of dyestuffs. When a shortage of artillery shells ruled out this method of delivery, he proposed instead that chlorine be released directly from pressurized gas cylinders, allowing the wind to carry the poisonous cloud over the enemy's trenches. [...]
>
> In mid-January [1915], Haber ordered the chemist Otto Hahn and several other colleagues to help prepare the chlorine attack. [...] The German chemists helped to organize a special unit for gas warfare called Pioneer Regiment 36. [...]
>
> In December 1915, the Germans fired shells containing phosgene, a gas used in the dye industry that was eighteen times more toxic than chlorine. [...]
>
> In an effort to circumvent the Allied use of protective masks and respirators, Haber and his colleagues developed a new chemical warfare agent that attacked the skin as well as the lungs. Called "mustard" because of its sharp, garlicky odor, it was an oily liquid that was readily absorbed through the skin, giving rise after several hours to severe chemical burns and blisters. In July 1917, once again at Ypres, the Germans began firing mustard-filled shells containing an explosive burster charge that shattered the liquid agent into a fine mist that was colorless or light yellow. Like phosgene, the effects of mustard were insidious: symptoms developed only after a delay of three to twenty-four hours (with a mean of ten to twelve hours), so that troops often did not realize that they had been exposed to the agent until it was too late.
>
> [...] Mustard soon became the most dreaded of chemical weapons and was dubbed "the king of the war gases." Not only was it highly persistent, clinging to clothing and equipment and contaminating the battlefield for days or even weeks, but its ability to penetrate the skin forced troops to augment their respirators with cumbersome oilskin capes, goggles, and leather or rubber garments. This protective gear could be worn only for short periods, however, because it caused heat stress and seriously impaired fighting efficiency.

Fritz Haber won the 1918 Nobel Prize in Chemistry for unrelated work to chemically synthesize ammonia on an industrial scale (p. 453).

During World War I, Fritz Wilhelm Lommel (German, 1875–1968) and Georg Wilhelm Steinkopf (German, 1879–1949) developed a chemical method for the large-scale synthesis of mustard agent. Ever since then, mustard agent has commonly been known in the German-speaking world as LOST, combining the first two letters of their last names.

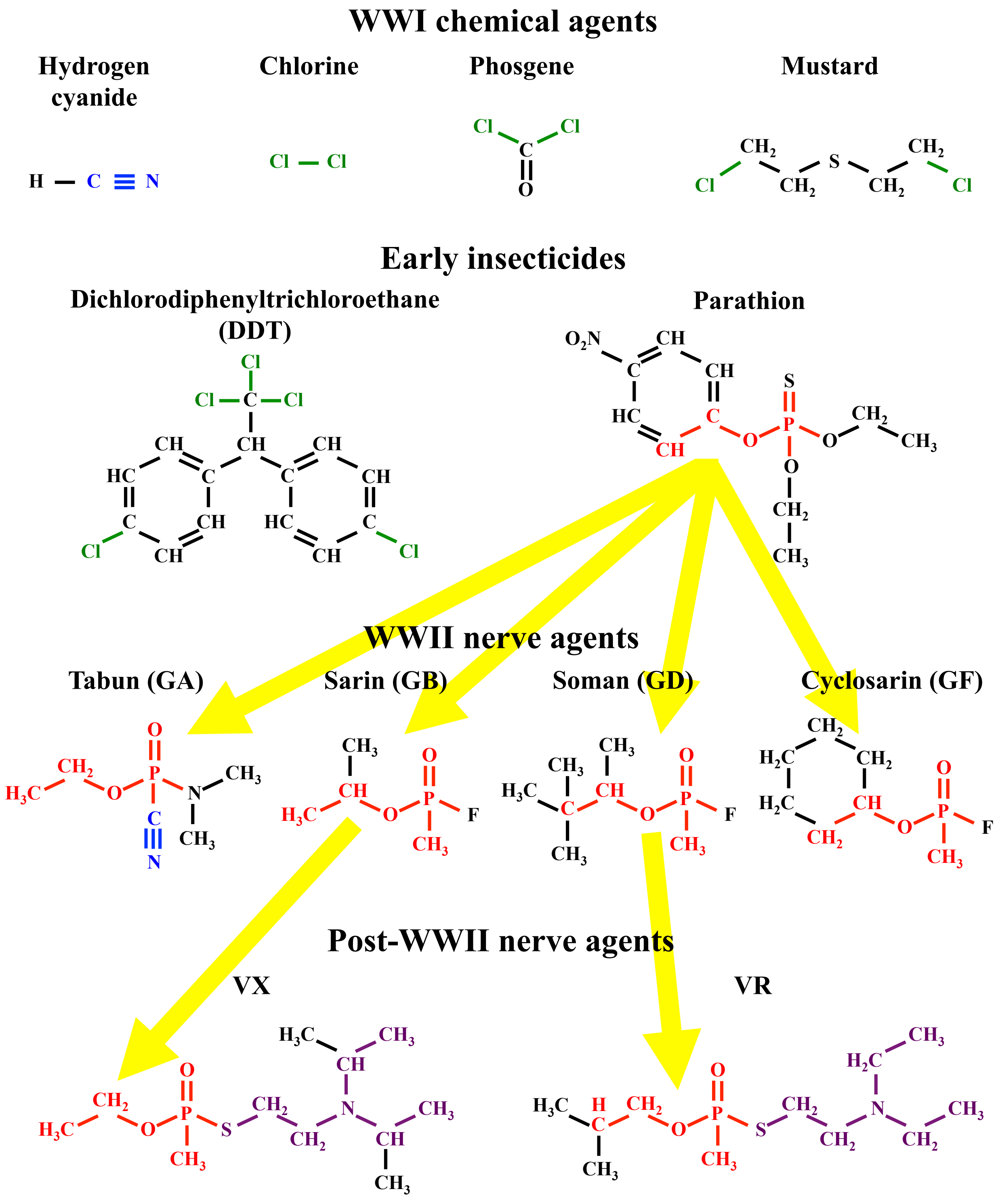
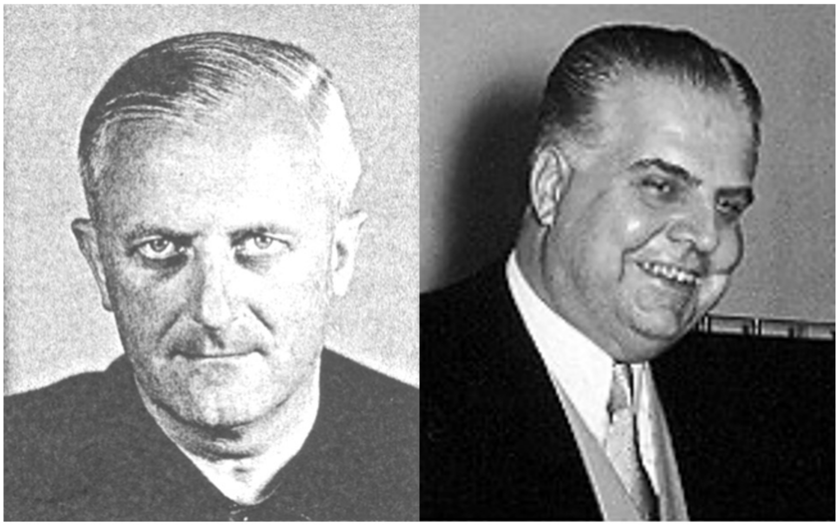


Figure 3.97: Chemical warfare agents and pesticides, including chemical agents used during World War I, some important early insecticides, nerve agents produced during World War II, and related nerve agents produced after World War II.

Wolfgang Alt
(19??–19??)

Otto Ambros
(1901–1990)
I.G. Farben

Otto Bayer
(1902–1982)
Leverkusen



?? von Bock
(19??–19??)
Dyhernfurth –1945;
USSR 1945--

Gerhard L. Bottger
(19??–19??)

Kurt Brand
(19??–19??)

Figure 3.98: Some creators who were involved in developing and testing chemical warfare agents and pesticides included Wolfgang Alt, Otto Ambros, Otto Bayer, ?? von Bock, Gerhard L. Bottger, and Kurt Brand.

Rudolf Criegee
(1902–1975)
Chemisches Institut
TU Karlsruhe

Gerhard Ehlers
(19??–19??)

Harry Endler
(19??–19??)

?? Fischer
(19??–19??)

Ferdinand Flury
(1877–1947)

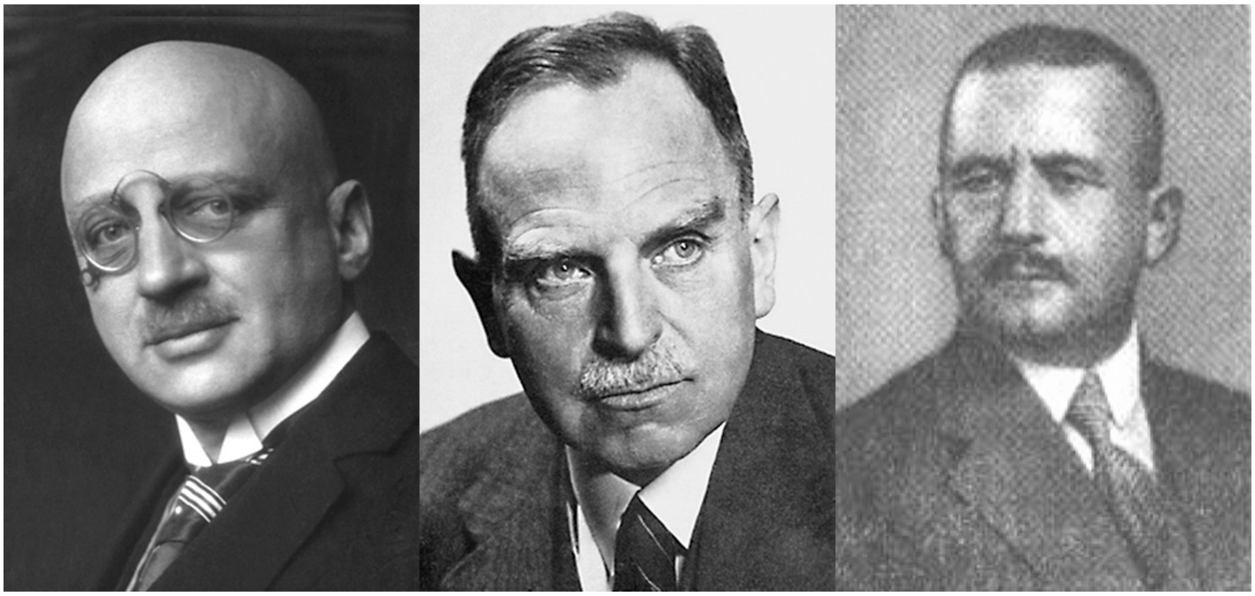
?? Gebauer
(19??–19??)

Figure 3.99: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Rudolf Criegee, Gerhard Ehlers, Harry Endler, ?? Fischer, Ferdinand Flury, and ?? Gebauer.

Siegfried Glupe
(1909–19??)
Army Ordnance Office

Eberhard Gross
(19??–19??)
IG Farben

Max Gruber
(19??–19??)
Gendorf Anorgana



Fritz Haber
(1868–1934)
WW I gases

Otto Hahn
(1879–1968)
WW I gases

Rudolf Hanslian
(1883–1954)

Figure 3.100: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Siegfried Glupe, Eberhard Gross, Max Gruber, Fritz Haber, Otto Hahn, and Rudolf Hanslian.

Paul Hartmann (19??–19??)

?? Heinman (19??–19??)

Hans Henke (19??–19??)

Walter Hirsch (19??–19??)

August Hirt (1898–1945) Testing

Friedrich Wilhelm Hoffmann (1910–1967) Organic synthesis

Figure 3.101: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Paul Hartmann, ?? Heinman, Hans Henke, Walter Hirsch, August Hirt, and Friedrich Wilhelm Hoffmann.

Heinrich Hörlein
(1882–1954)

?? Hoyer
(19??–19??)

Erich Hückel
(1896–1980)
New organophosphate nerve agents

?? Jannsen
(19??–19??)

?? Jung
(19??–19??)

L. Klebert
(19??–19??)
Leverkusen

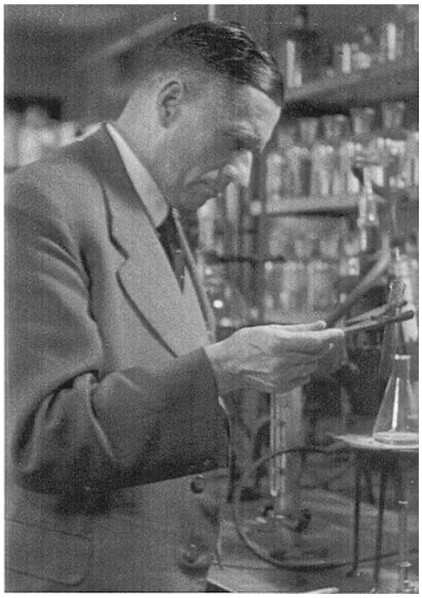
Figure 3.102: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Heinrich Hörlein, ?? Hoyer, Erich Hückel, ?? Jannsen, ?? Jung, and L. Klebert.

Wilhelm Kleinhans
(19??–19??)

Jürgen von Klenk
(1909–19??)

Otto Klimmer
(19??–19??)

Carl Krauch
(1887–1968)



Gerda von Krüger
(19??–19??)
1932 organophosphate nerve agent DFP

Richard Kuhn
(1900–1967)
Soman, etc.

Figure 3.103: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Wilhelm Kleinhans, Jürgen von Klenk, Otto Klimmer, Carl Krauch, Gerda von Krüger, and Richard Kuhn.

Hans Kükenthal
(19??–19??)
insecticide testing

Karl Küpper
(19??–19??)
Schrader's assistant

Willy Lange
(19??–19??)
1932 organophosphate nerve agent DFP

J. von der Linde
(19??–19??)

Fritz Wilhelm Lommel
(1875–1968)
Mass production of mustard agent

Walter Lorenz
(19??–19??)
VX-like agents

Figure 3.104: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Hans Kükenthal, Karl Küpper, Willy Lange, J. von der Linde, Fritz Wilhelm Lommel, and Walter Lorenz.

Paul Hermann Müller
(1899–1965)
DDT

Wilhelm Neumann
(1898–1965)

?? Nold
(19??–19??)

Hermann Ochsner
(1892–1951)

H. Oettel
(19??–19??)

Albert Palm
(19??–1994)
Dyhernfurth

Figure 3.105: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Paul Hermann Müller, Wilhelm Neumann, ?? Nold, Hermann Ochsner, H. Oettel, and Albert Palm.

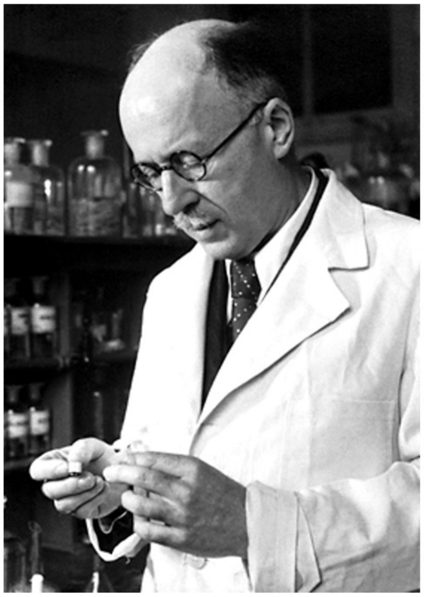
Karl Quasebart
(1882–19??)

Karl Rath
(19??–19??)

?? Rhein
(19??–19??)

Gerhard Ritter
(1902–19??)

Leopold Ružička
(1887–1976)
Pyrethroid insecticides



Wilhelm Sandermann
(1909–1994)

Figure 3.106: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Karl Quasebart, Karl Rath, ?? Rhein, Gerhard Ritter, Leopold Ružička, and Wilhelm Sandermann.

Ernst Schegk
(19??–19??)
VX-like agents

Walther Schieber
(1896–1960)

Hanshelmut Schlör
(19??–19??)
VX-like agents

?? Schmall
(19??–19??)

Siegfried Schmidt
(19??–19??)
Army Ordnance Office

Gerhard Schrader
(1903–1990)
Insecticides, tabun,
sarin, VX-like agents

Figure 3.107: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Ernst Schegk, Walther Schieber, Hanshelmut Schlör, ?? Schmall, Siegfried Schmidt, and Gerhard Schrader.

Erich Schumann
(1898–1985)
Army Ordnance Office
Chemical, biological, and nuclear weapons

Joseph Sextel
(19??–19??)

Leopold von Sicherer
(19??–19??)
Chemical munitions

Hermann Staudinger
(1881–1965)
Pyrethroid insecticides

Georg Wilhelm Steinkopf
(1879–1949)
Mass production of mustard agent

Hugo Stoltzenberg
(1883–1974)

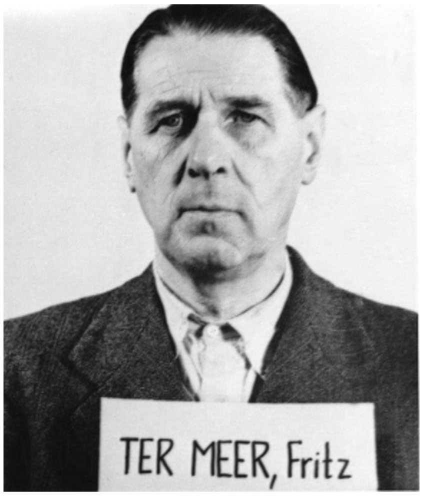
Figure 3.108: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Erich Schumann, Joseph Sextel, Leopold von Sicherer, Hermann Staudinger, Georg Wilhelm Steinkopf, and Hugo Stoltzenberg.

Gerhard Strauss
(19??–19??)

Ernst August Struss
(19??–19??)

Friedrich von Tempelhoff
(1878–1941)

Fritz ter Meer
(1884–1967)



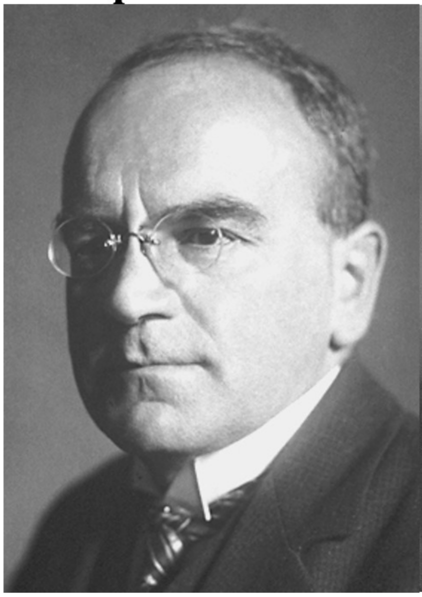
?? Tolkmitt
(19??–19??)

?? Vogel
(19??–19??)

Figure 3.109: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Gerhard Strauss, Ernst August Struss, Friedrich von Tempelhoff, Fritz ter Meer, ?? Tolkmitt, and ?? Vogel.

Theodor Wagner-Jauregg
(1903–1992)
Paperclip

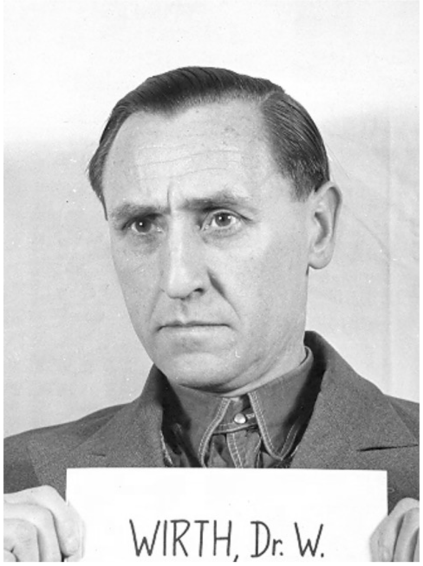
Heinrich Wieland
(1877–1957)
adamsite riot control agent, alpha amanitin



Richard Willstätter
(1872–1942)
Chemical warfare filters

Karl Wimmer
(1910–1946)
Testing

Wolfgang Wirth
(1898–1996)
Testing



Othmar Zeidler
(1850–1911)
DDT

Figure 3.110: Other creators who were involved in developing and testing chemical warfare agents and pesticides included Theodor Wagner-Jauregg, Heinrich Wieland, Richard Willstätter, Karl Wimmer, Wolfgang Wirth, and Othmar Zeidler.

3.5.2 Insecticides

The German-speaking world also produced the most important early insecticides, which had a worldwide impact and became the prototypes for improved insecticides. Dichloro-diphenyl-trichloromethylmethane (DDT, Fig. 3.97), with five chlorines coupled to two benzene rings, was first produced in 1874 by Othmar Zeidler (Austrian, 1850–1911). Paul Hermann Müller (Swiss, 1899–1965) discovered DDT's insecticidal properties in 1939. DDT was rapidly transferred from the German-speaking world to many other countries [Brooks 1974, pp. 7–17] and was widely used to curtail insect-borne diseases in the 1940s–1960s. Müller won the Nobel Prize in Physiology or Medicine in 1948 for DDT, drawing the praise of Professor G. Fischer, a member of the Staff of Professors of the Royal Caroline Institute [https://www.nobelprize.org/prizes/medicine/1948/ceremony-speech/]:

> The story of DDT illustrates the often wondrous ways of science when a major discovery has been made. A scientist, working with flies and Colorado beetles discovers a substance that proves itself effective in the battle against the most serious diseases in the world. Many there are who will say he was lucky, and so he was. Without a reasonable slice of luck hardly any discoveries whatever would be made. But the results are not simply based on luck. The discovery of DDT was made in the course of industrious and certainly sometimes monotonous labour; the real scientist is he who possesses the capacity to understand, interpret and evaluate the meaning of what at first sight may seem to be an unimportant discovery.
>
> Dr. Paul Müller. I have tried to give a brief survey of the historical development of DDT. Your discovery of the strong contact insecticidal action of dichloro-diphenyl-trichloromethylmethane is of the greatest importance in the field of medicine. Thanks to you, preventive medicine is now able to fight many diseases carried by insects on a way totally different from that employed heretofore. Your discovery furthermore has, throughout the world, stimulated successful research into newer insecticides.

DDT was phased out starting in the 1960s due to concerns about environmental side effects, as most famously articulated in Rachel Carson's 1962 book, *Silent Spring*. However, it was replaced by other insecticides that came from the German-speaking world.

Scientists in the German-speaking world developed a number of chemical derivatives of DDT that appeared (and in some cases still appear) to be safer. One was dichlorodiphenyldichloroethane (DDD), also known a ME-1700. Others were difluorodiphenyltrichloroethane (DFDT, also known as Lauseto) and monofluorodiphenyltrichloroethane (MFDT), which as of 2019 were still being considered as attractive and relatively safe insecticides [Zhu et al. 2019].

Hermann Staudinger (German, 1881–1965) and Leopold Ružička (Austro-Hungarian/Croatian, studied in Germany and worked in Switzerland, 1887–1976) identified pyrethroid insecticide molecules in 1924, and pyrethroid insecticides have been widely used from the 1960s onward as a safer replacement for DDT. Staudinger won the Nobel Prize in Chemistry in 1953 for his work on polymers (p. 480), and Ružička won the Nobel Prize in Chemistry in 1939 for his work on hormones (p. 355).

Other early insecticides had an even more profound impact. Organophosphate compounds, containing both a phosphorus atom and several carbons, were developed as insecticides by Paul Gerhard Schrader (German, 1903–1990). Parathion (Fig. 3.97) was one of the earliest and best-known examples, and numerous variations such as malathion were subsequently produced and used to the present day. Yet because some of the early organophosphate insecticides had some toxicity to humans as well as insects, they proved to be the key to developing more modern chemical warfare agents—rapidly acting nerve agents.

3.5.3 G-Series Nerve Agents

Scientists in the Third Reich produced and tested a wide variety of organophosphate nerve agents, and created several especially potent ones (which were given postwar codenames beginning with G for German): tabun (GA), sarin (GB), soman (GD), ethylsarin (GE), cyclosarin (GF), and isopentylsarin (GH). (The code name GC was not used, to avoid confusion with the U.S. code name for phosgene, CG [Tucker 2006, p. 105]. GG was likely skipped because of the double letters.) See Fig. 3.97. Schrader created all of the agents just listed, except for soman which was developed by Richard Kuhn (Austrian, 1900–1967). After their initial discovery and testing, the agents were mass-produced by I.G. Farben at several industrial plants led by the chemist Otto Ambros (German, 1901–1990). These G-series nerve agents were exclusively possessed by the Third Reich and were stockpiled but never used, due to fear that Allied nations would retaliate with much cruder but still effective first-generation chemical weapons such as mustard agent (pp. 2644–2663).

Jonathan Tucker described the sophistication of nerve agent research, development, and production during the Third Reich [Tucker 2006, pp. 42, 45, 47–48, 50–51]:

> Code-named "Hochwerk," it would eventually cover an area 1.5 kilometers long by 700 meters wide. [...]
>
> Because of shortages of key equipment and manpower, it took two years and an expenditure of 120 million reichsmarks to complete the Hochwerk plant at Dyhernfurth, which the Anorgana company headed by Ambros began to operate in the spring of 1942. The sprawling production complex included buildings for manufacturing basic chemical ingredients, intermediates, and final products; numerous warehouses and storage tanks; a bombproof bunker that could hold 1,000 tons of bulk agent; filling lines for loading Tabun into artillery shells and aerial bombs; a well-equipped medical clinic with a staff of trained physicians; and barracks for the plant workers. To reduce exposure to air raids, the main production facility was built partially underground and camouflaged with trees planted on the roof.
>
> Because of Tabun's extreme toxicity, the design of the Hochwerk facility included special features to protect the plant workers against exposure. Each kettle was housed in an enclosed operating chamber formed of two spaced glass walls. Between the glass walls, a ventilation system produced greater than atmospheric pressure, so that the flow of air was always toward the reaction kettle. Inside the operating chamber, the air above the kettle was continuously changed by means of a separate ventilating duct, creating negative pressure. This pressure differential meant that the air contaminated with Tabun fumes was retained inside the operating chamber. All pipes used to transfer solutions containing Tabun were double-walled, and their outer surfaces were sprayed frequently with a weak solution of ammonia and water to neutralize minor leaks. After each production run, the kettles were decontaminated with steam and ammonia.
>
> No technicians were allowed to enter the operating chambers while the production of Tabun was under way. Instead, the operators opened and closed valves with long-handled mechanical levers that penetrated the double glass walls through rubber-sealed gaskets. [...]

> Although the standard Germany Army gas mask protected against breathing contaminate air, Tabun could also be absorbed through the skin. For this reason, all mechanics who entered the sealed production chambers to perform repairs and maintenance wore not only a respirator but a protective suit, cap, boots, and gloves, encapsulating the entire body. The suit consisted of two layers of rubber separated by a layer of cloth, making it cumbersome and unbearably hot in summer. Despite these precautions, about a dozen fatal accidents occurred during the two and a half years of Tabun production, most of them affecting mechanics performing overhauls of the plant. In one incident, seven pipe fitters were struck in the face by a pressurized stream of liquid Tabun that forced itself between their respirators and rubberized suits. [...]
>
> All seven victims were given intramuscular injections of atropine and a new drug called Sympotal, but five did not respond to the antidotes and died. [...]
>
> Dyhernfurth had its own munition-loading facility, which was built underground and equipped with ventilation shafts. Steel artillery shells and bomb casings were manufactured in a separate building and place on conveyor belts that transported them to the filling plant. Liquid Tabun pumped from underground storage tanks was loaded into empty 105 mm and 150 mm artillery shells, 250-kilogram aerial bombs, and artillery rockets. [...] To compensate for Tabun's lack of volatility, the bombs contained a central "burster" tube filled with a high explosive that, detonated on impact with the ground, would shatter the liquid agent into a mist of tiny droplets, poisoning enemy soldiers through inhalation and skin contact.
>
> Once an aerial bomb had been loaded with Tabun, the filling port was closed with a plug that incorporated a tightening pin. Using a wrench, a technician applied seating pressure to the pin, causing it to shear off and leave the plug in a sealed position, flush with the surface of the weapon. The sealing plug and adjacent surface were then coated with a slow-drying pink lacquer that would turn a deep carmine if Tabun lead through the plug. Near the base of the bomb or shell, workers painted three green rings around the munition to indicate its contents, along with stenciled numbers providing the date of manufacture and a code letter indicating the ratio of Tabun to chlorobenzene. [...]
>
> The forced laborers were assigned the most menial, backbreaking, and dangerous tasks at the Tabun plant, including construction, maintenance, and loading munitions with the liquid agent. On the filling line, they wore protective clothing similar to a deep-sea diving suit, with a helmetlike mask covering the entire head and a hose providing a supply of fresh air. [...]

While Gerhard Schrader synthesized tabun, sarin, and hundreds of other possible nerve agents and pesticides, Jonathan Tucker described the role that Richard Kuhn also played in the program [Tucker 2006, pp. 54, 62–63]:

> In early 1943, Colonel Schmidt of the Army Ordnance Office asked Professor Richard Kuhn, the director of the Institute of Chemistry at the Kaiser Wilhelm Institute for Medical Research in Heidelberg, to analyze the effects of nerve agents on the central and peripheral nervous systems. [...]

> Based on these insights, Kuhn's research team developed a standardized assay that measured the ability of nerve agents to inhibit purified cholinesterase enzymes in the test tube. Over the next two years, they used this assay to screen a variety of candidate nerve agents, some of their own invention and others synthesized by the German Army chemists at Spandau Citadel. [...]
>
> [D]uring the spring of 1944, Richard Kuhn, working at the Kaiser Wilhelm Institute in Heidelberg, made a striking discovery. He was continuing his research for the German Army by screening a wide variety of organophosphorus compounds—some of which he had synthesized himself—for the ability to inhibit cholinesterase. Because of the Nazi obsession with secrecy, his research was "compartmented": he was not put into contact with other scientists in the nerve agent field and was completely unaware of Schrader's work.
>
> When Kuhn replaced the isopropyl alcohol used to make Sarin with a more complex alcohol known as pinacolyl, the resulting substance (which he called Compound 25075) had a camphorlike odor and was roughly twice as potent as Sarin in inhibiting cholinesterase. The War Office code-named this new compound "Soman," and Kuhn synthesized small amounts in the laboratory.
>
> Toxicological testing of Soman in animals by Dr. Gross at IG Elberfeld revealed that the new agent was twice as toxic as Sarin by inhalation, readily penetrated into the skin, and passed rapidly from the bloodstream into the brain, enhancing its lethal effects. Even more striking, Soman inactivated cholinesterase irreversibly within two minutes, severely limiting the effectiveness of atropine as an antidote. Over the next several months, Kuhn and his colleagues tested about fifty analogues of Sarin and Soman for their ability to inhibit cholinesterase in his test-tube system. The most promising compounds were then tested on dogs and apes. [...]

Unlike the view in conventional history books, both Axis and Allied forces very nearly used chemical weapons in World War II. Germany stockpiled and very seriously considered using its chemical weapons (both the newer ones like nerve agents and the older ones like mustard agent) against Allied targets, especially to halt Russian advances on the Eastern Front. The United States and United Kingdom stockpiled and very seriously considered using their own copies of the chemical weapons that Germany had invented in the previous war (mustard and phosgene) with the explicit goal of killing millions of civilians in German cities. The threats by both sides to use chemical weapons played an enormously important role in how and why the war was waged as it actually was. For more information, see pp. 2644–2663.

The G-series nerve agents and information on how to produce them were removed from Germany at the end of the war, and G-series agents have been mass-produced by a wide range of nations ever since. For example, the postwar U.S./U.K. chemical warfare program was directly copied from the wartime German program, making extensive use of German scientists, information, and materials [Tucker 2006, p. 116]:

> In addition to Schieber, EUCOM hired about thirty German chemical warfare experts, some of whom were later transferred to Edgewood Arsenal to continue their work on

> American soil. [...] Several of the German chemical weapons specialists recruited by Porton Down later moved to the United States, where they were granted U.S. citizenship and prominent positions.

Similarly, the postwar Soviet chemical warfare program was also directly copied from the wartime German program [Tucker 2006, pp. 106–107, 145]:

> In September 1946, with the aid of captured German scientists, Soviet engineers and pipe fitters had systematically dismantled the Tabun and Sarin plants at Dyhernfurth, which the Red Army had seized as war booty, and shipped the production equipment to Stalingrad. [...]
>
> To assist in rebuilding the nerve agent production lines, the Soviets brought to Stalingrad about a dozen German chemists and process engineers from Dyhernfurth who had been captured by the Red Army. The most senior of the German scientists were Dr. von Bock, the former production manager. Soon after his arrival, he was ordered to write a detailed technical report on Tabun production and was questioned at length about the metal corrosion problems associated with the manufacture of Sarin.
>
> The Sarin plant at Stalingrad started out as a copy of the one at Dyhernfurth, but for reasons of national pride [Zaharovich] Soborovsky and [Boris] Libman tried to improve on the German production process. In so doing, they ran into serious technical problems that resulted in lengthy delays. [...] Although the development had begun in 1948, it was not until 1959—more than a decade later—that Chemical Works No. 91 was churning out large amounts of Sarin with a satisfactory level of purity and stability.

For additional examples of the transfer of chemical weapons technologies from the German-speaking world to Allied countries, see:

> BIOS 110. *Drägerwerk Factories at Lübeck, Hamburg and Uetersen.* [Protective clothing, respiration filters, sensors, etc. for chemical warfare]
>
> BIOS 542. *Interrogation of Certain German Personalities Connected with Chemical Warfare.*
>
> BIOS 714. *The Development of New Insecticides and Chemical Warfare Agents.* [original edition; revised edition only covers insecticides and is less than half as long!]
>
> BIOS 760. *German War-Time Development in Fluid Turbulence with Particular Reference to the Lower Atmosphere and the Meteorology of Chemical Warfare.*
>
> BIOS 761. *German Bursting Coloured Smoke Shell. Interrogation of Dipl. Ing. C. von Watzdorf and Dr. W. Sauermilch.*
>
> BIOS 782. *Interrogation of Professor Ferdinand Flury and Dr. Wolfgang Wirth on the Toxicology of Chemical Warfare Agents.*

CIOS ER 33. *Interview with Dr. Klebert, Dr. Redies and Dr. Knonradi: Synthetic Rubber, Chemical Warfare.*

CIOS II-1. *German Chemical Warfare Activities in Paris Area.*

CIOS IX-4. *Interviews on Chemical Warfare.*

CIOS XI-12. *Production and Use of Aerosols.* [Chemical warfare aerosol production, medical treatment aerosols]

CIOS XXI-4. *Miscellaneous Chemical Warfare Information, I.G. Leverkusen.*

CIOS XXIV-19. *Anorgana G.m.b.H. Werke Gendorf.* [Chemical warfare, periston]

CIOS XXVI-49. *Heeresgasschutzschule I, Celle.* [chemical warfare]

CIOS XXVII-34. *War Gas Production and Miscellaneous Chemical Warfare Information, Anorgana G.m.b.H., Gendorf.*

CIOS XXVIII-59. *Aviation Medicine, General Medicine, Veterinary Medicine, and Chemical Warfare.*

CIOS XXX-19. *Chemical Warfare, I.G. Farbenindustrie AG, Frankfurt/Main.*

CIOS XXXI-86. *Chemical Warfare Installations in the Munsterlager Area.* [very long and very detailed, including personnel and molecular structures]

CIOS XXXII-13. *Production of Smoke, Incendiary and Chemical Warfare Weapons.*

NARA Still Pictures, RG 111 SCA---Records of the Chief Signal Officer. Prints: U.S. Army Signal Corps Photographs of Military Activity During WW II and the Korean Conflict, 1941-1954. Captured German Equipment, German, Box 3347, Book 8, SC 231579.

Figure 3.111: Stockpiled German chemical weapons found by U.S. forces in 1945. [NARA Still Pictures, RG 111 SCA—Records of the Chief Signal Officer. Prints: U.S. Army Signal Corps Photographs of Military Activity During WW II and the Korean Conflict, 1941–1954. Captured German Equipment, German, Box 3347, Book 8, SC 231579.]

3.5.4 V-Series Nerve Agents

A significant innovation in nerve agents first became publicly known after the war. Although G-series agents were relatively small molecules that dispersed fairly rapidly, if they were coupled to an oily hydrocarbon chain, they could persist on surfaces for long periods of time and also readily penetrate through human skin. These improved nerve agents became known as the V-series (for venomous); VX was the favorite in the United States and United Kingdom, and the similarly acting VR was the favorite in the Soviet Union (Fig. 3.97). Officially, the invention of this category of nerve agents was credited to postwar researchers not from the German-speaking world. In 1952, Ranajit Ghosh and J. F. Newman at the UK Imperial Chemical Industries (ICI) Plant Protection Laboratory produced a potent V-series agent, Amiton, that had been intended as an insecticide. Almost simultaneously, Lars-Erik Tammelin of the Swedish Institute of Chemical Defense produced similar compounds that came to be known as Tammelin esters.

In fact, V-series agents appear to have been invented, produced, and tested in Germany during World War II.

The chemical approach of coupling a toxic gas molecule to an oily hydrocarbon chain—in order to make the agent persist on surfaces and penetrate through human skin—is exactly the same strategy that German chemists used during World War I to upgrade chlorine gas to mustard agent (Fig. 3.97).

German chemists would be expected to consider the same approach to upgrade nerve agents during World War II. Making the most toxic German chemical agents persist much longer in the environment, so that they could be used to contaminate areas and block a Soviet advance (see p. 2645 for such plans), would be a very obvious and very high-priority goal.

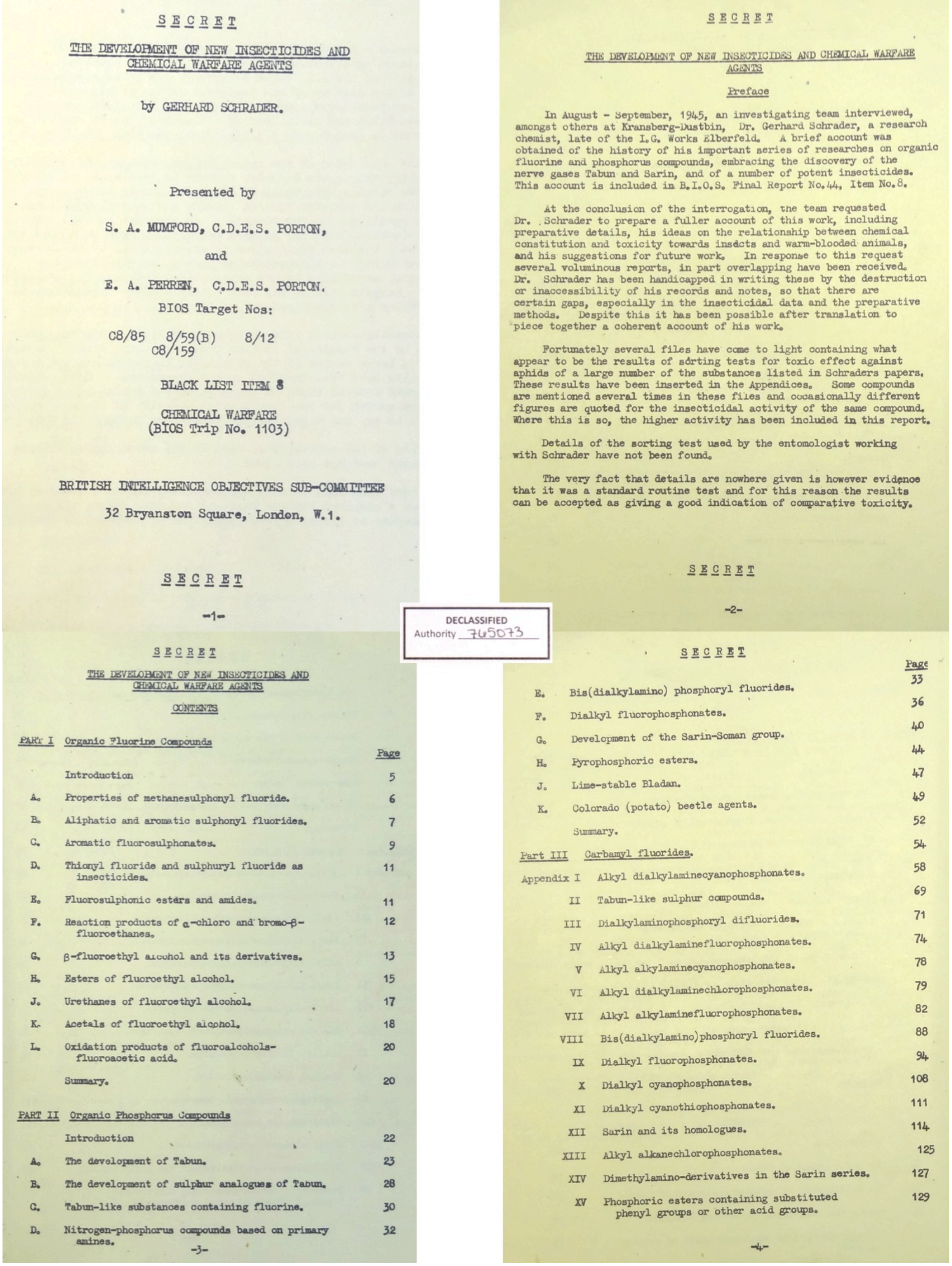
Indeed, in 1945 Gerhard Schrader gave U.K. and U.S. officials detailed information on many hundreds of nerve agents that he had developed and tested during the war [BIOS 714; see Fig. 3.112 and Section A.4]. Schrader's report included a wide variety of V-series agents, composed of G-series agents coupled to an oily hydrocarbon chain. Furthermore, many of Schrader's agents possessed the same molecular features as VX and VR, such as using a nitrogen atom to attach two branches of hydrocarbons to the toxic part of the molecule. After the war, Schrader, Ernst Schegk, and Hanshelmut Schlör of Bayer in Leverkusen (part of I.G. Farben during the war) filed patents on linking an oily hydrocarbon chain to a toxic organophosphate structure, although postwar restrictions both delayed public acknowledgement of that work and compelled them to focus on insecticide applications instead of chemical warfare applications; see Fig. 3.113 and Section A.4.

In the United States (and likely in other countries as well), German experts such as Friedrich Wilhelm Hoffmann (1910–1967) were employed after the war to mass produce V-series agents. Hoffmann was also deeply involved in the postwar U.S. development (or perhaps the postwar transfer/recapitulation of wartime German work) of the Agent Orange defoliant, dioxin, various other toxins, attempts to harness LSD, and other chemical agents.[11]

It is quite possible that Richard Kuhn or others also developed V-series agents in Germany during the war. Much more archival research is needed to clarify the history of the development and dissemination of knowledge about V-series agents.

---

[11] Albarelli 2009; Jacobsen 2014, pp. 384–389; Lindemann 2016; Möller et al. 2014; Sandermann 1984; Sorge 2017.



SECRET

THE DEVELOPMENT OF NEW INSECTICIDES AND CHEMICAL WARFARE AGENTS

by GERHARD SCHRADER.

Presented by

S. A. MUMFORD, C.D.E.S. PORTON,

and

E. A. PERREN, C.D.E.S. PORTON.

BIOS Target Nos:

C8/85 8/59(B) 8/12
C8/159

BLACK LIST ITEM 8

CHEMICAL WARFARE
(BIOS Trip No. 1103)

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

32 Bryanston Square, London, W.1.

SECRET

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SECRET

THE DEVELOPMENT OF NEW INSECTICIDES AND CHEMICAL WARFARE AGENTS

Preface

In August - September, 1945, an investigating team interviewed, amongst others at Kransberg-Dustbin, Dr. Gerhard Schrader, a research chemist, late of the I.G. Works Elberfeld. A brief account was obtained of the history of his important series of researches on organic fluorine and phosphorus compounds, embracing the discovery of the nerve gases Tabun and Sarin, and of a number of potent insecticides. This account is included in B.I.O.S. Final Report No.44, Item No.8.

At the conclusion of the interrogation, the team requested Dr. Schrader to prepare a fuller account of this work, including preparative details, his ideas on the relationship between chemical constitution and toxicity towards insects and warm-blooded animals, and his suggestions for future work. In response to this request several voluminous reports, in part overlapping have been received. Dr. Schrader has been handicapped in writing these by the destruction or inaccessibility of his records and notes, so that there are certain gaps, especially in the insecticidal data and the preparative methods. Despite this it has been possible after translation to piece together a coherent account of his work.

Fortunately several files have come to light containing what appear to be the results of sorting tests for toxic effect against aphids of a large number of the substances listed in Schraders papers. These results have been inserted in the Appendices. Some compounds are mentioned several times in these files and occasionally different figures are quoted for the insecticidal activity of the same compound. Where this is so, the higher activity has been included in this report.

Details of the sorting test used by the entomologist working with Schrader have not been found.

The very fact that details are nowhere given is however evidence that it was a standard routine test and for this reason the results can be accepted as giving a good indication of comparative toxicity.

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THE DEVELOPMENT OF NEW INSECTICIDES AND CHEMICAL WARFARE AGENTS

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Figure 3.112: Gerhard Schrader's description of the wartime development and testing of V-series nerve agents [BIOS 714].

AUSGEGEBEN AM
25. OKTOBER 1951

DEUTSCHES PATENTAMT

PATENTSCHRIFT

Nr. 818 352
KLASSE 12o GRUPPE 23 03
p 41994 IVd/12o D

Dr. Gerhard Schrader, Opladen-Bruchhausen
ist als Erfinder genannt worden

Farbenfabriken Bayer, Leverkusen

Verfahren zur Herstellung von neutralen Estern der Thiophosphorsäure

Patentiert im Gebiet der Bundesrepublik Deutschland vom 8. Mai 1949 an
Patenterteilung bekanntgemacht am 6. September 1951

Es ist bekannt, daß sich Salze der Thiophosphorsäureester folgender Konstitution:

mit Alkylhalogeniden zu den entsprechenden neutralen Estern umsetzen lassen. In vielen Fällen führt dieses Verfahren aber nur dann zum Ziel, wenn als Salze die der Schwermetalle, wie Blei oder Silber, und als Alkylhalogenide die Jodide gewählt werden. Es wurde nun gefunden, daß sich die neutralen Ester der Thiophosphorsäure leicht herstellen lassen, wenn beliebige Alkylrhodanide, die im Alkylrest in beliebiger Weise substituiert sein können, mit den technisch leicht herstellbaren Alkalisalzen der Dialkylphosphite zur Umsetzung gebracht werden. Unter Abspaltung von Alkalicyanid bilden sich die gewünschten Ester. Es war nicht vorauszusehen, daß die Reaktion diesen Verlauf nehmen würde. Das Schema der Reaktion ist folgendes:

Die Alkylreste R können gleich oder verschieden sein. Es lassen sich nach dem neuen Verfahren Verbindungen herstellen, die sich durch stärkste kontaktinsektizide Wirkungen auszeichnen. An folgenden Beispielen soll das Wesen der neuen Reaktion erläutert werden.

AUSGEGEBEN AM
15. OKTOBER 1951

DEUTSCHES PATENTAMT

PATENTSCHRIFT

Nr. 817 057
KLASSE 45l GRUPPE 3 01
L 58 IVa/45l

Dr. Gerhard Schrader, Opladen-Bruchhausen und
Dr. Walter Lorenz, Wuppertal-Elberfeld
sind als Erfinder genannt worden

Farbenfabriken Bayer, Leverkusen

Schädlingsbekämpfungsmittel

Patentiert im Gebiet der Bundesrepublik Deutschland vom 11. Oktober 1949 an
Patenterteilung bekanntgemacht am 23. August 1951

Es wurde gefunden, daß sich neutrale Ester der Thiolphosphorsäure folgender Zusammensetzung

(R_1 und R_2 stehen für beliebige Alkylreste, R_3 steht für einen beliebig substituierten Arylrest) hervorragend zur Bekämpfung von saugenden und fressenden Insekten aller Art eignen. Die genannten Ester sind z. B. durch Umsetzung von Dialkoxyphosphorsäurechloriden mit Thiophenolen nach an sich bekanntem Verfahren erhältlich.

Die neuen Ester können als Staub oder, vermischt mit einem Emulgator und Wasser, als Emulsionen zur Anwendung gebracht werden. Folgende Beispiele mögen das Gebiet der Erfindung erläutern:

Beispiele

1. Junge Apfelbäumchen, die von Blattläusen befallen sind, werden mit einer wäßrigen Lösung bespritzt, die 0,005% folgender Verbindung

(Kp. 1,5 mm/148°)

enthält. Bereits nach 3 Stunden beginnen die Blattläuse abzufallen. Nach 5 bis 6 Stunden sind alle Blattläuse abgetötet.

2. Petrischalen werden mit einem Staub einge-

AUSGEGEBEN AM
8. NOVEMBER 1951

DEUTSCHES PATENTAMT

PATENTSCHRIFT

Nr. 820 001
KLASSE 12o GRUPPE 23 03
p 54108 IVd/12o D

Dr. Walter Lorenz, Wuppertal-Elberfeld und
Dr. Gerhard Schrader, Opladen-Bruchhausen
sind als Erfinder genannt worden

Farbenfabriken Bayer, Leverkusen

Verfahren zur Herstellung von Thiopyrophosphorsäureestern

Patentiert im Gebiet der Bundesrepublik Deutschland vom 7. September 1949 an
Patenterteilung bekanntgemacht am 20. September 1951

Es wurde gefunden, daß sich Thiopyrophosphorsäureester folgender Zusammensetzung:

(R_1 bis R_4 können gleiche oder verschiedene Alkylreste sein), die bisher noch nicht bekanntgeworden sind, in technisch guter Ausbeute durch Umsetzung von Dialkylphosphiten mit Schwefeldichlorid oder dem durch eine sekundäre Base substituierten Schwefeldichlorid, den Dialkylaminosulfensäurechloriden herstellen lassen. Bei der Umsetzung wird im ersten Falle Salzsäure frei, die zweckmäßig durch Zugabe eines Säurebindemittels, z. B. Pyridin, Dimethylanilin u. a., gebunden werden kann. Im zweiten Fall wird die entstehende Salzsäure durch das gleichzeitige entstehende Dialkylamin gebunden. Die Umsetzung vollzieht sich nach folgenden beispielsweise angeführten Gleichungen:

(1)

bzw.

(2)

AUSLEGESCHRIFT 1 026 323

F 18573 IVb/12q
ANMELDETAG: 4. OKTOBER 1955
BEKANNTMACHUNG
DER ANMELDUNG
UND AUSGABE DER
AUSLEGESCHRIFT: 20. MÄRZ 1958

Verfahren zur Herstellung von insekticid wirksamen O,O-Dialkyl-S-phenyl-thiono-thiolphosphorsäureestern

Anmelder:
Farbenfabriken Bayer Aktiengesellschaft,
Leverkusen-Bayerwerk

Dr. Ernst Schegk, Wuppertal-Elberfeld,
und Dr. Gerhard Schrader, Wuppertal-Cronenberg,
sind als Erfinder genannt worden

1

Es wurde gefunden, daß man insekticid wirksame O,O-Dialkyl-S-phenyl-thiono-thiolphosphorsäureester durch Umsetzung von Dialkylthionophosphorsäurechloriden mit substituierten Phenylmercaptanen dadurch herstellen kann, daß als substituierte Phenylmercaptane Nitrophenylmercaptane, die gegebenenfalls im Phenylrest durch Halogen oder Alkylreste weitersubstituiert sind, verwendet werden.

Die neuen Thionothiolphosphate zeichnen sich durch hohe Beständigkeit gegen hydrolytische Einflüsse und durch sehr gute kontaktinsekticide Wirkungen aus. Gegenüber den vergleichbaren Thiolphosphorsäureestern, die z. B. aus der deutschen Patentschrift 817 753 bekannt sind, zeigen die neuen Thiono-thiolphosphorsäureester eine wesentlich geringere Toxizität gegenüber Warmblütern.

Außerdem sind die erfindungsgemäßen Verbindungen auch den aus der deutschen Patentschrift 885 176 her bekannten Verbindungen überlegen, und zwar sowohl hinsichtlich der Toxizität als auch hinsichtlich einer besseren Wirksamkeit. Aus der folgenden Gegenüberstellung sind diese Tatsachen zu ersehen:

Verglichen wurden der erfindungsgemäße Dithiophosphorsäureester

I

mit dem aus der deutschen Patentschrift 817 753 her bekannten Ester

II

und dem aus der deutschen Patentschrift 885 176 her bekannten Ester

III

Folgende Werte wurden gefunden:

Toxizität Ratte per os DL_{95} 50 mg/kg
I ... Spinnmilben 0,001% 100%
Raupen 0,1% 100%

2

Toxizität Ratte per os DL_{95} 2,5 mg/kg
II ... Spinnmilben 0,01% 100%
Raupen .... 0,1% keine Wirkung

Toxizität Ratte per os DL_{95} 20 mg/kg
III ... Spinnmilben 0,005% 100%
Raupen .... keine Wirkung

Beispiel 1

Fp. = 49°C

43 g p-Nitrothiophenol werden in 100 ccm wasserfreiem Pyridin gelöst. Unter Rühren gibt man, bei Zimmertemperatur beginnend, 76 g O,O-Diäthylthionophosphorsäuremonochlorid hinzu. Man sorgt durch Kühlen dafür, daß die Temperatur nicht über 40°C steigt. Nach dem Ausreagieren läßt man noch 1 bis 2 Stunden weiterrühren und gießt dann das Reaktionsprodukt in 100 ccm konzentrierte Salzsäure, die mit 50 g Eisstückchen versetzt ist. Das ausgeschiedene Rohprodukt wird ausgeäthert, und die Ätherschicht wird ein- bis zweimal mit einer

Figure 3.113: Examples from Gerhard Schrader's postwar patents on V-series nerve agents, based on wartime work.

3.5.5 Other Chemical Weapons

German-speaking scientists discovered and developed other categories of chemical weapons too. For example, R. P. Linstead and T. J. Betts, the British and American chairs of the Combined Intelligence Objectives Subcommittee (CIOS), described "N-Stoff" or chlorine trifluoride, a highly corrosive and incendiary German chemical weapon, in a September 1945 report [AFHRA A5186 electronic version pp. 904–1026, Ch. 4, p. 54]:

> A new method was discovered for the manufacture of chlorine trifluoride. The value of this compound is said to lie in its powerful oxidizing properties which causes organic materials to burst into flame immediately on contact. It also has a quality of liberating fluorine which attacks glass and rapidly obscures vision in planes or military vehicles.

Chemical weapons expert Dan Kaszeta provided more background information on N-Stoff/chlorine trifluoride [Kaszeta 2020, p. 39]:

> The Falkenhagen site was already in use for production of chemical warfare materiel unrelated to the nerve agent programme. In 1938, ground had been broken there for a complex to produce Chlorine Trifluoride (ClF_3), which the Army had nicknamed "N-stoff"—literally "substance N". It is a particularly vile substance. A very strong oxidizer, it is both extremely corrosive and poisonous and could be more readily considered to be an incendiary weapon. It burns many different things, even in the absence of oxygen and even ignites glass on contact. It reacts with water, including moisture on the skin. The German military had considered Chlorine Trifluoride as a possible weapon to attack fortifications such as the Maginot Line because it will burn through concrete.

Germany may have actually employed 5-kilogram shells of chlorine trifluoride[12] on the Eastern Front. An English translation of an Allied-intercepted 9 December 1944 Japanese message from Stockholm to Tokyo reported [NARA RG 457, Entry A1-9004, Japanese Army Attaché Messages Translations, SRA 14,200 thru 15,000. SRA 14628–14632. Photos in Pellas 2020, pp. 15–17]:

> [...] It is a fact that in June of 1942 the German Army tried out an utterly new type of weapon against the Russians at a location 150 kilometers southeast of Kursk. Although it was the entire 19th Infantry Regiment of the Russians which was thus attacked, only a few bombs (each round up to 5 kilograms) sufficed to utterly wipe them out to the last man. [...]
>
> The following is according to a statement by Lieutenant-Colonel UE(?K?)I KENJI, advisor to the attaché in Hungary and formerly (?on duty?) in this country, who by chance saw the actual scene immediately after the above took place:
>
> "All the men and the horses (?within the area of?) the explosion of the shells were charred black and even their ammunition had all been detonated."
>
> Moreover, it is a fact that the same type of war material was tried out in the Crimea, too. At that time the Russians claimed that this was poison-gas, and protested that if Germany were ever again to use it, Russia, too, would use poison-gas. [...]

A number of other German chemical agents with incendiary, freezing, neuropharmacological, and other properties were also reported.

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[12] Or perhaps fuel-air explosive shells or another novel weapon?

3.6 Physical Chemistry

Due to the dominance of creators from the greater German-speaking world both in the field of chemistry and in the field of physics, it is not surprising that they founded and led the area of physical chemistry, the intersection between chemical and physical phenomena.[13] Physical chemistry encompasses many topics such as thermochemistry, electrochemistry, photochemistry, and physical methods for analytical chemistry.

Some important creators in physical chemistry are shown in Figs. 3.114–3.123 and discussed in alphabetical order in Section 3.6.1.

Electrochemical battery and fuel cell technologies are discussed in more detail in Section 3.6.2.

For closely related creators and creations in quantum physics and statistical physics, see Sections 5.4 and 5.5, respectively.

3.6.1 General Physical Chemistry

Hermann Aron (German, 1845–1913) developed an improved lead-acid rechargeable battery in 1880, and it became widely used thereafter. He also developed improved methods of measuring electrical voltage and current [Katzir 2009, 2013].

Svante Arrhenius (1859–1927) was Swedish but studied and worked in Germany and Austria. In fact, throughout most of his education and career, he encountered considerable opposition to his scientific innovations in Sweden, but was given strong support and assistance by creators such as Ludwig Boltzmann, Rudolf Clausius, Friedrich Kohlrausch, Wilhelm Ostwald, and Jacobus van 't Hoff. Arrhenius was one of the founders of the field of physical chemistry and won the Nobel Prize in Chemistry in 1903 for his theoretical insights into electrolytic dissociation. H. R. Törnebladh, President of the Royal Swedish Academy of Sciences, explained the importance of Arrhenius's work [https://www.nobelprize.org/prizes/chemistry/1903/ceremony-speech/]:

> Around 1880 Svante Arrhenius—then studying for a doctorate in science—arrived, as a result of his researches into the movement of electric current through solutions, at a new explanation of the causes of chemical phenomena, i.e. he attributed them to electrical charges contained in the constituents of reacting substances. Electricity was thus introduced as a decisive factor into the theory of chemistry[...]
>
> In the time of Berzelius this notion rested on a qualitative basis only, whereas Arrhenius's theory determined it quantitatively, thus allowing it to be treated mathematically. In his doctor's thesis, twenty years ago, Arrhenius had deduced from this principle all known laws governing chemical changes, but despite this the new theory was very little understood. It so conflicted with current ideas as to disprove them. According to this theory, for instance, common salt, sodium chloride, when dissolved in water splits up to

---

[13] For more information on this area, see especially: Brock 1993; Laurie Brown et al. 1995; Bugge 1955; Coffey 2008; Engels et al. 1989; Farber 1961; Gamow 1966; Ihde 1984; Johnson 1990; Jones 2008; Jungnickel and McCormmach 1986, 2017; Kragh 2002; L'Annunziata 2016; von Meÿenn 1997; Ingo Müller 2007; Neufeldt 2003; Partington 1957, 1964; Teichmann et al. 2008; Weber 1988.

> a varying extent, in other words it is *dissociated* into its constituent parts which are diametrically opposed but charged with electricity, i.e. into *ions of chlorine* and of *sodium*, the only chemically effective substances in a solution of common salt. The theory also claimed that when an acid and a base react upon one another, water is the primary product and salt the secondary, and not reversely, as was then generally believed. Ideas so contrary to those current at that time could not be accepted immediately. A struggle lasting more than ten years and an enormous number of new experiments were required before the new theory was accepted by everyone. During this long battle over Arrhenius's theory of dissociation tremendous advances were made in chemistry and ever closer links were established between chemistry and physics—to the great benefit of both sciences.

Emil Bauer (Swiss, 1873–1944) developed novel fuel cells, such as a fuel cell using molten silver as the electrolyte. Together with Hans Preis, he developed the first fuel cell with a solid electrolyte, in this case one made of paste and metal oxides.

Henri Bernard Beer (Dutch, 1909–1994) invented improved electrodes made of titanium coated with mixed metal oxides containing metals such as rhodium, platinum, iridium, or ruthenium.

Jürgen Otto Besenhard (German, 1944–2006) played a major role in developing lithium batteries. It could be beneficial for historians to conduct much more archival research to investigate just how far back the history of the development of lithium batteries goes, and what contributions various scientists from the greater German-speaking world made during that development process.

Ludwig Boltzmann (Austrian, 1844–1906) developed an extensive framework of statistical physics equations for describing the thermodynamic behavior of large numbers of particles in solids, liquids, or gases [Boltzmann 1964]. As part of that work, he gave a precise mathematical definition of entropy for the second law of thermodynamics. In addition to its importance to physics, Boltzmann's work had enormous implications for chemical equilibria and chemical reactions.

Robert Bunsen (German, 1811–1899) made many important discoveries in physical chemistry. He invented the Bunsen cell battery using carbon electrodes (instead of more expensive platinum electrodes as had been used previously). He studied photochemical reactions, and he employed electrolysis to purify different metals. With Gustav Kirchhoff, he used spectroscopy to analyze and identify chemical elements.

Alexander Classen (German, 1843–1934) made important contributions to electrochemistry, including electrolytic gravimetry and rotating electrodes. The American Council of Learned Societies noted [ACLS 2000, p. 194]:

> First to make thorough study of electrogravimetric analysis (*Quantitative Analyse auf elektrolytischem Weg*, 1881); his innovative methods, which became standard practice, included use of warm solutions, introduction of measuring devices into the circuit, and substitution of storage cells for galvanic cells.

In 1850, Rudolf Clausius (German, 1822–1888) was the first to clearly articulate the second law of thermodynamics, that entropy cannot decrease, or equivalently that heat flows from regions of higher temperature to regions of lower temperature. He also did important work on phase transitions and other aspects of physical chemistry.

Peter Debye (Dutch, 1884–1966) studied and worked in Germany and Switzerland for many years. He developed statistical models of the behavior of molecules, chemical solutions, and crystalline solids. For his work, he won the Nobel Prize in Chemistry in 1936 (p. 922).

Manfred Eigen (German, 1927–2019) developed methods of measuring very fast chemical reactions. He won the Nobel Prize in Chemistry in 1967 for those innovations. Professor H. A. Ölander of the Nobel Committee for Chemistry announced the award [https://www.nobelprize.org/prizes/chemistry/1967/ceremony-speech/]:

> Professor Dr. Manfred Eigen. Although chemists had long been talking of instantaneous reactions, they had no way of determining the actual reaction rates. There were many very important reactions of this type, such as the neutralization of acids with alkalis. Thanks to you, chemists now have a whole range of methods that can be used to follow these rapid processes, so that this large gap in our chemical knowledge has now been filled.

Tibor Erdey-Grúz (Hungarian, 1902–1976) studied the electrochemistry of ionic conductivity, corrosion, and catalysis. Together with Max Volmer, he developed an equation describing the relation between voltage and current in electrolytic solutions.

Richard Ernst (Swiss, 1933–) developed nuclear magnetic resonance (NMR) spectroscopy methods that are useful for studying chemical molecules and biological systems. For that work, he won the Nobel Prize in Chemistry in 1991. Professor Sture Forsén of the Royal Swedish Academy of Sciences praised his research [https://www.nobelprize.org/prizes/chemistry/1991/ceremony-speech/]:

> Professor Ernst,
>
> You have played a leading role in several of the most significant methodological developments that have taken place in the field of NMR spectroscopy over the past two decades; developments that have had a lasting impact on the way modern chemistry is conducted. You have, in an admirable way, combined excellent experimental know-how with extraordinary theoretical insight. In recognition of your services to chemistry, and to natural science as a whole, the Royal Swedish Academy of Sciences has decided to confer upon you this year's Nobel Prize for Chemistry.

Joseph von Fraunhofer (German states, 1787–1826) invented the spectroscope and was the first to use spectroscopy to analyze chemical elements. Robert Bunsen and Gustav Kirchhoff later built upon his work on spectroscopic chemical analysis. Von Fraunhofer also made important innovations in the production of high-quality glass. See pp. 686, 970, and 1269.

In 1885, Carl Gassner (German, 1855–1942) demonstrated and patented the world's first dry batteries, which used zinc, carbon, and a paste electrolyte. See Fig. 3.126.

Heinz Gerischer (German, 1919–1994) began his research on electrochemistry during World War II and continued in that field for the rest of his career, making a number of major discoveries regarding electrode kinetics, electrode reactions, and electrode diagnostics. He also made important contributions to photochemistry.

Michael Grätzel (German, 1944–) invented dye-sensitized photoelectrochemical cells for converting sunlight to electricity more cheaply and efficiently than had previously been possible.

Theodor Grotthuß (German states, 1785–1822) conducted early experiments on electrolysis and developed the first theory of charge transport in electrolytes (now called the Grotthuß mechanism) in 1806. He also developed important early theoretical explanations of photochemical reactions.

Fritz Haber (German, 1868–1934) made tremendously important contributions not only to most other areas of chemistry, but also to physical chemistry, particularly with regard to electrochemistry, combustion, and chemical bond energies [Hager 2008; Stoltzenberg 1994; Szöllösi-Janze 2015]. He won the Nobel Prize in Chemistry in 1918 for his development of industrial-scale ammonia synthesis (p. 453).

Wilhelm Heinrich Heintz (German, 1817–1880) analyzed the physical structure of molecules, including fatty acids, uric acid, amines, and others. He also studied chemical reaction kinetics and the properties of a number of metals.

Frederik Wilhelm Hellesen (Danish but closely tied to the German-speaking research world, 1836–1892) produced dry zinc-carbon batteries in 1887.

Hermann von Helmholtz (German, 1821–1894) made foundational contributions to the thermodynamics of chemical reactions, most notably by defining what came to be known as the Helmholtz free energy. In 1847, he published a more detailed treatment of the first law of thermodynamics, *Über die Erhaltung der Kraft* (*On the Conservation of Energy*), and also studied the thermodynamics of fluids. Von Helmholtz also made major discoveries in biology (pp. 240, 283, 299, 313) and physics (p. 867) [Cahan 2018].

Gerhard Herzberg (German, 1904–1999) made important discoveries regarding molecular structures, molecular spectroscopy, and highly reactive free radical molecules. He won the Nobel Prize in Chemistry in 1971 for his work in those areas. Professor Stig Claesson of the Royal Swedish Academy of Sciences explained the importance of Herzberg's research [https://www.nobelprize.org/prizes/chemistry/1971/ceremony-speech/]:

> Herzberg began as a physicist and his first contributions to molecular spectroscopy were published at the end of the 1920's. In such investigations one measures how molecules absorb light-energy—also outside the visible region—i.e. in the ultraviolet and infrared. Since light-energy is packaged as quanta, these measurements can provide accurate information about energy contents in molecules. From this information their size, shape and other properties can be derived. Such calculations must be based on the description of matter given by quantum mechanics. The development of this subject during the 1920's and 30's is regarded as one of the most exciting periods in the history of physical science. Herzberg's elegant experimental investigations combined with his theoretical insight into their interpretation contributed to the progress of quantum mechanics while being decisive for the rapid development of molecular spectroscopy.
>
> One may now ask why Herzberg—originally a physicist and even famous as an astrophysicist—finally was awarded the Nobel Prize in chemistry.
>
> The explanation is that around 1950 molecular spectroscopy had progressed so far that one could begin to study even complicated systems of great chemical interest. This is brilliantly demonstrated by Herzberg's pioneering investigations of free radicals. Knowledge of their properties is of fundamental importance to our understanding of

> how chemical reactions proceed.
>
> For a chemical reaction to occur the original molecules must in some way break up into fragments which rearrange to form the new molecules. These fragments, or intermediates, are called free radicals.
>
> Free radicals are very difficult to study due to their short life-times—measured in millionths of a second. Herzberg therefore had ample opportunity to repeatedly demonstrate his exceptional experimental skill when the necessary spectroscopic technique was worked out.
>
> Herzberg has so far performed extensive precision determinations of the properties of over thirty free radicals among which are to be found the radicals methyl and methylene—well known from organic chemistry. Among his exciting discoveries may be mentioned that radicals drastically change their shape with increasing energy. For example, methylene is linear in its ground state but bent in states of higher energy. Many of the most important results were only achieved after several years' work and some of the most exciting as late as at the end of the 1960's. One can therefore note that this year's prize is truly an award for contributions of great current interest.

In 1840, Germain Hess (Swiss, 1802–1850) formulated what is now known as Hess's law, a form of the first law of thermodynamics (conservation of energy) applied to a series of chemical reactions. He also studied the thermodynamics of the dissolution of various salts in water.

Jaroslav Heyrovský (Austrian/Czech, 1890–1967) developed polarographic and electroanalytic methods of analyzing chemical samples. For those innovations, he won the Nobel Prize in Chemistry in 1959. The Royal Swedish Academy of Sciences summarized his work [https://www.nobelprize.org/prizes/chemistry/1959/ceremony-speech/]:

> Chemical and electrical phenomena are often associated, as in the case of redox reactions, when electrons are emitted and absorbed. In 1922 Jaroslav Heyrovský discovered a method for analyzing the occurrence and content of various substances in solutions using electrical measurements. The solution is analyzed with two electrodes, one of which is a dropping mercury electrode. At a voltage specific for different substances, redox reactions cause the current to rapidly increase to a level dependent on the concentration of the substance.

Johann Wilhelm Hittorf (German, 1824–1914) conducted very careful electrolytic experiments to measure the mobilities of different ions in solution, the values of which are now called Hittorf ion transport numbers. He was also one of the earliest scientists to experiment with high-voltage tubes and electron beams (p. 870).

Roald Hoffmann (born Roald Safran, Polish, 1937–) made important discoveries regarding the behavior of electrons in chemical bonds, for which he won the Nobel Prize in Chemistry in 1981. The Royal Swedish Academy of Sciences described his research [https://www.nobelprize.org/prizes/chemistry/1981/ceremony-speech/]:

> In chemical reactions, molecules composed of atoms meet and form new compounds. Electrons orbiting around the atoms' nuclei play an important role here. After Kenichi

> Fukui proved that the properties of the electron orbits that most weakly bound to the atom are critical in chemical reactions, Roald Hoffmann went on to further develop these theories from the mid-1960s. Independently of one another, Roald Hoffmann and Kenichi Fukui both demonstrated how the symmetrical properties of electron orbitals explain the course of chemical reactions.

Erich Hückel (German, 1896–1980) developed the Hückel molecular orbital theory to explain double and triple covalent bonds in molecules. He also worked with Peter Debye to create the Debye-Hückel theory of electrolytic solutions. Oxford University's *Biographical Dictionary of Scientists* summarized some of his research accomplishments [Porter 1994, pp. 350–351]:

> Debye and Hückel suggested that strong electrolytes dissociate completely into ions, explaining the deviations from expected behaviour in terms of attraction and repulsion between the ions. In a series of highly mathematical investigations they found formulae for calculating the electrical and thermodynamic properties of electrolytic solutions, principally dilute solutions of strong electrolytes. [...]
>
> In 1930, Hückel began his work on aromaticity, the basis of the chemical behaviour of benzene, pyridine and similar compounds. The benzene molecule is held together by electrons that are delocalized and contribute to one large hexagonal bond above and below the plane of the molecule. This accounts for its planar shape and its ability to preserve its structure through chemical reactions. Hückel developed a mathematical approximation for the evaluation of certain integrals in the calculations concerned with the exact nature of the bonding in benzene.
>
> Later in the 1930s, he extended his research to other chemical systems that appear to possess the same kind of aromatic nature as benzene (although usually to a lower degree). From this study emerged the Hückel rule for monocyclic systems[...]
>
> Hückel also carried out research into unsaturated compounds (those with double or triple bonds) and into the chemistry of free radical compounds (those with a free, non-bonding electron).

In 1899, Ernst Waldemar Jungner (Swedish but closely tied to the German-speaking research world, 1869–1924) created nickel-cadmium, nickel-iron, and silver cadmium rechargeable batteries (Fig. 3.127). He also developed improved fuel cells and electrolytic systems. Nickel-cadmium and other rechargeable batteries were mass-produced and harnessed for a variety of applications in the German-speaking world.

Karl Kellner (Austrian, 1851–1905) developed an industrial electrolytic process for producing chlorine gas and sodium hydroxide, both of which were useful reagents for manufacturing other commercial chemical products.

Gustav Kirchhoff (German, 1824–1887) derived equations to predict the heat of reaction in thermochemistry. Working with Robert Bunsen, he used spectroscopy to analyze and identify chemical elements. Kirchhoff made major discoveries in many areas of chemistry, physics, and engineering (see also pp. 433, 866, 923, 953, and 966).

Friedrich Kohlrausch (German, 1840–1910), the son of Rudolf Kohlrausch (p. 867), was an experimentalist who worked on a wide range of topics in chemistry, physics, and physical chemistry over his career. He developed and used accurate methods of measuring the electrical conductivity of electrolytes, and he also studied the properties of mercury. In addition, he developed experimental techniques and instruments for measuring thermal conductivity, elasticity, magnetic fields, and optical properties.

Walter Kohn (Austrian, 1923–2016) developed new methods to calculate the behavior of electrons in large molecules and in solid materials. For that work, he won the Nobel Prize in Chemistry in 1998, as explained by Professor Björn Roos of the Royal Swedish Academy of Sciences [https://www.nobelprize.org/prizes/chemistry/1998/ceremony-speech/]:

> In two landmark articles from 1964 and 1965, Walter Kohn showed an alternative way in which quantum mechanical equations can be approximated. He showed that there is a one-to-one correspondence between the energy of a quantum mechanical system and its electron density, which is a function of three positional coordinates only and is, therefore, much easier to handle than the complicated wave function, which depend on the positions of all electrons. He also developed a method which made it possible to construct a set of equations, which could be used to determine the energy and electron density. This approach, called density functional theory, has developed during the last ten years into a versatile computational tool with many applications in chemistry. Due to its simplicity, it can be applied to larger molecules than the wave function based methods. Density functional theory has made it possible to study the mechanisms of chemical reactions in enzymes, for example when water is transformed into oxygen in photosynthesis.

Hermann Kolbe (German, 1818–1884) developed methods of using electrolysis with carboxylic acids and fatty acids, now called Kolbe electrolysis. He was also one of the founders of organic chemistry (p. 477).

Karl Kordesch (Austrian, 1922–2011) worked on advanced battery programs in wartime and early postwar Austria, then came to the United States as part of Operation Paperclip. Drawing upon his experience with advanced battery research in Austria, he headed the battery development program at the U.S. Army's Fort Monmouth laboratory, then headed two Union Carbide groups to develop fuel cells and batteries in parallel. He and the other members of his Union Carbide battery group filed the first patents on alkaline (manganese dioxide) dry batteries (Fig. 3.129). He also invented hydrazine-air fuel cells and developed thin carbon electrodes that revolutionized hydrogen-oxygen fuel cells (Fig. 3.130). In view of the great importance that the United States placed on importing Kordesch in Operation Paperclip, putting him in charge of a battery development program for the Army, and placing him in charge simultaneously of two different programs at Union Carbide, it seems highly likely that Kordesch's postwar U.S. projects were based on earlier discoveries by him or others in Austria and Germany. It is difficult to trace that history from the publicly available documentation, but more archival research in this area could be quite enlightening.

Irving Langmuir (American but studied in Germany, 1881–1957) did important work on surface chemistry, the study of chemical reactions that occur at the surface of a liquid or solid. For his discoveries, he won the Nobel Prize in Chemistry in 1932. The Royal Swedish Academy of Sciences described Langmuir's research [https://www.nobelprize.org/prizes/chemistry/1932/langmuir/facts/]:

> Chemical reactions often take place more easily next to surfaces where substances in different phases, such as solids and gases, come in contact. In studies of incandescent

> light bulbs with rarefied hydrogen gas, Irving Langmuir discovered that a layer of hydrogen atoms only one atom thick formed on the inside of the incandescent light bulb. Further studies of oil films and other materials led him in 1917 to a theory postulating that surfaces resemble a chessboard on which every square can be occupied by only one atom or molecule. As a result, atoms or molecules that wind up next to each other can more easily react with one another.

Max Le Blanc (German, 1865–1943) created many innovations in electrochemistry, including the hydrogen electrode for pH measurement, control of voltage during electrolysis to selectively deposit different metals, and improved methods of measuring voltages and currents in solutions.

Johann Josef Loschmidt (Austrian, 1821–1895) studied the physical structures and sizes of molecules. He developed methods to determine the number of gas molecules within a given volume of air. In his honor, that number for standard temperature and pressure is now called the Loschmidt constant, approximately 2.69×10^{25} molecules/m^3 at 0^oC and 1 atmosphere of pressure. Loschmidt also used the then-new second law of thermodynamics in theoretical explanations of the behavior of chemical compounds and solutions.

Julius von Mayer (German, 1814–1878) expressed the first law of thermodynamics, the law of conservation of energy (including heat energy and work), in 1841. He was also the first to find equations for the specific heat of an ideal gas, or the relationship between the amount of heat energy absorbed by a substance and the corresponding temperature rise for that substance. He was one of the first to attempt a scientific analysis of photosynthesis, and he created Mayer's reagent for detecting alkaloids.

Karl Friedrich Mohr (German, 1806–1879) developed improved methods of volumetric analysis and chemical titration. In an 1837 journal article, he became the first known scientist to state the first law of thermodynamics (conservation of energy) [Mohr 1837]:

> Ausser den bekannten 54 chemischen Elementen gibt es in der Natur der Dinge nur noch ein Agens, und dieses heisst Kraft; es kann unter den passenden Verhältnissen als Bewegung, chemische Affinität, Cohäsion, Elektricität, Licht, Wärme und Magnetismus hervortreten, und aus jeder dieser Erscheinungsarten können alle übrigen hervorgebracht werden.

> Apart from the known 54 chemical elements, there is only one agent in the physical world, and this is called energy; it can appear under the appropriate conditions as motion, chemical affinity, cohesion, electricity, light, heat, and magnetism, and from any one of these forms it can be transformed into any of the others.

Ludwig Mond (German, 1839–1909) developed and improved electrochemical methods for extracting and depositing nickel and other metals. Mond also founded the field of organometallic chemistry (p. 503).

Adolph Müller (German, 1852–1928) was responsible for first producing lead-acid storage batteries on an industrial scale in Germany in 1886. His battery company became known as Accumulatoren Fabrik Aktiengesellschaft Berlin-Hagen (AFA) until 1945, and as VARTA (Vertrieb, Aufladung, Reparatur transportabler Akkumulatoren) after 1945.

Walther Nernst (German, 1864–1941) was one of the founders of the field of physical chemistry. He made important discoveries regarding the statistical physics underlying thermodynamics, chemical reactions, electrochemistry, and the physics of solids. He derived the Nernst equation relating voltages and ion concentrations in electrochemistry. In 1905, he discovered the third law of thermodynamics (as a system approaches absolute zero temperature, its entropy approaches a constant value), for which he won the Nobel Prize in Chemistry in 1920 (p. 921).

Wilhelm Ostwald (German, 1853–1932) was another founder of the field of physical chemistry. He developed statistical methods that were applicable to thermodynamic processes in both chemistry and physics. He also made key discoveries regarding the dissociation constants of electrolytes (Ostwald's dilution law) and polymorphism in solid materials (Ostwald's rule). Ostwald's work earned him the Nobel Prize in Chemistry in 1909 (p. 921).

In 1842, Johann Christian Poggendorff (German, 1796–1877) invented an improved battery, now called the Poggendorff cell, that used chromic acid as the electrolyte. Poggendorff also developed and used a number of sensitive instruments for measuring voltage, current, and other parameters in electrochemistry experiments.

John Polanyi (German/Hungarian, 1929–) is the son of Michael Polanyi. He won the Nobel Prize in Chemistry in 1986 for developing methods of using infrared chemiluminescence and other techniques to make high-speed measurements of chemical reactions as they occur. The Royal Swedish Academy of Sciences explained his work [https://www.nobelprize.org/prizes/chemistry/1986/ceremony-speech/]:

> Chemical reactions in which molecules comprised of atoms collide and form new compounds represent one of nature's fundamental processes. At the end of the 1950s John Polanyi began developing methods to carefully study the dynamics of chemical reactions. During chemical reactions, the newly formed molecules are sometimes infused with energy that then is emitted in the form of infrared light. By measuring this very weak radiation, the quantum mechanical energy state of the molecules can be determined and the reaction mapped.

Michael Polanyi (Hungarian, 1891–1976) made major discoveries in many areas of physical chemistry, including the kinetics of chemical reactions, X-ray diffraction, the adsorption of gases by solids, fiber diffraction analysis, and the theory of dislocations in materials under plastic deformation. He also made important contributions in a number of other fields, including medicine, economics, philosophy, and epistemology. He was the father of John Polanyi. The American Council of Learned Societies summarized his contributions to physical chemistry [ACLS 2000, p. 717]:

> Earned his Ph.D. from the University of Budapest in 1917 with a dissertation on the thermodynamics of gas adsorption. In 1920 he was hired by the Kaiser Wilhelm Institute for Fiber Chemistry in Berlin, where he did research on plant fibers, using X-ray diffraction. At the Kaiser Wilhelm Institute for Physical Chemistry, which he joined in 1923, he established his well-known dislocation theory. His work with Eugene Wigner concerned the uncertainty principle for angular momentum and the absolute rate of unimolecular dissociation. In 1933 he immigrated to England, where his main work was in reaction kinetics. At the University of Manchester, he helped develop the theory of bimolecular activation energy and the theory of absolute rates of reaction; he also did studies on ionic reactions in solution, on bond dissociation energies, and on the mechanism of polymerization.

Hans Preis (Swiss, 18??–19??) worked together with Emil Bauer to develop the first fuel cell with a solid electrolyte, in this case one made of paste and metal oxides.

Johann Ritter (Prussian/Bavarian, 1776–1810) built the first or one of the first electrolysis cells around 1800 and studied the electrolysis of water. He also built and conducted experiments with very early batteries. In addition, Ritter discovered ultraviolet light in 1801 (p. 970).

Beginning in 1896, Paul Schmidt (German, 1868–1948, not to be confused with the later designer of the V-1 cruise missile's pulsejet engine) mass-produced zinc-carbon dry batteries and founded the Daimon electronics company.

Christian Schönbein (German states, 1799–1868) invented and demonstrated the first fuel cells (using hydrogen and oxygen) no later than 1838, as shown in Fig. 3.124. He also discovered ozone and did groundbreaking work in explosives (p. 534) and chromatography (p. 717).

Wilhelm Sinsteden (German, 1803–1891) invented and demonstrated lead-acid rechargeable batteries during the period 1850–1854, published his results in 1854 (Fig. 3.125), and studied many other areas of electricity and electrical components.

While Otto Stern (German, 1888–1969) is more famous for his physics experiments (p. 905), he made several important contributions to physical chemistry. He discovered what is now known as the Stern electrochemical double layer, developed the Stern-Volmer equation for photochemical reaction kinetics with Max Volmer, and studied entropy and statistical effects in chemical systems.

Ignatz Stroof (German, 1838–1920) developed industrial-scale electrolysis systems for producing chemical elements of high purity.

Julius Tafel (Swiss, 1862–1918) made several discoveries in electrochemistry that are now named after him, such as the Tafel equation relating voltage and the electrochemical reaction rate, the Tafel mechanism for catalytic hydrogen production, and the Tafel rearrangement for electrochemical hydrocarbon synthesis.

Johannes van der Waals (Dutch, 1837–1923, photo p. 919) developed detailed thermodynamic equations relating the pressure, density, and temperature of gases and liquids. He won the Nobel Prize in Physics in 1910 (p. 920).

Jacobus Henricus van 't Hoff (Dutch, 1852–1911) was another founder of the field of physical chemistry, making vital discoveries regarding chemical affinity, chemical equilibrium, chemical kinetics, chemical thermodynamics, osmotic pressure in solutions, and stereochemistry. In 1901, he became the first winner of the Nobel Prize in Chemistry (p. 481).

Max Volmer (German, 1885–1965) made several contributions to physical chemistry. One was discovering what is now known as Volmer diffusion of adsorbed molecules. Working with Tibor Erdey-Grúz, he also developed an equation describing the relation between voltage and current in electrolytic solutions. With Otto Stern, he developed the Stern-Volmer equation describing the kinetics of photochemical reactions. Moreover, Volmer played an important role in the wartime German nuclear program (Section 8.8) and the postwar Soviet nuclear program (Section 8.9).

In 1874, Emil Wohlwill (German, 1835–1912) invented what is now known as the Wohlwill process, an electrochemical process for refining gold or silver to very high purity, which is still used today. He was the father of Heinrich Wohlwill.

Heinrich Wohlwill (German, 1874–1943) was the son of Emil Wohlwill. He invented an electrolytic process for purifying and recycling copper, and became the technical director of Norddeutsche Affinerie to apply that process on an industrial scale. Unfortunately he was taken to the Theresienstadt concentration camp in 1942 and died there in 1943.

Kurt Wüthrich (Swiss, 1938–) developed methods to use nuclear magnetic resonance (NMR) to study large molecules. For that work, he won the Nobel Prize in Chemistry in 2002. Professor Astrid Gräslund of the Royal Swedish Academy of Sciences emphasized the importance of his innovations [https://www.nobelprize.org/prizes/chemistry/2002/ceremony-speech/]:

> Using nuclear magnetic resonance, or NMR, a method that Kurt Wüthrich has further refined, it is now possible to determine the three-dimensional structure of protein molecules in a water solution. NMR is one of the chemist's best methods for examining molecules, and it has been used extensively for small molecules since the mid-20th century. But large molecules like proteins involve special problems. One of the fine points of NMR is that it enables us to see individual signals, for example, from each hydrogen nucleus in a molecule. But because a protein can contain thousands of hydrogen nuclei, how do you know which signal belongs to which nucleus?
>
> Wüthrich devised a way of systematically determining how each signal fits together with its special hydrogen nucleus. In the bargain, he was also able to determine a large number of pairwise distances between hydrogen nuclei. This enabled him to calculate a three-dimensional structure for the protein molecule. It is something like drawing a picture of a house if you know a large number of distances in the house. So thanks to Wüthrich's discovery, we can now use NMR to examine and depict proteins in their natural environment, surrounded by water like in a cell.

Physical chemistry

Hermann Aron
(1845–1913)

Svante Arrhenius
(1859–1927)

Emil Bauer
(1873–1944)

Henri Bernard Beer
(1909–1994)

Jürgen Besenhard
(1944–2006)

Ludwig Boltzmann
(1844–1906)

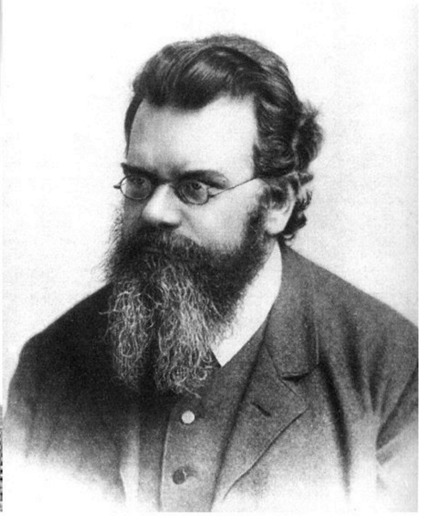


Figure 3.114: Some creators who made important contributions to physical chemistry included Hermann Aron, Svante Arrhenius, Emil Bauer, Henri Bernard Beer, Jürgen Besenhard, and Ludwig Boltzmann.

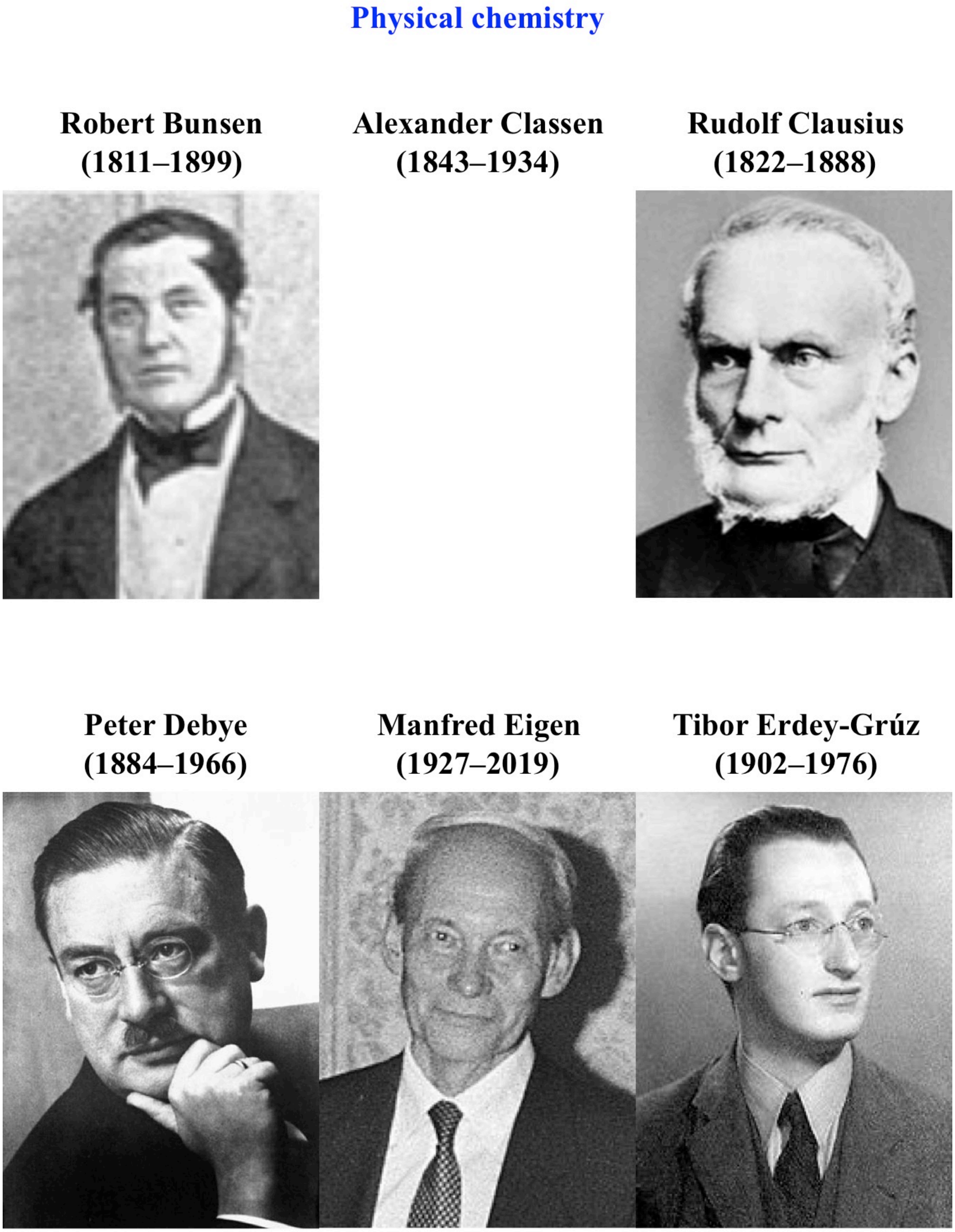
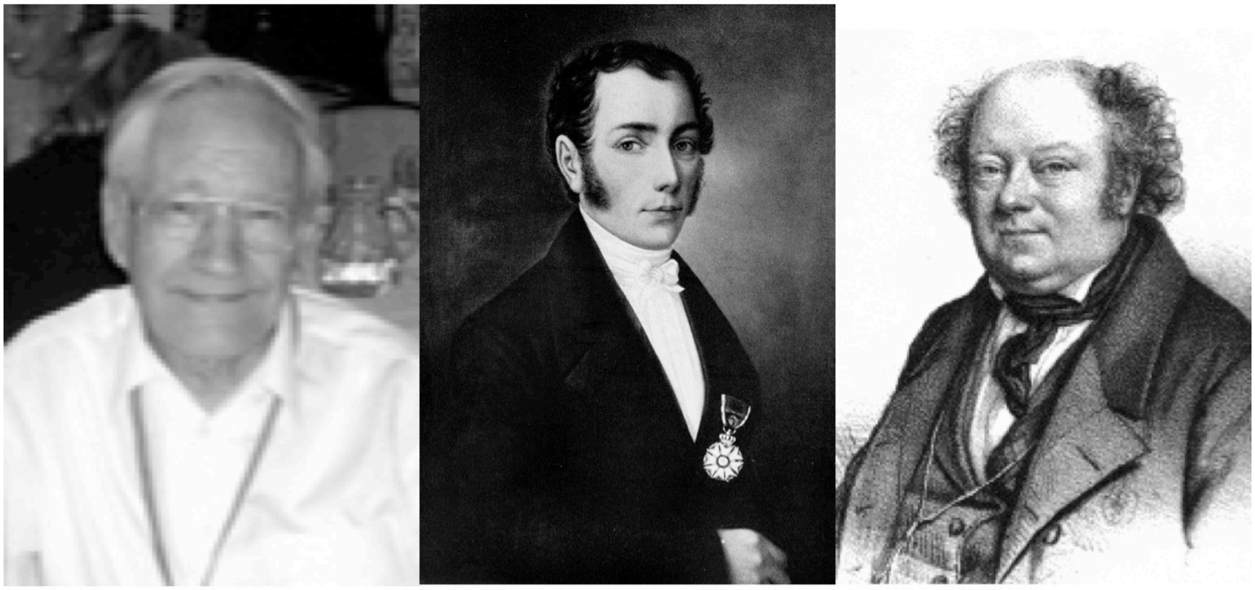


Figure 3.115: Other creators who made important contributions to physical chemistry included Robert Bunsen, Alexander Classen, Rudolf Clausius, Peter Debye, Manfred Eigen, and Tibor Erdey-Grúz.

Physical chemistry



Richard Ernst (1933–)

Joseph von Fraunhofer (1787–1826)

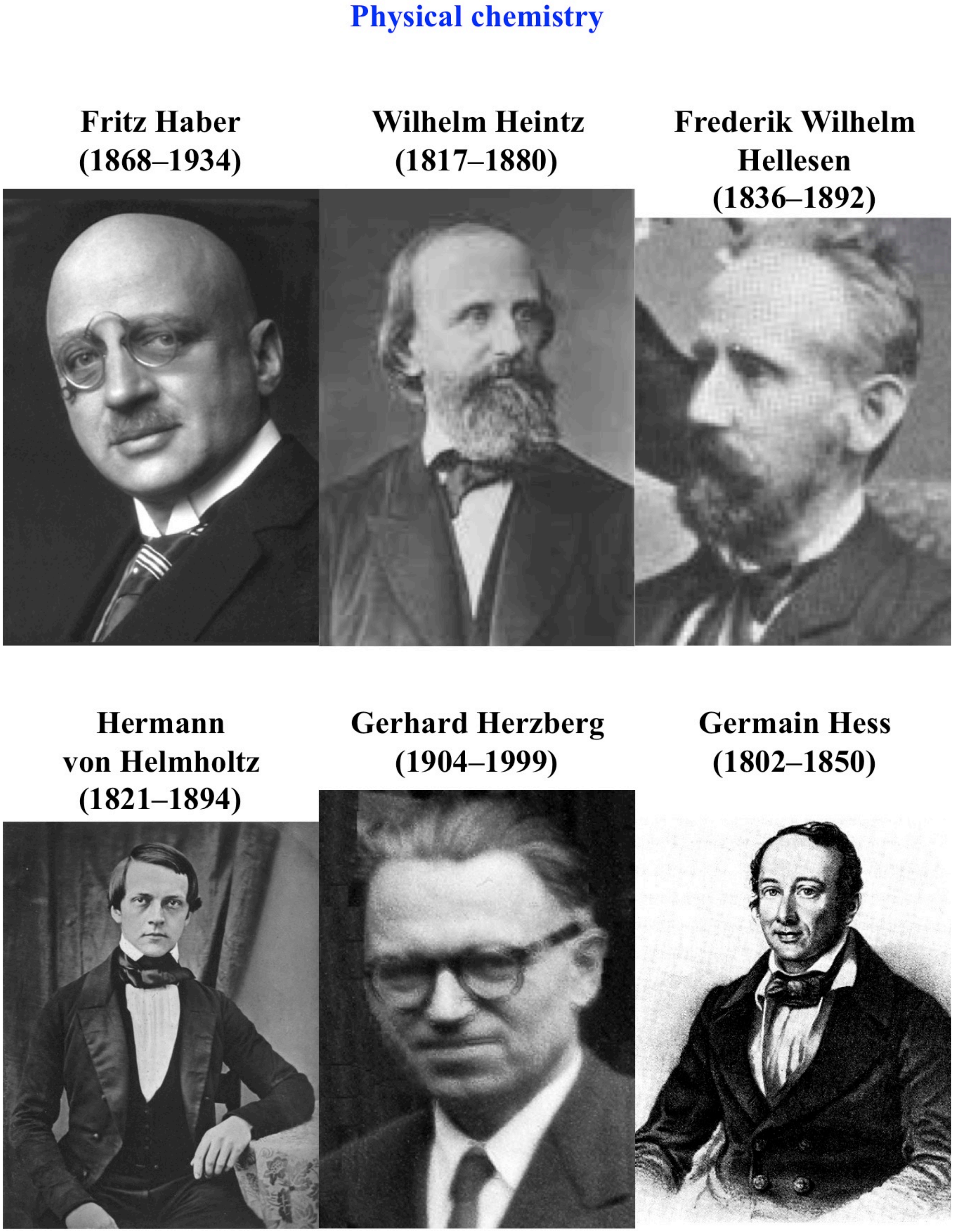
Carl Gassner (1855–1942)

Heinz Gerischer (1919–1994)

Michael Grätzel (1944–)

Theodor Grotthuß (1785–1822)

Figure 3.116: Other creators who made important contributions to physical chemistry included Richard Ernst, Joseph von Fraunhofer, Carl Gassner, Heinz Gerischer, Michael Grätzel, and Theodor Grotthuß.



Physical chemistry

Fritz Haber (1868–1934)

Wilhelm Heintz (1817–1880)

Frederik Wilhelm Hellesen (1836–1892)

Hermann von Helmholtz (1821–1894)

Gerhard Herzberg (1904–1999)

Germain Hess (1802–1850)

Figure 3.117: Other creators who made important contributions to physical chemistry included Fritz Haber, Wilhelm Heintz, Frederik Wilhelm Hellesen, Hermann von Helmholtz, Gerhard Herzberg, and Germain Hess.

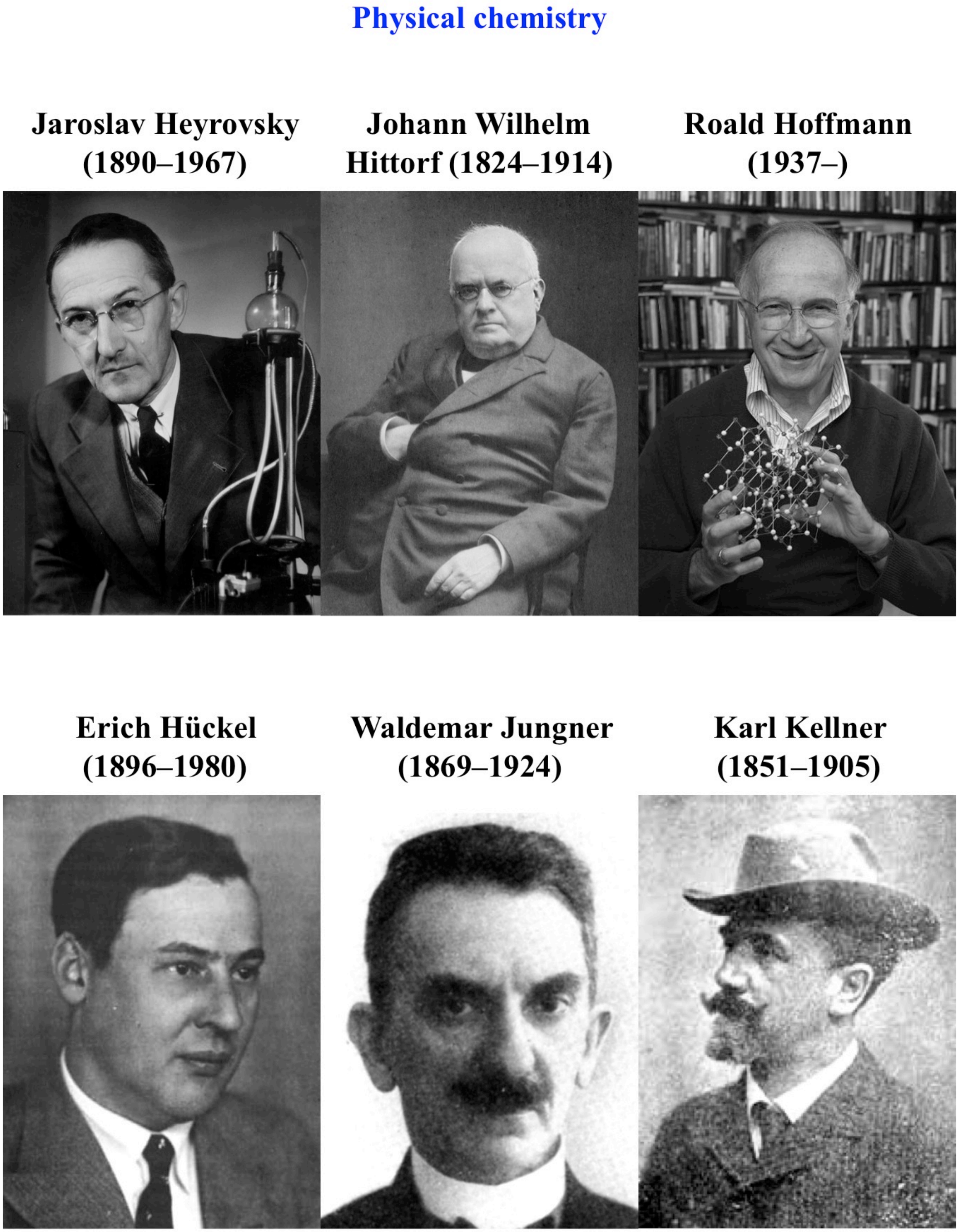


Figure 3.118: Other creators who made important contributions to physical chemistry included Jaroslav Heyrovský, Johann Wilhelm Hittorf, Roald Hoffmann, Erich Hückel, Waldemar Jungner, and Karl Kellner.

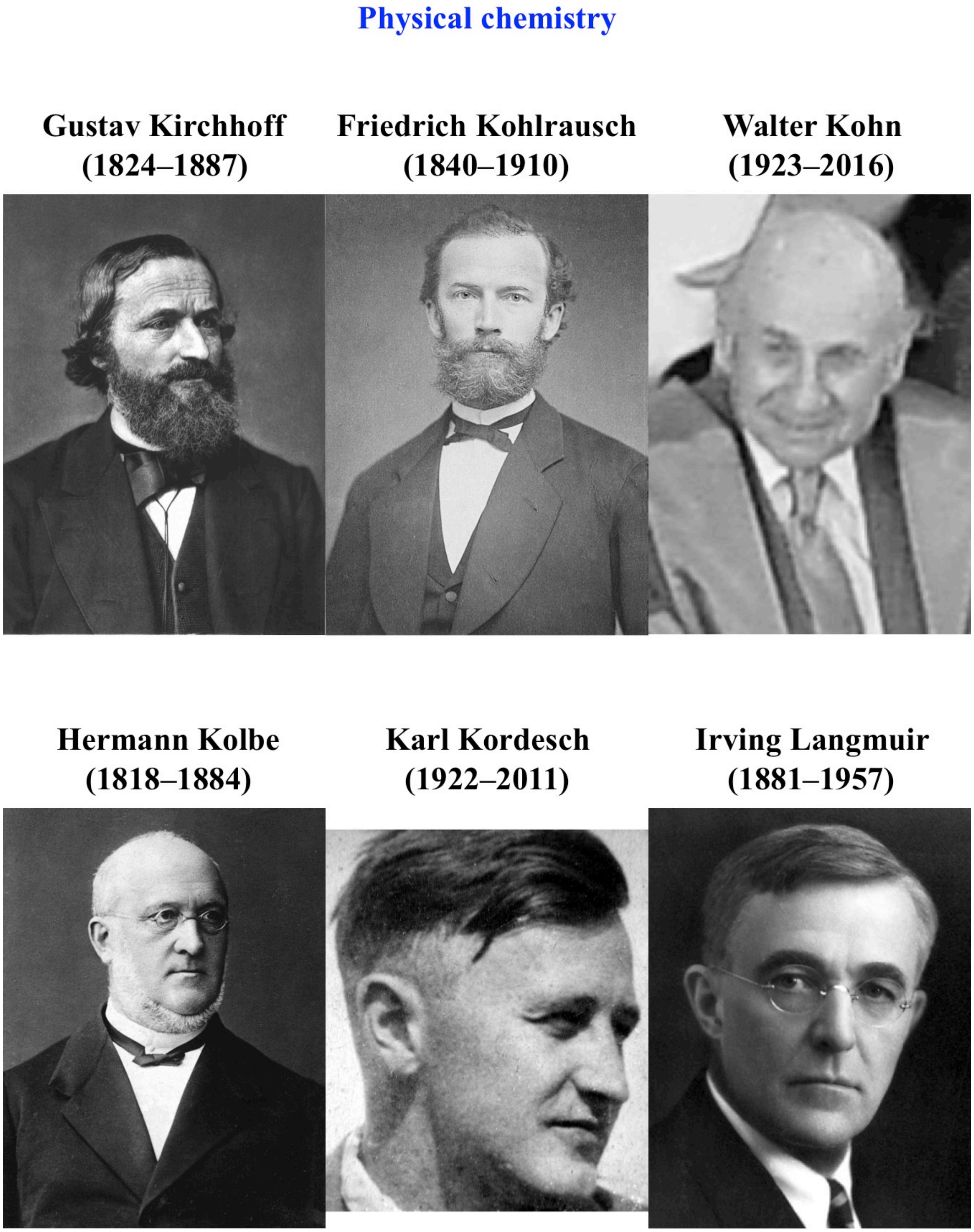
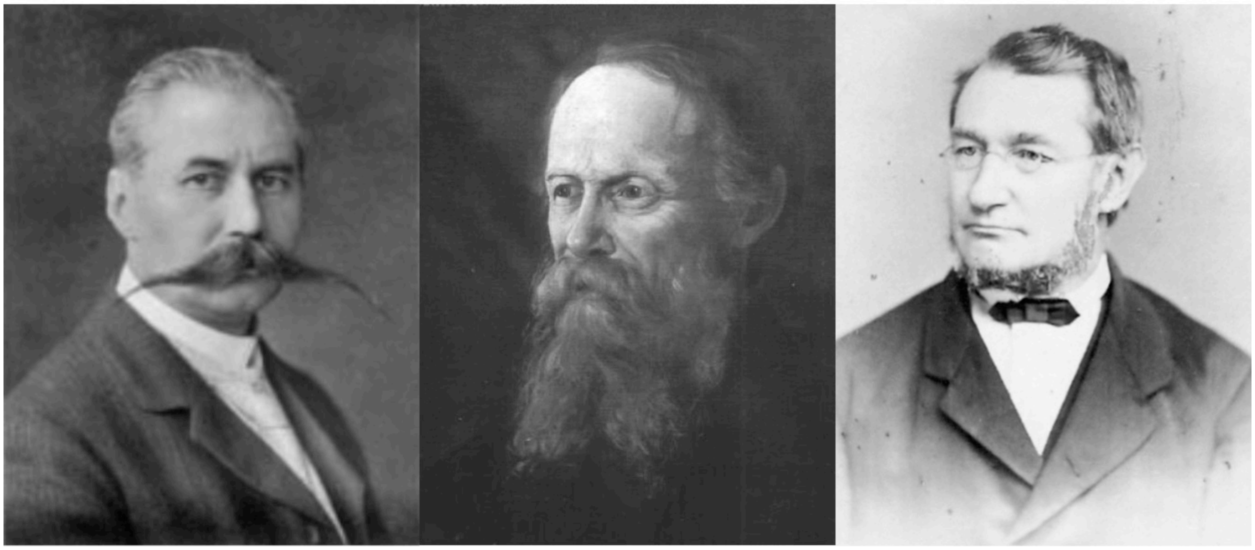


Figure 3.119: Other creators who made important contributions to physical chemistry included Gustav Kirchhoff, Friedrich Kohlrausch, Walter Kohn, Hermann Kolbe, Karl Kordesch, and Irving Langmuir.

Physical chemistry

Max Le Blanc (1865–1943) **Johann Loschmidt (1821–1895)** **Julius von Mayer (1814–1878)**



Karl Friedrich Mohr (1806–1879) **Ludwig Mond (1839–1909)** **Adolph Müller (1852–1928)**

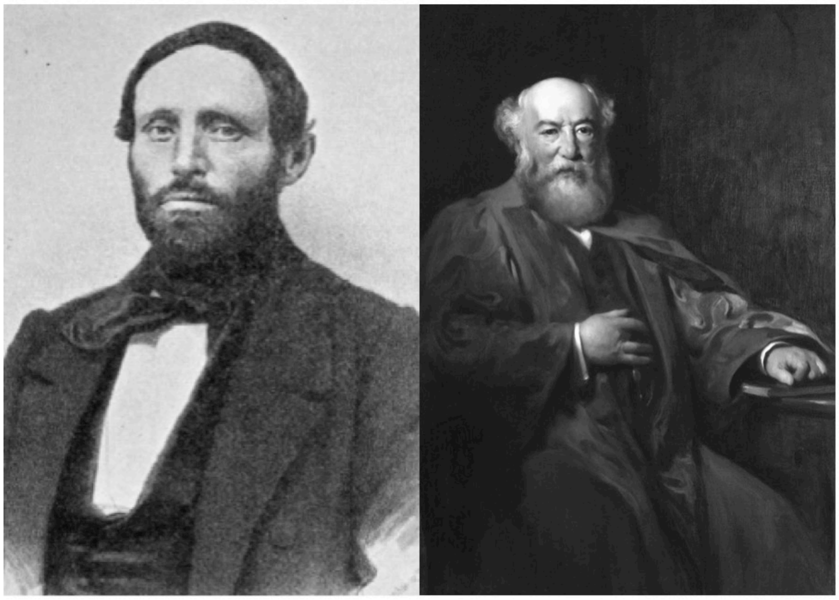


Figure 3.120: Other creators who made important contributions to physical chemistry included Max Le Blanc, Johann Loschmidt, Julius von Mayer, Karl Friedrich Mohr, Ludwig Mond, and Adolph Müller.

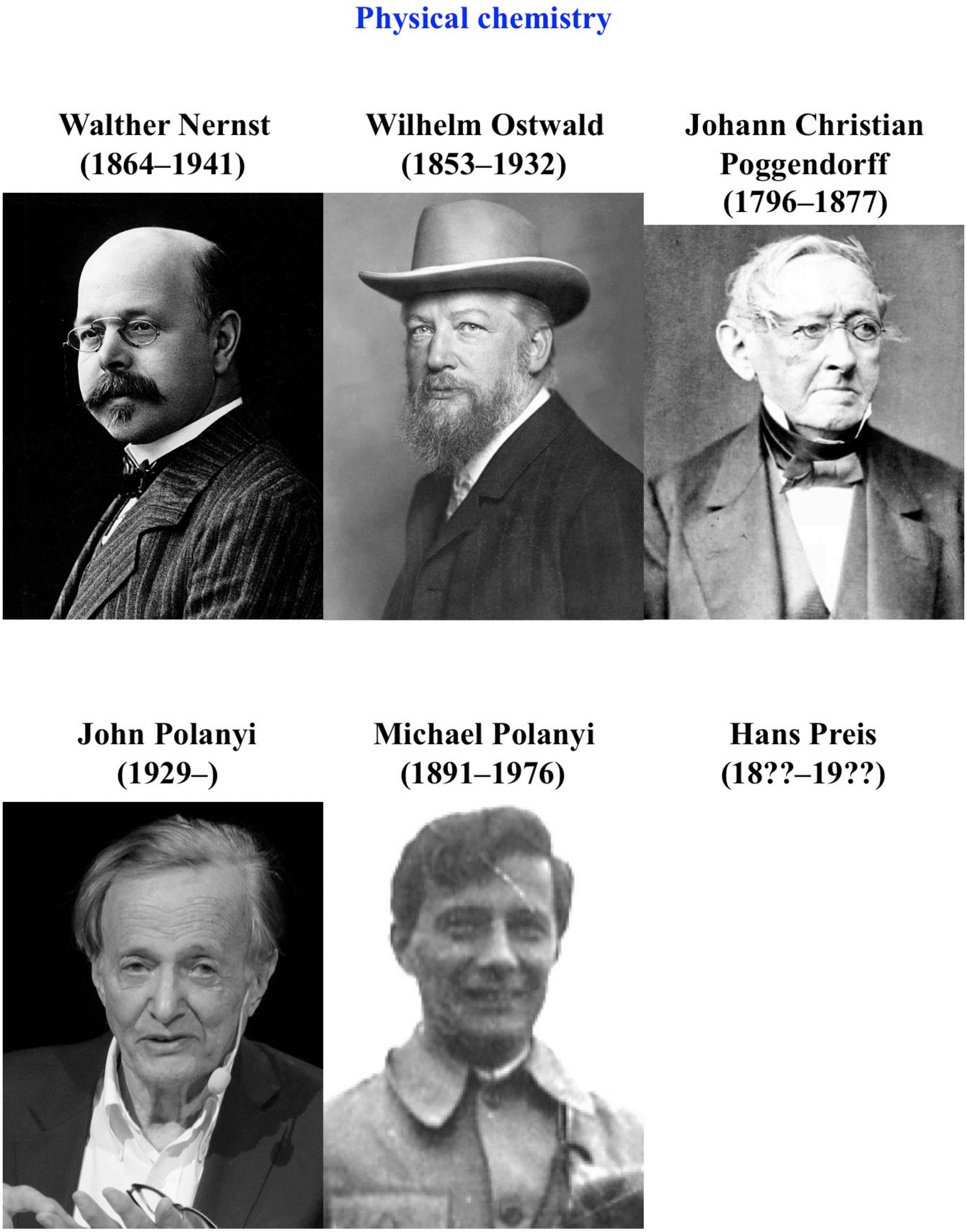
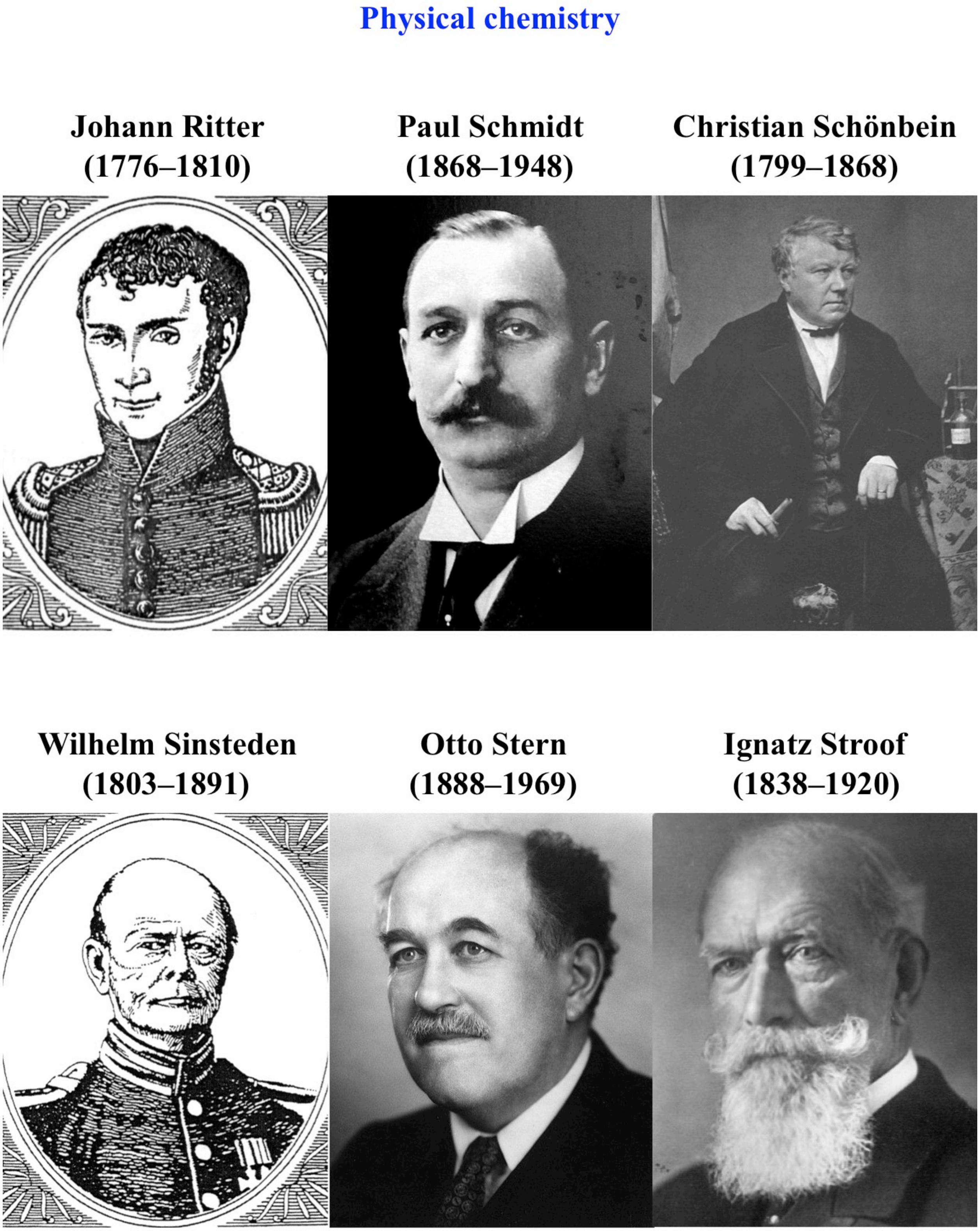


Figure 3.121: Other creators who made important contributions to physical chemistry included Walther Nernst, Wilhelm Ostwald, Johann Christian Poggendorff, John Polanyi, Michael Polanyi, and Hans Preis.



Physical chemistry

Johann Ritter
(1776–1810)

Paul Schmidt
(1868–1948)

Christian Schönbein
(1799–1868)

Wilhelm Sinsteden
(1803–1891)

Otto Stern
(1888–1969)

Ignatz Stroof
(1838–1920)

Figure 3.122: Other creators who made important contributions to physical chemistry included Johann Ritter, Paul Schmidt, Christian Schönbein, Wilhelm Sinsteden, Otto Stern, and Ignatz Stroof.

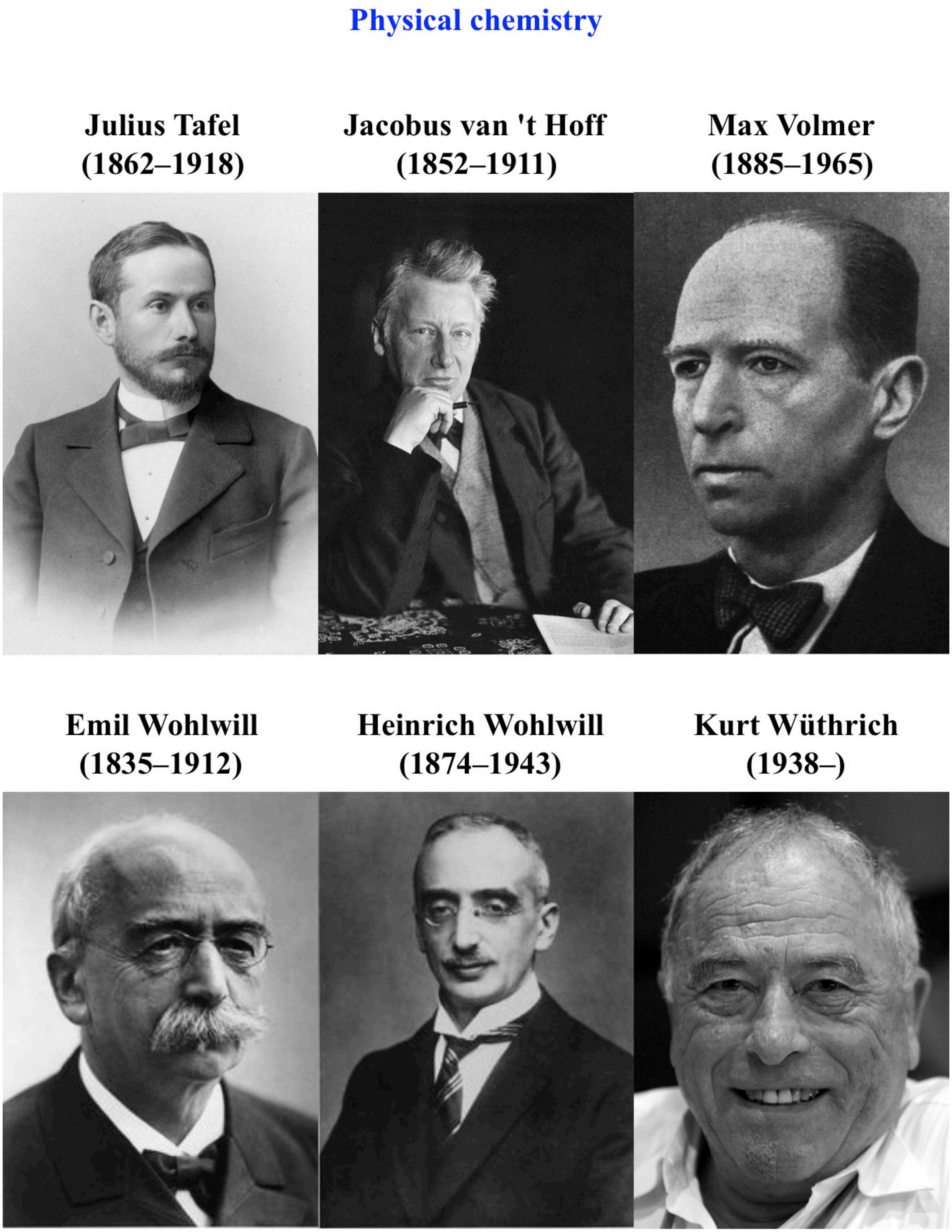


Figure 3.123: Other creators who made important contributions to physical chemistry included Julius Tafel, Jacobus Henricus van 't Hoff, Max Volmer, Emil Wohlwill, Heinrich Wohlwill, and Kurt Wüthrich.

3.6.2 Batteries and Fuel Cells

Most modern battery and fuel cell technologies were invented and developed in the German-speaking world, as discussed above for individual creators and as shown in Figs. 3.124–3.130. Advanced German battery technologies were used for everything from the world's first hybrid electric automobiles in 1900 (p. 1363) to electric submarines in World Wars I and II (p. 1468).

Many of those battery technologies were transferred out of the German-speaking world before 1945 in the form of patents, commercial transactions, and immigrant scientists. However, there were a number of additional, advanced battery and fuel cell technologies that were transferred out of the German-speaking world in the immediate aftermath of World War II (Fig. 3.128), as shown by numerous reports such as:

> BIOS 307. *German Secondary Batteries (with Special Reference to Those Used by Army Signals).*
>
> BIOS 362. *German Primary Battery Industry.*
>
> BIOS 384. *German Battery Electric Vehicles and the German Storage Battery Industry.*
>
> BIOS 467. *German Secondary Battery Industry.*
>
> BIOS 490. *Primary Battery Development by the Chemische-Physikalische Versuchsanstalt, Danisch Nienhof.*
>
> BIOS 557. *Visits to Radio Targets in Germany.*
>
> BIOS 1097. *German Battery Electric Road Vehicles.*
>
> CIOS XXX-53. *German Development of the Primary Battery.*
>
> CIOS XXXII-81. *The Manufacture of Hard Rubber Parts for Storage Batteries.*
>
> FIAT 615. *Battery Production Capacities for Automotive Purposes in Germany.*
>
> FIAT 670. *Survey of a New Storage Battery.*
>
> FIAT 800. *Nickel Cadmium Storage Batteries in Germany.*
>
> NavTecMisEu 210-45. *Submarine Batteries The Accumulaturen Fabrik AG Hagen—Hannover Plants.*
>
> NavTecMisEu 211-45. *Torpedo Propulsion Batteries (Secondary) The Accumulatoren Fabrik, AG Hagon—Hannover Plants.*
>
> NavTecMisEu 212-45. *Aircraft Batteries (Lead and Alkaline) The Accumulatoren Fabrick AG Hagon—Hannover Plants.*

NavTecMisEu 213-45. *Manufacture of Hard Rubber Parts for Storage Batteries and Battery Ventilating Equipment for German Submarines.*

NavTecMisEu 283-45. *German Development of the Primary Battery.*

NavTecMisEu 310-45. *German Submarine Battery Installation and Battery Ventilation.*

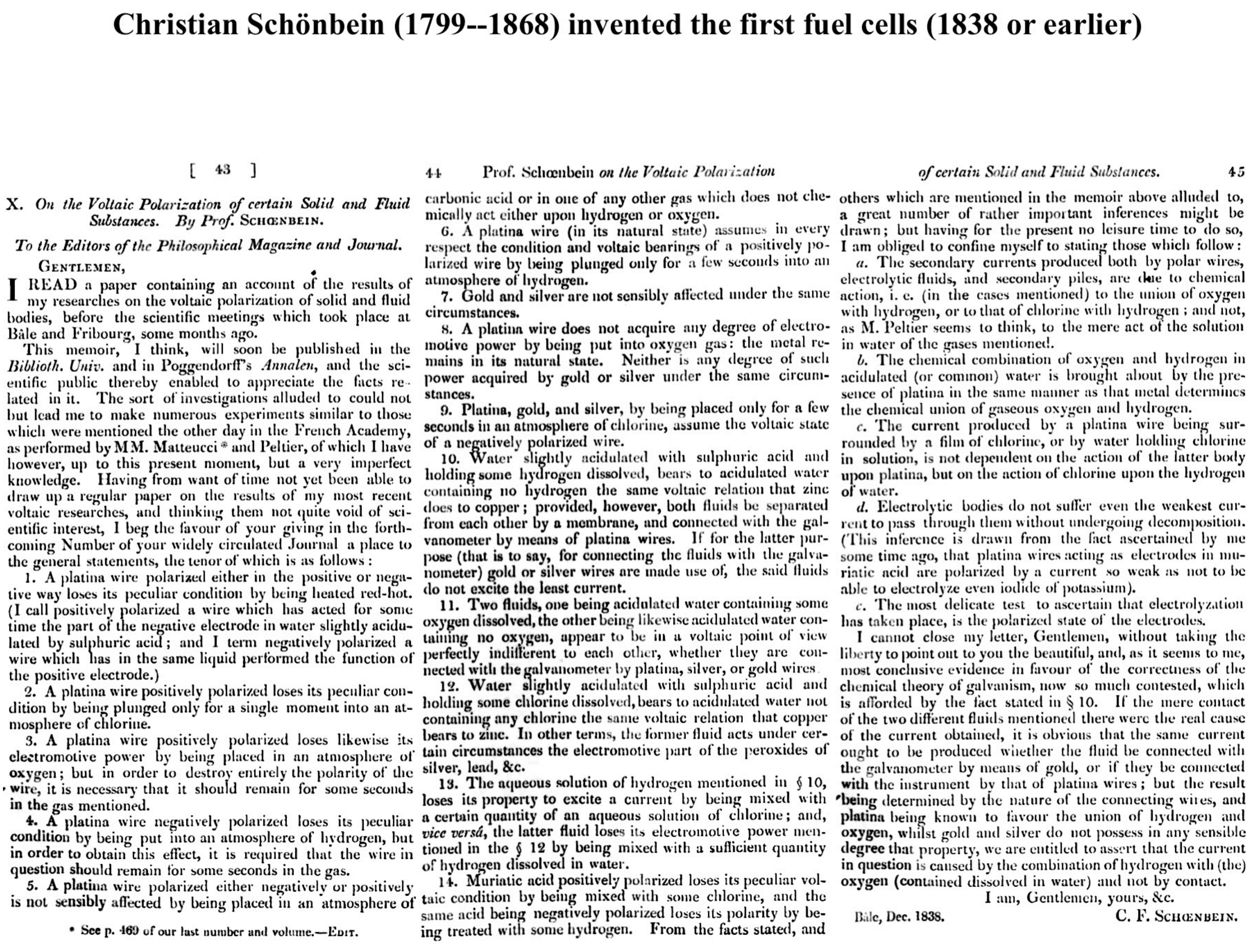
Karl Kordesch and many other German-speaking experts on advanced battery and fuel cell technologies were also transferred along with all of that information.

In addition to battery and fuel cell technologies, many other physical-chemistry-based technologies were transferred too, such as physical methods of making chemical measurements. See for example:

BIOS 1007. *Instrumentation and Control in the German Chemical Industry.* [Magnetic oxygen recorder, CO_2 recorder, etc.]

BIOS 1321. *Control Instruments in the German Chemical Industry.* [Chemical control in production, infrared chemical analyzer, etc.]

FIAT 708. *A Survey of the Use of Infra-Red Spectra in Chemical Analysis in Germany.*



Christian Schönbein (1799--1868) invented the first fuel cells (1838 or earlier)

[43]

X. *On the Voltaic Polarization of certain Solid and Fluid Substances. By Prof.* SCHŒNBEIN.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

I READ a paper containing an account of the results of my researches on the voltaic polarization of solid and fluid bodies, before the scientific meetings which took place at Bâle and Fribourg, some months ago.

This memoir, I think, will soon be published in the *Biblioth. Univ.* and in Poggendorff's *Annalen*, and the scientific public thereby enabled to appreciate the facts related in it. The sort of investigations alluded to could not but lead me to make numerous experiments similar to those which were mentioned the other day in the French Academy, as performed by MM. Matteucci* and Peltier, of which I have however, up to this present moment, but a very imperfect knowledge. Having from want of time not yet been able to draw up a regular paper on the results of my most recent voltaic researches, and thinking them not quite void of scientific interest, I beg the favour of your giving in the forthcoming Number of your widely circulated Journal a place to the general statements, the tenor of which is as follows:

1. A platina wire polarized either in the positive or negative way loses its peculiar condition by being heated red-hot. (I call positively polarized a wire which has acted for some time the part of the negative electrode in water slightly acidulated by sulphuric acid; and I term negatively polarized a wire which has in the same liquid performed the function of the positive electrode.)

2. A platina wire positively polarized loses its peculiar condition by being plunged only for a single moment into an atmosphere of chlorine.

3. A platina wire positively polarized loses likewise its electromotive power by being placed in an atmosphere of oxygen; but in order to destroy entirely the polarity of the wire, it is necessary that it should remain for some seconds in the gas mentioned.

4. A platina wire negatively polarized loses its peculiar condition by being put into an atmosphere of hydrogen, but in order to obtain this effect, it is required that the wire in question should remain for some seconds in the gas.

5. A platina wire polarized either negatively or positively is not sensibly affected by being placed in an atmosphere of carbonic acid or in one of any other gas which does not chemically act either upon hydrogen or oxygen.

6. A platina wire (in its natural state) assumes in every respect the condition and voltaic bearings of a positively polarized wire by being plunged only for a few seconds into an atmosphere of hydrogen.

7. Gold and silver are not sensibly affected under the same circumstances.

8. A platina wire does not acquire any degree of electromotive power by being put into oxygen gas: the metal remains in its natural state. Neither is any degree of such power acquired by gold or silver under the same circumstances.

9. Platina, gold, and silver, by being placed only for a few seconds in an atmosphere of chlorine, assume the voltaic state of a negatively polarized wire.

10. Water slightly acidulated with sulphuric acid and holding some hydrogen dissolved, bears to acidulated water containing no hydrogen the same voltaic relation that zinc does to copper; provided, however, both fluids be separated from each other by a membrane, and connected with the galvanometer by means of platina wires. If for the latter purpose (that is to say, for connecting the fluids with the galvanometer) gold or silver wires are made use of, the said fluids do not excite the least current.

11. Two fluids, one being acidulated water containing some oxygen dissolved, the other being likewise acidulated water containing no oxygen, appear to be in a voltaic point of view perfectly indifferent to each other, whether they are connected with the galvanometer by platina, silver, or gold wires.

12. Water slightly acidulated with sulphuric acid and holding some chlorine dissolved, bears to acidulated water not containing any chlorine the same voltaic relation that copper bears to zinc. In other terms, the former fluid acts under certain circumstances the electromotive part of the peroxides of silver, lead, &c.

13. The aqueous solution of hydrogen mentioned in § 10, loses its property to excite a current by being mixed with a certain quantity of an aqueous solution of chlorine; and, *vice versâ*, the latter fluid loses its electromotive power mentioned in the § 12 by being mixed with a sufficient quantity of hydrogen dissolved in water.

14. Muriatic acid positively polarized loses its peculiar voltaic condition by being mixed with some chlorine, and the same acid being negatively polarized loses its polarity by being treated with some hydrogen. From the facts stated, and others which are mentioned in the memoir above alluded to, a great number of rather important inferences might be drawn; but having for the present no leisure time to do so, I am obliged to confine myself to stating those which follow:

a. The secondary currents produced both by polar wires, electrolytic fluids, and secondary piles, are due to chemical action, i. e. (in the cases mentioned) to the union of oxygen with hydrogen, or to that of chlorine with hydrogen; and not, as M. Peltier seems to think, to the mere act of the solution in water of the gases mentioned.

b. The chemical combination of oxygen and hydrogen in acidulated (or common) water is brought about by the presence of platina in the same manner as that metal determines the chemical union of gaseous oxygen and hydrogen.

c. The current produced by a platina wire being surrounded by a film of chlorine, or by water holding chlorine in solution, is not dependent on the action of the latter body upon platina, but on the action of chlorine upon the hydrogen of water.

d. Electrolytic bodies do not suffer even the weakest current to pass through them without undergoing decomposition. (This inference is drawn from the fact ascertained by me some time ago, that platina wires acting as electrodes in muriatic acid are polarized by a current so weak as not to be able to electrolyze even iodide of potassium).

e. The most delicate test to ascertain that electrolyzation has taken place, is the polarized state of the electrodes.

I cannot close my letter, Gentlemen, without taking the liberty to point out to you the beautiful, and, as it seems to me, most conclusive evidence in favour of the correctness of the chemical theory of galvanism, now so much contested, which is afforded by the fact stated in § 10. If the mere contact of the two different fluids mentioned there were the real cause of the current obtained, it is obvious that the same current ought to be produced whether the fluid be connected with the galvanometer by means of gold, or if they be connected with the instrument by that of platina wires; but the result being determined by the nature of the connecting wires, and platina being known to favour the union of hydrogen and oxygen, whilst gold and silver do not possess in any sensible degree that property, we are entitled to assert that the current in question is caused by the combination of hydrogen with (the) oxygen (contained dissolved in water) and not by contact.

I am, Gentlemen, yours, &c.

Bâle, Dec. 1838.

C. F. SCHŒNBEIN.

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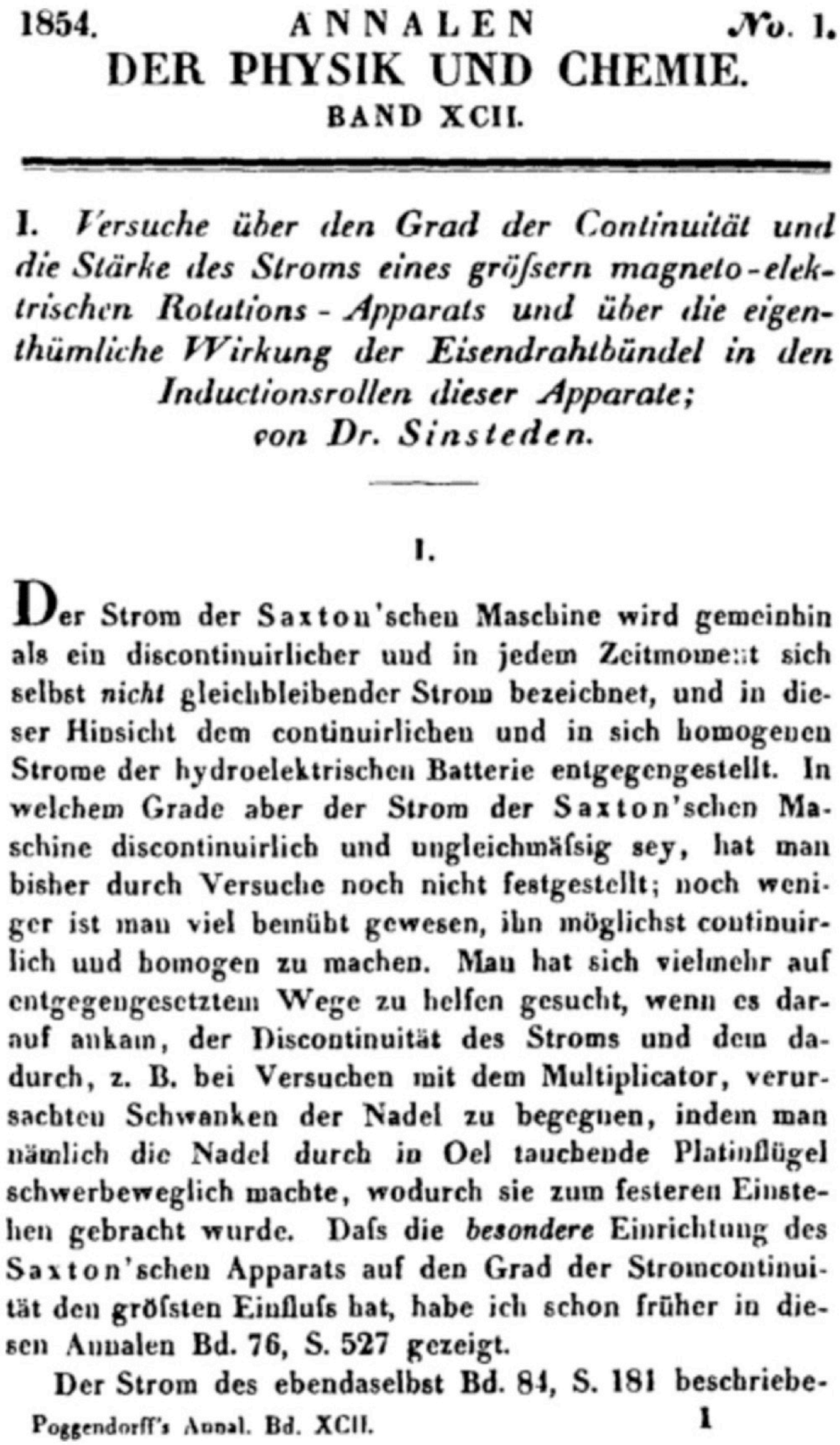
[*] See p. 469 of our last number and volume.—EDIT.

Figure 3.124: Christian Schönbein invented and demonstrated the first fuel cells in 1838 or earlier [Schönbein 1839].

Wilhelm Sinsteden (1803–1891) invented lead-acid rechargeable batteries (1854 or earlier)



1854. ANNALEN No. 1.
DER PHYSIK UND CHEMIE.
BAND XCII.

I. *Versuche über den Grad der Continuität und die Stärke des Stroms eines gröſsern magneto-elektrischen Rotations-Apparats und über die eigenthümliche Wirkung der Eisendrahtbündel in den Inductionsrollen dieser Apparate;*
von Dr. Sinsteden.

I.

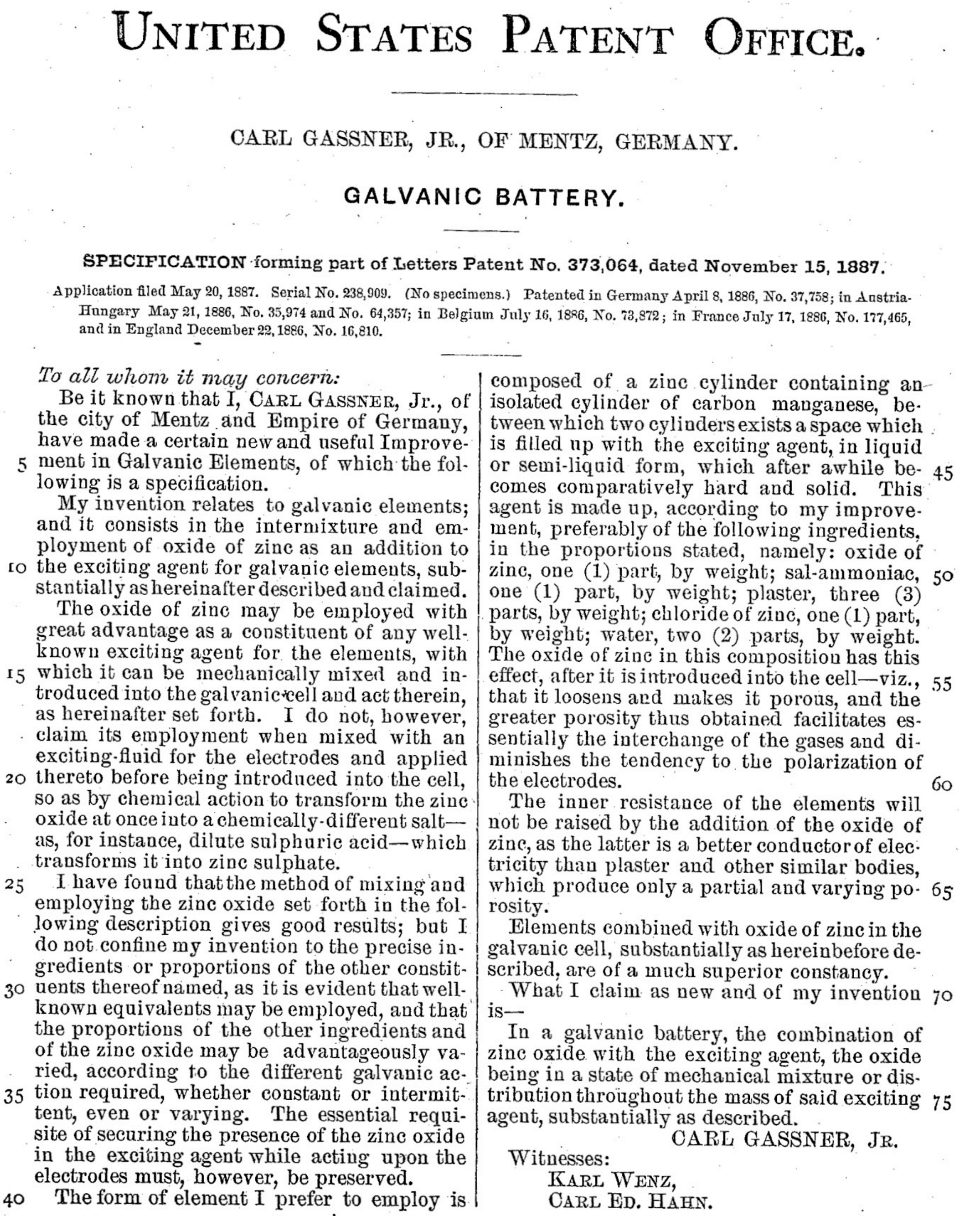
Der Strom der Saxton'schen Maschine wird gemeinhin als ein discontinuirlicher und in jedem Zeitmoment sich selbst *nicht* gleichbleibender Strom bezeichnet, und in dieser Hinsicht dem continuirlichen und in sich homogenen Strome der hydroelektrischen Batterie entgegengestellt. In welchem Grade aber der Strom der Saxton'schen Maschine discontinuirlich und ungleichmäſsig sey, hat man bisher durch Versuche noch nicht festgestellt; noch weniger ist man viel bemüht gewesen, ihn möglichst continuirlich und homogen zu machen. Man hat sich vielmehr auf entgegengesetztem Wege zu helfen gesucht, wenn es darauf ankam, der Discontinuität des Stroms und dem dadurch, z. B. bei Versuchen mit dem Multiplicator, verursachten Schwanken der Nadel zu begegnen, indem man nämlich die Nadel durch in Oel tauchende Platinflügel schwerbeweglich machte, wodurch sie zum festeren Einstehen gebracht wurde. Daſs die *besondere* Einrichtung des Saxton'schen Apparats auf den Grad der Stromcontinuität den gröſsten Einfluſs hat, habe ich schon früher in diesen Annalen Bd. 76, S. 527 gezeigt.

Der Strom des ebendaselbst Bd. 84, S. 181 beschriebe-

Poggendorff's Annal. Bd. XCII. 1

Figure 3.125: Wilhelm Sinsteden invented and demonstrated lead-acid rechargeable batteries in 1854 or earlier [Sinsteden 1854].

Carl Gassner (1855–1942) invented zinc-carbon dry batteries (1885)



UNITED STATES PATENT OFFICE.

CARL GASSNER, JR., OF MENTZ, GERMANY.

GALVANIC BATTERY.

SPECIFICATION forming part of Letters Patent No. 373,064, dated November 15, 1887.

Application filed May 20, 1887. Serial No. 238,909. (No specimens.) Patented in Germany April 8, 1886, No. 37,758; in Austria-Hungary May 21, 1886, No. 35,974 and No. 64,357; in Belgium July 16, 1886, No. 73,872; in France July 17, 1886, No. 177,465, and in England December 22, 1886, No. 16,810.

To all whom it may concern:

Be it known that I, CARL GASSNER, Jr., of the city of Mentz and Empire of Germany, have made a certain new and useful Improvement in Galvanic Elements, of which the following is a specification.

My invention relates to galvanic elements; and it consists in the intermixture and employment of oxide of zinc as an addition to the exciting agent for galvanic elements, substantially as hereinafter described and claimed.

The oxide of zinc may be employed with great advantage as a constituent of any well-known exciting agent for the elements, with which it can be mechanically mixed and introduced into the galvanic cell and act therein, as hereinafter set forth. I do not, however, claim its employment when mixed with an exciting-fluid for the electrodes and applied thereto before being introduced into the cell, so as by chemical action to transform the zinc oxide at once into a chemically-different salt—as, for instance, dilute sulphuric acid—which transforms it into zinc sulphate.

I have found that the method of mixing and employing the zinc oxide set forth in the following description gives good results; but I do not confine my invention to the precise ingredients or proportions of the other constituents thereof named, as it is evident that well-known equivalents may be employed, and that the proportions of the other ingredients and of the zinc oxide may be advantageously varied, according to the different galvanic action required, whether constant or intermittent, even or varying. The essential requisite of securing the presence of the zinc oxide in the exciting agent while acting upon the electrodes must, however, be preserved.

The form of element I prefer to employ is composed of a zinc cylinder containing an isolated cylinder of carbon manganese, between which two cylinders exists a space which is filled up with the exciting agent, in liquid or semi-liquid form, which after awhile becomes comparatively hard and solid. This agent is made up, according to my improvement, preferably of the following ingredients, in the proportions stated, namely: oxide of zinc, one (1) part, by weight; sal-ammoniac, one (1) part, by weight; plaster, three (3) parts, by weight; chloride of zinc, one (1) part, by weight; water, two (2) parts, by weight. The oxide of zinc in this composition has this effect, after it is introduced into the cell—viz., that it loosens and makes it porous, and the greater porosity thus obtained facilitates essentially the interchange of the gases and diminishes the tendency to the polarization of the electrodes.

The inner resistance of the elements will not be raised by the addition of the oxide of zinc, as the latter is a better conductor of electricity than plaster and other similar bodies, which produce only a partial and varying porosity.

Elements combined with oxide of zinc in the galvanic cell, substantially as hereinbefore described, are of a much superior constancy.

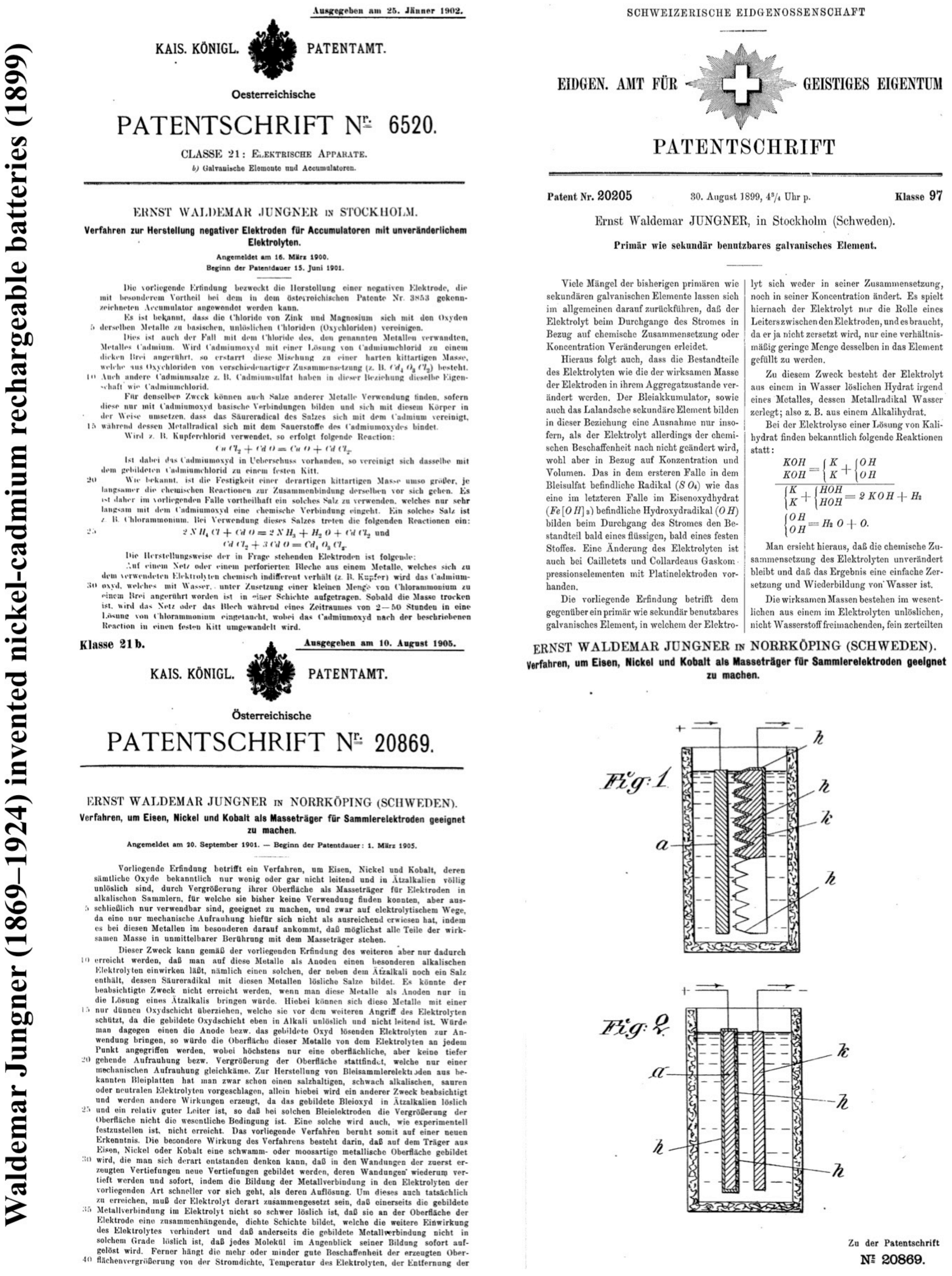
What I claim as new and of my invention is—

In a galvanic battery, the combination of zinc oxide with the exciting agent, the oxide being in a state of mechanical mixture or distribution throughout the mass of said exciting agent, substantially as described.

CARL GASSNER, JR.

Witnesses:
KARL WENZ,
CARL ED. HAHN.

Figure 3.126: Carl Gassner demonstrated and patented zinc-carbon dry batteries in 1885.



Waldemar Jungner (1869–1924) invented nickel-cadmium rechargeable batteries (1899)

Ausgegeben am 25. Jänner 1902.

KAIS. KÖNIGL. PATENTAMT.

Oesterreichische

PATENTSCHRIFT Nr. 6520.

CLASSE 21: ELEKTRISCHE APPARATE.
b) Galvanische Elemente und Accumulatoren.

ERNST WALDEMAR JUNGNER IN STOCKHOLM.

Verfahren zur Herstellung negativer Elektroden für Accumulatoren mit unveränderlichem Elektrolyten.

Angemeldet am 16. März 1900.
Beginn der Patentdauer 15. Juni 1901.

Die vorliegende Erfindung bezweckt die Herstellung einer negativen Elektrode, die mit besonderem Vortheil bei dem in dem österreichischen Patente Nr. 3853 gekennzeichneten Accumulator angewendet werden kann.

Es ist bekannt, dass die Chloride von Zink und Magnesium sich mit den Oxyden derselben Metalle zu basischen, unlöslichen Chloriden (Oxychloriden) vereinigen.

Dies ist auch der Fall mit dem Chloride des, den genannten Metallen verwandten, Metalles Cadmium. Wird Cadmiumoxyd mit einer Lösung von Cadmiumchlorid zu einem dicken Brei angerührt, so erstarrt diese Mischung zu einer harten kittartigen Masse, welche aus Oxychloriden von verschiedenartiger Zusammensetzung (z. B. $Cd_4O_3Cl_2$) besteht. Auch andere Cadmiumsalze z. B. Cadmiumsulfat haben in dieser Beziehung dieselbe Eigenschaft wie Cadmiumchlorid.

Für denselben Zweck können auch Salze anderer Metalle Verwendung finden, sofern diese nur mit Cadmiumoxyd basische Verbindungen bilden und sich mit diesem Körper in der Weise umsetzen, dass das Säureradical des Salzes sich mit dem Cadmium vereinigt, während dessen Metallradical sich mit dem Sauerstoffe des Cadmiumoxydes bindet.

Wird z. B. Kupferchlorid verwendet, so erfolgt folgende Reaction:

$$CuCl_2 + CdO = CuO + CdCl_2.$$

Ist dabei das Cadmiumoxyd in Ueberschuss vorhanden, so vereinigt sich dasselbe mit dem gebildeten Cadmiumchlorid zu einem festen Kitt.

Wie bekannt, ist die Festigkeit einer derartigen kittartigen Masse umso größer, je langsamer die chemischen Reactionen zur Zusammenbindung derselben vor sich gehen. Es ist daher im vorliegenden Falle vortheilhaft ein solches Salz zu verwenden, welches nur sehr langsam mit dem Cadmiumoxyd eine chemische Verbindung eingeht. Ein solches Salz ist z. B. Chlorammonium. Bei Verwendung dieses Salzes treten die folgenden Reactionen ein:

$$2\,NH_4Cl + CdO = 2\,NH_3 + H_2O + CdCl_2 \text{ und}$$
$$CdCl_2 + 3\,CdO = Cd_4O_3Cl_2.$$

Die Herstellungsweise der in Frage stehenden Elektroden ist folgende:

Auf einem Netz oder einem perforierten Bleche aus einem Metalle, welches sich zu dem verwendeten Elektrolyten chemisch indifferent verhält (z. B. Kupfer) wird das Cadmiumoxyd, welches mit Wasser, unter Zusetzung einer kleinen Menge von Chlorammonium zu einem Brei angerührt worden ist in einer Schichte aufgetragen. Sobald die Masse trocken ist, wird das Netz oder das Blech während eines Zeitraumes von 2—50 Stunden in eine Lösung von Chlorammonium eingetaucht, wobei das Cadmiumoxyd nach der beschriebenen Reaction in einen festen Kitt umgewandelt wird.

Klasse 21 b.

Ausgegeben am 10. August 1905.

KAIS. KÖNIGL. PATENTAMT.

Österreichische

PATENTSCHRIFT Nr. 20869.

ERNST WALDEMAR JUNGNER IN NORRKÖPING (SCHWEDEN).

Verfahren, um Eisen, Nickel und Kobalt als Masseträger für Sammlerelektroden geeignet zu machen.

Angemeldet am 20. September 1901. — Beginn der Patentdauer: 1. März 1905.

Vorliegende Erfindung betrifft ein Verfahren, um Eisen, Nickel und Kobalt, deren sämtliche Oxyde bekanntlich nur wenig oder gar nicht leitend und in Ätzalkalien völlig unlöslich sind, durch Vergrößerung ihrer Oberfläche als Masseträger für Elektroden in alkalischen Sammlern, für welche sie bisher keine Verwendung finden konnten, aber ausschließlich nur verwendbar sind, geeignet zu machen, und zwar auf elektrolytischem Wege, da eine nur mechanische Aufrauhung hiefür sich nicht als ausreichend erwiesen hat, indem es bei diesen Metallen im besonderen darauf ankommt, daß möglichst alle Teile der wirksamen Masse in unmittelbarer Berührung mit dem Masseträger stehen.

Dieser Zweck kann gemäß der vorliegenden Erfindung des weiteren aber nur dadurch erreicht werden, daß man auf diese Metalle als Anoden einen besonderen alkalischen Elektrolyten einwirken läßt, nämlich einen solchen, der neben dem Ätzalkali noch ein Salz enthält, dessen Säureradikal mit diesen Metallen lösliche Salze bildet. Es könnte der beabsichtigte Zweck nicht erreicht werden, wenn man diese Metalle als Anoden nur in die Lösung eines Ätzalkalis bringen würde. Hiebei können sich diese Metalle mit einer nur dünnen Oxydschicht überziehen, welche sie vor dem weiteren Angriff des Elektrolyten schützt, da die gebildete Oxydschicht eben in Alkali unlöslich und nicht leitend ist. Würde man dagegen einen die Anode bezw. das gebildete Oxyd lösenden Elektrolyten zur Anwendung bringen, so würde die Oberfläche dieser Metalle von dem Elektrolyten an jedem Punkt angegriffen werden, wobei höchstens nur eine oberflächliche, aber keine tiefer gehende Aufrauhung bezw. Vergrößerung der Oberfläche stattfindet, welche nur einer mechanischen Aufrauhung gleichkäme. Zur Herstellung von Bleisammlerelektroden aus bekannten Bleiplatten hat man zwar schon einen salzhaltigen, schwach alkalischen, sauren oder neutralen Elektrolyten vorgeschlagen, allein hiebei wird ein anderer Zweck beabsichtigt und werden andere Wirkungen erzeugt, da das gebildete Bleioxyd in Ätzalkalien löslich und ein relativ guter Leiter ist, so daß bei solchen Bleielektroden die Vergrößerung der Oberfläche nicht die wesentliche Bedingung ist. Eine solche wird auch, wie experimentell festzustellen ist, nicht erreicht. Das vorliegende Verfahren beruht somit auf einer neuen Erkenntnis. Die besondere Wirkung des Verfahrens besteht darin, daß auf dem Träger aus Eisen, Nickel oder Kobalt eine schwamm- oder moosartige metallische Oberfläche gebildet wird, die man sich derart entstanden denken kann, daß in den Wandungen der zuerst erzeugten Vertiefungen neue Vertiefungen gebildet werden, deren Wandungen wiederum vertieft werden und sofort, indem die Bildung der Metallverbindung in den Elektrolyten der vorliegenden Art schneller vor sich geht, als deren Auflösung. Um dieses auch tatsächlich zu erreichen, muß der Elektrolyt derart zusammengesetzt sein, daß einerseits die gebildete Metallverbindung im Elektrolyt nicht so schwer löslich ist, daß sie an der Oberfläche der Elektrode eine zusammenhängende, dichte Schichte bildet, welche die weitere Einwirkung des Elektrolytes verhindert und daß anderseits die gebildete Metallverbindung nicht in solchem Grade löslich ist, daß jedes Molekül im Augenblick seiner Bildung sofort aufgelöst wird. Ferner hängt die mehr oder minder gute Beschaffenheit der erzeugten Oberflächenvergrößerung von der Stromdichte, Temperatur des Elektrolyten, der Entfernung der

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SCHWEIZERISCHE EIDGENOSSENSCHAFT

EIDGEN. AMT FÜR GEISTIGES EIGENTUM

PATENTSCHRIFT

Patent Nr. 20205 30. August 1899, $4^3/_4$ Uhr p. **Klasse 97**

Ernst Waldemar JUNGNER, in Stockholm (Schweden).

Primär wie sekundär benutzbares galvanisches Element.

Viele Mängel der bisherigen primären wie sekundären galvanischen Elemente lassen sich im allgemeinen darauf zurückführen, daß der Elektrolyt beim Durchgange des Stromes in Bezug auf chemische Zusammensetzung oder Koncentration Veränderungen erleidet.

Hieraus folgt auch, dass die Bestandteile des Elektrolyten wie die der wirksamen Masse der Elektroden in ihrem Aggregatzustande verändert werden. Der Bleiakkumulator, sowie auch das Lalandsche sekundäre Element bilden in dieser Beziehung eine Ausnahme nur insofern, als der Elektrolyt allerdings der chemischen Beschaffenheit nach nicht geändert wird, wohl aber in Bezug auf Konzentration und Volumen. Das in dem ersteren Falle in dem Bleisulfat befindliche Radikal (SO_4) wie das eine im letzteren Falle im Eisenoxydhydrat ($Fe[OH]_3$) befindliche Hydroxydradikal (OH) bilden beim Durchgang des Stromes den Bestandteil bald eines flüssigen, bald eines festen Stoffes. Eine Änderung des Elektrolyten ist auch bei Cailletets und Collardeaus Gaskompressionselementen mit Platinelektroden vorhanden.

Die vorliegende Erfindung betrifft dem gegenüber ein primär wie sekundär benutzbares galvanisches Element, in welchem der Elektrolyt sich weder in seiner Zusammensetzung, noch in seiner Koncentration ändert. Es spielt hiernach der Elektrolyt nur die Rolle eines Leiters zwischen den Elektroden, und es braucht, da er ja nicht zersetzt wird, nur eine verhältnismäßig geringe Menge desselben in das Element gefüllt zu werden.

Zu diesem Zweck besteht der Elektrolyt aus einem in Wasser löslichen Hydrat irgend eines Metalles, dessen Metallradikal Wasser zerlegt; also z. B. aus einem Alkalihydrat.

Bei der Elektrolyse einer Lösung von Kalihydrat finden bekanntlich folgende Reaktionen statt:

$$\begin{array}{l}\begin{matrix}KOH\\KOH\end{matrix}=\left\{\begin{matrix}K\\K\end{matrix}\right.+\left\{\begin{matrix}OH\\OH\end{matrix}\right.\\ \hline \left\{\begin{matrix}K\\K\end{matrix}\right.+\left\{\begin{matrix}HOH\\HOH\end{matrix}\right.=2\,KOH+H_2\\ \left\{\begin{matrix}OH\\OH\end{matrix}\right.=H_2O+O.\end{array}$$

Man ersieht hieraus, daß die chemische Zusammensetzung des Elektrolyten unverändert bleibt und daß das Ergebnis eine einfache Zersetzung und Wiederbildung von Wasser ist.

Die wirksamen Massen bestehen im wesentlichen aus einem im Elektrolyten unlöslichen, nicht Wasserstoff freimachenden, fein zerteilten

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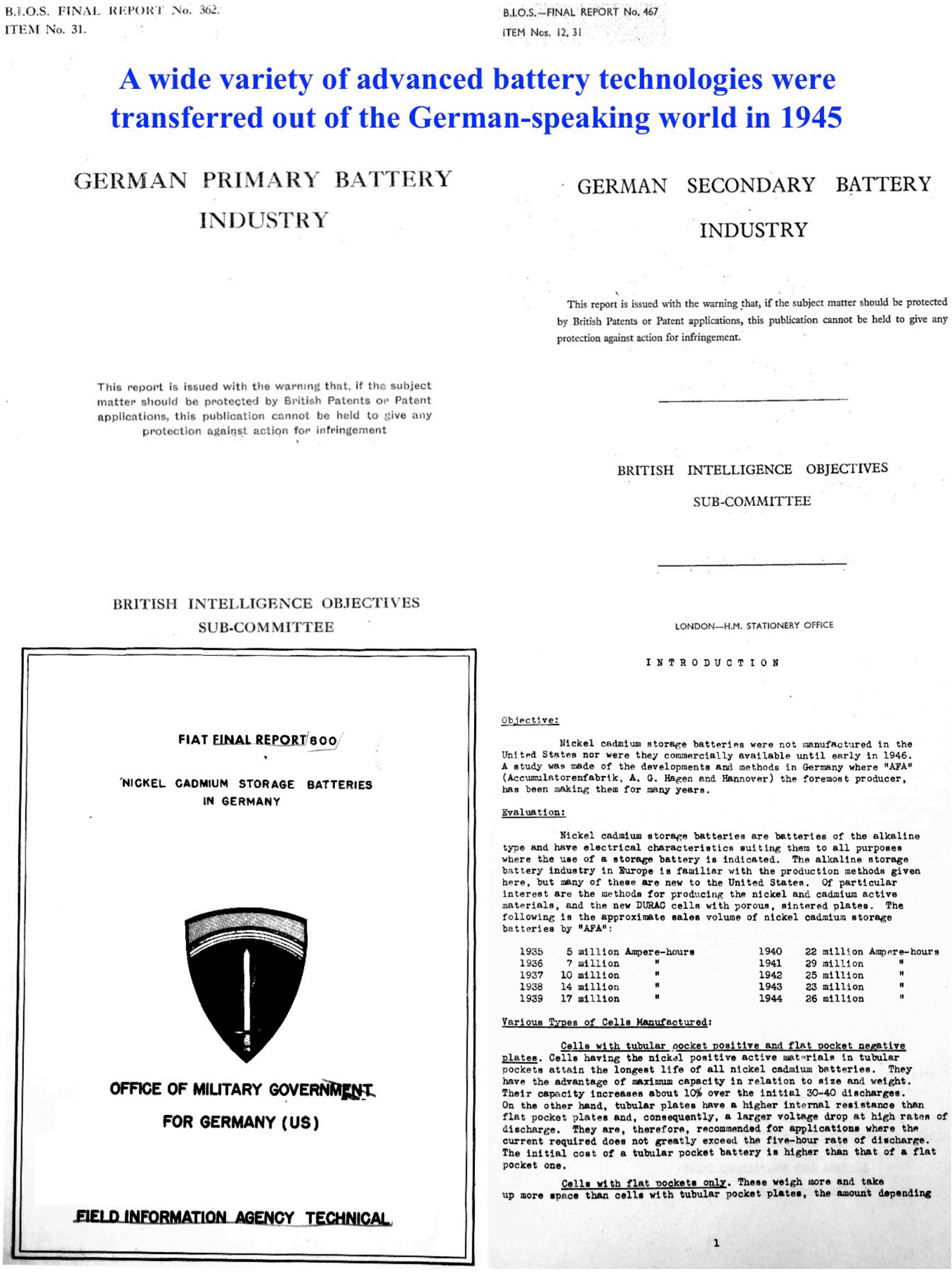
ERNST WALDEMAR JUNGNER IN NORRKÖPING (SCHWEDEN).

Verfahren, um Eisen, Nickel und Kobalt als Masseträger für Sammlerelektroden geeignet zu machen.

Zu der Patentschrift
Nr. 20869.

Figure 3.127: Waldemar Jungner invented nickel-cadmium rechargeable batteries in 1899.



A wide variety of advanced battery technologies were transferred out of the German-speaking world in 1945

B.I.O.S. FINAL REPORT No. 362.
ITEM No. 31.

GERMAN PRIMARY BATTERY
INDUSTRY

This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

B.I.O.S.—FINAL REPORT No. 467
ITEM Nos. 12, 31

GERMAN SECONDARY BATTERY
INDUSTRY

This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement.

BRITISH INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

FIAT FINAL REPORT 800

NICKEL CADMIUM STORAGE BATTERIES
IN GERMANY

OFFICE OF MILITARY GOVERNMENT
FOR GERMANY (US)

FIELD INFORMATION AGENCY TECHNICAL

INTRODUCTION

Objective:

Nickel cadmium storage batteries were not manufactured in the United States nor were they commercially available until early in 1946. A study was made of the developments and methods in Germany where "AFA" (Accumulatorenfabrik, A. G. Hagen and Hannover) the foremost producer, has been making them for many years.

Evaluation:

Nickel cadmium storage batteries are batteries of the alkaline type and have electrical characteristics suiting them to all purposes where the use of a storage battery is indicated. The alkaline storage battery industry in Europe is familiar with the production methods given here, but many of these are new to the United States. Of particular interest are the methods for producing the nickel and cadmium active materials, and the new DURAC cells with porous, sintered plates. The following is the approximate sales volume of nickel cadmium storage batteries by "AFA":

1935	5 million Ampere-hours	1940	22 million Ampere-hours
1936	7 million "	1941	29 million "
1937	10 million "	1942	25 million "
1938	14 million "	1943	23 million "
1939	17 million "	1944	26 million "

Various Types of Cells Manufactured:

Cells with tubular pocket positive and flat pocket negative plates. Cells having the nickel positive active materials in tubular pockets attain the longest life of all nickel cadmium batteries. They have the advantage of maximum capacity in relation to size and weight. Their capacity increases about 10% over the initial 30-40 discharges. On the other hand, tubular plates have a higher internal resistance than flat pocket plates and, consequently, a larger voltage drop at high rates of discharge. They are, therefore, recommended for applications where the current required does not greatly exceed the five-hour rate of discharge. The initial cost of a tubular pocket battery is higher than that of a flat pocket one.

Cells with flat pockets only. These weigh more and take up more space than cells with tubular pocket plates, the amount depending

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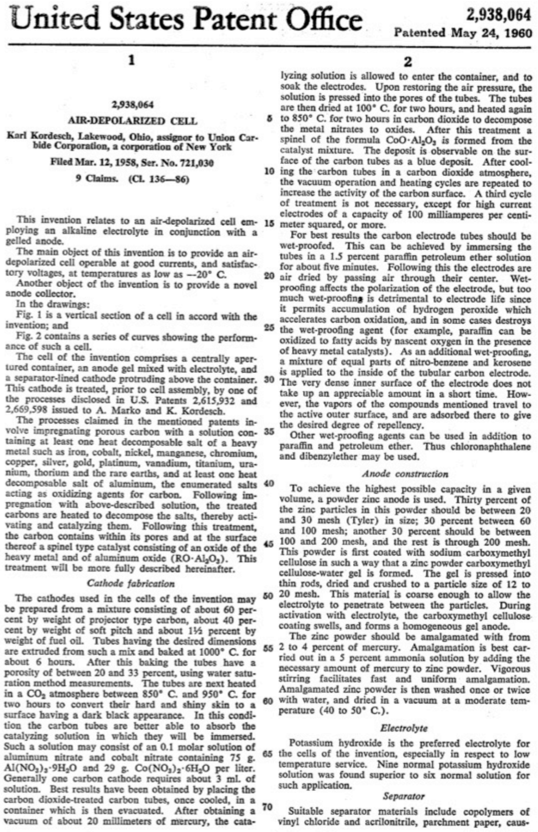
Figure 3.128: A wide variety of advanced battery technologies were transferred out of the German-speaking world in 1945, as shown by numerous BIOS, CIOS, FIAT, NavTecMisEu, and other reports.

Karl Kordesch (1922–2011) invented alkaline dry batteries (1957 or earlier)



United States Patent Office

2,938,064
Patented May 24, 1960

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2,938,064
AIR-DEPOLARIZED CELL
Karl Kordesch, Lakewood, Ohio, assignor to Union Carbide Corporation, a corporation of New York
Filed Mar. 12, 1958, Ser. No. 721,030
9 Claims. (Cl. 136—86)

This invention relates to an air-depolarized cell employing an alkaline electrolyte in conjunction with a gelled anode.

The main object of this invention is to provide an air-depolarized cell operable at good currents, and satisfactory voltages, at temperatures as low as —20° C.

Another object of the invention is to provide a novel anode collector.

In the drawings:

Fig. 1 is a vertical section of a cell in accord with the invention; and

Fig. 2 contains a series of curves showing the performance of such a cell.

The cell of the invention comprises a centrally apertured container, an anode gel mixed with electrolyte, and a separator-lined cathode protruding above the container. This cathode is treated, prior to cell assembly, by one of the processes disclosed in U.S. Patents 2,615,932 and 2,669,598 issued to A. Marko and K. Kordesch.

The processes claimed in the mentioned patents involve impregnating porous carbon with a solution containing at least one heat decomposable salt of a heavy metal such as iron, cobalt, nickel, manganese, chromium, copper, silver, gold, platinum, vanadium, titanium, uranium, thorium and the rare earths, and at least one heat decomposable salt of aluminum, the enumerated salts acting as oxidizing agents for carbon. Following impregnation with above-described solution, the treated carbons are heated to decompose the salts, thereby activating and catalyzing them. Following this treatment, the carbon contains within its pores and at the surface thereof a spinel type catalyst consisting of an oxide of the heavy metal and of aluminum oxide ($RO \cdot Al_2O_3$). This treatment will be more fully described hereinafter.

Cathode fabrication

The cathodes used in the cells of the invention may be prepared from a mixture consisting of about 60 percent by weight of projector type carbon, about 40 percent by weight of soft pitch and about 1½ percent by weight of fuel oil. Tubes having the desired dimensions are extruded from such a mix and baked at 1000° C. for about 6 hours. After this baking the tubes have a porosity of between 20 and 33 percent, using water saturation method measurements. The tubes are next heated in a CO_2 atmosphere between 850° C. and 950° C. for two hours to convert their hard and shiny skin to a surface having a dark black appearance. In this condition the carbon tubes are better able to absorb the catalyzing solution in which they will be immersed. Such a solution may consist of an 0.1 molar solution of aluminum nitrate and cobalt nitrate containing 75 g. $Al(NO_3)_3 \cdot 9H_2O$ and 29 g. $Co(NO_3)_2 \cdot 6H_2O$ per liter. Generally one carbon cathode requires about 3 ml. of solution. Best results have been obtained by placing the carbon dioxide-treated carbon tubes, once cooled, in a container which is then evacuated. After obtaining a vacuum of about 20 millimeters of mercury, the catalyzing solution is allowed to enter the container, and to soak the electrodes. Upon restoring the air pressure, the solution is pressed into the pores of the tubes. The tubes are then dried at 100° C. for two hours, and heated again to 850° C. for two hours in carbon dioxide to decompose the metal nitrates to oxides. After this treatment a spinel of the formula $CoO \cdot Al_2O_3$ is formed from the catalyst mixture. The deposit is observable on the surface of the carbon tubes as a blue deposit. After cooling the carbon tubes in a carbon dioxide atmosphere, the vacuum operation and heating cycles are repeated to increase the activity of the carbon surface. A third cycle of treatment is not necessary, except for high current electrodes of a capacity of 100 milliamperes per centimeter squared, or more.

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For best results the carbon electrode tubes should be wet-proofed. This can be achieved by immersing the tubes in a 1.5 percent paraffin petroleum ether solution for about five minutes. Following this the electrodes are air dried by passing air through their center. Wet-proofing affects the polarization of the electrode, but too much wet-proofing is detrimental to electrode life since it permits accumulation of hydrogen peroxide which accelerates carbon oxidation, and in some cases destroys the wet-proofing agent (for example, paraffin can be oxidized to fatty acids by nascent oxygen in the presence of heavy metal catalysts). As an additional wet-proofing, a mixture of equal parts of nitro-benzene and kerosene is applied to the inside of the tubular carbon electrode. The very dense inner surface of the electrode does not take up an appreciable amount in a short time. However, the vapors of the compounds mentioned travel to the active outer surface, and are adsorbed there to give the desired degree of repellency.

Other wet-proofing agents can be used in addition to paraffin and petroleum ether. Thus chloronaphthalene and dibenzylether may be used.

Anode construction

To achieve the highest possible capacity in a given volume, a powder zinc anode is used. Thirty percent of the zinc particles in this powder should be between 20 and 30 mesh (Tyler) in size; 30 percent between 60 and 100 mesh; another 30 percent should be between 100 and 200 mesh, and the rest is through 200 mesh. This powder is first coated with sodium carboxymethyl cellulose in such a way that a zinc powder carboxymethyl cellulose-water gel is formed. The gel is pressed into thin rods, dried and crushed to a particle size of 12 to 20 mesh. This material is coarse enough to allow the electrolyte to penetrate between the particles. During activation with electrolyte, the carboxymethyl cellulose coating swells, and forms a homogeneous gel anode.

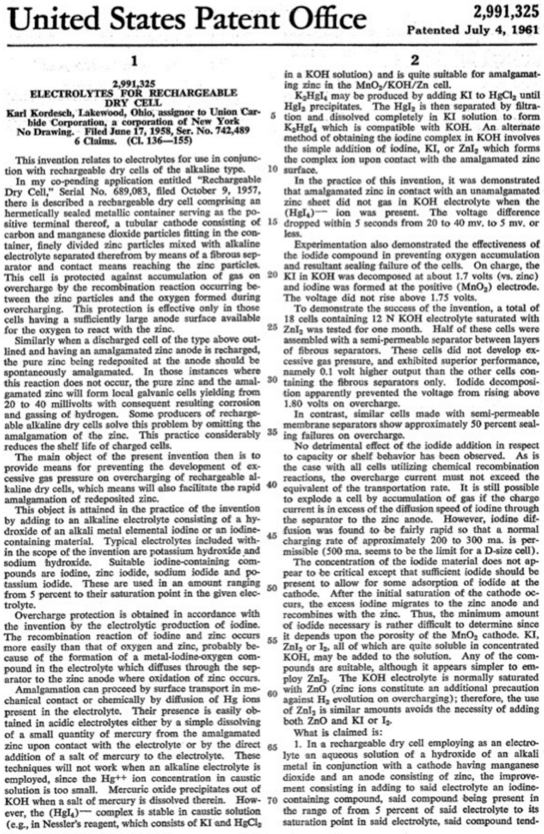
The zinc powder should be amalgamated with from 2 to 4 percent of mercury. Amalgamation is best carried out in a 5 percent ammonia solution by adding the necessary amount of mercury to zinc powder. Vigorous stirring facilitates fast and uniform amalgamation. Amalgamated zinc powder is then washed once or twice with water, and dried in a vacuum at a moderate temperature (40 to 50° C.).

Electrolyte

Potassium hydroxide is the preferred electrolyte for the cells of the invention, especially in respect to low temperature service. Nine normal potassium hydroxide solution was found superior to six normal solution for such application.

Separator

Suitable separator materials include copolymers of vinyl chloride and acrilonitrile, parchment paper, caus-



United States Patent Office

2,991,325
Patented July 4, 1961

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2,991,325
ELECTROLYTES FOR RECHARGEABLE DRY CELL
Karl Kordesch, Lakewood, Ohio, assignor to Union Carbide Corporation, a corporation of New York
No Drawing. Filed June 17, 1958, Ser. No. 742,489
6 Claims. (Cl. 136—155)

This invention relates to electrolytes for use in conjunction with rechargeable dry cells of the alkaline type.

In my co-pending application entitled "Rechargeable Dry Cell," Serial No. 689,083, filed October 9, 1957, there is described a rechargeable dry cell comprising an hermetically sealed metallic container serving as the positive terminal thereof, a tubular cathode consisting of carbon and manganese dioxide particles fitting in the container, finely divided zinc particles mixed with alkaline electrolyte separated therefrom by means of a fibrous separator and contact means reaching the zinc particles. This cell is protected against accumulation of gas on overcharge by the recombination reaction occurring between the zinc particles and the oxygen formed during overcharging. This protection is effective only in those cells having a sufficiently large anode surface available for the oxygen to react with the zinc.

Similarly when a discharged cell of the type above outlined and having an amalgamated zinc anode is recharged, the pure zinc being redeposited at the anode should be spontaneously amalgamated. In those instances where this reaction does not occur, the pure zinc and the amalgamated zinc will form local galvanic cells yielding from 20 to 40 millivolts with consequent resulting corrosion and gassing of hydrogen. Some producers of rechargeable alkaline dry cells solve this problem by omitting the amalgamation of the zinc. This practice considerably reduces the shelf life of charged cells.

The main object of the present invention then is to provide means for preventing the development of excessive gas pressure on overcharging of rechargeable alkaline dry cells, which means will also facilitate the rapid amalgamation of redeposited zinc.

This object is attained in the practice of the invention by adding to an alkaline electrolyte consisting of a hydroxide of an alkali metal elemental iodine or an iodine-containing material. Typical electrolytes included within the scope of the invention are potassium hydroxide and sodium hydroxide. Suitable iodine-containing compounds are iodine, zinc iodide, sodium iodide and potassium iodide. These are used in an amount ranging from 5 percent to their saturation point in the given electrolyte.

Overcharge protection is obtained in accordance with the invention by the electrolytic production of iodine. The recombination reaction of iodine and zinc occurs more easily than that of oxygen and zinc, probably because of the formation of a metal-iodine-oxygen compound in the electrolyte which diffuses through the separator to the zinc anode where oxidation of zinc occurs.

Amalgamation can proceed by surface transport in mechanical contact or chemically by diffusion of Hg ions present in the electrolyte. Their presence is easily obtained in acidic electrolytes either by a simple dissolving of a small quantity of mercury from the amalgamated zinc upon contact with the electrolyte or by the direct addition of a salt of mercury to the electrolyte. These techniques will not work when an alkaline electrolyte is employed, since the Hg^{++} ion concentration in caustic solution is too small. Mercuric oxide precipitates out of KOH when a salt of mercury is dissolved therein. However, the $(HgI_4)^{--}$ complex is stable in caustic solution (e.g., in Nessler's reagent, which consists of KI and $HgCl_2$ in a KOH solution) and is quite suitable for amalgamating zinc in the $MnO_2/KOH/Zn$ cell.

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K_2HgI_4 may be produced by adding KI to $HgCl_2$ until HgI_2 precipitates. The HgI_2 is then separated by filtration and dissolved completely in KI solution to form K_2HgI_4 which is compatible with KOH. An alternate method of obtaining the iodine complex in KOH involves the simple addition of iodine, KI, or ZnI_2 which forms the complex ion upon contact with the amalgamated zinc surface.

In the practice of this invention, it was demonstrated that amalgamated zinc in contact with an unamalgamated zinc sheet did not gas in KOH electrolyte when the $(HgI_4)^{--}$ ion was present. The voltage difference dropped within 5 seconds from 20 to 40 mv. to 5 mv. or less.

Experimentation also demonstrated the effectiveness of the iodide compound in preventing oxygen accumulation and resultant sealing failure of the cells. On charge, the KI in KOH was decomposed at about 1.7 volts (vs. zinc) and iodine was formed at the positive (MnO_2) electrode. The voltage did not rise above 1.75 volts.

To demonstrate the success of the invention, a total of 18 cells containing 12 N KOH electrolyte saturated with ZnI_2 was tested for one month. Half of these cells were assembled with a semi-permeable separator between layers of fibrous separators. These cells did not develop excessive gas pressure, and exhibited superior performance, namely 0.1 volt higher output than the other cells containing the fibrous separators only. Iodide decomposition apparently prevented the voltage from rising above 1.80 volts on overcharge.

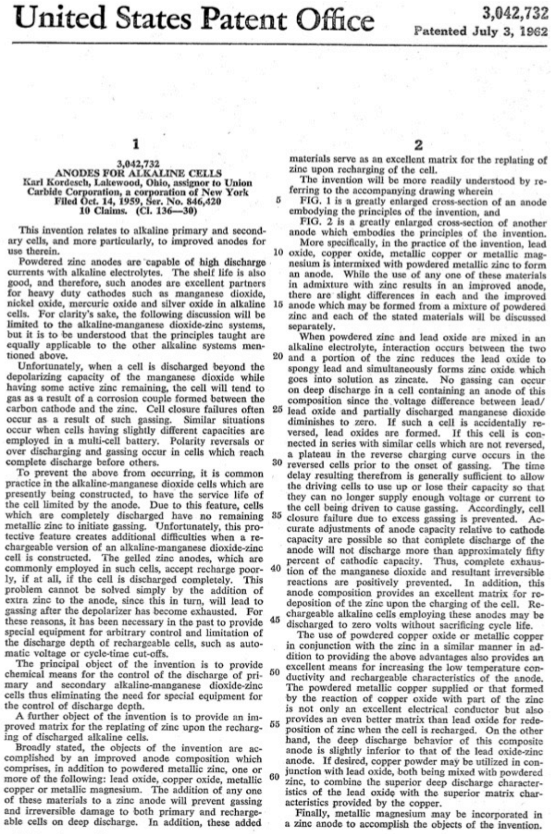
In contrast, similar cells made with semi-permeable membrane separators show approximately 50 percent sealing failures on overcharge.

No detrimental effect of the iodide addition in respect to capacity or shelf behavior has been observed. As is the case with all cells utilizing chemical recombination reactions, the overcharge current must not exceed the equivalent of the transportation rate. It is still possible to explode a cell by accumulation of gas if the charge current is in excess of the diffusion speed of iodine through the separator to the zinc anode. However, iodine diffusion was found to be fairly rapid so that a normal charging rate of approximately 200 to 300 ma. is permissible (500 ma. seems to be the limit for a D-size cell).

The concentration of the iodide material does not appear to be critical except that sufficient iodide should be present to allow for some adsorption of iodide at the cathode. After the initial saturation of the cathode occurs, the excess iodine migrates to the zinc anode and recombines with the zinc. Thus, the minimum amount of iodide necessary is rather difficult to determine since it depends upon the porosity of the MnO_2 cathode. KI, ZnI_2 or I_2, all of which are quite soluble in concentrated KOH, may be added to the solution. Any of the compounds are suitable, although it appears simpler to employ ZnI_2. The KOH electrolyte is normally saturated with ZnO (zinc ions constitute an additional precaution against H_2 evolution on overcharging); therefore, the use of ZnI_2 is similar amounts avoids the necessity of adding both ZnO and KI or I_2.

What is claimed is:

1. In a rechargeable dry cell employing as an electrolyte an aqueous solution of a hydroxide of an alkali metal in conjunction with a cathode having manganese dioxide and an anode consisting of zinc, the improvement consisting in adding to said electrolyte an iodine-containing compound, said compound being present in the range of from 5 percent of said electrolyte to its saturation point in said electrolyte, said compound tend-



United States Patent Office

3,042,732
Patented July 3, 1962

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3,042,732
ANODES FOR ALKALINE CELLS
Karl Kordesch, Lakewood, Ohio, assignor to Union Carbide Corporation, a corporation of New York
Filed Oct. 14, 1959, Ser. No. 846,420
10 Claims. (Cl. 136—30)

This invention relates to alkaline primary and secondary cells, and more particularly, to improved anodes for use therein.

Powdered zinc anodes are capable of high discharge currents with alkaline electrolytes. The shelf life is also good, and therefore, such anodes are excellent partners for heavy duty cathodes such as manganese dioxide, nickel oxide, mercuric oxide and silver oxide in alkaline cells. For clarity's sake, the following discussion will be limited to the alkaline-manganese dioxide-zinc systems, but it is to be understood that the principles taught are equally applicable to the other alkaline systems mentioned above.

Unfortunately, when a cell is discharged beyond the depolarizing capacity of the manganese dioxide while having some active zinc remaining, the cell will tend to gas as a result of a corrosion couple formed between the carbon cathode and the zinc. Cell closure failures often occur as a result of such gassing. Similar situations occur when cells having slightly different capacities are employed in a multi-cell battery. Polarity reversals or over discharging and gassing occur in cells which reach complete discharge before others.

To prevent the above from occurring, it is common practice in the alkaline-manganese dioxide cells which are presently being constructed, to have the service life of the cell limited by the anode. Due to this feature, cells which are completely discharged have no remaining metallic zinc to initiate gassing. Unfortunately, this protective feature creates additional difficulties when a rechargeable version of an alkaline-manganese dioxide-zinc cell is constructed. The gelled zinc anodes, which are commonly employed in such cells, accept recharge poorly, if at all, if the cell is discharged completely. This problem cannot be solved simply by the addition of extra zinc to the anode, since this in turn, will lead to gassing after the depolarizer has become exhausted. For these reasons, it has been necessary in the past to provide special equipment for arbitrary control and limitation of the discharge depth of rechargeable cells, such as automatic voltage or cycle-time cut-offs.

The principal object of the invention is to provide chemical means for the control of the discharge of primary and secondary alkaline-manganese dioxide-zinc cells thus eliminating the need for special equipment for the control of discharge depth.

A further object of the invention is to provide an improved matrix for the replating of zinc upon the recharging of discharged alkaline cells.

Broadly stated, the objects of the invention are accomplished by an improved anode composition which comprises, in addition to powdered metallic zinc, one or more of the following: lead oxide, copper oxide, metallic copper or metallic magnesium. The addition of any one of these materials to a zinc anode will prevent gassing and irreversible damage to both primary and rechargeable cells on deep discharge. In addition, these added

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materials serve as an excellent matrix for the replating of zinc upon recharging of the cell.

The invention will be more readily understood by referring to the accompanying drawing wherein

FIG. 1 is a greatly enlarged cross-section of an anode embodying the principles of the invention, and

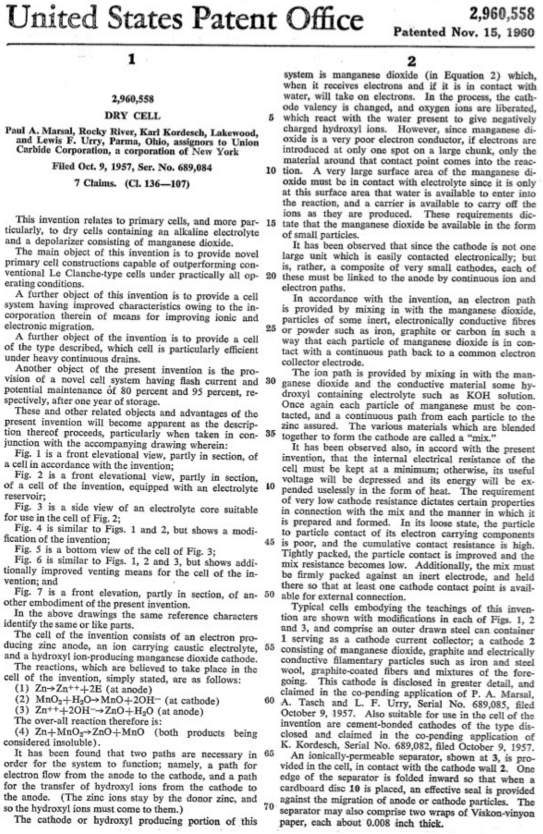
FIG. 2 is a greatly enlarged cross-section of another anode which embodies the principles of the invention.

More specifically, in the practice of the invention, lead oxide, copper oxide, metallic copper or metallic magnesium is intermixed with powdered metallic zinc to form an anode. While the use of any one of these materials in admixture with zinc results in an improved anode, there are slight differences in each and the improved anode which may be formed from a mixture of powdered zinc and each of the stated materials will be discussed separately.

When powdered zinc and lead oxide are mixed in an alkaline electrolyte, interaction occurs between the two and a portion of the zinc reduces the lead oxide to spongy lead and simultaneously forms zinc oxide which goes into solution as zincate. No gassing can occur on deep discharge in a cell containing an anode of this composition since the voltage difference between lead/lead oxide and partially discharged manganese dioxide diminishes to zero. If such a cell is accidentally reversed, lead oxides are formed. If this cell is connected in series with similar cells which are not reversed, a plateau in the reverse charging curve occurs in the reversed cells prior to the onset of gassing. The time delay resulting therefrom is generally sufficient to allow the driving cells to use up or lose their capacity so that they can no longer supply enough voltage or current to the cell being driven to cause gassing. Accordingly, cell closure failure due to excess gassing is prevented. Accurate adjustments of anode capacity relative to cathode capacity are possible so that complete discharge of the anode will not discharge more than approximately fifty percent of cathodic capacity. Thus, complete exhaustion of the manganese dioxide and resultant irreversible reactions are positively prevented. In addition, this anode composition provides an excellent matrix for redeposition of the zinc upon the charging of the cell. Rechargeable alkaline cells employing these anodes may be discharged to zero volts without sacrificing cycle life.

The use of powdered copper oxide or metallic copper in conjunction with the zinc in a similar manner in addition to providing the above advantages also provides an excellent means for increasing the low temperature conductivity and rechargeable characteristics of the anode. The powdered metallic copper supplied or that formed by the reaction of copper oxide with part of the zinc is not only an excellent electrical conductor but also provides an even better matrix than lead oxide for redeposition of zinc when the cell is recharged. On the other hand, the deep discharge behavior of this composite anode is slightly inferior to that of the lead oxide-zinc anode. If desired, copper powder may be utilized in conjunction with lead oxide, both being mixed with powdered zinc, to combine the superior deep discharge characteristics of the lead oxide with the superior matrix characteristics provided by the copper.

Finally, metallic magnesium may be incorporated in a zinc anode to accomplish the objects of the invention.



United States Patent Office

2,960,558
Patented Nov. 15, 1960

1

2,960,558
DRY CELL
Paul A. Marsal, Rocky River, Karl Kordesch, Lakewood, and Lewis F. Urry, Parma, Ohio, assignors to Union Carbide Corporation, a corporation of New York
Filed Oct. 9, 1957, Ser. No. 689,084
7 Claims. (Cl. 136—107)

This invention relates to primary cells, and more particularly, to dry cells containing an alkaline electrolyte and a depolarizer consisting of manganese dioxide.

The main object of this invention is to provide novel primary cell constructions capable of outperforming conventional Le Clanche-type cells under practically all operating conditions.

A further object of this invention is to provide a cell system having improved characteristics owing to the incorporation therein of means for improving ionic and electronic migration.

A further object of the invention is to provide a cell of the type described, which cell is particularly efficient under heavy continuous drains.

Another object of the present invention is the provision of a novel cell system having flash current and potential maintenance of 80 percent and 95 percent, respectively, after one year of storage.

These and other related objects and advantages of the present invention will become apparent as the description thereof proceeds, particularly when taken in conjunction with the accompanying drawing wherein:

Fig. 1 is a front elevational view, partly in section, of a cell in accordance with the invention;

Fig. 2 is a front elevational view, partly in section, of a cell of the invention, equipped with an electrolyte reservoir;

Fig. 3 is a side view of an electrolyte core suitable for use in the cell of Fig. 2;

Fig. 4 is similar to Figs. 1 and 2, but shows a modification of the invention;

Fig. 5 is a bottom view of the cell of Fig. 3;

Fig. 6 is similar to Figs. 1, 2 and 3, but shows additionally improved venting means for the cell of the invention; and

Fig. 7 is a front elevation, partly in section, of another embodiment of the present invention.

In the above drawings the same reference characters identify the same or like parts.

The cell of the invention consists of an electron producing zinc anode, an ion carrying caustic electrolyte, and a hydroxyl ion-producing manganese dioxide cathode.

The reactions, which are believed to take place in the cell of the invention, simply stated, are as follows:

(1) $Zn \rightarrow Zn^{++} + 2E$ (at anode)
(2) $MnO_2 + H_2O \rightarrow MnO + 2OH^-$ (at cathode)
(3) $Zn^{++} + 2OH^- \rightarrow ZnO + H_2O$ (at anode)

The over-all reaction therefore is:

(4) $Zn + MnO_2 \rightarrow ZnO + MnO$ (both products being considered insoluble).

It has been found that two paths are necessary in order for the system to function; namely, a path for electron flow from the anode to the cathode, and a path for the transfer of hydroxyl ions from the cathode to the anode. (The zinc ions stay by the donor zinc, and so the hydroxyl ions must come to them.)

The cathode or hydroxyl producing portion of this system is manganese dioxide (in Equation 2) which, when it receives electrons and if it is in contact with water, will take on electrons. In the process, the cathode valency is changed, and oxygen ions are liberated, which react with the water present to give negatively charged hydroxyl ions. However, since manganese dioxide is a very poor electron conductor, if electrons are introduced at only one spot on a large chunk, only the material around that contact point comes into the reaction. A very large surface area of the manganese dioxide must be in contact with electrolyte since it is only at this surface area that water is available to enter into the reaction, and a carrier is available to carry off the ions as they are produced. These requirements dictate that the manganese dioxide be available in the form of small particles.

2

It has been observed that since the cathode is not one large unit which is easily contacted electronically; but is, rather, a composite of very small cathodes, each of these must be linked to the anode by continuous ion and electron paths.

In accordance with the invention, an electron path is provided by mixing in with the manganese dioxide, particles of some inert, electronically conductive fibres or powder such as iron, graphite or carbon in such a way that each particle of manganese dioxide is in contact with a continuous path back to a common electron collector electrode.

The ion path is provided by mixing in with the manganese dioxide and the conductive material some hydroxyl containing electrolyte such as KOH solution. Once again each particle of manganese must be contacted, and a continuous path from each particle to the zinc assured. The various materials which are blended together to form the cathode are called a "mix."

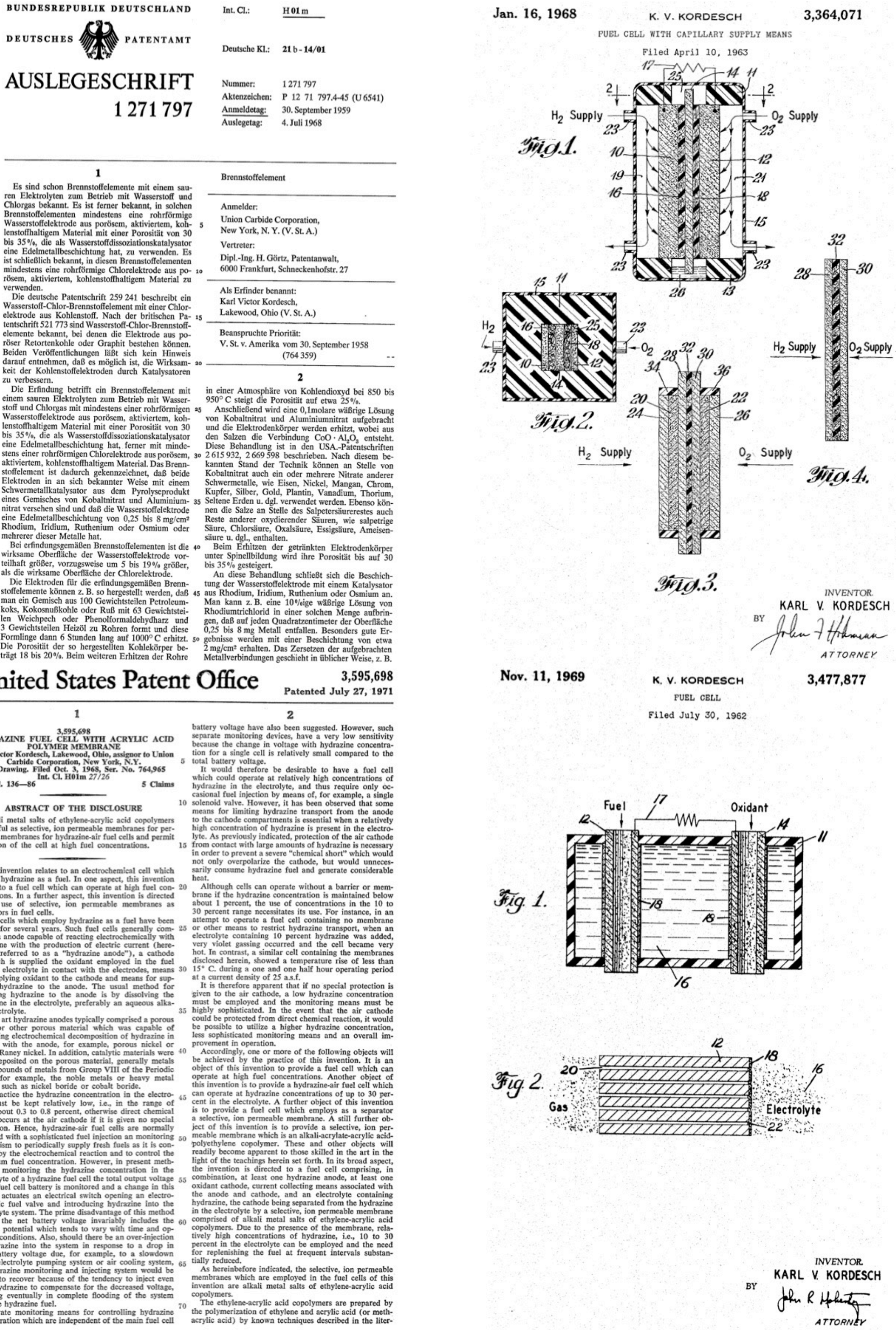
It has been observed also, in accord with the present invention, that the internal electrical resistance of the cell must be kept at a minimum; otherwise, its useful voltage will be depressed and its energy will be expended uselessly in the form of heat. The requirement of very low cathode resistance dictates certain properties in connection with the mix and the manner in which it is prepared and formed. In its loose state, the particle to particle contact of its electron carrying components is poor, and the cumulative contact resistance is high. Tightly packed, the particle contact is improved and the mix resistance becomes low. Additionally, the mix must be firmly packed against an inert electrode, and held there so that at least one cathode contact point is available for external connection.

Typical cells embodying the teachings of this invention are shown with modifications in each of Figs. 1, 2 and 3, and comprise an outer drawn steel can container 1 serving as a cathode current collector; a cathode 2 consisting of manganese dioxide, graphite and electrically conductive filamentary particles such as iron and steel wool, graphite-coated fibers and mixtures of the foregoing. This cathode is disclosed in greater detail, and claimed in the co-pending application of P. A. Marsal, A. Tasch and L. F. Urry, Serial No. 689,085, filed October 9, 1957. Also suitable for use in the cell of the invention are cement-bonded cathodes of the type disclosed and claimed in the co-pending application of K. Kordesch, Serial No. 689,082, filed October 9, 1957.

An ionically-permeable separator, shown at 3, is provided in the cell, in contact with the cathode wall 2. One edge of the separator is folded inward so that when a cardboard disc 10 is placed, an effective seal is provided against the migration of anode or cathode particles. The separator may also comprise two wraps of Viskon-vinyon paper, each about 0.008 inch thick.

Figure 3.129: Karl Kordesch, an Austrian battery expert who was brought to the United States as part of Operation Paperclip, invented alkaline dry batteries in 1957 or earlier.

Karl Kordesch (1922–2011) invented improved fuel cells



BUNDESREPUBLIK DEUTSCHLAND
DEUTSCHES PATENTAMT

AUSLEGESCHRIFT
1 271 797

Int. Cl.: H 01 m
Deutsche Kl.: 21 b - 14/01
Nummer: 1 271 797
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Anmeldetag: 30. September 1959
Auslegetag: 4. Juli 1968

Brennstoffelement

Anmelder:
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Beanspruchte Priorität:
V. St. v. Amerika vom 30. September 1958
(764 359)

1

Es sind schon Brennstoffelemente mit einem sauren Elektrolyten zum Betrieb mit Wasserstoff und Chlorgas bekannt. Es ist ferner bekannt, in solchen Brennstoffelementen mindestens eine rohrförmige Wasserstoffelektrode aus porösem, aktiviertem, kohlenstoffhaltigem Material mit einer Porosität von 30 bis 35%, die als Wasserstoffdissoziationskatalysator eine Edelmetallbeschichtung hat, zu verwenden. Es ist schließlich bekannt, in diesen Brennstoffelementen mindestens eine rohrförmige Chlorelektrode aus porösem, aktiviertem, kohlenstoffhaltigem Material zu verwenden.

Die deutsche Patentschrift 259 241 beschreibt ein Wasserstoff-Chlor-Brennstoffelement mit einer Chlorelektrode aus Kohlenstoff. Nach der britischen Patentschrift 521 773 sind Wasserstoff-Chlor-Brennstoffelemente bekannt, bei denen die Elektrode aus poröser Retortenkohle oder Graphit bestehen können. Beiden Veröffentlichungen läßt sich kein Hinweis darauf entnehmen, daß es möglich ist, die Wirksamkeit der Kohlenstoffelektroden durch Katalysatoren zu verbessern.

Die Erfindung betrifft ein Brennstoffelement mit einem sauren Elektrolyten zum Betrieb mit Wasserstoff und Chlorgas mit mindestens einer rohrförmigen Wasserstoffelektrode aus porösem, aktiviertem, kohlenstoffhaltigem Material mit einer Porosität von 30 bis 35%, die als Wasserstoffdissoziationskatalysator eine Edelmetallbeschichtung hat, ferner mit mindestens einer rohrförmigen Chlorelektrode aus porösem, aktiviertem, kohlenstoffhaltigem Material. Das Brennstoffelement ist dadurch gekennzeichnet, daß beide Elektroden in an sich bekannter Weise mit einem Schwermetallkatalysator aus dem Pyrolyseprodukt eines Gemisches von Kobaltnitrat und Aluminiumnitrat versehen sind und daß die Wasserstoffelektrode eine Edelmetallbeschichtung von 0,25 bis 8 mg/cm² Rhodium, Iridium, Ruthenium oder Osmium oder mehrerer dieser Metalle hat.

Bei erfindungsgemäßen Brennstoffelementen ist die wirksame Oberfläche der Wasserstoffelektrode vorteilhaft größer, vorzugsweise um 5 bis 19% größer, als die wirksame Oberfläche der Chlorelektrode.

Die Elektroden für die erfindungsgemäßen Brennstoffelemente können z. B. so hergestellt werden, daß man ein Gemisch aus 100 Gewichtsteilen Petroleumkoks, Kokosnußkohle oder Ruß mit 63 Gewichtsteilen Weichpech oder Phenolformaldehydharz und 3 Gewichtsteilen Heizöl zu Rohren formt und diese Formlinge dann 6 Stunden lang auf 1000° C erhitzt. Die Porosität der so hergestellten Kohlekörper beträgt 18 bis 20%. Beim weiteren Erhitzen der Rohre

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in einer Atmosphäre von Kohlendioxyd bei 850 bis 950° C steigt die Porosität auf etwa 25%.

Anschließend wird eine 0,1molare wäßrige Lösung von Kobaltnitrat und Aluminiumnitrat aufgebracht und die Elektrodenkörper werden erhitzt, wobei aus den Salzen die Verbindung $CoO \cdot Al_2O_3$ entsteht. Diese Behandlung ist in den USA.-Patentschriften 2 615 932, 2 669 598 beschrieben. Nach diesem bekannten Stand der Technik können an Stelle von Kobaltnitrat auch ein oder mehrere Nitrate anderer Schwermetalle, wie Eisen, Nickel, Mangan, Chrom, Kupfer, Silber, Gold, Plantin, Vanadium, Thorium, Seltene Erden u. dgl. verwendet werden. Ebenso können die Salze an Stelle des Salpetersäurerestes auch Reste anderer oxydierender Säuren, wie salpetrige Säure, Chlorsäure, Oxalsäure, Essigsäure, Ameisensäure u. dgl., enthalten.

Beim Erhitzen der getränkten Elektrodenkörper unter Spinellbildung wird ihre Porosität bis auf 30 bis 35% gesteigert.

An diese Behandlung schließt sich die Beschichtung der Wasserstoffelektrode mit einem Katalysator aus Rhodium, Iridium, Ruthenium oder Osmium an. Man kann z. B. eine 10%ige wäßrige Lösung von Rhodiumtrichlorid in einer solchen Menge aufbringen, daß auf jeden Quadratzentimeter der Oberfläche 0,25 bis 8 mg Metall entfallen. Besonders gute Ergebnisse werden mit einer Beschichtung von etwa 2 mg/cm² erhalten. Das Zersetzen der aufgebrachten Metallverbindungen geschieht in üblicher Weise, z. B.

United States Patent Office

3,595,698
Patented July 27, 1971

1

3,595,698
HYDRAZINE FUEL CELL WITH ACRYLIC ACID POLYMER MEMBRANE
Karl Victor Kordesch, Lakewood, Ohio, assignor to Union Carbide Corporation, New York, N.Y.
No Drawing. Filed Oct. 3, 1968, Ser. No. 764,965
Int. Cl. H01m *27/26*
U.S. Cl. 136—86 5 Claims

ABSTRACT OF THE DISCLOSURE

Alkali metal salts of ethylene-acrylic acid copolymers are useful as selective, ion permeable membranes for permeable membranes for hydrazine-air fuel cells and permit operation of the cell at high fuel concentrations.

This invention relates to an electrochemical cell which utilizes hydrazine as a fuel. In one aspect, this invention relates to a fuel cell which can operate at high fuel concentrations. In a further aspect, this invention is directed to the use of selective, ion permeable membranes as separators in fuel cells.

Fuel cells which employ hydrazine as a fuel have been known for several years. Such fuel cells generally comprise an anode capable of reacting electrochemically with hydrazine with the production of electric current (hereinafter referred to as a "hydrazine anode"), a cathode to which is supplied the oxidant employed in the fuel cell, an electrolyte in contact with the electrodes, means for supplying oxidant to the cathode and means for supplying hydrazine to the anode. The usual method for supplying hydrazine to the anode is by dissolving the hydrazine in the electrolyte, preferably an aqueous alkaline electrolyte.

Prior art hydrazine anodes typically comprised a porous metal or other porous material which was capable of promoting electrochemical decomposition of hydrazine in contact with the anode, for example, porous nickel or porous Raney nickel. In addition, catalytic materials were often deposited on the porous material, generally metals or compounds of metals from Group VIII of the Periodic Table, for example, the noble metals or heavy metal borides such as nickel boride or cobalt boride.

In practice the hydrazine concentration in the electrolyte must be kept relatively low, i.e., in the range of from about 0.3 to 0.8 percent, otherwise direct chemical attack occurs at the air cathode if it is given no special protection. Hence, hydrazine-air fuel cells are normally provided with a sophisticated fuel injection an monitoring mechanism to periodically supply fresh fuels as it is consumed by the electrochemical reaction and to control the maximum fuel concentration. However, in present methods of monitoring the hydrazine concentration in the electrolyte of a hydrazine fuel cell the total output voltage of the fuel cell battery is monitored and a change in this voltage actuates an electrical switch opening an electromagnetic fuel valve and introducing hydrazine into the electrolyte system. The prime disadvantage of this method is that the net battery voltage invariably includes the cathode potential which tends to vary with time and operating conditions. Also, should there be an over-injection of hydrazine into the system in response to a drop in total battery voltage due, for example, to a slowdown in the electrolyte pumping system or air cooling system, the hydrazine monitoring and injecting system would be unable to recover because of the tendency to inject even more hydrazine to compensate for the decreased voltage, resulting eventually in complete flooding of the system with the hydrazine fuel.

Separate monitoring means for controlling hydrazine concentration which are independent of the main fuel cell

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battery voltage have also been suggested. However, such separate monitoring devices, have a very low sensitivity because the change in voltage with hydrazine concentration for a single cell is relatively small compared to the total battery voltage.

It would therefore be desirable to have a fuel cell which could operate at relatively high concentrations of hydrazine in the electrolyte, and thus require only occasional fuel injection by means of, for example, a single solenoid valve. However, it has been observed that some means for limiting hydrazine transport from the anode to the cathode compartments is essential when a relatively high concentration of hydrazine is present in the electrolyte. As previously indicated, protection of the air cathode from contact with large amounts of hydrazine is necessary in order to prevent a severe "chemical short" which would not only overpolarize the cathode, but would unnecessarily consume hydrazine fuel and generate considerable heat.

Although cells can operate without a barrier or membrane if the hydrazine concentration is maintained below about 1 percent, the use of concentrations in the 10 to 30 percent range necessitates its use. For instance, in an attempt to operate a fuel cell containing no membrane or other means to restrict hydrazine transport, when an electrolyte containing 10 percent hydrazine was added, very violet gassing occurred and the cell became very hot. In contrast, a similar cell containing the membranes disclosed herein, showed a temperature rise of less than 15° C. during a one and one half hour operating period at a current density of 25 a.s.f.

It is therefore apparent that if no special protection is given to the air cathode, a low hydrazine concentration must be employed and the monitoring means must be highly sophisticated. In the event that the air cathode could be protected from direct chemical reaction, it would be possible to utilize a higher hydrazine concentration, less sophisticated monitoring means and an overall improvement in operation.

Accordingly, one or more of the following objects will be achieved by the practice of this invention. It is an object of this invention to provide a fuel cell which can operate at high fuel concentrations. Another object of this invention is to provide a hydrazine-air fuel cell which can operate at hydrazine concentrations of up to 30 percent in the electrolyte. A further object of this invention is to provide a fuel cell which employs as a separator a selective, ion permeable membrane. A still further object of this invention is to provide a selective, ion permeable membrane which is an alkali-acrylate-acrylic acid-polyethylene copolymer. These and other objects will readily become apparent to those skilled in the art in the light of the teachings herein set forth. In its broad aspect, the invention is directed to a fuel cell comprising, in combination, at least one hydrazine anode, at least one oxidant cathode, current collecting means associated with the anode and cathode, and an electrolyte containing hydrazine, the cathode being separated from the hydrazine in the electrolyte by a selective, ion permeable membrane comprised of alkali metal salts of ethylene-acrylic acid copolymers. Due to the presence of the membrane, relatively high concentrations of hydrazine, i.e., 10 to 30 percent in the electrolyte can be employed and the need for replenishing the fuel at frequent intervals substantially reduced.

As hereinbefore indicated, the selective, ion permeable membranes which are employed in the fuel cells of this invention are alkali metal salts of ethylene-acrylic acid copolymers.

The ethylene-acrylic acid copolymers are prepared by the polymerization of ethylene and acrylic acid (or methacrylic acid) by known techniques described in the liter-

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Jan. 16, 1968 K. V. KORDESCH 3,364,071
FUEL CELL WITH CAPILLARY SUPPLY MEANS
Filed April 10, 1963

INVENTOR.
KARL V. KORDESCH
BY
ATTORNEY

Nov. 11, 1969 K. V. KORDESCH 3,477,877
FUEL CELL
Filed July 30, 1962

INVENTOR.
KARL V. KORDESCH
BY
ATTORNEY

Figure 3.130: Karl Kordesch also invented improved fuel cells.

3.7 Film Photography

While early film photography was being developed and practiced in France, the United Kingdom, the United States, and other countries, most of the key technological advances were made in the German-speaking world (Section 3.7.1) and then transferred to other countries (Section 3.7.2).[14] See Figs. 3.131–3.144.

Even the American chemist and chemical historian Aaron Ihde admitted [Ihde 1984, p. 464]:

> The German industry held a virtual monopoly until World War I as a supplier of photographic chemicals, optical glass, and high quality cameras.

3.7.1 Development of Photography

In 1717, Johann Heinrich Schulze (German states, 1687–1744, Fig. 3.132) discovered that light causes some silver solutions to become darker. He used that process to reproduce clear images such as words, although he found that the images in the silver solutions faded with time. Schulze published his results in books that were freely circulated within the European chemical community, thus launching the field of chemical photography.

Building upon Schulze's research, in 1777 Carl Wilhelm Scheele (German states, 1742–1786, Fig. 3.132) developed a chemical fixer for silver solutions to make the light-induced images permanent and to prevent further light from altering the images. Scheele also discovered the need for working with light-sensitive silver solutions in red light until they were fixed. Scheele's research findings, like the earlier discoveries of Schulze, were circulated within the community of European chemists. Thus Schulze and Scheele were responsible for establishing the fundamental chemical and physical principles upon which film photography has been based ever since.

It appears that the German-speaking scientific world reduced the discoveries of Schulze and Scheele to practical and commercial applications by the early nineteenth century. No later than 1839, the brothers Friedrich Wilhelm Enzmann (German states, 1802–1866, Fig. 3.131) and Carl Heinrich Enzmann (German states, 18??–18??) were producing and selling cameras and photographic film as a regular commercial business.

These early German developments in photography spread to other countries, where they were adopted and further publicized by other scientists such as Louis Daguerre (French, 1787–1851) and William Henry Fox Talbot (English, 1800–1877). Especially in the English-speaking world, some historians erroneously assigned credit for the invention of photography to those later scientists, although the original discoveries and inventions clearly arose earlier and in the German-speaking world.

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[14] See for example: Flueckiger 2020; Gill and Mustroph 2014, 2015a, 2015b; BIOS 61; BIOS 252; BIOS 262; BIOS 397; BIOS 435; BIOS 484; BIOS 492; BIOS 658; BIOS 772; BIOS 773; BIOS 1180; BIOS 1355; BIOS 1605; BIOS 1627; BIOS Overall 19; CIOS ER 217; CIOS ER 345; CIOS XII-22; CIOS XIII-5; CIOS XVII-10; CIOS XXVI-7; CIOS XXVI-61; CIOS XXX-15; CIOS XXX-17; FIAT 153; FIAT 351; FIAT 355; FIAT 356; FIAT 357; FIAT 358; FIAT 359; FIAT 360; FIAT 678; FIAT 698; FIAT 721; FIAT 891; FIAT 893; FIAT 943; FIAT 953; FIAT 976; FIAT 977; JIOA 13; NavTecMisEu 96-45; NavTecMisEu 140-45.

In 1873, Hermann Wilhelm Vogel (German, 1834–1898, not to be confused with the astronomer Hermann Carl Vogel) invented dye color sensitization, which enabled photographic emulsions to be made sensitive to different colors of light, and thereby led to color photography. His results were widely publicized (Fig. 3.133) and became the basis of almost all color photography. *Chronologie Chemie* described Vogel's revolutionary innovation [Neufeldt 2003, p. 74]:

> Die Entdeckung der optischen Sensibilisierung photographischer Schichten, so daß diese außer für blau auch für weitere Spektralbereiche lichtempfindlich werden, führt zu naturgetreuen Schattierungen in der Schwarz-Weiß-Photographie. Vogel beobachtet dieses Phänomen zuerst am Farbstoff Korallin, die Weiterentwicklung führt zur Sensibilisierung für grünes und gelbes Licht (orthochromatische Filme) und schließlich mit Hilfe der Polymethin-Farbstoffe zur Sensibilisierung für den gesamten sichtbaren Spektralbereich (panchromatische Filme).

> The discovery of optical sensitization of photographic layers, so that they become light-sensitive to other spectral ranges in addition to blue, led to lifelike shading in black-and-white photography. Vogel first observed this phenomenon with the dye coralline; further development led to sensitization for green and yellow light (orthochromatic films) and finally, with the help of polymethine dyes, to sensitization for the entire visible spectral range (panchromatic films).

Ferdinand Hurter (Swiss, 1844–1898, Fig. 3.131) worked to make photography more rigorously systematic, such as defining and measuring film speed, optical density, and other properties.

As shown in Fig. 3.134, Ottomar Anschütz (German, 1846–1907) invented high-speed camera shutters in 1881 and compact portable cameras in 1896.

Momme Andresen (German/Danish, 1857–1951) invented new and improved chemical developers and fixers for photography from the 1880s onward. He helped to build what became known as the Agfa photography company (derived and rebranded from the earlier Aktiengesellschaft für Anilinfabrikation) and employed other chemists such as Ernst Leupold (German, 18??–19??). See Fig. 3.135.

As shown in Fig. 3.136, the brothers Max Skladanowsky (German, 1863–1939) and Emil Skladanowsky (German, 1866–1945) created the Bioscop motion picture camera and projector in 1892 and presented the first public films in 1895.

Adolf Miethe (German, 1862–1927) produced high-quality color photographs using a three-color process beginning in 1901 (Fig. 3.137). He also invented the first practical flash powder for photography.

Raphael Eduard Liesegang (German, 1869–1947, Fig. 3.132) conducted numerous experimental and theoretical analyses of the photochemistry of both black-and-white photography and color photography.

Rudolf Fischer (German, 1881–1957) invented Agfa color film in 1911 (Fig. 3.138). He worked closely with Wilhelm Siegrist (German, 1881–19??) for part of that period.

In 1913, Oskar Barnack (German, 1879–1936) invented the first modern 35 mm still camera, which later was dubbed Leica (for Leitz Camera); see Fig. 3.139. The *Encyclopedia Britannica* described his invention [EB 2010]:

> [D]esigner of the first precision miniature camera to become available commercially, the Leica I, which was introduced in 1924 by the Ernst Leitz optical firm at Wetzlar, Ger.
>
> Barnack was a master mechanic and inventor who joined the Leitz optical firm in 1911. Barnack had completed a prototype of the Leica by 1913, but World War I and the postwar chaos in Germany delayed production. The success of the Leica I promoted the use of 35-millimetre and other small cameras. Barnack determined the standard 24 × 36-millimetre picture size for 35-millimetre film and was partly responsible for the Leitz Elmar lens.

As shown in Fig. 3.140, Max Hagedorn (German, 18??–19??) created improved film stock from 1924 onward.

Ernst Bauer (German, 18??–19??), Wilhelm Schneider (German, 18??–19??), and Gustav Wilmanns (German, 18??–19??) invented Agfa Neu improved color film in 1935. Their technology was showcased in films such as *Frauen sind doch bessere Diplomaten* (Fig. 3.141) and became the basis for most color film around the world after World War II.

Joseph Joshua Weiss (Austrian, 1905–1972, Fig. 3.132) carried out a series of analyses on the photochemical reaction mechanisms in photographic film.

Artur Fischer (German, 1919–2016, Fig. 3.131) invented a system for synchronizing a photo flash with the camera shutter.

The German-speaking world also developed very high-quality optical components and optical devices that were important for photography (p. 686 and Section 6.9).

3.7.2 Transfer of Photography-Related Technologies

As illustrated by the examples above, a wide variety of advanced technologies, components, and methods for photography were created in the German-speaking world. Some were transferred to other countries via patents, publications, and commerce before World War II, but many of the most advanced photographic technologies were only transferred after the war. For some examples of transferred technologies, see Figs. 3.142–3.144 and the following reports:

> BIOS 61. *Weapons Section of the LFA, Volkenrode, with Notes on Photographic Methods Used in German Ballistics.*
>
> BIOS 252. *I. G. Photopapier Fabrik (AGFA), Leverkusen, Near Cologne.*
>
> BIOS 262. *German Photographic Film Base Industry.*
>
> BIOS 397. *Agfa Colour.*

BIOS 435. *Ozalid Light-Sensitive Materials, Kalle & Co., Wiesbaden—Biebrich (I.G. Farbenindustrie A.G.).*

BIOS 484. *The German Printing Industry.*

BIOS 492. *Explosives Work and Associated Photographic Technique.*

BIOS 658. *German Photographic Industry.*

BIOS 772. *Manufacture of Diazo Chemicals, Kalle & Co., Wiesbaden/Biebrich.*

BIOS 773. *Manufacture of Photographic Developing Substances at I.G. Farbenfabrik, Wolfen.*

BIOS 1180. *German Between-Lens Photographic Shutter Production.*

BIOS 1355. *Further Investigation of Agfa Filmfabrik (Photographic Plant), Wolfen, Near Leipzig.*

BIOS 1605. *I.G. Farbenindustrie. The Manufacture of Intermediates and "Colour Formers" for Agfa Farbenfilm.*

BIOS 1627. *German Organic and Inorganic Photographic Chemicals Manufacture.*

BIOS Overall 19. *Photographic Industry.*

CIOS ER 217. *Report on Manufacture of Air Photography Apparatus.*

CIOS ER 345. *Report on: I.G. Agfa, Wolfen; I.G. Farben, Wolfen.*

CIOS XII-22. *Electronic Test Instruments Spark and Flash Discharge Photographic Equipment Philips, Eindhoven.*

CIOS XIII-5. *Photographic Lenses and Optical Instruments.*

CIOS XVII-10. *Gervart Photo Material Manufacturer, Antwerp.*

CIOS XXVI-7. *Focke Wulf Photo Reproduction Department, Bad Eilsen.*

CIOS XXVI-61. *Film Production and Methods, Agfa Film Fabrik Plant, Wolfen.*

CIOS XXX-15. *Agfa Film Factory, Wolfen.*

CIOS XXX-17. *I.G. Farben, Agfa Subsidiary, Wolfen.*

FIAT 153. *Punching of Spinnerets, I.G. Farbenindustrie, Agfa Camera Werke, Munich.*

FIAT 351. *Photosensitive Products, Kalle & Company.*

FIAT 355. *Interviews with Technical Personnel, Agfa, Wolfen.*

FIAT 356. *Report on Photographic Silver Nitrate as Manufactured by Degussa, Frankfurt/M.*

FIAT 357. *Photographic Gelatin Plants.*

FIAT 358. *The Manufacture of Photosensitive Products at the Schleussner Film Werke.*

FIAT 359. *Report on Goebel, A. G. Darmstadt.* [photosensitive materials]

FIAT 360. *Report on AGFA Photo Paper Plant, at Leverkusen.*

FIAT 678. *Status of Exploitation of Photography and Optics in Germany.*

FIAT 698. *Photographing a Single Fuel Injection.*

FIAT 721. *Agfacolor Negative-Positive Method for Professional Motion Pictures.*

FIAT 891. *Duxochrome Photo Color Prints.*

FIAT 893. *Introduction to Technical Photographic X-Ray.*

FIAT 943. *The Manufacture of Agfacolor Material.*

FIAT 953. *Color Photography.*

FIAT 976. *Agfa Color Process.*

FIAT 977. *Color Reproduction by Color Photography.*

JIOA 13. *Photo-Mapping and Map Reproduction.*

NavTecMisEu 96-45. *Investigation of Film Production and Methods at the Agfa Film Fabrik Plant, Wolfen, Germany.*

NavTecMisEu 140-45. *Agfa Paper Formulae.*

Scientists from the German-speaking world also developed technologies for electronic photography and transferred those technologies to other countries, especially after World War II. See Sections 6.3, 6.5, and 6.6. Over the course of several decades after World War II, German-derived chemical film technologies for photography were slowly and ultimately almost completely eclipsed by German-derived electronic photography technologies.

Photography

Carl Heinrich Enzmann (18??–18??)

Friedrich Wilhelm Enzmann (1802–1866)

Artur Fischer (1919–2016)

Ferdinand Hurter (1844–1898)

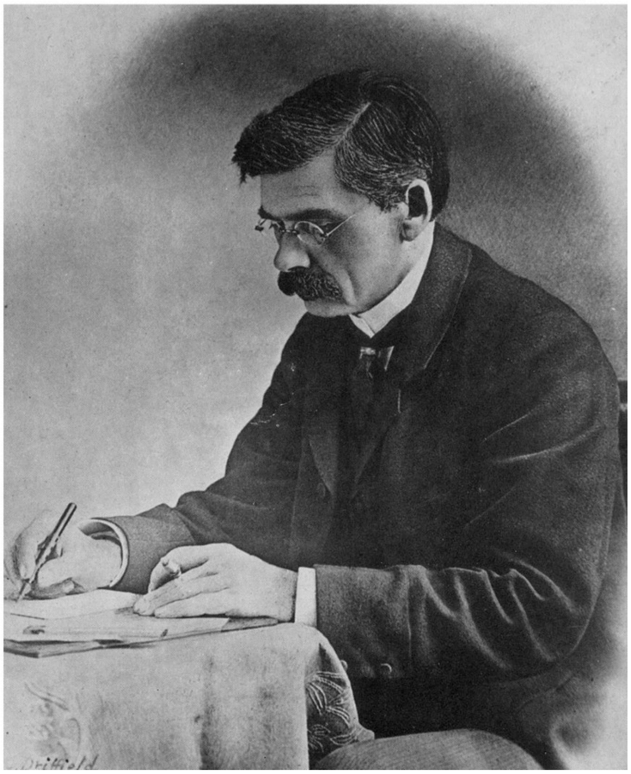


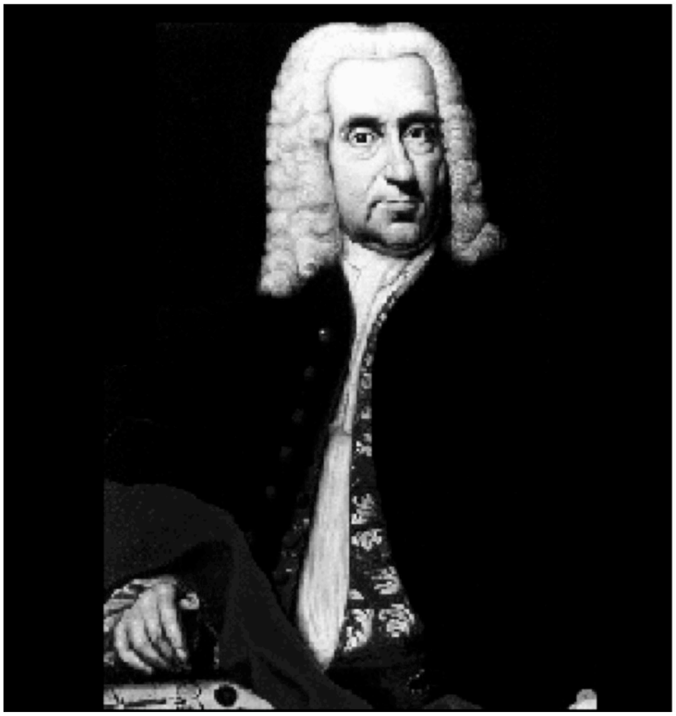
Figure 3.131: Some creators who made important contributions to photography included Carl Heinrich Enzmann, Friedrich Wilhelm Enzmann, Artur Fischer, and Ferdinand Hurter.

Photography

Raphael Eduard Liesegang (1869–1947)

Carl Wilhelm Scheele (1742–1786)

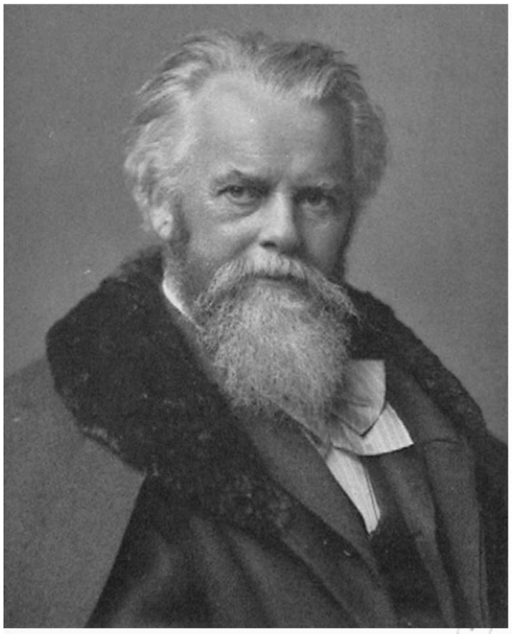
Johann Heinrich Schulze (1687–1744)

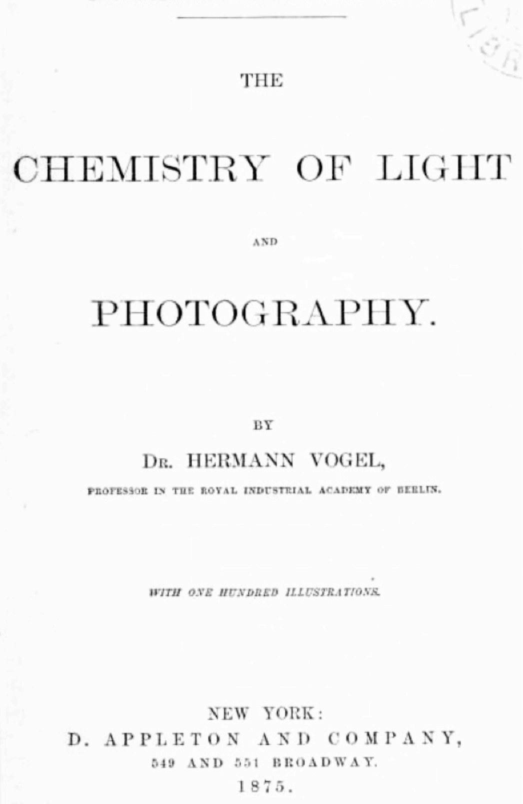


Joseph Joshua Weiss (1905–1972)

Figure 3.132: Other creators who made important contributions to photography included Raphael Eduard Liesegang, Carl Wilhelm Scheele, Johann Heinrich Schulze, and Joseph Joshua Weiss.

Hermann Wilhelm
Vogel (1834–1898)
invented dye sensitization
for color photography (1873)





THE INTERNATIONAL SCIENTIFIC SERIES.

THE

CHEMISTRY OF LIGHT

AND

PHOTOGRAPHY.

BY

Dr. HERMANN VOGEL,

PROFESSOR IN THE ROYAL INDUSTRIAL ACADEMY OF BERLIN.

WITH ONE HUNDRED ILLUSTRATIONS.

NEW YORK:
D. APPLETON AND COMPANY,
549 AND 551 BROADWAY.
1875.

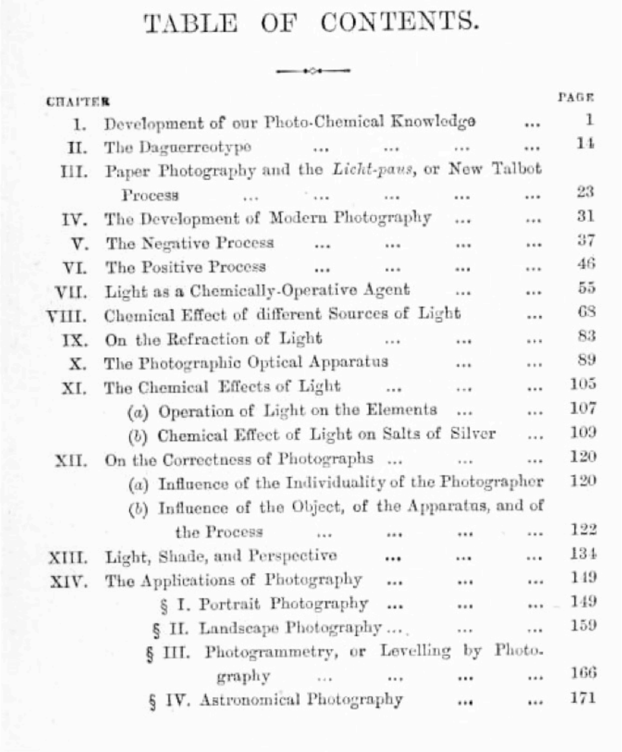


TABLE OF CONTENTS.

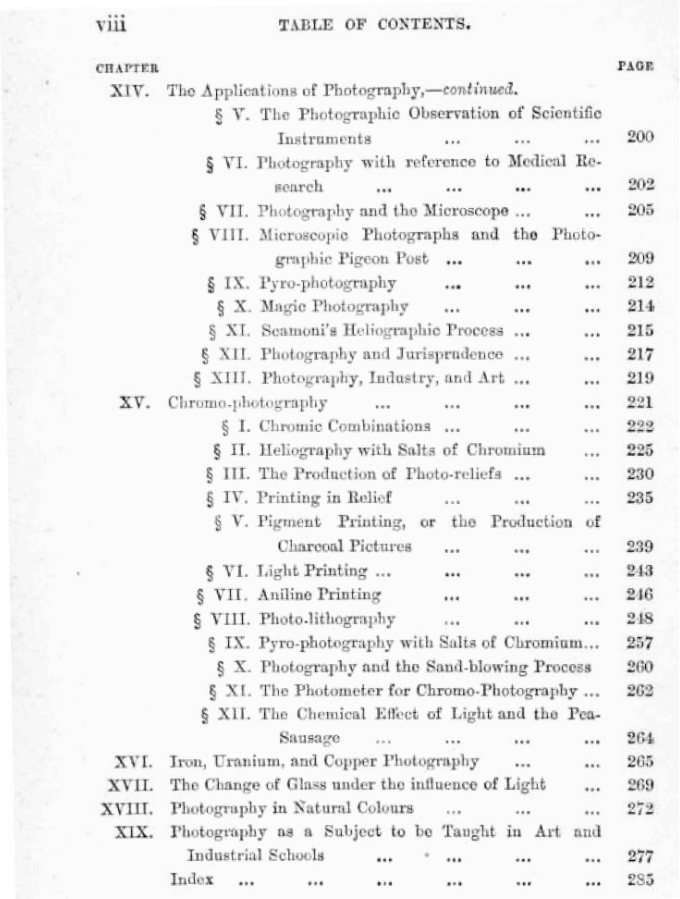


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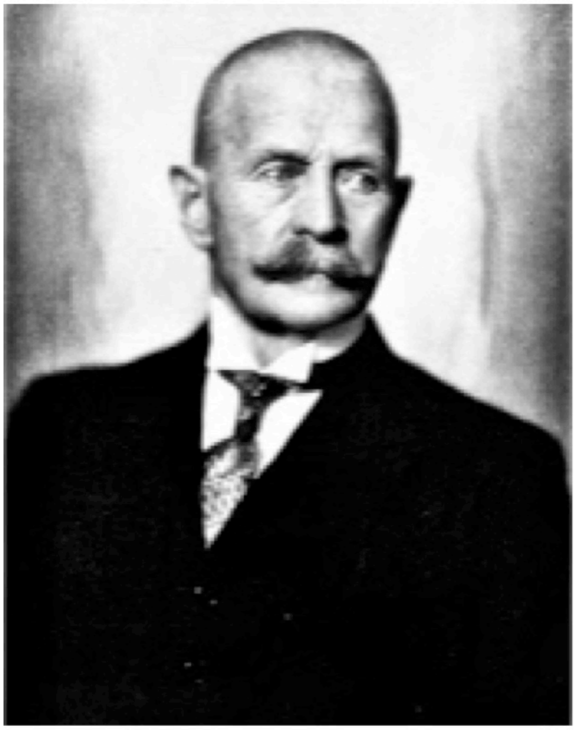
Figure 3.133: Hermann Wilhelm Vogel invented dye sensitization for color photography in 1873.

Figure 3.134: Ottomar Anschütz invented high-speed shutters in 1881 and compact portable cameras in 1896.

Momme Andresen (1857–1951)



Ernst Leupold (18??–19??)

Chemical developers and fixers for photography

UNITED STATES PATENT OFFICE.

MOMME ANDRÉSEN, OF BERLIN, GERMANY.

PROCESS OF DEVELOPING PHOTOGRAPHIC PICTURES.

SPECIFICATION forming part of Letters Patent No. 475,372, dated May 24, 1892.

Application filed April 15, 1889. Serial No. 307,326. (No specimens.) Patented in Germany February 10, 1889, No. 50,265; in Belgium March 26, 1889, No. 85,553; in France March 26, 1889, No. 196,980; in England March 26, 1889, No. 5,207; in Norway March 26, 1889, No. 1,233; in Sweden March 26, 1889, No. 2,028; in Italy March 31, 1889, XXIII, 25,190, L, 27; in Spain June 4, 1889, No. 9,403, and in Austria-Hungary February 20, 1890, No. 39,968 and No. 79.

To all whom it may concern:

Be it known that I, MOMME ANDRÉSEN, chemist, a subject of the King of Prussia, residing at 44 Melchiorstrasse, Berlin, Prussia, German Empire, have invented certain new and useful Improvements in and Relating to the Development of Photographic Pictures, (for which Letters Patent have been obtained in Austria-Hungary, No. 39,968 and No. 79, dated February 20, 1890; in Belgium, No. 85,553, dated March 26, 1889; in France, No. 196,980, dated March 26, 1889; in Germany, No. 50,265, dated February 10, 1889; in Great Britain, No. 5,207, dated March 26, 1889; in Italy, Vol. XXIII, 25,190, Vol. L, 27, dated March 31, 1889; in Norway, No. 1,233, dated March 26, 1889; in Spain, No. 9,403, dated June 4, 1889, and in Sweden, No. 2,028, dated March 26, 1889;) and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

My invention relates to the development of photographic pictures by means of diamido-naphthaline, amido-naphthol, and dioxynaphthaline, as well as their sulpho-acids.

As is well known in photography, it is the practice to treat the sensitive plates (prepared with chloride, bromide, or iodide of silver, or with two or all of these salts) after exposure with a developing solution in order to bring to view the image produced on the sensitive plate. The developing solution hitherto employed for this purpose has usually consisted of a solution of oxalate of iron, sulphate of iron, or pyrogallic acid. Now I have found by experiment that a derivative of naphthaline, or of a naphthol, or their sulpho-acids—as, for instance, diamido-naphthaline, amido-naphthol, and dioxynaphthaline, as well as their sulpho-acids—gives much better results than the well-known alkaline pyrogallol developers, and are exceptionally suitable for developing photographic pictures, whenever, in the production of such pictures, a sensitizing agent is used that will be chemically affected by the developer, as is the case in the use of a silver salt or salts—for instance, the effect being to impart to the plate a blue-black tint similar to that produced when the picture is developed in a bath of oxalate of iron, with the advantage that the sensitized plate is not in the least colored. On the other hand, the developers forming the subject-matter of this invention are more durable in an aqueous alkaline solution than the pyrogallol developers hitherto used. I thus obtain the advantages possessed by known developing agents without their disadvantages.

A developing-bath prepared with my naphthol developer, in which it is intended to immerse the sensitive plate after having been exposed for the purpose of producing a visible picture, is for instantaneous photography advantageously composed of the following ingredients: five grams of the hereinbefore-described napthol developer, fifteen grams of sulphite of soda, two hundred and fifty grams of distilled water, and five grams of carbonate of potash. The above proportions can, however, be varied, or one or the other of the ingredients can be substituted by others, providing the essential part—namely, the before-mentioned napthol developer—is contained in the developing-bath. After having immersed the photographic plate in this bath till the picture becomes completely developed it is then fixed in the usual way.

Having thus described my invention, what I claim as new therein, and desire to secure by Letters Patent, is—

1. In the art of photography, the improvement which consists in subjecting sensitized and exposed surfaces to the developing action of a solution of a derivative of naphthaline, substantially as set forth.

2. In the art of photography, the improvement which consists in subjecting sensitized and exposed surfaces to the developing action of an alkaline solution of a derivative of naphthaline, substantially as set forth.

3. In the art of photography, the improvement which consists in subjecting sensitized

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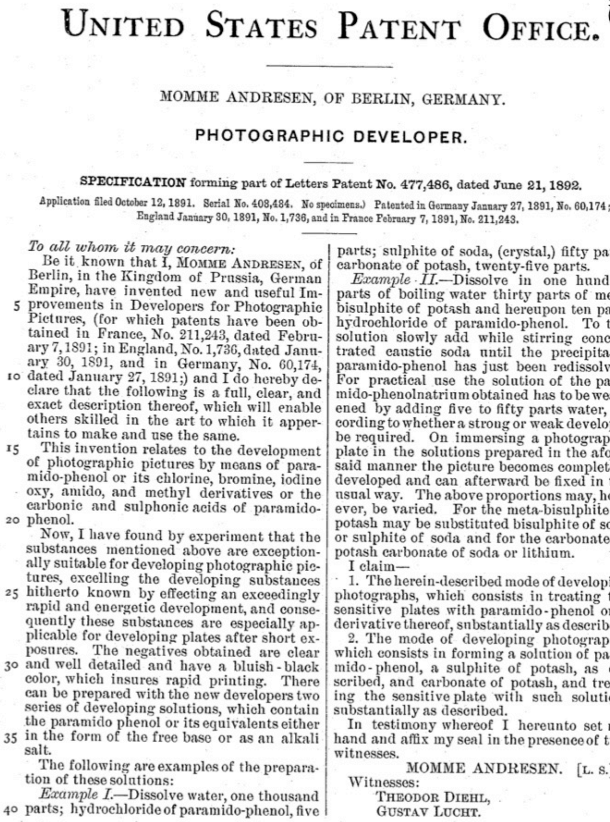


UNITED STATES PATENT OFFICE.

MOMME ANDRESEN, OF BERLIN, GERMANY.

PHOTOGRAPHIC DEVELOPER.

SPECIFICATION forming part of Letters Patent No. 477,486, dated June 21, 1892.

Application filed October 12, 1891. Serial No. 408,484. No specimens.) Patented in Germany January 27, 1891, No. 60,174; in England January 30, 1891, No. 1,736, and in France February 7, 1891, No. 211,243.

To all whom it may concern:

Be it known that I, MOMME ANDRESEN, of Berlin, in the Kingdom of Prussia, German Empire, have invented new and useful Improvements in Developers for Photographic Pictures, (for which patents have been obtained in France, No. 211,243, dated February 7, 1891; in England, No. 1,736, dated January 30, 1891, and in Germany, No. 60,174, dated January 27, 1891;) and I do hereby declare that the following is a full, clear, and exact description thereof, which will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the development of photographic pictures by means of paramido-phenol or its chlorine, bromine, iodine oxy, amido, and methyl derivatives or the carbonic and sulphonic acids of paramido-phenol.

Now, I have found by experiment that the substances mentioned above are exceptionally suitable for developing photographic pictures, excelling the developing substances hitherto known by effecting an exceedingly rapid and energetic development, and consequently these substances are especially applicable for developing plates after short exposures. The negatives obtained are clear and well detailed and have a bluish-black color, which insures rapid printing. There can be prepared with the new developers two series of developing solutions, which contain the paramido phenol or its equivalents either in the form of the free base or as an alkali salt.

The following are examples of the preparation of these solutions:

Example I.—Dissolve water, one thousand parts; hydrochloride of paramido-phenol, five parts; sulphite of soda, (crystal,) fifty parts; carbonate of potash, twenty-five parts.

Example II.—Dissolve in one hundred parts of boiling water thirty parts of meta-bisulphite of potash and hereupon ten parts hydrochloride of paramido-phenol. To this solution slowly add while stirring concentrated caustic soda until the precipitated paramido-phenol has just been redissolved. For practical use the solution of the paramido-phenolnatrium obtained has to be weakened by adding five to fifty parts water, according to whether a strong or weak developer be required. On immersing a photographic plate in the solutions prepared in the aforesaid manner the picture becomes completely developed and can afterward be fixed in the usual way. The above proportions may, however, be varied. For the meta-bisulphite of potash may be substituted bisulphite of soda or sulphite of soda and for the carbonate of potash carbonate of soda or lithium.

I claim—

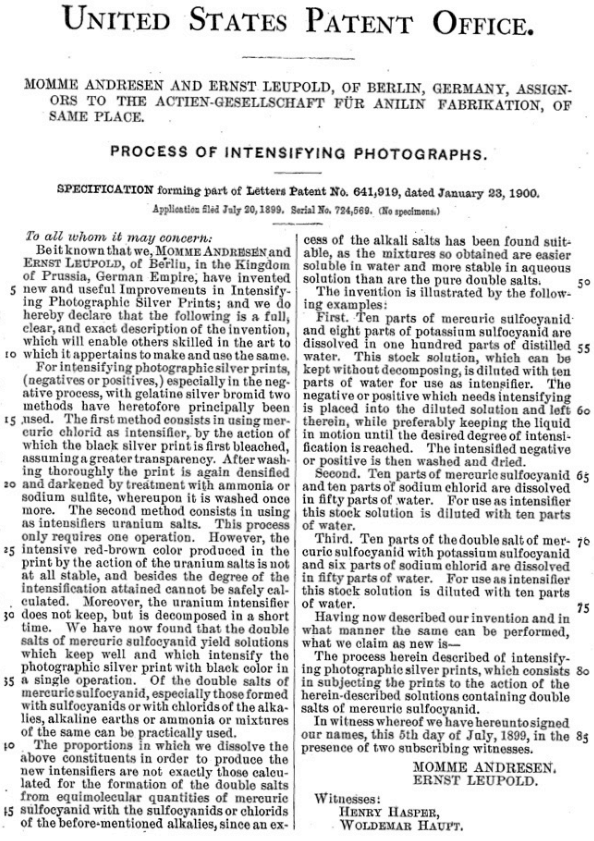
1. The herein-described mode of developing photographs, which consists in treating the sensitive plates with paramido-phenol or a derivative thereof, substantially as described.

2. The mode of developing photographs, which consists in forming a solution of paramido-phenol, a sulphite of potash, as described, and carbonate of potash, and treating the sensitive plate with such solution, substantially as described.

In testimony whereof I hereunto set my hand and affix my seal in the presence of two witnesses.

MOMME ANDRESEN. [L. S.]

Witnesses:
THEODOR DIEHL,
GUSTAV LUCHT.



UNITED STATES PATENT OFFICE.

MOMME ANDRESEN AND ERNST LEUPOLD, OF BERLIN, GERMANY, ASSIGNORS TO THE ACTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION, OF SAME PLACE.

PROCESS OF INTENSIFYING PHOTOGRAPHS.

SPECIFICATION forming part of Letters Patent No. 641,919, dated January 23, 1900.

Application filed July 20, 1899. Serial No. 724,569. (No specimens.)

To all whom it may concern:

Be it known that we, MOMME ANDRESEN and ERNST LEUPOLD, of Berlin, in the Kingdom of Prussia, German Empire, have invented new and useful Improvements in Intensifying Photographic Silver Prints; and we do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

For intensifying photographic silver prints, (negatives or positives,) especially in the negative process, with gelatine silver bromid two methods have heretofore principally been used. The first method consists in using mercuric chlorid as intensifier, by the action of which the black silver print is first bleached, assuming a greater transparency. After washing thoroughly the print is again densified and darkened by treatment with ammonia or sodium sulfite, whereupon it is washed once more. The second method consists in using as intensifiers uranium salts. This process only requires one operation. However, the intensive red-brown color produced in the print by the action of the uranium salts is not at all stable, and besides the degree of the intensification attained cannot be safely calculated. Moreover, the uranium intensifier does not keep, but is decomposed in a short time. We have now found that the double salts of mercuric sulfocyanid yield solutions which keep well and which intensify the photographic silver print with black color in a single operation. Of the double salts of mercuric sulfocyanid, especially those formed with sulfocyanids or with chlorids of the alkalies, alkaline earths or ammonia or mixtures of the same can be practically used.

The proportions in which we dissolve the above constituents in order to produce the new intensifiers are not exactly those calculated for the formation of the double salts from equimolecular quantities of mercuric sulfocyanid with the sulfocyanids or chlorids of the before-mentioned alkalies, since an excess of the alkali salts has been found suitable, as the mixtures so obtained are easier soluble in water and more stable in aqueous solution than are the pure double salts.

The invention is illustrated by the following examples:

First. Ten parts of mercuric sulfocyanid and eight parts of potassium sulfocyanid are dissolved in one hundred parts of distilled water. This stock solution, which can be kept without decomposing, is diluted with ten parts of water for use as intensifier. The negative or positive which needs intensifying is placed into the diluted solution and left therein, while preferably keeping the liquid in motion until the desired degree of intensification is reached. The intensified negative or positive is then washed and dried.

Second. Ten parts of mercuric sulfocyanid and ten parts of sodium chlorid are dissolved in fifty parts of water. For use as intensifier this stock solution is diluted with ten parts of water.

Third. Ten parts of the double salt of mercuric sulfocyanid with potassium sulfocyanid and six parts of sodium chlorid are dissolved in fifty parts of water. For use as intensifier this stock solution is diluted with ten parts of water.

Having now described our invention and in what manner the same can be performed, what we claim as new is—

The process herein described of intensifying photographic silver prints, which consists in subjecting the prints to the action of the herein-described solutions containing double salts of mercuric sulfocyanid.

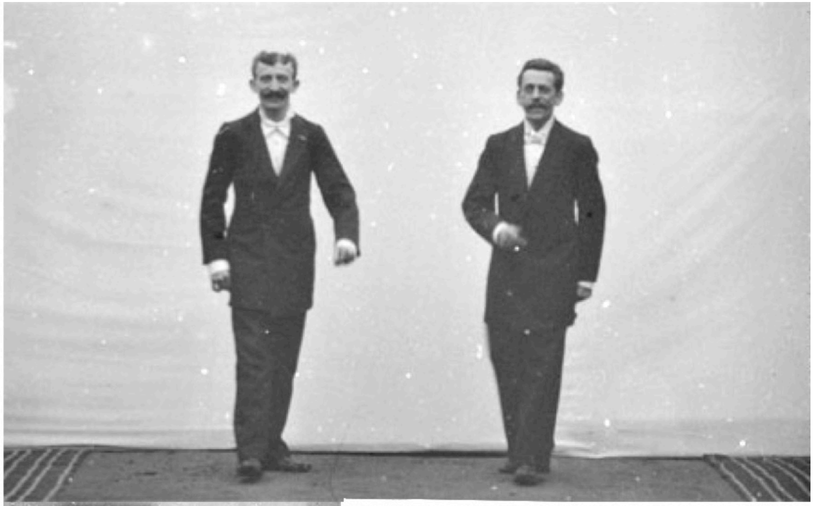
In witness whereof we have hereunto signed our names, this 5th day of July, 1899, in the presence of two subscribing witnesses.

MOMME ANDRESEN.
ERNST LEUPOLD.

Witnesses:
HENRY HASPER,
WOLDEMAR HAUPT.

Figure 3.135: Momme Andresen invented new and improved chemical developers and fixers for photography from the 1880s onward. He helped to build what became known as the Agfa photography company and employed other chemists such as Ernst Leupold.

Max Skladanowsky (1863–1939) and Emil Skladanowsky (1866–1945) created the Bioscop motion picture camera and projector (1892) and presented the first public films (1895)



Max Skladanowsky with a Bioscop projector

Paris, den 31. December 1895.

Sensationelle Neuheit! In Deutschland gesetzlich geschützt

Sensationelle Neuheit! In Deutschland gesetzlich geschützt.

Gebrüder Skladanowsky's

BIOSCOP

Die amüsanteste und interessanteste Erfindung des 19. Jahrhunderts!

„Man muss das Bioscop gesehen haben", war der Ausspruch sämmtlicher Zeitungen Berlins.

Gebr. Skladanowsky's Bioscop hat gegenwärtig folgendes Repertoir:

1. Italienischer Bauerntanz, ausgeführt von 2 Kindern.
2. Komisches Reck.
3. Das boxende Känguruh.
4. Jongleur.
5. Akrobatisches Potpourri (8 Personen).
6. Kamarinskij, russischer Nationaltanz.
7. Ringkampf zwischen Greiner und Sandow.
8. Die Erfinder des Bioscopes (Gebr. Skladanowsky).

Ein volles Variété-Programm in 15 Minuten.

Die lebensgrossen Darstellungen im Bioscop sind die Projectionen eigener Original-Serien-Aufnahmen, sie geben genau das Leben in voller Natürlichkeit vermittelst der Electricität wieder, man glaubt die Wirklichkeit vor sich zu haben, so greifbar plastisch ist die Wirkung des Bioscopes.

Frei für Februar und März 1896.

Paris, den 31. December 1895.

Hochachtungsvoll

Gebr. Skladanowsky.

Ständige Adresse: Berlin N., Pankow.

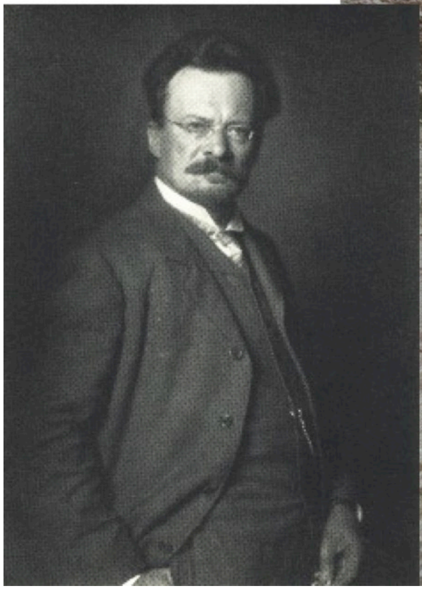
Avis! Machen hiermit bekannt, dass am 1. Februar ein Bioscop unseres deutschen Patentes mit sämmtlichen dazu gehörigen electrischen Apparaten, Bogenlampen, Schaltbretter, Original-Serien-Aufnahmen (laut Repertoir), vollständiger Prosceniums-Einrichtung, complet verpackt, für den Preis von 2500 Mark zu verkaufen ist. Weitere Bioscope sind erst 2 Monate nach der Bestellung lieferbar.

A frame from one of the 1895 Bioscop films

Figure 3.136: The brothers Max and Emil Skladanowsky created the Bioscop motion picture camera and projector in 1892 and presented the first public films in 1895.

Color photograph by Miethe (1902)

Adolf Miethe (1862–1927) produced high-quality color photographs



Color photograph by Miethe (1903)

Figure 3.137: Adolf Miethe produced high-quality color photographs using a three-color process beginning in 1901. He also invented the first practical flash powder.

Rudolf Fischer (1881–1957)

KAISERLICHES PATENTAMT.

PATENTSCHRIFT

— № 257160 —

KLASSE 57*b*. GRUPPE 18.

AUSGEGEBEN DEN 17. APRIL 1913.

NEUE PHOTOGRAPHISCHE GESELLSCHAFT AKT.-GES.
IN BERLIN-STEGLITZ.

Verfahren zur Herstellung von Farbenphotographien.

Patentiert im Deutschen Reiche vom 14. Juni 1911 ab.

Es ist bekannt, daß man durch Baden von belichteten Halogensilberschichten in geeigneten Lösungen unmittelbar einfarbige Bilder erhalten kann, indem das belichtete Halogensilber den in den Lösungen vorhandenen Stoff zu einem unlöslichen Farbstoff oxydiert, der sich auf dem reduzierten Silber niederschlägt. In der Folge soll diese Art der Entwicklung als »farbige Entwicklung« und die dieselbe verursachenden Stoffe als »Farbbildner« bezeichnet werden.

Das vorliegende Verfahren benutzt diese stärkere Oxydationsfähigkeit von belichtetem Halogensilber gegenüber unbelichtetem zur Erzeugung von Farbenphotographien. Diese ist auf verschiedene Arten möglich, und zwar können ebenso gut additive als auch subtraktive Farbenbilder hergestellt werden.

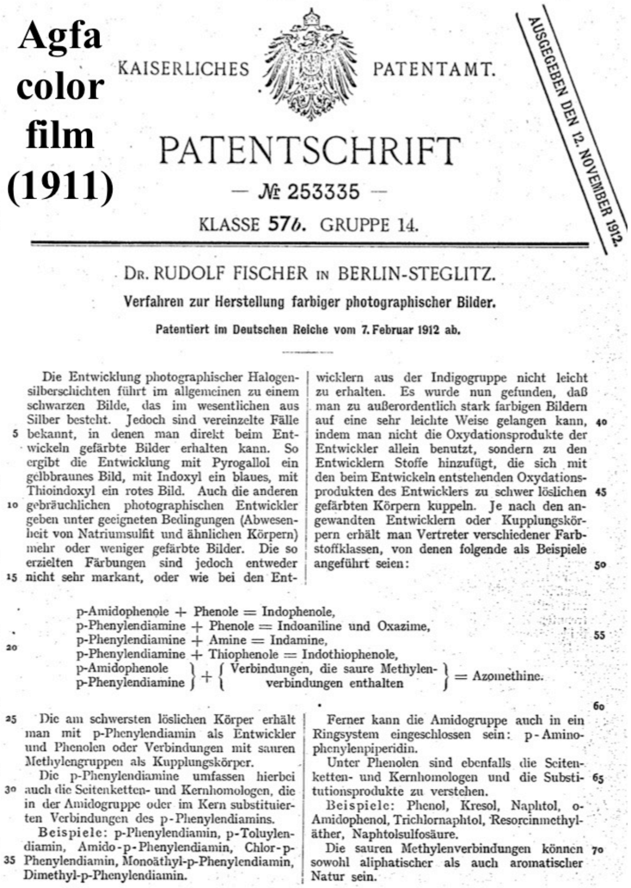
I. Soll z. B. ein Farbraster als ein additives Farbbild hergestellt werden, so belichtet man eine lichtempfindliche Halogensilberschicht unter einem Raster, der zu etwa einem Drittel seiner Fläche lichtdurchlässig und zu zwei Dritteln gedeckt ist, badet die Schicht dann in einer einen blauen Farbstoff erzeugenden Lösung, z. B. Indoxyl, kopiert unter einem zweiten Raster so, daß wiederum ein Drittel der Fläche belichtet wird, und badet in einer einen roten Farbstoff erzeugenden Lösung, z. B. Thioindoxyl. Man belichtet dann die ganze Fläche ohne das Rasternegativ; dabei wird der Rest, also das bisher unbelichtete Halogensilber, beeinflußt, das sich nunmehr beim Baden in einer einen grünen Farbstoff ergebenden Lösung, z. B. Chlorindoxyl, grün färbt. Bei der zweiten und dritten Belichtung schützt das unter den Farbkörpern liegende Silber das unter diesem liegende unveränderte Halogensilber vor weiterer Belichtung und Entwicklung. Dieser Schutz kann außerdem schon durch den erzeugten Farbstoff hervorgerufen werden, wenn man bei den späteren Belichtungen solches Licht anwendet, das durch den bereits erzeugten Farbstoff absorbiert wird. Das so hergestellte dreifarbige Bild (Raster) kann nach Entfernung des unter den Farbkörpern liegenden Silbers, z. B. mit Farmerschem Abschwächer, und nach Entfernung des nicht veränderten Halogensilbers mittels eines Fixiermittels als Dreifarbenraster dienen.

II. Für subtraktive Bilder werden, wie üblich, drei Teilnegative verwendet, deren jedes einer der Grundfarben entspricht. Hiervon werden auf Halogensilberschichten drei Teilpositive kopiert und diese in der oben angegebenen Weise in den entsprechenden Farbbildnern entwickelt und alsdann übereinander gelegt.

Die Teilpositive kann man auch direkt aus einem mittels Raster hergestellten komplementärfarbigen Negativ erhalten, indem man von

Wilhelm Siegrist (1881–19??)

Agfa color film (1911)



KAISERLICHES PATENTAMT.

PATENTSCHRIFT

— № 253335 —

KLASSE 57*b*. GRUPPE 14.

AUSGEGEBEN DEN 12. NOVEMBER 1912.

DR. RUDOLF FISCHER IN BERLIN-STEGLITZ.

Verfahren zur Herstellung farbiger photographischer Bilder.

Patentiert im Deutschen Reiche vom 7. Februar 1912 ab.

Die Entwicklung photographischer Halogensilberschichten führt im allgemeinen zu einem schwarzen Bilde, das im wesentlichen aus Silber besteht. Jedoch sind vereinzelte Fälle bekannt, in denen man direkt beim Entwickeln gefärbte Bilder erhalten kann. So ergibt die Entwicklung mit Pyrogallol ein gelbbraunes Bild, mit Indoxyl ein blaues, mit Thioindoxyl ein rotes Bild. Auch die anderen gebräuchlichen photographischen Entwickler geben unter geeigneten Bedingungen (Abwesenheit von Natriumsulfit und ähnlichen Körpern) mehr oder weniger gefärbte Bilder. Die so erzielten Färbungen sind jedoch entweder nicht sehr markant, oder wie bei den Entwicklern aus der Indigogruppe nicht leicht zu erhalten. Es wurde nun gefunden, daß man zu außerordentlich stark farbigen Bildern auf eine sehr leichte Weise gelangen kann, indem man nicht die Oxydationsprodukte der Entwickler allein benutzt, sondern zu den Entwicklern Stoffe hinzufügt, die sich mit den beim Entwickeln entstehenden Oxydationsprodukten des Entwicklers zu schwer löslichen gefärbten Körpern kuppeln. Je nach den angewandten Entwicklern oder Kupplungskörpern erhält man Vertreter verschiedener Farbstoffklassen, von denen folgende als Beispiele angeführt seien:

p-Amidophenole + Phenole = Indophenole,
p-Phenylendiamine + Phenole = Indoaniline und Oxazime,
p-Phenylendiamine + Amine = Indamine,
p-Phenylendiamine + Thiophenole = Indothiophenole,

$$\left.\begin{array}{l}\text{p-Amidophenole}\\ \text{p-Phenylendiamine}\end{array}\right\}+\left\{\begin{array}{c}\text{Verbindungen, die saure Methylen-}\\ \text{verbindungen enthalten}\end{array}\right\}=\text{Azomethine.}$$

Die am schwersten löslichen Körper erhält man mit p-Phenylendiamin als Entwickler und Phenolen oder Verbindungen mit sauren Methylengruppen als Kupplungskörper.

Die p-Phenylendiamine umfassen hierbei auch die Seitenketten- und Kernhomologen, die in der Amidogruppe oder im Kern substituierten Verbindungen des p-Phenylendiamins.

Beispiele: p-Phenylendiamin, p-Toluylendiamin, Amido-p-Phenylendiamin, Chlor-p-Phenylendiamin, Monoäthyl-p-Phenylendiamin, Dimethyl-p-Phenylendiamin.

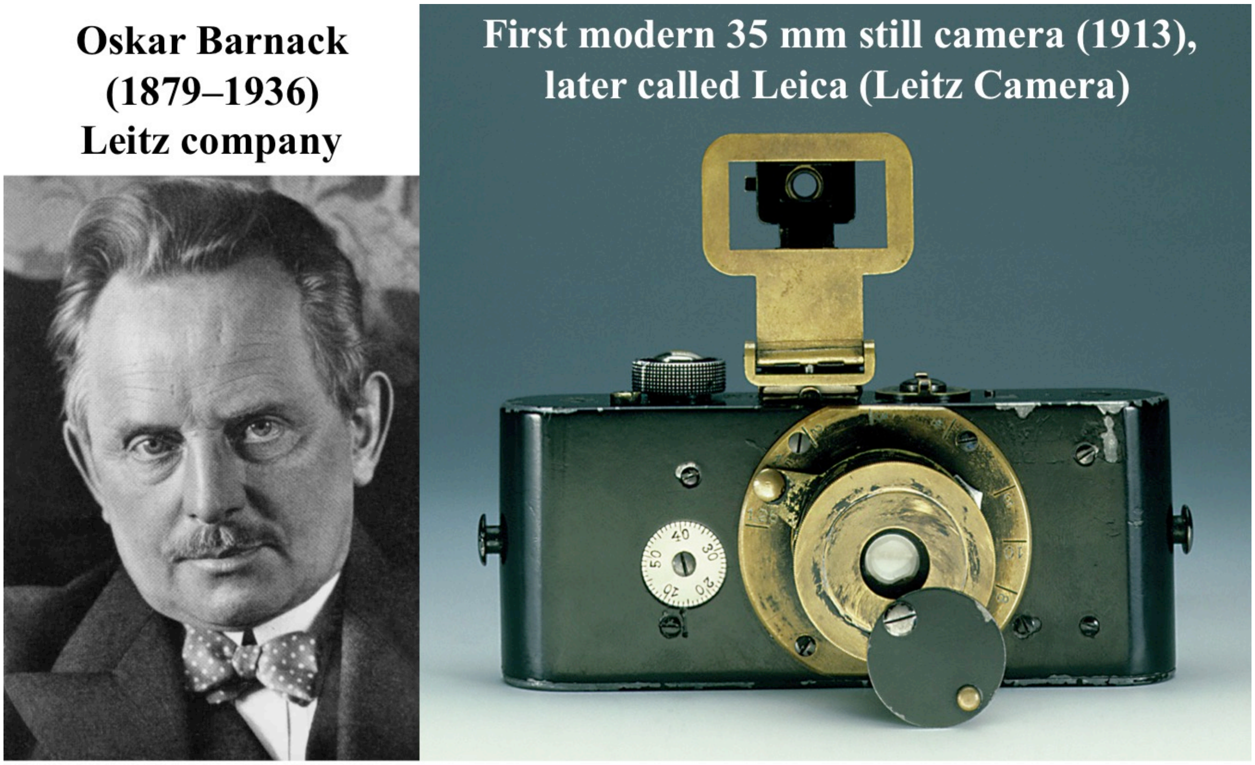
Ferner kann die Amidogruppe auch in ein Ringsystem eingeschlossen sein: p-Aminophenylenpiperidin.

Unter Phenolen sind ebenfalls die Seitenketten- und Kernhomologen und die Substitutionsprodukte zu verstehen.

Beispiele: Phenol, Kresol, Naphtol, o-Amidophenol, Trichlornaphtol, Resorcinmethyläther, Naphtolsulfosäure.

Die sauren Methylenverbindungen können sowohl aliphatischer als auch aromatischer Natur sein.

Figure 3.138: Rudolf Fischer invented Agfa color film in 1911. He worked closely with Wilhelm Siegrist for part of that period.

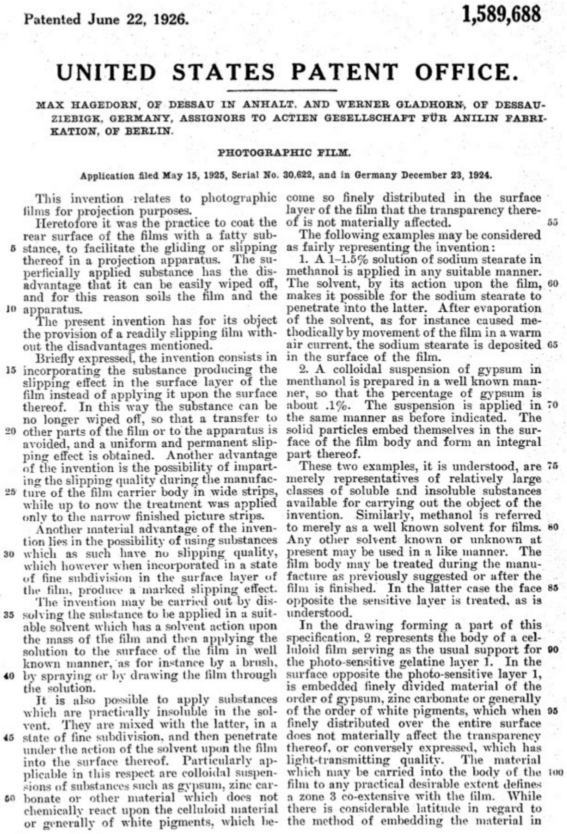


Oskar Barnack (1879–1936) Leitz company

First modern 35 mm still camera (1913), later called Leica (Leitz Camera)

First photo with that camera (Wetzlar, 1913)

Figure 3.139: In 1913, Oskar Barnack invented the first modern 35 mm still camera, which later was dubbed Leica (Leitz Camera).



Patented June 22, 1926. **1,589,688**

UNITED STATES PATENT OFFICE.

MAX HAGEDORN, OF DESSAU IN ANHALT, AND WERNER GLADHORN, OF DESSAU-ZIEBIGK, GERMANY, ASSIGNORS TO ACTIEN GESELLSCHAFT FÜR ANILIN FABRIKATION, OF BERLIN.

PHOTOGRAPHIC FILM.

Application filed May 15, 1925, Serial No. 30,622, and in Germany December 23, 1924.

This invention relates to photographic films for projection purposes.

Heretofore it was the practice to coat the rear surface of the films with a fatty substance, to facilitate the gliding or slipping thereof in a projection apparatus. The superficially applied substance has the disadvantage that it can be easily wiped off, and for this reason soils the film and the apparatus.

The present invention has for its object the provision of a readily slipping film without the disadvantages mentioned.

Briefly expressed, the invention consists in incorporating the substance producing the slipping effect in the surface layer of the film instead of applying it upon the surface thereof. In this way the substance can be no longer wiped off, so that a transfer to other parts of the film or to the apparatus is avoided, and a uniform and permanent slipping effect is obtained. Another advantage of the invention is the possibility of imparting the slipping quality during the manufacture of the film carrier body in wide strips, while up to now the treatment was applied only to the narrow finished picture strips.

Another material advantage of the invention lies in the possibility of using substances which as such have no slipping quality, which however when incorporated in a state of fine subdivision in the surface layer of the film, produce a marked slipping effect.

The invention may be carried out by dissolving the substance to be applied in a suitable solvent which has a solvent action upon the mass of the film and then applying the solution to the surface of the film in well known manner, as for instance by a brush, by spraying or by drawing the film through the solution.

It is also possible to apply substances which are practically insoluble in the solvent. They are mixed with the latter, in a state of fine subdivision, and then penetrate under the action of the solvent upon the film into the surface thereof. Particularly applicable in this respect are colloidal suspensions of substances such as gypsum, zinc carbonate or other material which does not chemically react upon the celluloid material or generally of white pigments, which become so finely distributed in the surface layer of the film that the transparency thereof is not materially affected.

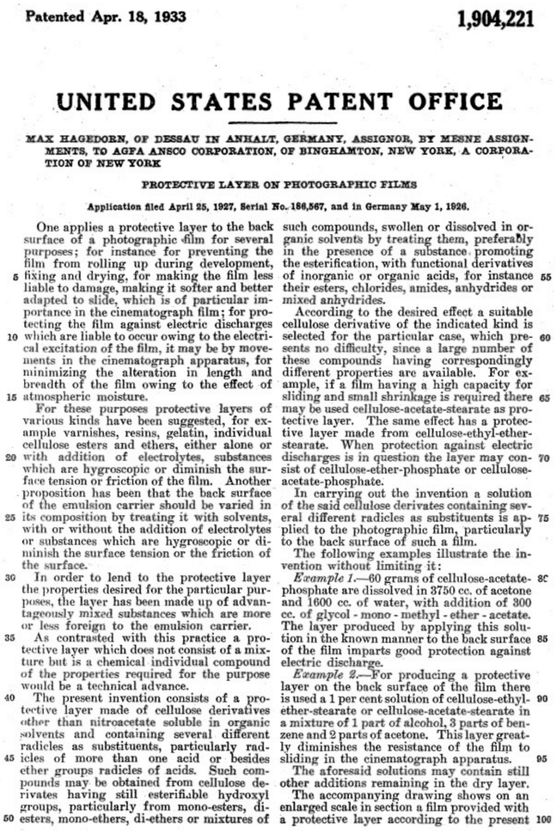
The following examples may be considered as fairly representing the invention:

1. A 1–1.5% solution of sodium stearate in methanol is applied in any suitable manner. The solvent, by its action upon the film, makes it possible for the sodium stearate to penetrate into the latter. After evaporation of the solvent, as for instance caused methodically by movement of the film in a warm air current, the sodium stearate is deposited in the surface of the film.

2. A colloidal suspension of gypsum in menthanol is prepared in a well known manner, so that the percentage of gypsum is about .1%. The suspension is applied in the same manner as before indicated. The solid particles embed themselves in the surface of the film body and form an integral part thereof.

These two examples, it is understood, are merely representatives of relatively large classes of soluble and insoluble substances available for carrying out the object of the invention. Similarly, methanol is referred to merely as a well known solvent for films. Any other solvent known or unknown at present may be used in a like manner. The film body may be treated during the manufacture as previously suggested or after the film is finished. In the latter case the face opposite the sensitive layer is treated, as is understood.

In the drawing forming a part of this specification, 2 represents the body of a celluloid film serving as the usual support for the photo-sensitive gelatine layer 1. In the surface opposite the photo-sensitive layer 1, is embedded finely divided material of the order of gypsum, zinc carbonate or generally of the order of white pigments, which when finely distributed over the entire surface does not materially affect the transparency thereof, or conversely expressed, which has light-transmitting quality. The material which may be carried into the body of the film to any practical desirable extent defines a zone 3 co-extensive with the film. While there is considerable latitude in regard to the method of embedding the material in



Patented Apr. 18, 1933 **1,904,221**

UNITED STATES PATENT OFFICE

MAX HAGEDORN, OF DESSAU IN ANHALT, GERMANY, ASSIGNOR, BY MESNE ASSIGNMENTS, TO AGFA ANSCO CORPORATION, OF BINGHAMTON, NEW YORK, A CORPORATION OF NEW YORK

PROTECTIVE LAYER ON PHOTOGRAPHIC FILMS

Application filed April 25, 1927, Serial No. 186,567, and in Germany May 1, 1926.

One applies a protective layer to the back surface of a photographic film for several purposes; for instance for preventing the film from rolling up during development, fixing and drying, for making the film less liable to damage, making it softer and better adapted to slide, which is of particular importance in the cinematograph film; for protecting the film against electric discharges which are liable to occur owing to the electrical excitation of the film, it may be by movements in the cinematograph apparatus, for minimizing the alteration in length and breadth of the film owing to the effect of atmospheric moisture.

For these purposes protective layers of various kinds have been suggested, for example varnishes, resins, gelatin, individual cellulose esters and ethers, either alone or with addition of electrolytes, substances which are hygroscopic or diminish the surface tension or friction of the film. Another proposition has been that the back surface of the emulsion carrier should be varied in its composition by treating it with solvents, with or without the addition of electrolytes or substances which are hygroscopic or diminish the surface tension or the friction of the surface.

In order to lend to the protective layer the properties desired for the particular purposes, the layer has been made up of advantageously mixed substances which are more or less foreign to the emulsion carrier.

As contrasted with this practice a protective layer which does not consist of a mixture but is a chemical individual compound of the properties required for the purpose would be a technical advance.

The present invention consists of a protective layer made of cellulose derivatives other than nitroacetate soluble in organic solvents and containing several different radicles as substituents, particularly radicles of more than one acid or besides ether groups radicles of acids. Such compounds may be obtained from cellulose derivates having still esterifiable hydroxyl groups, particularly from mono-esters, di-esters, mono-ethers, di-ethers or mixtures of such compounds, swollen or dissolved in organic solvents by treating them, preferably in the presence of a substance promoting the esterification, with functional derivatives of inorganic or organic acids, for instance their esters, chlorides, amides, anhydrides or mixed anhydrides.

According to the desired effect a suitable cellulose derivative of the indicated kind is selected for the particular case, which presents no difficulty, since a large number of these compounds having correspondingly different properties are available. For example, if a film having a high capacity for sliding and small shrinkage is required there may be used cellulose-acetate-stearate as protective layer. The same effect has a protective layer made from cellulose-ethyl-ether-stearate. When protection against electric discharges is in question the layer may consist of cellulose-ether-phosphate or cellulose-acetate-phosphate.

In carrying out the invention a solution of the said cellulose derivates containing several different radicles as substituents is applied to the photographic film, particularly to the back surface of such a film.

The following examples illustrate the invention without limiting it:

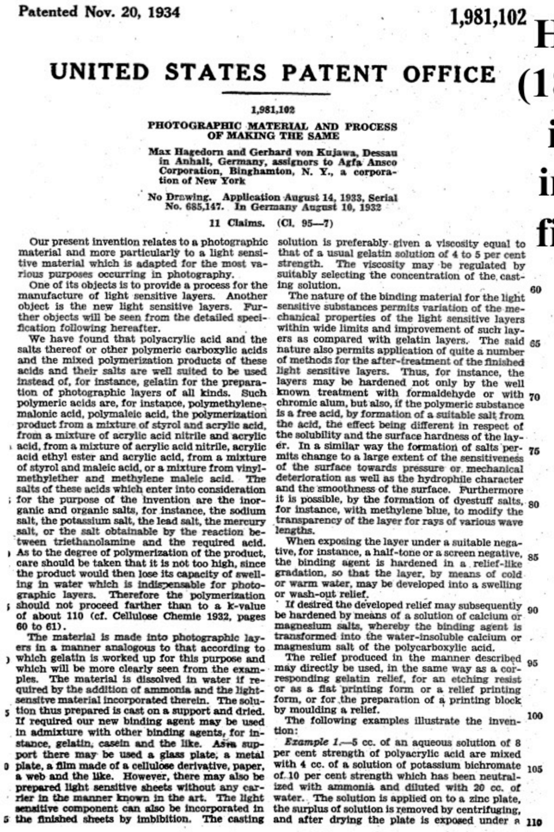
Example 1.—60 grams of cellulose-acetate-phosphate are dissolved in 3750 cc. of acetone and 1600 cc. of water, with addition of 300 cc. of glycol - mono - methyl - ether - acetate. The layer produced by applying this solution in the known manner to the back surface of the film imparts good protection against electric discharge.

Example 2.—For producing a protective layer on the back surface of the film there is used a 1 per cent solution of cellulose-ethyl-ether-stearate or cellulose-acetate-stearate in a mixture of 1 part of alcohol, 3 parts of benzene and 2 parts of acetone. This layer greatly diminishes the resistance of the film to sliding in the cinematograph apparatus.

The aforesaid solutions may contain still other additions remaining in the dry layer.

The accompanying drawing shows on an enlarged scale in section a film provided with a protective layer according to the present

Max Hagedorn (18??–19??) invented improved film stock (1924–)



Patented Nov. 20, 1934 **1,981,102**

UNITED STATES PATENT OFFICE

1,981,102

PHOTOGRAPHIC MATERIAL AND PROCESS OF MAKING THE SAME

Max Hagedorn and Gerhard von Kujawa, Dessau in Anhalt, Germany, assignors to Agfa Ansco Corporation, Binghamton, N. Y., a corporation of New York

No Drawing. Application August 14, 1933, Serial No. 685,147. In Germany August 10, 1932

11 Claims. (Cl. 95—7)

Our present invention relates to a photographic material and more particularly to a light sensitive material which is adapted for the most various purposes occurring in photography.

One of its objects is to provide a process for the manufacture of light sensitive layers. Another object is the new light sensitive layers. Further objects will be seen from the detailed specification following hereafter.

We have found that polyacrylic acid and the salts thereof or other polymeric carboxylic acids and the mixed polymerization products of these acids and their salts are well suited to be used instead of, for instance, gelatin for the preparation of photographic layers of all kinds. Such polymeric acids are, for instance, polymethylene-malonic acid, polymaleic acid, the polymerization product from a mixture of styrol and acrylic acid, from a mixture of acrylic acid nitrile and acrylic acid, from a mixture of acrylic acid nitrile, acrylic acid ethyl ester and acrylic acid, from a mixture of styrol and maleic acid, or a mixture from vinylmethylether and methylene maleic acid. The salts of these acids which enter into consideration for the purpose of the invention are the inorganic and organic salts, for instance, the sodium salt, the potassium salt, the lead salt, the mercury salt, or the salt obtainable by the reaction between triethanolamine and the required acid. As to the degree of polymerization of the product, care should be taken that it is not too high, since the product would then lose its capacity of swelling in water which is indispensable for photographic layers. Therefore the polymerization should not proceed farther than to a k-value of about 110 (cf. Cellulose Chemie 1932, pages 60 to 61).

The material is made into photographic layers in a manner analogous to that according to which gelatin is worked up for this purpose and which will be more clearly seen from the examples. The material is dissolved in water if required by the addition of ammonia and the light-sensitve material incorporated therein. The solution thus prepared is cast on a support and dried. If required our new binding agent may be used in admixture with other binding agents, for instance, gelatin, casein and the like. As a support there may be used a glass plate, a metal plate, a film made of a cellulose derivative, paper, a web and the like. However, there may also be prepared light sensitive sheets without any carrier in the manner known in the art. The light sensitive component can also be incorporated in the finished sheets by imbibition. The casting solution is preferably given a viscosity equal to that of a usual gelatin solution of 4 to 5 per cent strength. The viscosity may be regulated by suitably selecting the concentration of the casting solution.

The nature of the binding material for the light sensitive substances permits variation of the mechanical properties of the light sensitive layers within wide limits and improvement of such layers as compared with gelatin layers. The said nature also permits application of quite a number of methods for the after-treatment of the finished light sensitive layers. Thus, for instance, the layers may be hardened not only by the well known treatment with formaldehyde or with chromic alum, but also, if the polymeric substance is a free acid, by formation of a suitable salt from the acid, the effect being different in respect of the solubility and the surface hardness of the layer. In a similar way the formation of salts permits change to a large extent of the sensitiveness of the surface towards pressure or mechanical deterioration as well as the hydrophile character and the smoothness of the surface. Furthermore it is possible, by the formation of dyestuff salts, for instance, with methylene blue, to modify the transparency of the layer for rays of various wave lengths.

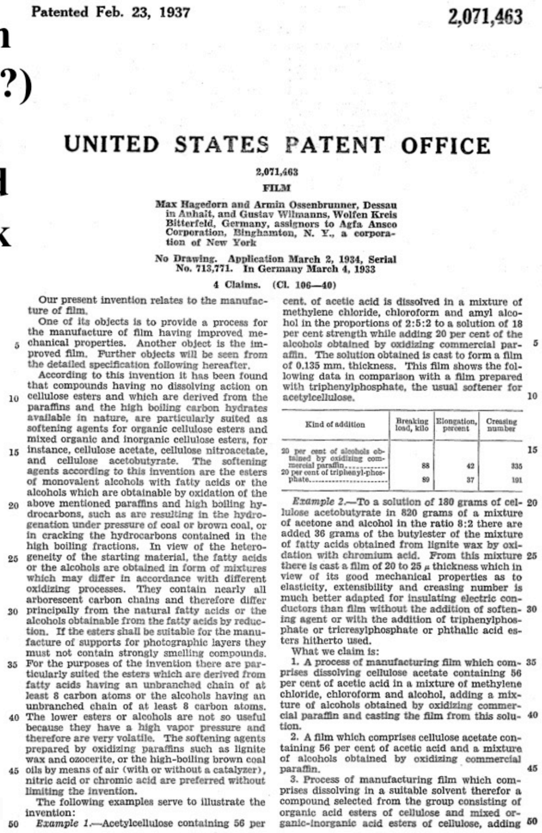
When exposing the layer under a suitable negative, for instance, a half-tone or a screen negative, the binding agent is hardened in a relief-like gradation, so that the layer, by means of cold or warm water, may be developed into a swelling or wash-out relief.

If desired the developed relief may subsequently be hardened by means of a solution of calcium or magnesium salts, whereby the binding agent is transformed into the water-insoluble calcium or magnesium salt of the polycarboxylic acid.

The relief produced in the manner described may directly be used, in the same way as a corresponding gelatin relief, for an etching resist or as a flat printing form or a relief printing form, or for the preparation of a printing block by moulding a relief.

The following examples illustrate the invention:

Example 1.—5 cc. of an aqueous solution of 8 per cent strength of polyacrylic acid are mixed with 4 cc. of a solution of potassium bichromate of 10 per cent strength which has been neutralized with ammonia and diluted with 20 cc. of water. The solution is applied on to a zinc plate, the surplus of solution is removed by centrifuging, and after drying the plate is exposed under a



Patented Feb. 23, 1937 **2,071,463**

UNITED STATES PATENT OFFICE

2,071,463

FILM

Max Hagedorn and Armin Ossenbrunner, Dessau in Anhalt, and Gustav Wilmanns, Wolfen Kreis Bitterfeld, Germany, assignors to Agfa Ansco Corporation, Binghamton, N. Y., a corporation of New York

No Drawing. Application March 2, 1934, Serial No. 713,771. In Germany March 4, 1933

4 Claims. (Cl. 106—40)

Our present invention relates to the manufacture of film.

One of its objects is to provide a process for the manufacture of film having improved mechanical properties. Another object is the improved film. Further objects will be seen from the detailed specification following hereafter.

According to this invention it has been found that compounds having no dissolving action on cellulose esters and which are derived from the paraffins and the high boiling carbon hydrates available in nature, are particularly suited as softening agents for organic cellulose esters and mixed organic and inorganic cellulose esters, for instance, cellulose acetate, cellulose nitroacetate, and cellulose acetobutyrate. The softening agents according to this invention are the esters of monovalent alcohols with fatty acids or the alcohols which are obtainable by oxidation of the above mentioned paraffins and high boiling hydrocarbons, such as are resulting in the hydrogenation under pressure of coal or brown coal, or in cracking the hydrocarbons contained in the high boiling fractions. In view of the heterogeneity of the starting material, the fatty acids or the alcohols are obtained in form of mixtures which may differ in accordance with different oxidizing processes. They contain nearly all arborescent carbon chains and therefore differ principally from the natural fatty acids or the alcohols obtainable from the fatty acids by reduction. If the esters shall be suitable for the manufacture of supports for photographic layers they must not contain strongly smelling compounds. For the purposes of the invention there are particularly suited the esters which are derived from fatty acids having an unbranched chain of at least 8 carbon atoms or the alcohols having an unbranched chain of at least 8 carbon atoms. The lower esters or alcohols are not so useful because they have a high vapor pressure and therefore are very volatile. The softening agents prepared by oxidizing paraffins such as lignite wax and ozocerite, or the high-boiling brown coal oils by means of air (with or without a catalyzer), nitric acid or chromic acid are preferred without limiting the invention.

The following examples serve to illustrate the invention:

Example 1.—Acetylcellulose containing 56 per cent. of acetic acid is dissolved in a mixture of methylene chloride, chloroform and amyl alcohol in the proportions of 2:5:2 to a solution of 18 per cent strength while adding 20 per cent of the alcohols obtained by oxidizing commercial paraffin. The solution obtained is cast to form a film of 0.135 mm. thickness. This film shows the following data in comparison with a film prepared with triphenylphosphate, the usual softener for acetylcellulose.

Kind of addition	Breaking load, kilo	Elongation, percent	Creasing number
20 per cent of alcohols obtained by oxidizing commercial paraffin	88	42	335
20 per cent of triphenyl-phosphate	89	37	191

Example 2.—To a solution of 180 grams of cellulose acetobutyrate in 820 grams of a mixture of acetone and alcohol in the ratio 8:2 there are added 36 grams of the butylester of the mixture of fatty acids obtained from lignite wax by oxidation with chromium acid. From this mixture there is cast a film of 20 to 25 μ thickness which in view of its good mechanical properties as to elasticity, extensibility and creasing number is much better adapted for insulating electric conductors than film without the addition of softening agent or with the addition of triphenylphosphate or tricresylphosphate or phthalic acid esters hitherto used.

What we claim is:

1. A process of manufacturing film which comprises dissolving cellulose acetate containing 56 per cent of acetic acid in a mixture of methylene chloride, chloroform and alcohol, adding a mixture of alcohols obtained by oxidizing commercial paraffin and casting the film from this solution.

2. A film which comprises cellulose acetate containing 56 per cent of acetic acid and a mixture of alcohols obtained by oxidizing commercial paraffin.

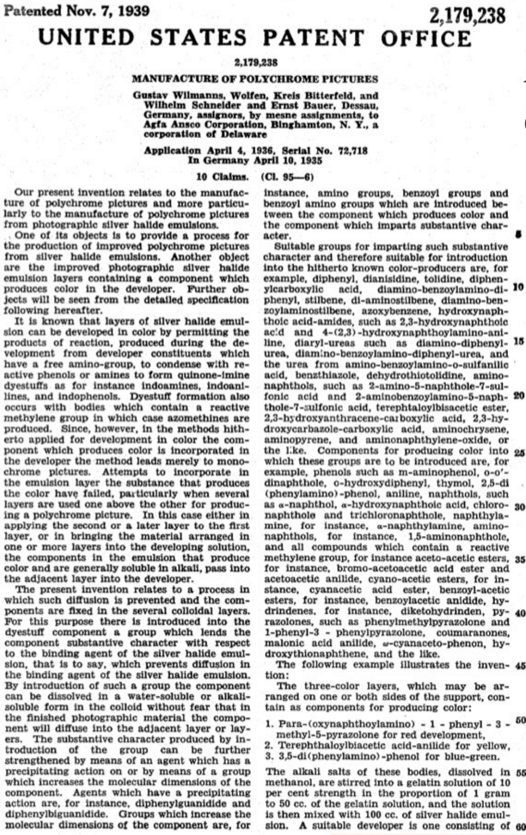
3. Process of manufacturing film which comprises dissolving in a suitable solvent therefor a compound selected from the group consisting of organic acid esters of cellulose and mixed organic-inorganic acid esters of cellulose, adding

Figure 3.140: Max Hagedorn created improved film stock from 1924 onward.

Ernst Bauer
(18??–19??)

Wilhelm Schneider
(18??–19??)

Gustav Wilmanns
(18??–19??)



Patented Nov. 7, 1939

2,179,238

UNITED STATES PATENT OFFICE

2,179,238

MANUFACTURE OF POLYCHROME PICTURES

Gustav Wilmanns, Wolfen, Kreis Bitterfeld, and Wilhelm Schneider and Ernst Bauer, Dessau, Germany, assignors, by mesne assignments, to Agfa Ansco Corporation, Binghamton, N. Y., a corporation of Delaware

Application April 4, 1936, Serial No. 72,718
In Germany April 10, 1935

10 Claims. (Cl. 95—6)

Our present invention relates to the manufacture of polychrome pictures and more particularly to the manufacture of polychrome pictures from photographic silver halide emulsions.

One of its objects is to provide a process for the production of improved polychrome pictures from silver halide emulsions. Another object are the improved photographic silver halide emulsion layers containing a component which produces color in the developer. Further objects will be seen from the detailed specification following hereafter.

It is known that layers of silver halide emulsion can be developed in color by permitting the products of reaction, produced during the development from developer constituents which have a free amino-group, to condense with reactive phenols or amines to form quinone-imine dyestuffs as for instance indoamines, indoanilines, and indophenols. Dyestuff formation also occurs with bodies which contain a reactive methylene group in which case azomethines are produced. Since, however, in the methods hitherto applied for development in color the component which produces color is incorporated in the developer the method leads merely to monochrome pictures. Attempts to incorporate in the emulsion layer the substance that produces the color have failed, particularly when several layers are used one above the other for producing a polychrome picture. In this case either in applying the second or a later layer to the first layer, or in bringing the material arranged in one or more layers into the developing solution, the components in the emulsion that produce color and are generally soluble in alkali, pass into the adjacent layer into the developer.

The present invention relates to a process in which such diffusion is prevented and the components are fixed in the several colloidal layers. For this purpose there is introduced into the dyestuff component a group which lends the component substantive character with respect to the binding agent of the silver halide emulsion, that is to say, which prevents diffusion in the binding agent of the silver halide emulsion. By introduction of such a group the component can be dissolved in a water-soluble or alkali-soluble form in the colloid without fear that in the finished photographic material the component will diffuse into the adjacent layer or layers. The substantive character produced by introduction of the group can be further strengthened by means of an agent which has a precipitating action on or by means of a group which increases the molecular dimensions of the component. Agents which have a precipitating action are, for instance, diphenylguanidide and diphenylbiguanidide. Groups which increase the molecular dimensions of the component are, for instance, amino groups, benzoyl groups and benzoyl amino groups which are introduced between the component which produces color and the component which imparts substantive character.

Suitable groups for imparting such substantive character and therefore suitable for introduction into the hitherto known color-producers are, for example, diphenyl, dianisidine, tolidine, diphenylcarboxylic acid, diamino-benzoylamino-diphenyl, stilbene, di-aminostilbene, diamino-benzoylaminostilbene, azoxybenzene, hydroxynaphthoic acid-amides, such as 2,3-hydroxynaphthoic acid and 4-(2,3)-hydroxynaphthoylamino-aniline, diaryl-ureas such as diamino-diphenyl-urea, diamino-benzoylamino-diphenyl-urea, and the urea from amino-benzoylamino-o-sulfanilic acid, benzthiazole, dehydrothiotolidine, amino-naphthols, such as 2-amino-5-naphthole-7-sulfonic acid and 2-aminobenzoylamino-5-naphthole-7-sulfonic acid, terephtaloylbisacetic ester, 2,3-hydroxyanthracene-carboxylic acid, 2,3-hydroxycarbazole-carboxylic acid, aminochrysene, aminopyrene, and aminonaphthylene-oxide, or the like. Components for producing color into which these groups are to be introduced are, for example, phenols such as m-aminophenol, o-o′-dinaphthole, o-hydroxydiphenyl, thymol, 2,5-di (phenylamino)-phenol, aniline, naphthols, such as α-naphthol, α-hydroxynaphthoic acid, chloronaphthole and trichloronaphthole, naphthylamine, for instance, α-naphthylamine, aminonaphthols, for instance, 1,5-aminonaphthole, and all compounds which contain a reactive methylene group, for instance aceto-acetic esters, for instance, bromo-acetoacetic acid ester and acetoacetic anilide, cyano-acetic esters, for instance, cyanacetic acid ester, benzoyl-acetic esters, for instance, benzoylacetic anidide, hydrindenes, for instance, diketohydrinden, pyrazolones, such as phenylmethylpyrazolone and 1-phenyl-3 - phenylpyrazolone, coumaranones, malonic acid anilide, ω-cyanaceto-phenon, hydroxythionaphthene, and the like.

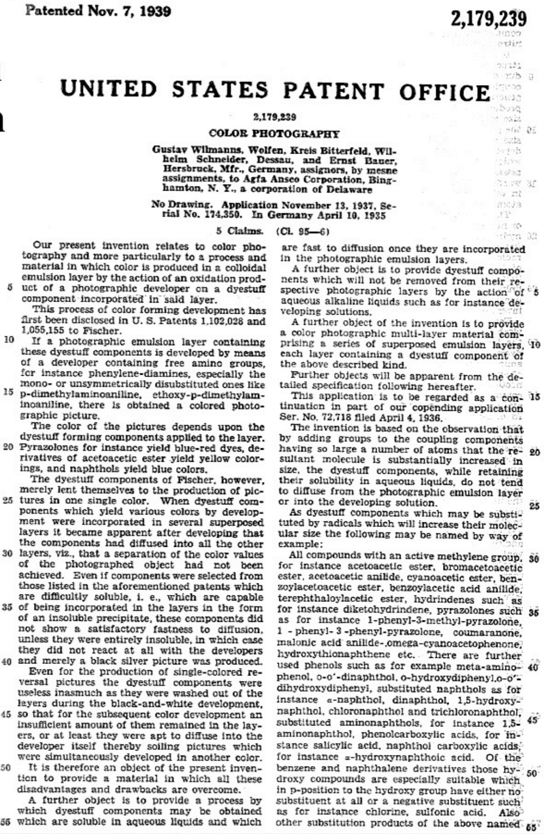
The following example illustrates the invention:

The three-color layers, which may be arranged on one or both sides of the support, contain as components for producing color:

1. Para-(oxynaphthoylamino) - 1 - phenyl - 3 - methyl-5-pyrazolone for red development,
2. Terephthaloylbiacetic acid-anilide for yellow,
3. 3,5-di(phenylamino)-phenol for blue-green.

The alkali salts of these bodies, dissolved in methanol, are stirred into a gelatin solution of 10 per cent strength in the proportion of 1 gram to 50 cc. of the gelatin solution, and the solution is then mixed with 100 cc. of silver halide emulsion. A suitable developer is one consisting of

Agfa Neu
color film
(1935)



Patented Nov. 7, 1939

2,179,239

UNITED STATES PATENT OFFICE

2,179,239

COLOR PHOTOGRAPHY

Gustav Wilmanns, Wolfen, Kreis Bitterfeld, Wilhelm Schneider, Dessau, and Ernst Bauer, Hersbruck, Mfr., Germany, assignors, by mesne assignments, to Agfa Ansco Corporation, Binghamton, N. Y., a corporation of Delaware

No Drawing. Application November 13, 1937, Serial No. 174,350. In Germany April 10, 1935

5 Claims. (Cl. 95—6)

Our present invention relates to color photography and more particularly to a process and material in which color is produced in a colloidal emulsion layer by the action of an oxidation product of a photographic developer on a dyestuff component incorporated in said layer.

This process of color forming development has first been disclosed in U. S. Patents 1,102,028 and 1,055,155 to Fischer.

If a photographic emulsion layer containing these dyestuff components is developed by means of a developer containing free amino groups, for instance phenylene-diamines, especially the mono- or unsymmetrically disubstituted ones like p-dimethylaminoaniline, ethoxy-p-dimethylaminoaniline, there is obtained a colored photographic picture.

The color of the pictures depends upon the dyestuff forming components applied to the layer. Pyrazolones for instance yield blue-red dyes, derivatives of acetoacetic ester yield yellow colorings, and naphthols yield blue colors.

The dyestuff components of Fischer, however, merely lent themselves to the production of pictures in one single color. When dyestuff components which yield various colors by development were incorporated in several superposed layers it became apparent after developing that the components had diffused into all the other layers, viz., that a separation of the color values of the photographed object had not been achieved. Even if components were selected from those listed in the aforementioned patents which are difficultly soluble, i. e., which are capable of being incorporated in the layers in the form of an insoluble precipitate, these components did not show a satisfactory fastness to diffusion, unless they were entirely insoluble, in which case they did not react at all with the developers and merely a black silver picture was produced.

Even for the production of single-colored reversal pictures the dyestuff components were useless inasmuch as they were washed out of the layers during the black-and-white development, so that for the subsequent color development an insufficient amount of them remained in the layers, or at least they were apt to diffuse into the developer itself thereby soiling pictures which were simultaneously developed in another color.

It is therefore an object of the present invention to provide a material in which all these disadvantages and drawbacks are overcome.

A further object is to provide a process by which dyestuff components may be obtained which are soluble in aqueous liquids and which are fast to diffusion once they are incorporated in the photographic emulsion layers.

A further object is to provide dyestuff components which will not be removed from their respective photographic layers by the action of aqueous alkaline liquids such as for instance developing solutions.

A further object of the invention is to provide a color photographic multi-layer material comprising a series of superposed emulsion layers, each layer containing a dyestuff component of the above described kind.

Further objects will be apparent from the detailed specification following hereafter.

This application is to be regarded as a continuation in part of our copending application Ser. No. 72,718 filed April 4, 1936.

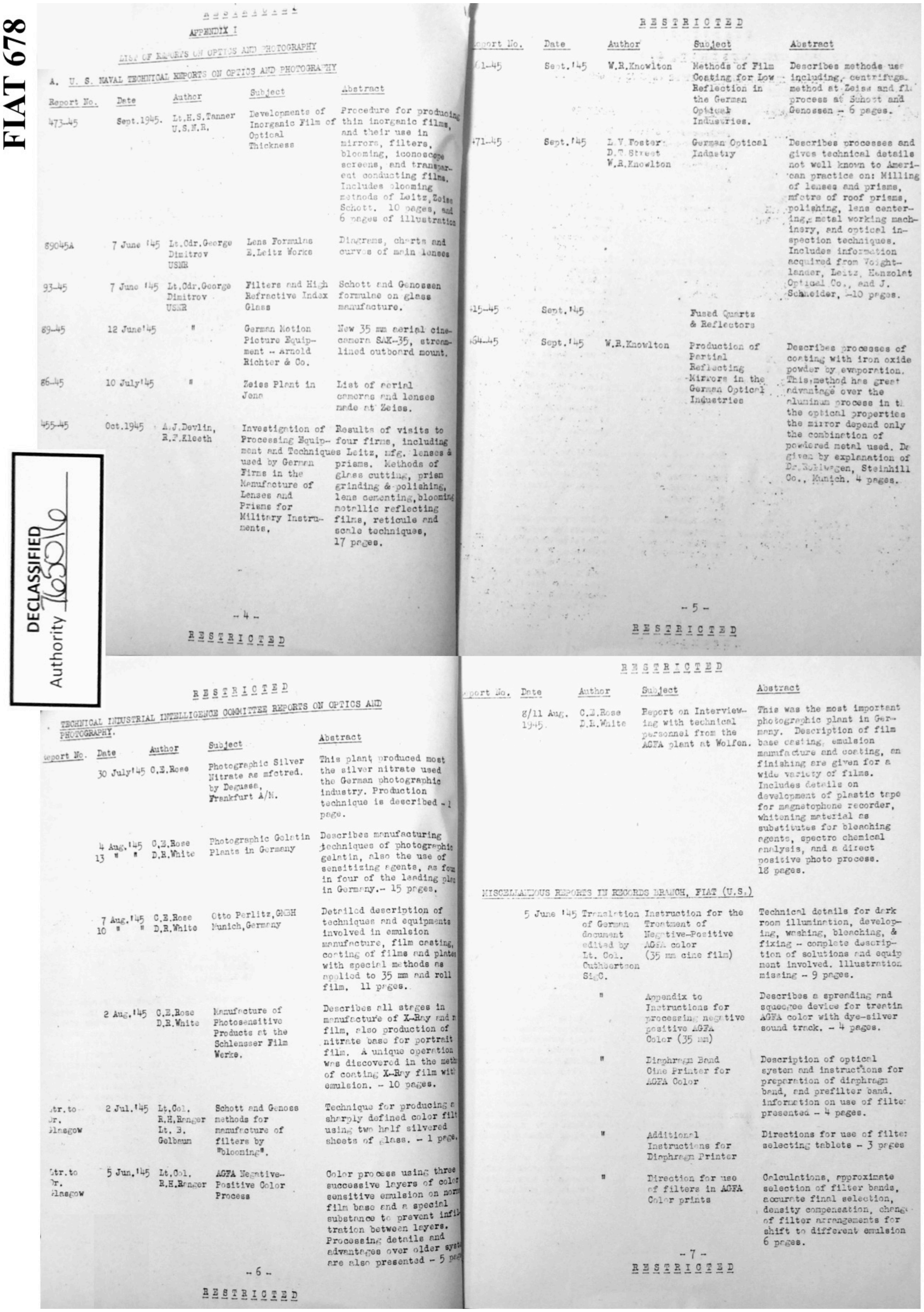
The invention is based on the observation that by adding groups to the coupling components having so large a number of atoms that the resultant molecule is substantially increased in size, the dyestuff components, while retaining their solubility in aqueous liquids, do not tend to diffuse from the photographic emulsion layer or into the developing solution.

As dyestuff components which may be substituted by radicals which will increase their molecular size the following may be named by way of example:

All compounds with an active methylene group, for instance acetoacetic ester, bromacetoacetic ester, acetoacetic anilide, cyanoacetic ester, benzoylacetoacetic ester, benzoylacetic acid anilide, terephthaloylacetic ester, hydrindenes such as for instance diketohydrindene, pyrazolones such as for instance 1-phenyl-3-methyl-pyrazolone, 1 - phenyl- 3 -phenyl-pyrazolone, coumaranone, malonic acid anilide-.omega-cyanoacetophenone, hydroxythionaphthene etc. There are further used phenols such as for example meta-aminophenol, o-o′-dinaphthol, o-hydroxydiphenyl.o-o′-dihydroxydiphenyl, substituted naphthols as for instance α-naphthol, dinaphthol, 1,5-hydroxynaphthol, chloronaphthol and trichloronaphthol, substituted aminonaphthols, for instance 1,5-aminonaphthol, phenolcarboxylic acids, for instance salicylic acid, naphthol carboxylic acids, for instance α-hydroxynaphthoic acid. Of the benzene and naphthalene derivatives those hydroxy compounds are especially suitable which in p-position to the hydroxy group have either no substituent at all or a negative substituent such as for instance chlorine, sulfonic acid. Also other substitution products of the above named

***Frauen sind doch bessere Diplomaten* (filmed 1939–1940)**

Figure 3.141: Ernst Bauer, Wilhelm Schneider, and Gustav Wilmanns invented Agfa Neu improved color film in 1935. Their technology was showcased in films such as *Frauen sind doch bessere Diplomaten* and became the basis for most color film around the world after World War II.



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APPENDIX I

LIST OF REPORTS ON OPTICS AND PHOTOGRAPHY

A. U. S. NAVAL TECHNICAL REPORTS ON OPTICS AND PHOTOGRAPHY

Report No.	Date	Author	Subject	Abstract
473-45	Sept.1945.	Lt.H.S.Tanner U.S.N.R.	Developments of Inorganic Film of Optical Thickness	Procedure for producing thin inorganic films, and their use in mirrors, filters, blooming, iconoscope screens, and transparent conducting films. Includes blooming methods of Leitz, Zeiss Schott. 10 pages, and 6 pages of illustration
89045A	7 June '45	Lt.Cdr.George Dimitrov USNR	Lens Formulas E.Leitz Works	Diagrams, charts and curves of main lenses
93-45	7 June '45	Lt.Cdr.George Dimitrov USNR	Filters and High Refractive Index Glass	Schott and Genossen formulae on glass manufacture.
89-45	12 June'45	"	German Motion Picture Equipment -- Arnold Richter & Co.	New 35 mm aerial cinecamera SAK-35, streamlined outboard mount.
86-45	10 July'45	"	Zeiss Plant in Jena	List of aerial cameras and lenses made at Zeiss.
455-45	Oct.1945	A.J.Devlin, R.F.Kleeth	Investigation of Processing Equipment and Techniques used by German Firms in the Manufacture of Lenses and Prisms for Military Instruments.	Results of visits to four firms, including Leitz, mfg. lenses & prisms. Methods of glass cutting, prism grinding & polishing, lens cementing, blooming metallic reflecting films, reticule and scale techniques, 17 pages.

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port No.	Date	Author	Subject	Abstract
1-45	Sept.'45	W.R.Knowlton	Methods of Film Coating for Low Reflection in the German Optical Industries.	Describes methods us including, centrifuga method at Zeiss and fl process at Schott and Genossen – 6 pages.
71-45	Sept.'45	L.V.Foster D.T.Street W.R.Knowlton	German Optical Industry	Describes processes and gives technical details not well known to American practice on: Milling of lenses and prisms, mfctre of roof prisms, polishing, lens centering, metal working machinery, and optical inspection techniques. Includes information acquired from Voightlander, Leitz, Henzolat Optical Co., and J. Schneider, –10 pages.
15-45	Sept.'45		Fused Quartz & Reflectors	
64-45	Sept.'45	W.R.Knowlton	Production of Partial Reflecting Mirrors in the German Optical Industries	Describes processes of coating with iron oxide powder by evaporation. This method has great advantage over the aluminum process in t the optical properties the mirror depend only the combination of powdered metal used. D given by explanation of Dr.Schlwagen, Steinhill Co., Munich. 4 pages.

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TECHNICAL INDUSTRIAL INTELLIGENCE COMMITTEE REPORTS ON OPTICS AND PHOTOGRAPHY.

eport No.	Date	Author	Subject	Abstract
	30 July'45	C.E.Rose	Photographic Silver Nitrate as mfctred. by Degussa, Frankfurt A/M.	This plant produced most the silver nitrate used the German photographic industry. Production technique is described - 1 page.
	4 Aug.'45 13 " "	C.E.Rose D.R.White	Photographic Gelatin Plants in Germany	Describes manufacturing techniques of photographic gelatin, also the use of sensitizing agents, as fou in four of the leading pla in Germany.- 15 pages.
	7 Aug.'45 10 " "	C.E.Rose D.R.White	Otto Perlitz, GMBH Munich, Germany	Detailed description of techniques and equipments involved in emulsion manufacture, film casting, coating of films and plates with special methods as applied to 35 mm and roll film. 11 pages.
	2 Aug.'45	C.E.Rose D.R.White	Manufacture of Photosensitive Products at the Schlensser Film Werke.	Describes all stages in manufacture of X-Ray and n film, also production of nitrate base for portrait film. A unique operation was discovered in the meth of coating X-Ray film wit emulsion. - 10 pages.
tr. to r. lasgow	2 Jul.'45	Lt.Col. R.H.Ranger Lt. B. Gelbaum	Schott and Genoss methods for manufacture of filters by "blooming".	Technique for producing a sharply defined color filt using two half silvered sheets of glass. – 1 page.
tr. to r. lasgow	5 Jun.'45	Lt.Col. R.H.Ranger	AGFA Negative-Positive Color Process	Color process using three successive layers of color sensitive emulsion on nor film base and a special substance to prevent infil tration between layers. Processing details and advantages over older syst are also presented – 5 pa

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port No.	Date	Author	Subject	Abstract
	8/11 Aug. 1945.	C.E.Rose D.R.White	Report on Interviewing with technical personnel from the AGFA plant at Wolfen.	This was the most important photographic plant in Germany. Description of film base casting, emulsion manufacture and coating, an finishing are given for a wide variety of films. Includes details on development of plastic tape for magnetophone recorder, whitening material as substitutes for bleaching agents, spectro chemical analysis, and a direct positive photo process. 18 pages.

MISCELLANEOUS REPORTS IN RECORDS BRANCH, FIAT (U.S.)

	5 June '45	Translation of German document edited by Lt. Col. Cuthbertson SigC.	Instruction for the Treatment of Negative-Positive AGFA color (35 mm cine film)	Technical details for dark room illumination, developing, washing, bleaching, & fixing – complete description of solutions and equipment involved. Illustration missing – 9 pages.
	"		Appendix to Instructions for processing negative positive AGFA Color (35 mm)	Describes a spreading and squeegee device for treatin AGFA color with dye-silver sound track. – 4 pages.
	"		Diaphragm Band Cine Printer for AGFA Color	Description of optical system and instructions for preparation of diaphragm band, and prefilter band. information on use of filte presented – 4 pages.
	"		Additional Instructions for Diaphragm Printer	Directions for use of filte selecting tablets – 3 pages
	"		Direction for use of filters in AGFA Color prints	Calculations, approximate selection of filter bands, accurate final selection, density compensation, chang of filter arrangements for shift to different emulsion 6 pages.

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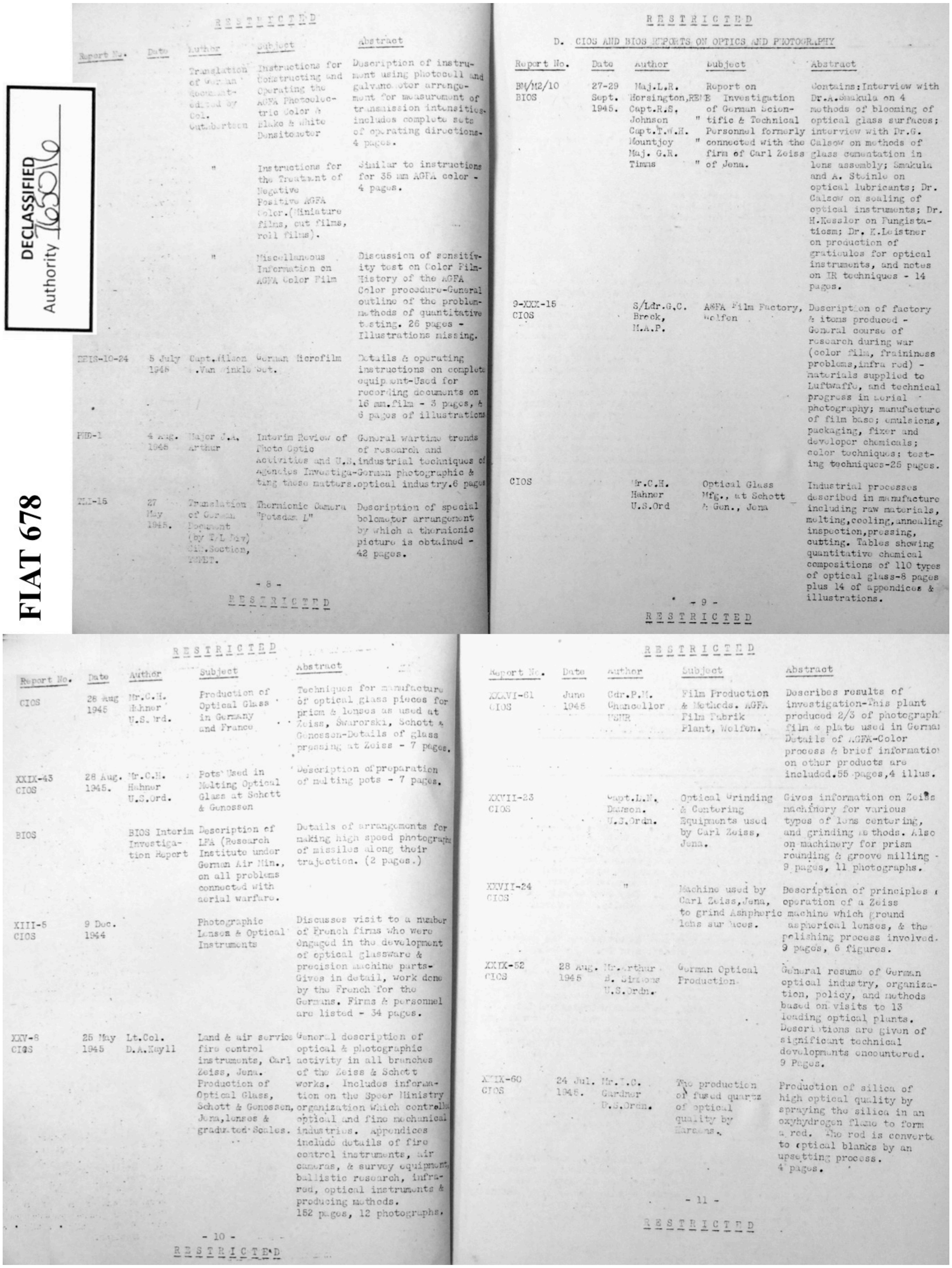
Figure 3.142: A wide variety of advanced technologies, components, and methods for photography were developed in the German-speaking world and transferred to other countries after World War II [FIAT 678].



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FIAT 678

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Report No.	Date	Author	Subject	Abstract
		Translation of German document-edited by Col. Cuthbertson	Instructions for Constructing and Operating the AGFA Photoelectric Color & Black & White Densitometer	Description of instrument using photocell and galvanometer arrangement for measurement of transmission intensities. includes complete sets of operating directions. 4 pages.
		"	Instructions for the Treatment of Negative Positive AGFA Color. (Miniature films, cut films, roll films).	Similar to instructions for 35 mm AGFA color - 4 pages.
		"	Miscellaneous Information on AGFA Color Film	Discussion of sensitivity test on Color Film-History of the AGFA Color procedure-General outline of the problem-methods of quantitative testing. 26 pages - Illustrations missing.
EEIS-10-24	5 July 1945	Capt.Wilson .Van Winkle	German Microfilm Set.	Details & operating instructions on complete equipment-Used for recording documents on 16 mm.film - 3 pages, & 6 pages of illustrations
PHD-1	4 Aug. 1945	Major J.A. Arthur	Interim Review of Photo Optic Activities and U.S. Agencies Investigating these matters.	General wartime trends of research and industrial techniques of German photographic & optical industry. 6 pages
TLI-15	27 May 1945.	Translation of German Document (by T/L Div) Cit.Section, TSFET.	Thermionic Camera "Potsdam L"	Description of special bolometer arrangement by which a thermionic picture is obtained - 42 pages.

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D. CIOS AND BIOS REPORTS ON OPTICS AND PHOTOGRAPHY

Report No.	Date	Author	Subject	Abstract
BM/M2/10 BIOS	27-29 Sept. 1945.	Maj.L.R. Horsington,REME Capt.R.S. Johnson " Capt.T.W.H. Mountjoy " Maj. G.R. Timms "	Report on Investigation of German Scientific & Technical Personnel formerly connected with the firm of Carl Zeiss of Jena.	Contains: Interview with Dr.A.Smakula on 4 methods of blooming of optical glass surfaces; interview with Dr.G. Calsow on methods of glass cementation in lens assembly; Smakula and A. Steinle on optical lubricants; Dr. Calsow on sealing of optical instruments; Dr. H.Kessler on Fungistaticsm; Dr. K.Leistner on production of graticules for optical instruments, and notes on IR techniques - 14 pages.
9-XXX-15 CIOS		S/Ldr.G.C. Breck, M.A.P.	AGFA Film Factory, Wolfen	Description of factory & items produced - General course of research during war (color film, graininess problems, infra red) - materials supplied to Luftwaffe, and technical progress in aerial photography; manufacture of film base; emulsions, packaging, fixer and developer chemicals; color techniques; testing techniques-25 pages.
CIOS		Mr.C.H. Hahner U.S.Ord	Optical Glass Mfg., at Schott & Gen., Jena	Industrial processes described in manufacture including raw materials, melting,cooling,annealing inspection,pressing, cutting. Tables showing quantitative chemical compositions of 110 types of optical glass-8 pages plus 14 of appendices & illustrations.

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Report No.	Date	Author	Subject	Abstract
CIOS	28 Aug 1945	Mr.C.H. Hahner U.S. Ord.	Production of Optical Glass in Germany and France	Techniques for manufacture of optical glass pieces for prism & lenses as used at Zeiss, Swarorski, Schott & Genossen-Details of glass pressing at Zeiss - 7 pages.
XXIX-43 CIOS	28 Aug. 1945.	Mr.C.H. Hahner U.S.Ord.	Pots Used in Melting Optical Glass at Schott & Genossen	Description of preparation of melting pots - 7 pages.
BIOS		BIOS Interim Investigation Report	Description of LFA (Research Institute under German Air Min., on all problems connected with aerial warfare.	Details of arrangements for making high speed photographs of missiles along their trajection. (2 pages.)
XIII-5 CIOS	9 Dec. 1944		Photographic Lenses & Optical Instruments	Discusses visit to a number of French firms who were engaged in the development of optical glassware & precision machine parts-Gives in detail, work done by the French for the Germans. Firms & personnel are listed - 34 pages.
XXV-8 CIOS	25 May 1945	Lt.Col. D.A.Kayll	Land & air service fire control instruments, Carl Zeiss, Jena. Production of Optical Glass, Schott & Genossen, Jena,lenses & graduated Scales.	General description of optical & photographic activity in all branches of the Zeiss & Schott works. Includes information on the Speer Ministry organization which controlled optical and fine mechanical industries. Appendices include details of fire control instruments, air cameras, & survey equipment, ballistic research, infra-red, optical instruments & producing methods. 152 pages, 12 photographs.

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Report No.	Date	Author	Subject	Abstract
XXXVI-61 CIOS	June 1945	Cdr.P.M. Chancellor USNR	Film Production & Methods. AGFA Film Fabrik Plant, Wolfen.	Describes results of investigation-This plant produced 2/3 of photographic film & plate used in German. Details of AGFA-Color process & brief information on other products are included. 55 pages,4 illus.
XXVII-23 CIOS		Capt.L.N. Dawson. U.S.Ordn.	Optical Grinding & Centering Equipments used by Carl Zeiss, Jena.	Gives information on Zeiss machinery for various types of lens centering, and grinding methods. Also on machinery for prism rounding & groove milling - 9 pages, 11 photographs.
XXVII-24 CIOS		"	Machine used by Carl Zeiss,Jena, to grind Ashpheric lens surfaces.	Description of principles of operation of a Zeiss machine which ground aspherical lenses, & the polishing process involved. 9 pages, 6 figures.
XXIX-52 CIOS	28 Aug. 1945	Mr.Arthur B. Simmons U.S.Ordn.	German Optical Production	General resume of German optical industry, organization, policy, and methods based on visits to 13 leading optical plants. Descriptions are given of significant technical developments encountered. 9 Pages.
XXIX-60 CIOS	24 Jul. 1945.	Mr.I.C. Gardner U.S.Ordn.	The production of fused quartz of optical quality by Heraeus.	Production of silica of high optical quality by spraying the silica in an oxyhydrogen flame to form a rod. The rod is converted to optical blanks by an upsetting process. 4 pages.

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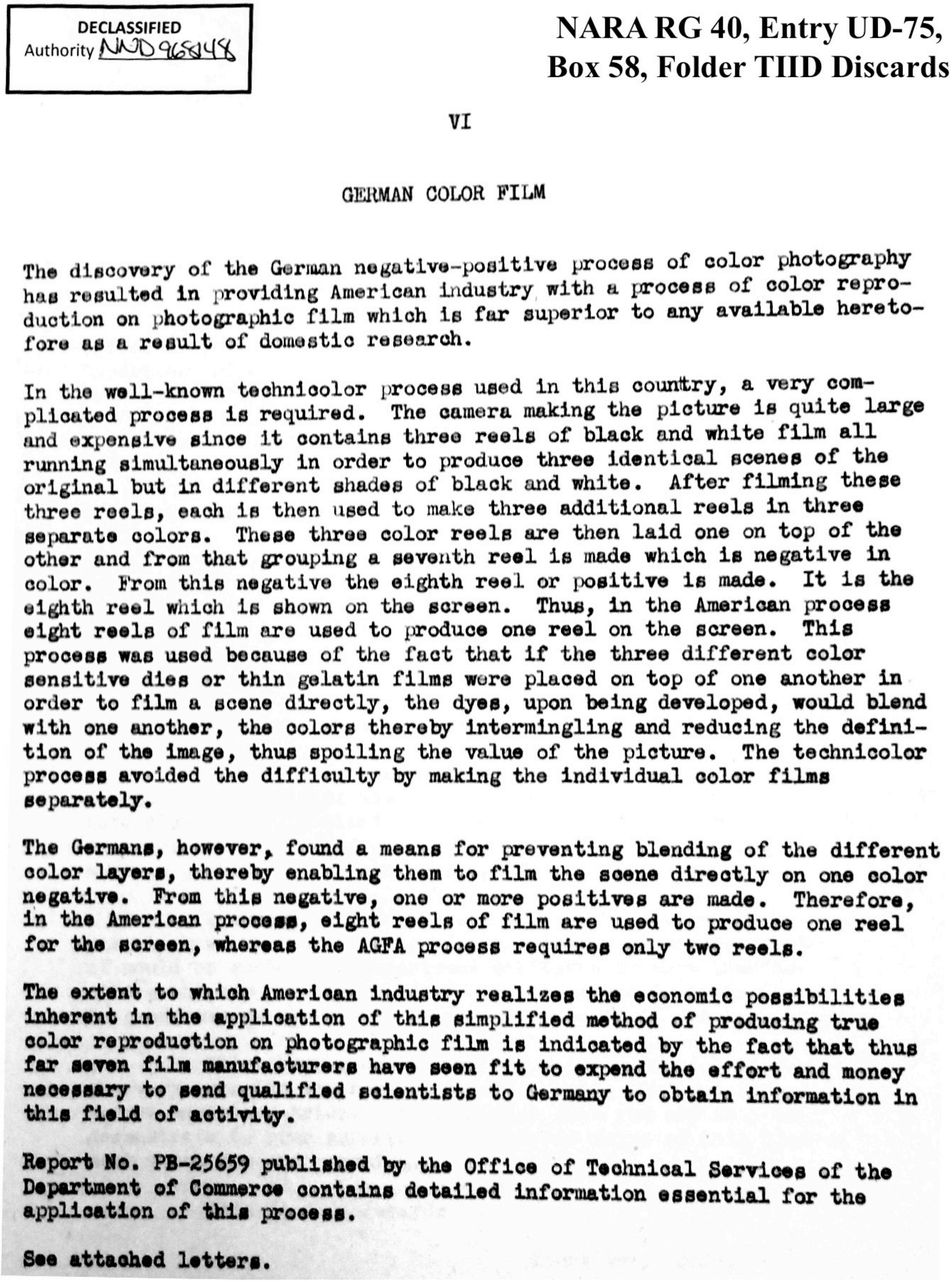
Figure 3.143: A wide variety of advanced technologies, components, and methods for photography were developed in the German-speaking world and transferred to other countries after World War II [FIAT 678].



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**NARA RG 40, Entry UD-75,
Box 58, Folder TIID Discards**

VI

GERMAN COLOR FILM

The discovery of the German negative-positive process of color photography has resulted in providing American industry with a process of color reproduction on photographic film which is far superior to any available heretofore as a result of domestic research.

In the well-known technicolor process used in this country, a very complicated process is required. The camera making the picture is quite large and expensive since it contains three reels of black and white film all running simultaneously in order to produce three identical scenes of the original but in different shades of black and white. After filming these three reels, each is then used to make three additional reels in three separate colors. These three color reels are then laid one on top of the other and from that grouping a seventh reel is made which is negative in color. From this negative the eighth reel or positive is made. It is the eighth reel which is shown on the screen. Thus, in the American process eight reels of film are used to produce one reel on the screen. This process was used because of the fact that if the three different color sensitive dies or thin gelatin films were placed on top of one another in order to film a scene directly, the dyes, upon being developed, would blend with one another, the colors thereby intermingling and reducing the definition of the image, thus spoiling the value of the picture. The technicolor process avoided the difficulty by making the individual color films separately.

The Germans, however, found a means for preventing blending of the different color layers, thereby enabling them to film the scene directly on one color negative. From this negative, one or more positives are made. Therefore, in the American process, eight reels of film are used to produce one reel for the screen, whereas the AGFA process requires only two reels.

The extent to which American industry realizes the economic possibilities inherent in the application of this simplified method of producing true color reproduction on photographic film is indicated by the fact that thus far seven film manufacturers have seen fit to expend the effort and money necessary to send qualified scientists to Germany to obtain information in this field of activity.

Report No. PB-25659 published by the Office of Technical Services of the Department of Commerce contains detailed information essential for the application of this process.

See attached letters.

Figure 3.144: Advanced technology to produce and process color film was developed in the German-speaking world and transferred to other countries after World War II [NARA RG 40, Entry UD-75, Box 58, Folder TIID Discards].

3.8 Materials Science

Materials science covers the creation of solid chemical compounds that make useful materials for various applications and products. For simplicity, this field can be divided into several areas, and German-speaking scientists played major roles in all of them:

3.8.1. Polymers

3.8.2. Ceramics and crystallography

3.8.3. Glass

3.8.4. Metals

3.8.1 Polymers

Creators from the German-speaking world led most of the development of polymers, including plastics and synthetic rubbers, which are now ubiquitous in consumer products.[15]

As shown in Fig. 3.145, polystyrene was first created in 1839 by Johann Eduard Simon (German states, 1789–1856), and developed further in 1845 by August Wilhelm von Hofmann (1818–1892) and John Blyth (Scottish but studied in Germany, 1814–1871). In 1929, Hermann Mark (Austrian, 1895–1992) and Carl Wulff (German?, 18??–19??) greatly improved the process of producing polystyrene. In the 1940s, Fritz Stastny (Austrian, 1908–1985) created expanded or porous polystyrene (Styrofoam). Polystyrene is used to make a wide variety of consumer products, and Styrofoam is used to make thermally insulated containers and protective packaging (Fig. 3.146).

Cellulose acetate was first created in 1865 by Paul Schützenberger (Franco-German, 1829–1897), and produced in larger quantities in 1903 by Arthur Eichengrün (German, 1867–1949) and Theodore Becker (German?, 18??–19??). The brothers Camille Dreyfus (Swiss, 1878–1956) and Henri Dreyfus (Swiss, 1882–1944) developed cellulose acetate yarn in 1913. Cellulose acetate has been used for photographic film, eyeglass frames, yarn, clothing, and other products, as illustrated in Fig. 3.147.

Eugen Baumann (German, 1846–1896) discovered photopolymerization and created polyvinyl chloride in 1872 (Fig. 3.148). Friedrich (Fritz) Klatte (German, 1880–1934) developed an improved method of producing polyvinyl chloride in 1913. Polyvinyl chloride is widely used for making water drain pipes and pipe fittings.

Phenol formaldehyde (phenolic) resin was first created in 1891 by Adolf von Baeyer (German, 1835–1917) and Werner Kleeberg (German, 18??–19??), and developed further in 1902 by Adolf Luft (German?, 18??–19??). Adolf von Baeyer won the Nobel Prize in Chemistry in 1905 (p. 465). In 1907, Leo Baekeland (Belgian but studied under August Kekulé, 1863–1944) began producing and commercializing phenolic resin under the trade name of Bakelite; phenolic resin was also sold under other trade names. Phenolic resin was used to make early plastic products such as telephone cases. See Fig. 3.149.

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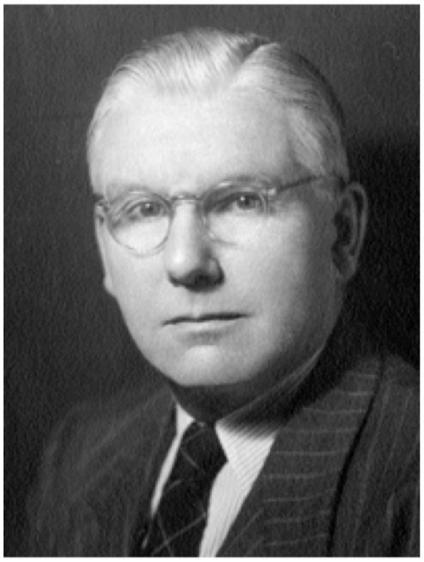
[15] Dietrich Braun 2017; Feichtinger 2017; Kline 1946; Herman Mark 1993; Morris 2005; Schwedt 2013; Seymour 2013; Strom and Rasmussen 2012; Tuttle 1981; so many BIOS, CIOS, and FIAT reports that they cannot all be listed here.

Eduard Simon (1789–1856) created polystyrene (1839)

August Wilhelm von Hofmann (1818–1892) produced more polystyrene (1845)

John Blyth (studied in Germany, 1814–1871) produced more polystyrene (1845)

Hermann Mark (1895–1992) improved production of polystyrene (1929)



Carl Wulff (18??–19??) improved production of polystyrene (1929)

Fritz Stastny (1908–1985) created expanded polystyrene (Styrofoam, ca. 1945)

Figure 3.145: Polystyrene was first created in 1839 by Eduard Simon, and developed further by August Wilhelm von Hofmann, John Blyth, Hermann Mark, Carl Wulff, and Fritz Stastny.

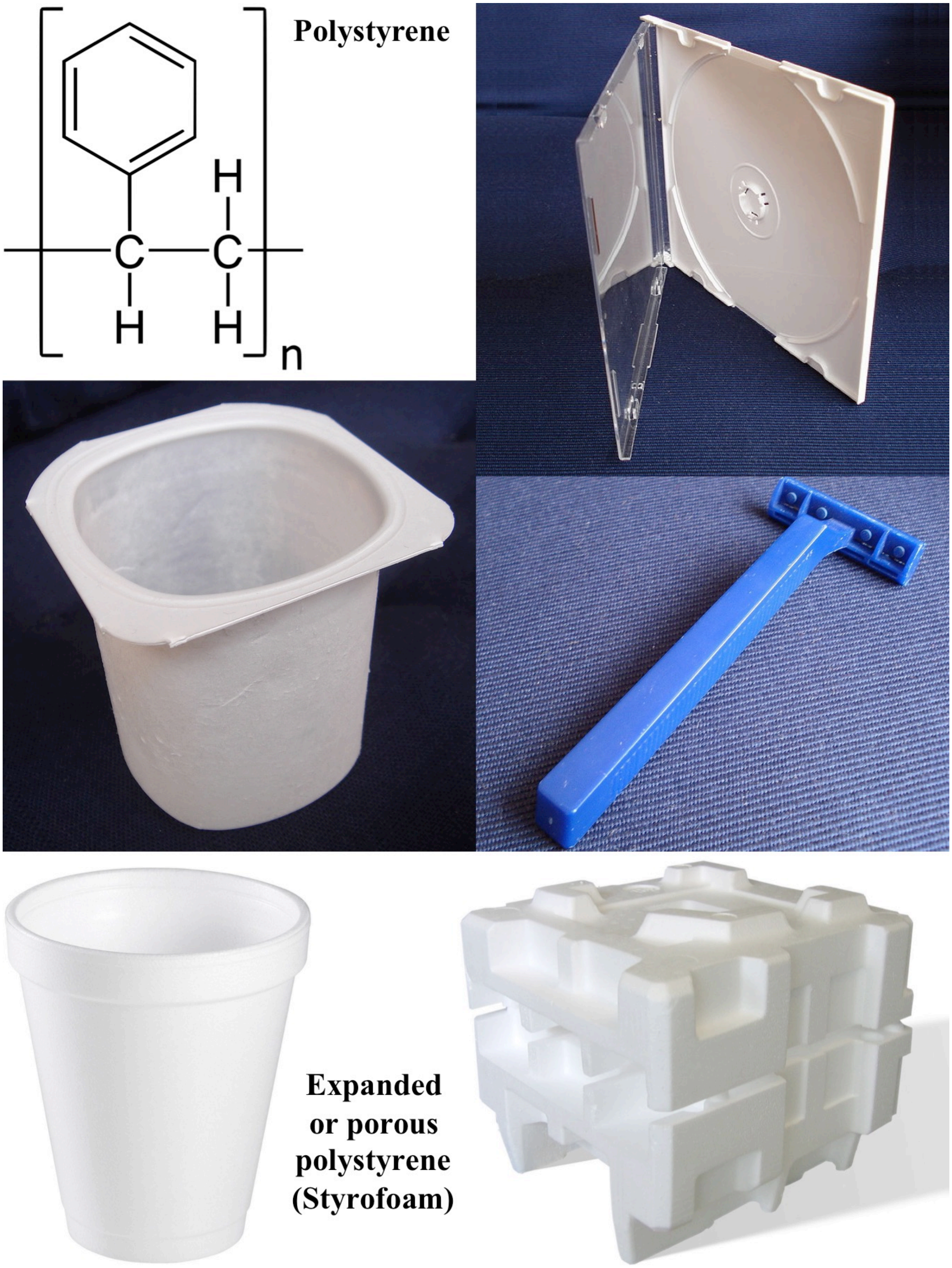


Figure 3.146: Polystyrene is used to make a wide variety of consumer products. Expanded or porous polystyrene (Styrofoam) is used to make thermally insulated containers and protective packaging.

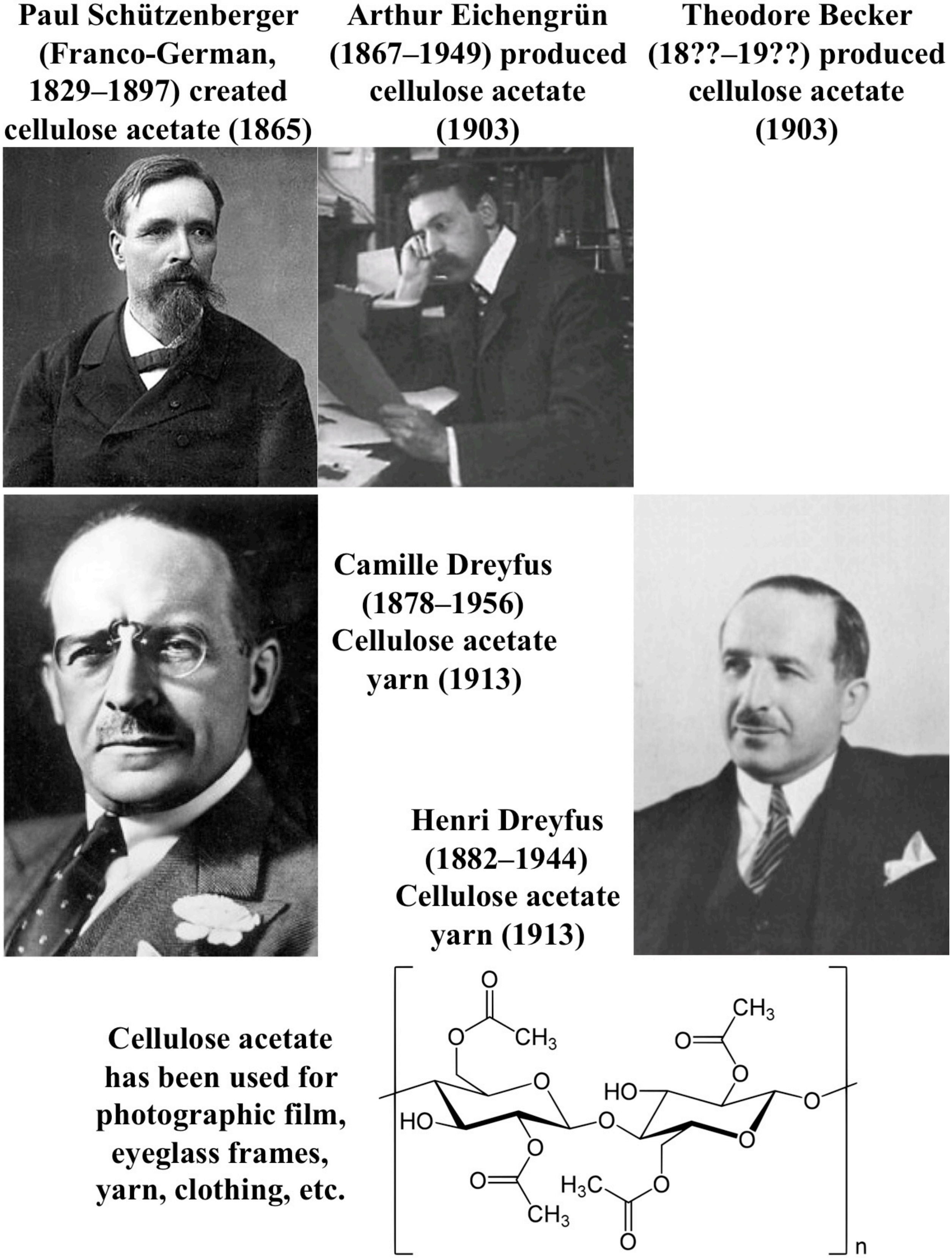


Figure 3.147: Cellulose acetate was first created in 1865 by Paul Schützenberger, and developed further by Arthur Eichengrün, Theodore Becker, Camille Dreyfus, and Henri Dreyfus. Cellulose acetate has been used for photographic film, eyeglass frames, yarn, clothing, and other products.

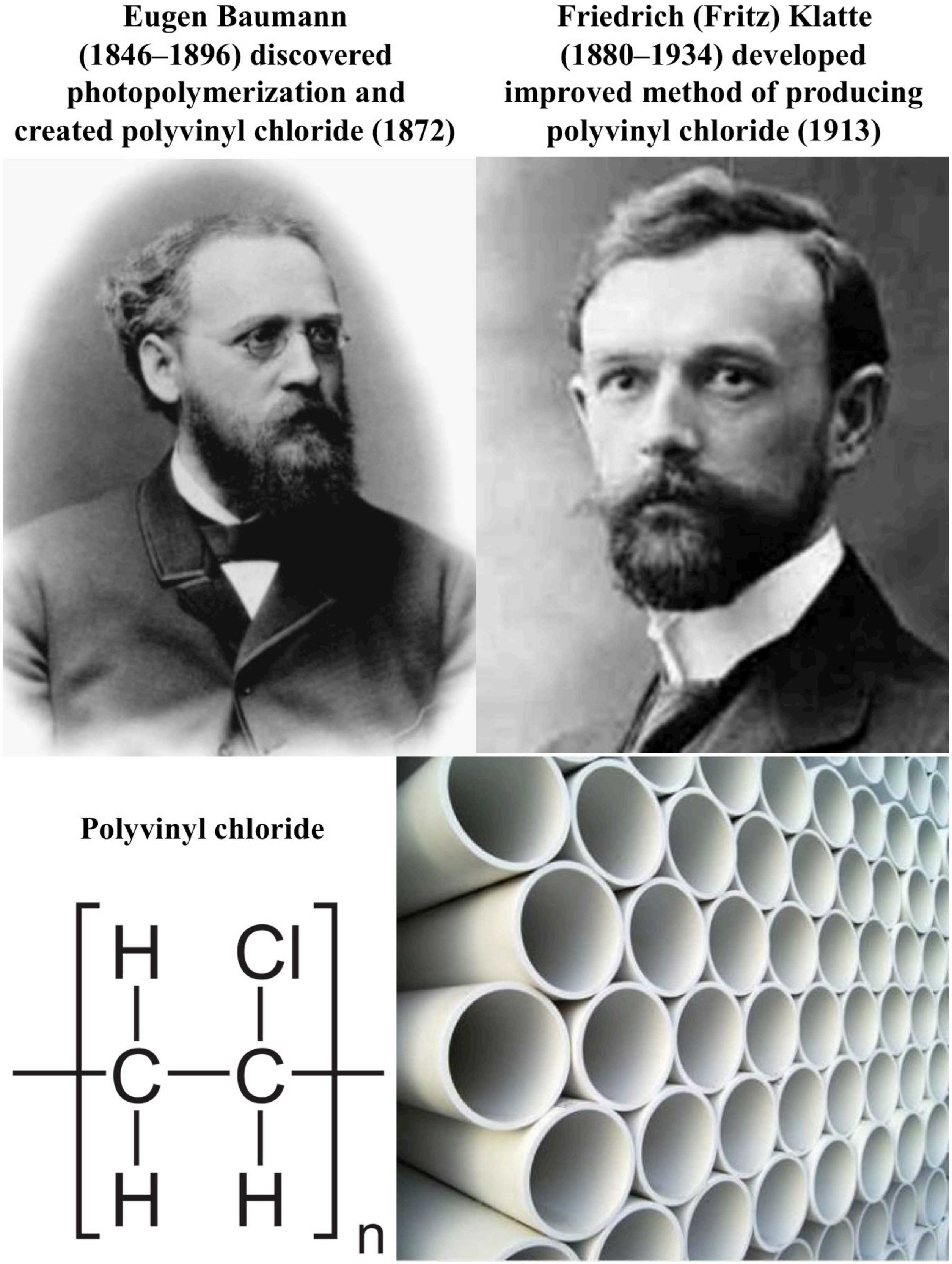


Figure 3.148: Eugen Baumann discovered photopolymerization and created polyvinyl chloride in 1872. Friedrich (Fritz) Klatte developed an improved method of producing polyvinyl chloride in 1913. Polyvinyl chloride is widely used for making water drain pipes and pipe fittings.

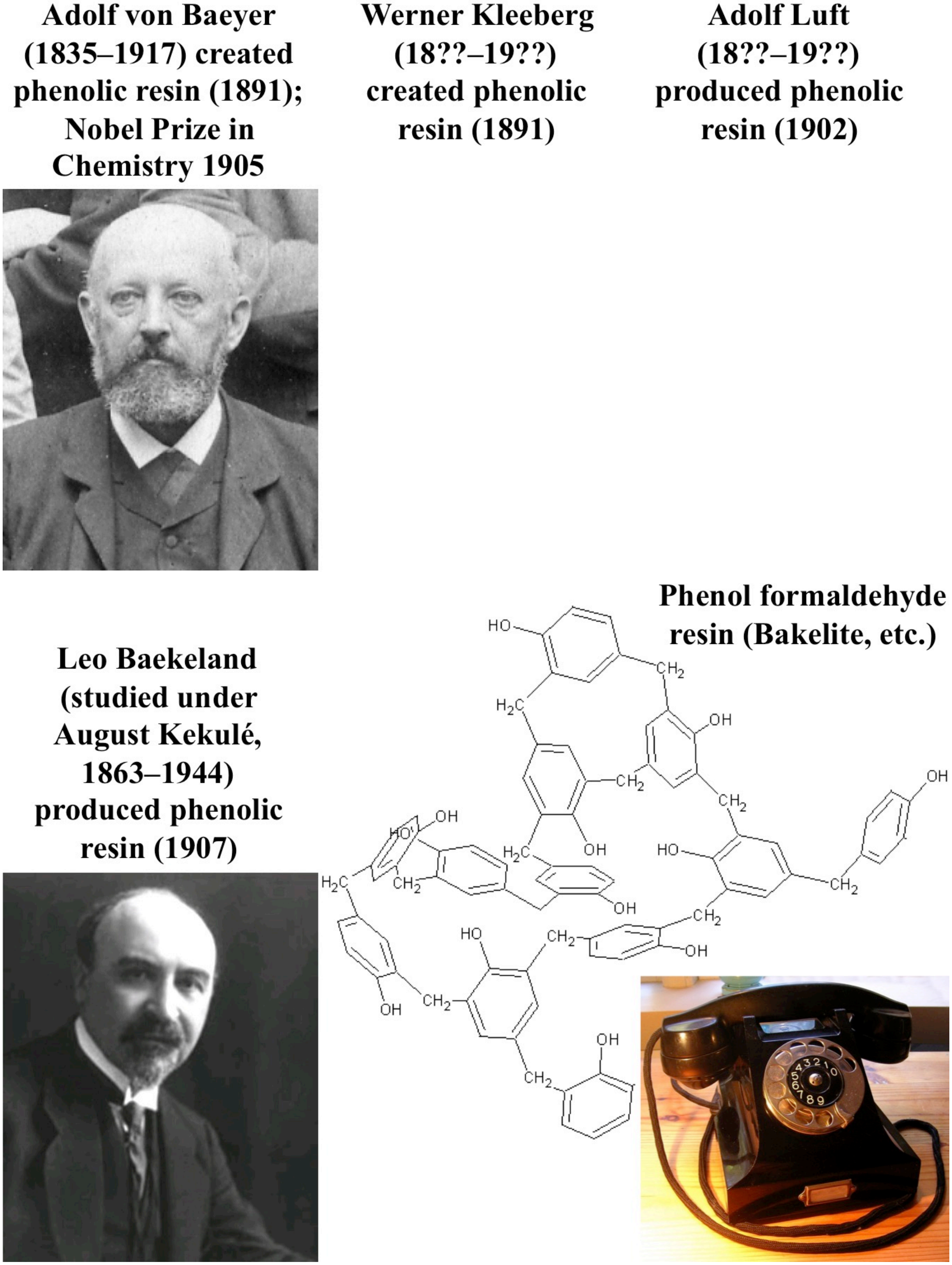


Figure 3.149: Phenol formaldehyde (phenolic) resin was first created in 1891 by Adolf von Baeyer and Werner Kleeberg, and developed further by Adolf Luft and Leo Baekeland. Phenolic resin was commercialized as Bakelite and other trade names and used to make early plastic products such as telephone cases.

In 1897, Wilhelm Krische (German, 1859–19??) and Friedrich Adolph Spitteler (German, 1846–1940) created a natural plastic (later dubbed Galalith) by purifying and crosslinking casein milk protein, as shown in Fig. 3.150. Galalith was also used to make a number of early plastic products.

Polyethylene was first created in 1898 by Hans von Pechmann (German, 1850–1902). In 1900, Eugen Bamberger (German, 1857–1932) and Friedrich Tschirner (German?, 18??–19??) determined the chemical structure of polyethylene. Karl Ziegler (German, 1898–1973) developed an improved method of producing polyethylene in 1952, and won the Nobel Prize in Chemistry in 1963 (p. 504). Polyethylene has been widely used to make plastic bags (Fig. 3.151), due to its flexibility and the low cost of Ziegler's production process.

Polycarbonate was first created in 1898 by Alfred Einhorn (German, 1856–1917). In 1953, Hermann Schnell (German, 1916–1999) developed an improved method of producing polycarbonate. Because polycarbonate is very rugged, it is used to make products such as compact discs, water bottles, cell phone cases, and safety glasses. See Fig. 3.152.

Friedrich (Fritz) Klatte (German, 1880–1934), shown in Fig. 3.153, created polyvinyl acetate in 1912. It has been used worldwide as white glue ever since.

Otto Röhm (German, 1876–1939) and Walter Hermann Bauer (German, 1893–1968) created polymethylacrylic (plexiglass) in 1928. Plexiglass pieces from a circa 1942 German aircraft windshield are shown in Fig. 3.154.

Some German-speaking scientists who made important contributions to rubber included (Fig. 3.155):

- Carl Harries (German, 1866–1923) studied the polymer structure of rubber.
- Fritz Hofmann (German, 1866–1956) produced synthetic rubbers.
- Kurt Gottlob (Austrian, 1881–1925) developed emulsion polymerization and improved vulcanization.
- Kurt Meyer (German, 1883–1952) studied the structure of cellulose and the effect of entropy on rubber elasticity.
- Herman(n) Mark (Austrian, 1895–1992) studied the structure of cellulose.
- Eugen(e) Guth (Hungarian, 1905–1990) developed a mathematical model using entropy to calculate the elasticity of rubber.

As shown in Fig. 3.156, Eduard Tschunkur (German, 1874–1946) and Walter Bock (German, 1895–1948) created styrene-butadiene synthetic rubber (Buna S) in 1929. It is now used to make most tires.

Similarly, Eduard Tschunkur, Helmut Kleiner (German, 1902–1987), and Erich Konrad (German, 1894–1975) created acrylonitrile butadiene synthetic rubber (Buna N) in 1930. It is now used for products such as latex-free nitrile rubber gloves (Fig. 3.157).

Wilhelm Krische (1859–19??) **Adolph Spitteler (1846–1940)**

Created a natural plastic from casein milk protein (Galalith, 1897)

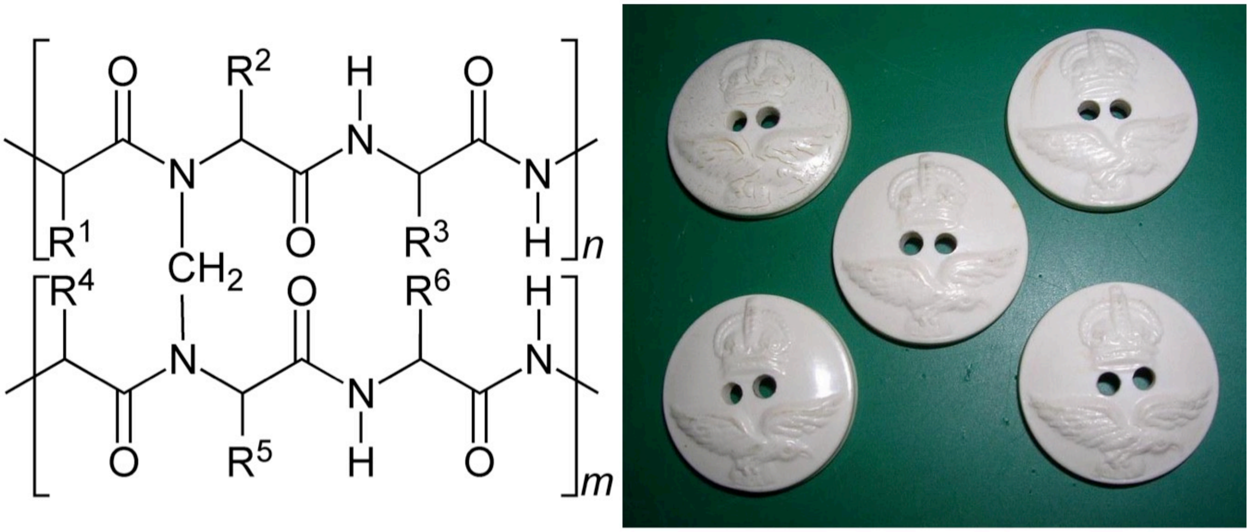


Figure 3.150: Wilhelm Krische and Adolph Spitteler created a natural plastic (later dubbed Galalith) from casein milk protein in 1897.

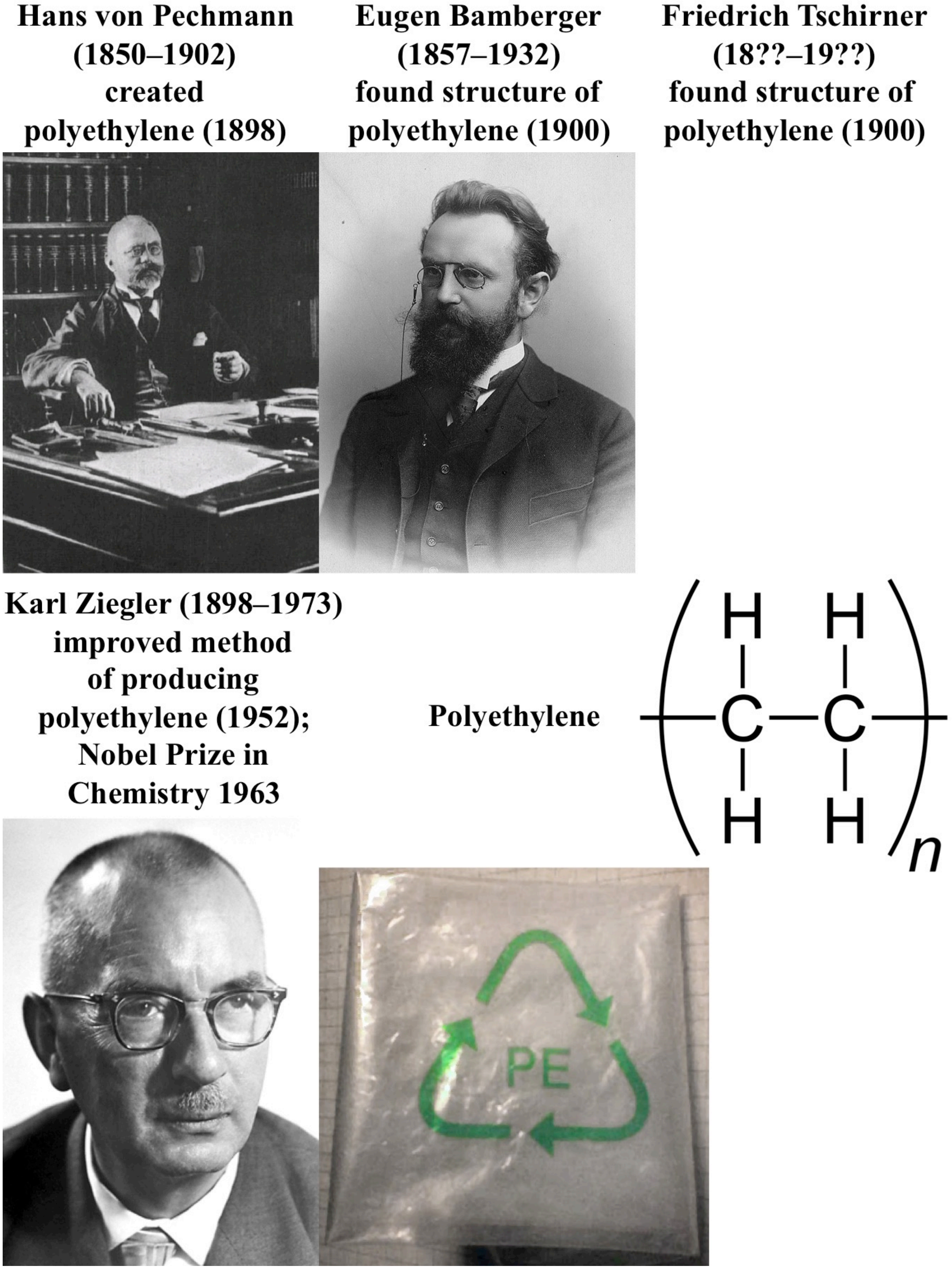


Figure 3.151: Polyethylene was first created in 1898 by Hans von Pechmann, and developed further by Eugen Bamberger, Friedrich Tschirner, and Karl Ziegler. Polyethylene has been widely used to make plastic bags.

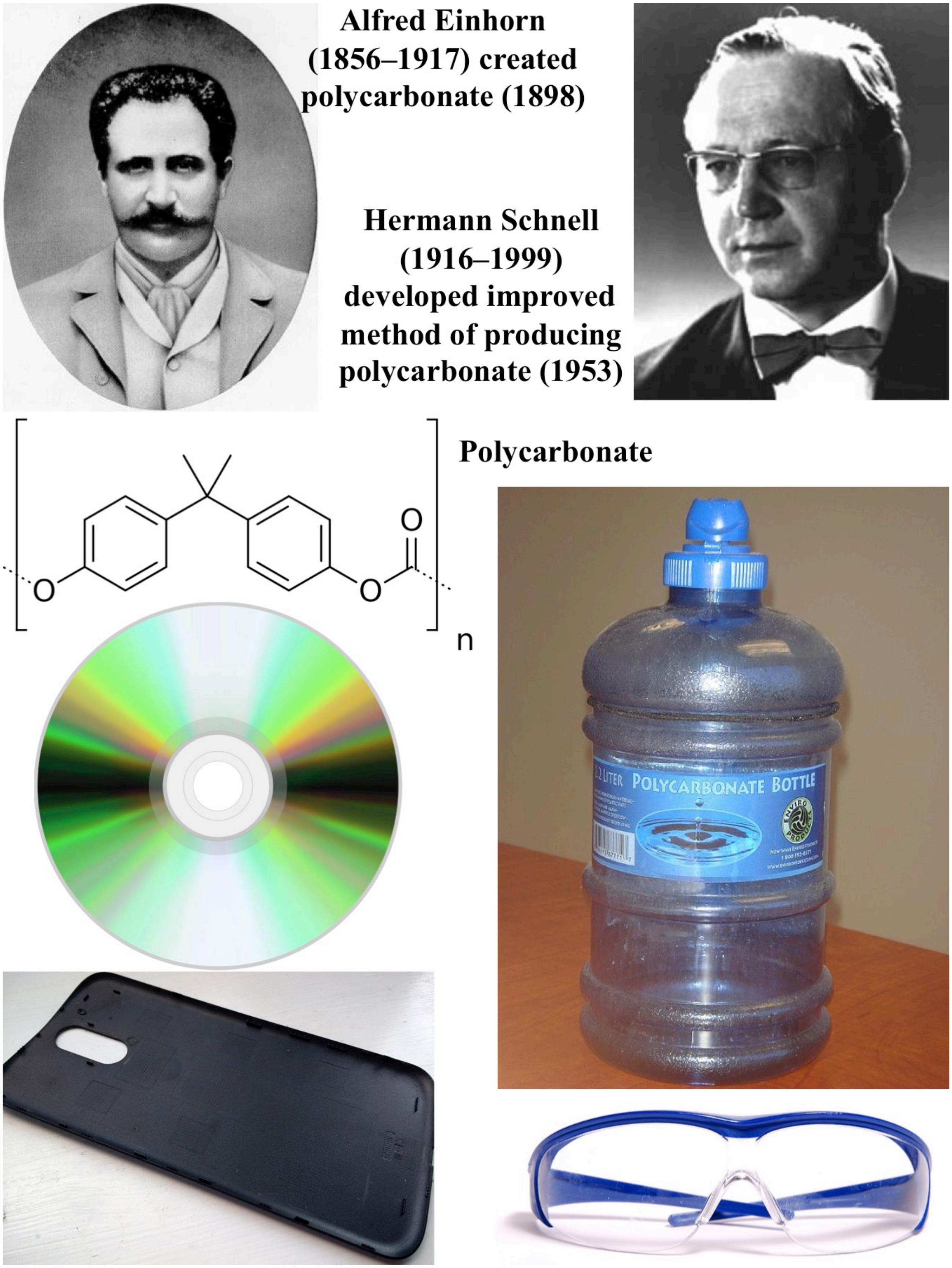


Figure 3.152: Polycarbonate was first created in 1898 by Alfred Einhorn, and developed further by Hermann Schnell. Because polycarbonate is very rugged, it is used to make products such as compact discs, water bottles, cell phone cases, and safety glasses.

Figure 3.153: Friedrich (Fritz) Klatte created polyvinyl acetate (white glue) in 1912.

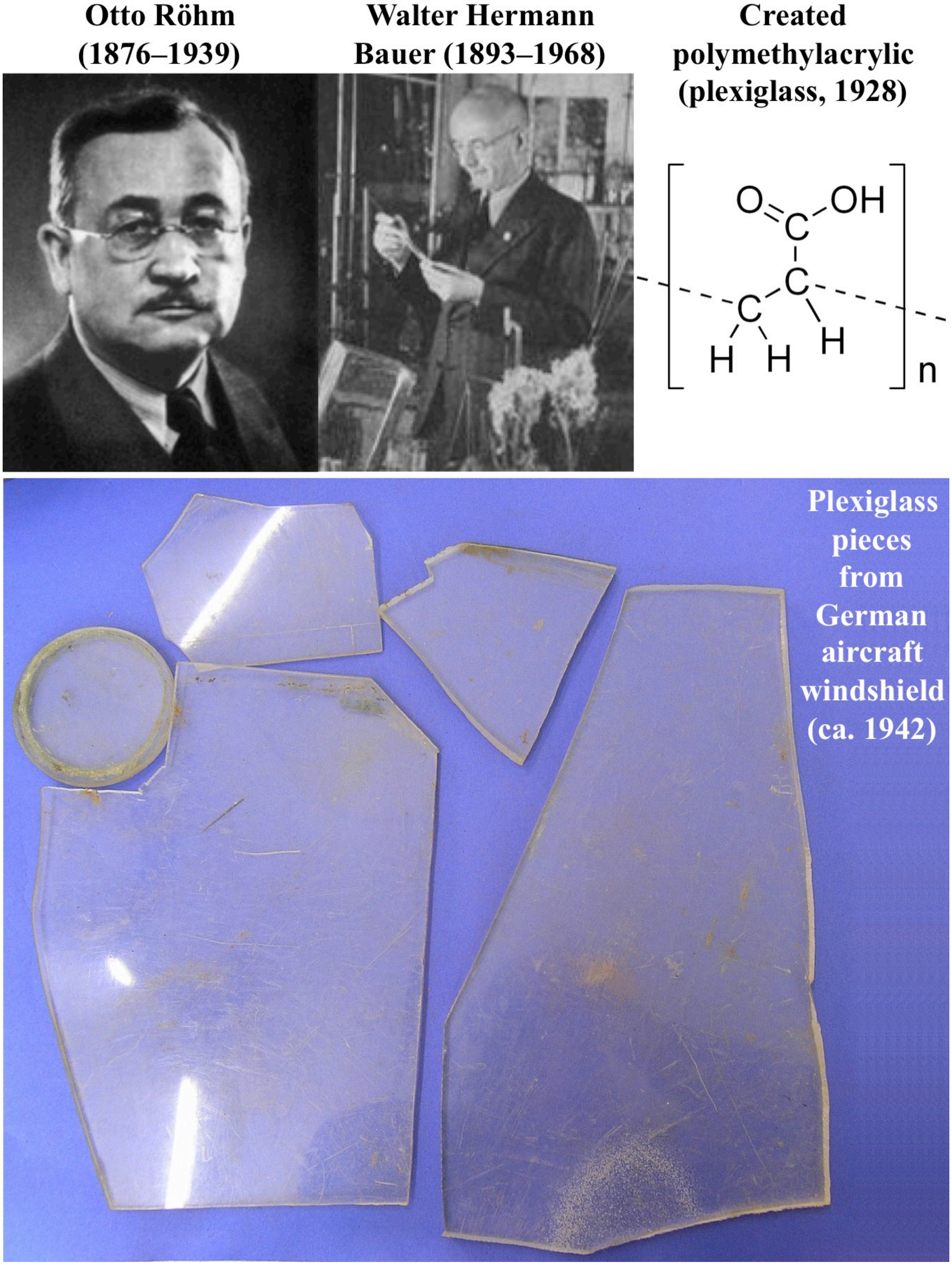


Figure 3.154: Otto Röhm and Walter Hermann Bauer created polymethylacrylic (plexiglass) in 1928. Plexiglass pieces from German aircraft windshield (ca. 1942).

Carl Harries (1866–1923) Polymer structure of rubber

Fritz Hofmann (1866–1956) Synthetic rubbers

Kurt Gottlob (1881–1925) Emulsion polymerization, improved vulcanization

Kurt Meyer (1883–1952) Cellulose structure, entropy of rubber elasticity

Hermann Mark (1895–1992) Cellulose structure

Eugene Guth (1905–1990) Entropy model of rubber elasticity

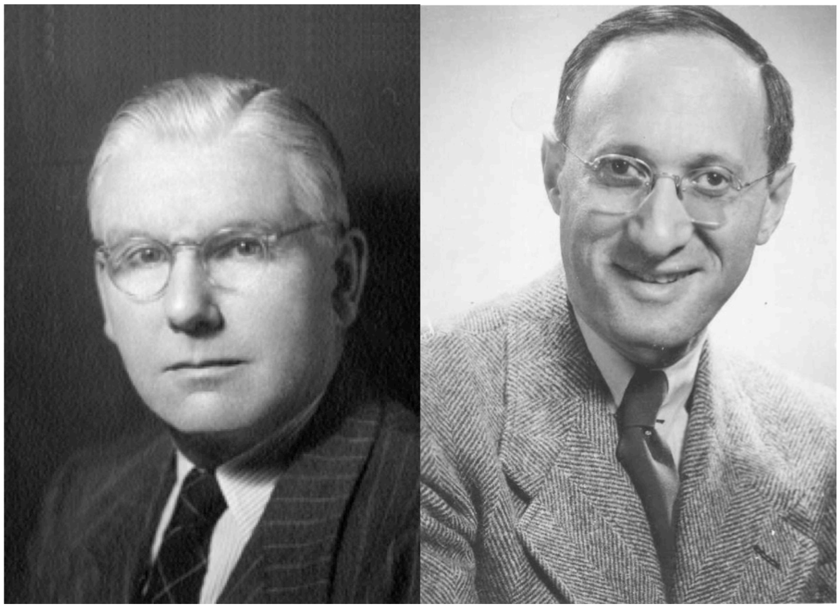


Figure 3.155: Some German-speaking scientists who made important contributions to rubber included Carl Harries, Fritz Hofmann, Kurt Gottlob, Kurt Meyer, Herman(n) Mark, and Eugen(e) Guth.

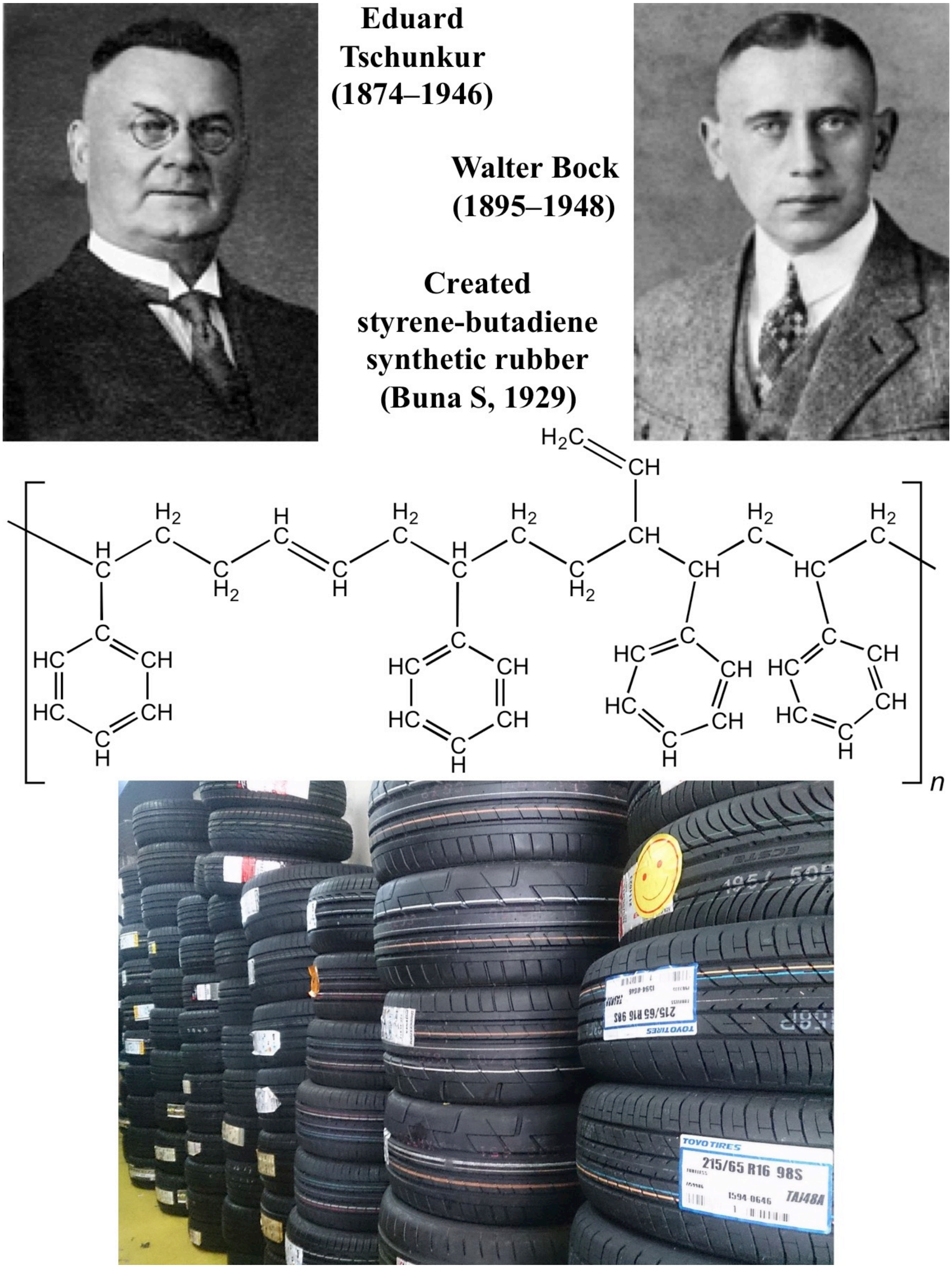
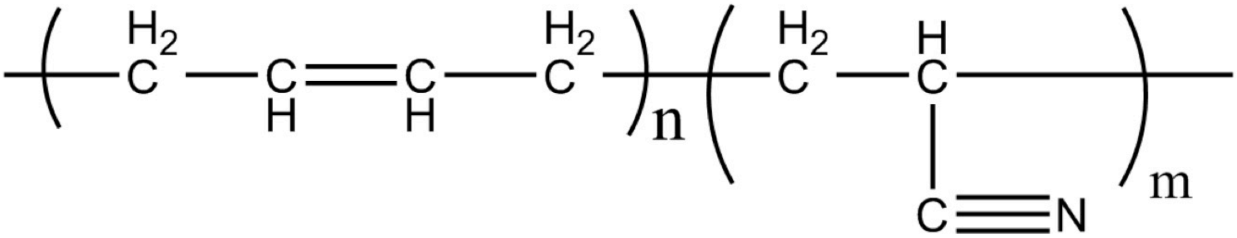


Figure 3.156: Eduard Tschunkur and Walter Bock created styrene-butadiene synthetic rubber (Buna S) in 1929; it is now used to make most tires.

Eduard Tschunkur (1874–1946) **Helmut Kleiner (1902–1987)** **Erich Konrad (1894–1975)**

Created acrylonitrile butadiene synthetic rubber (Buna N, 1930)



Buna N production at Bayer Leverkusen (19??)

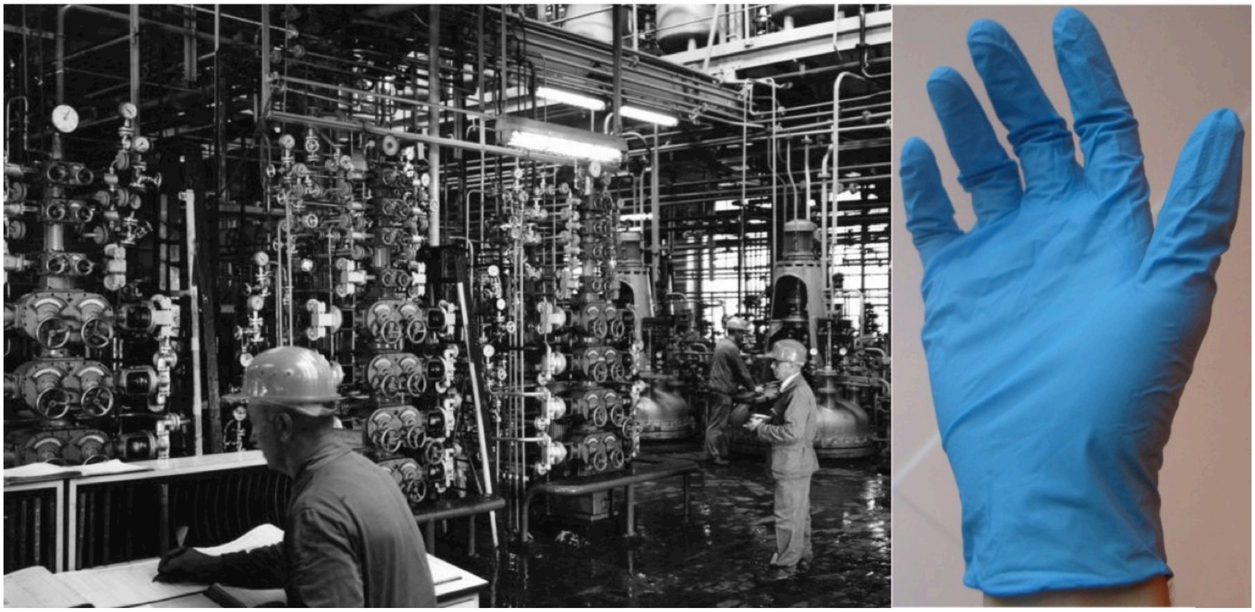


Figure 3.157: Eduard Tschunkur, Helmut Kleiner, and Erich Konrad created acrylonitrile butadiene synthetic rubber (Buna N) in 1930; it is now used for products such as latex-free nitrile rubber gloves.

Figure 3.158: I.G. Farben headquarters in Frankfurt am Main (1930–1945) and production of butadiene or buna synthetic rubber.

Polyacrylonitrile (Orlon) was first created in 1930 by Hans Fikentscher (German, 1896–1983) and Claus Heuck (German?, 18??–19??). Beginning in 1938, it was produced in the form of fibers by Herbert Rein (German, 1899–1955). See Fig. 3.159.

As illustrated in Fig. 3.160, Otto Bayer (German, 1902–1982) created polyurethane in 1937. Polyurethane is now used for sprayable thermal insulation, surface coatings [BIOS 629], memory foam, Spandex, and other products.

Paul Schlack (German, 1897–1987) created polyamide (better known as Nylon or Perlon) in the 1930s. Wallace Carothers (American, 1896–1937) independently produced Nylon around the same time in the United States but became much better known than Schlack. Nylon/Perlon is widely used now to make thread, rope, and solid objects (Fig. 3.161).

Karl Rehn (German, 19??–19??) and Karl Ziegler (German, 1898–1973), shown in Fig. 3.162, produced polypropylene in 1951. Ziegler won the Nobel Prize in Chemistry in 1963 (p. 504). Polypropylene is widely used for products that must not crack even after repeated bending and stress, such as plastic hinges and centrifuge tubes.

Some other creators who made important contributions to polymers included (Fig. 3.163):

- Wilhelm Rudolph Fittig (German, 1835–1910) studied the chemistry of polymers.
- Bernhard Tollens (German, 1841–1918) developed urea-formaldehyde resin polymers.
- Oscar Troplowitz (German, 1863–1918) created adhesive bandages and adhesive tape in 1901.
- Hermann Staudinger (German, 1881–1965) studied polymer structures. He won the Nobel Prize in Chemistry in 1953 (p. 480).
- Werner Kuhn (Swiss, 1899–1963) was especially noted for his work on the physical chemistry of polymers. He applied the laws of statistical physics to polymer molecules to explain the temperature dependence of viscosity and elasticity in rubber and other polymers.
- Victor Garten (German, 19??–19??) conducted advanced research on polymers in Germany during World War II, then moved to Australia after the war to continue his research. In Australia, he produced revolutionary electrically conducting polymers that were quite likely based on wartime German work. The 2000 Nobel Prize in Chemistry was awarded to Alan Heeger, Alan MacDiarmid, and Hedeki Shiakawa for rediscovering electrically conducting polymers much later.

Polymer production also makes extensive use of the Diels-Alder reaction, which was developed by Otto Diels (German, 1876–1954) and Kurt Alder (German, 1902–1958). They both won the Nobel Prize in Chemistry in 1950 for that discovery. See pp. 474 and 489.

As shown in Fig. 3.164, George de Mestral (Swiss, 1907–1990) invented Velcro hook-and-loop fasteners in 1941. They were subsequently used in everything from the space program to sportswear.

After World War II, vast amounts of information on polymers were transferred from the German-speaking world to Allied countries: large numbers of scientists, reports on interrogations of scientists, patents, BIOS/CIOS/FIAT reports, samples, hardware, and even complete factories. See for example Fig. 3.165. Thus it was the innovations of German-speaking creators that dominated the field of polymers from the first inventions of polymers in the nineteenth century to the boom in commercial polymer production and applications in the latter half of the twentieth century.

Hans Fikentscher (1896–1983) created polyacrylonitrile (1930)

Claus Heuck (18??–19??) created polyacrylonitrile (1930)

Herbert Rein (1899–1955) produced polyacrylonitrile fibers (1938)

Polyacrylonitrile (Orlon)

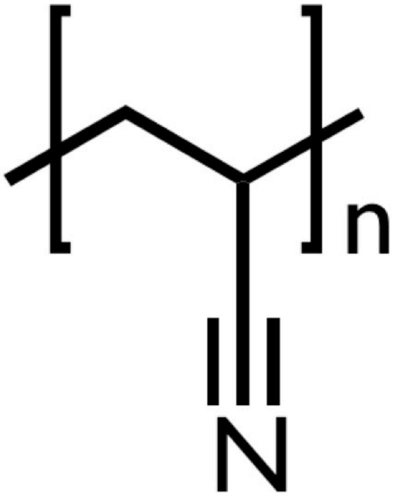


Figure 3.159: Polyacrylonitrile (Orlon) was first created in 1930 by Hans Fikentscher and Claus Heuck, and produced as fibers by Herbert Rein in 1938.

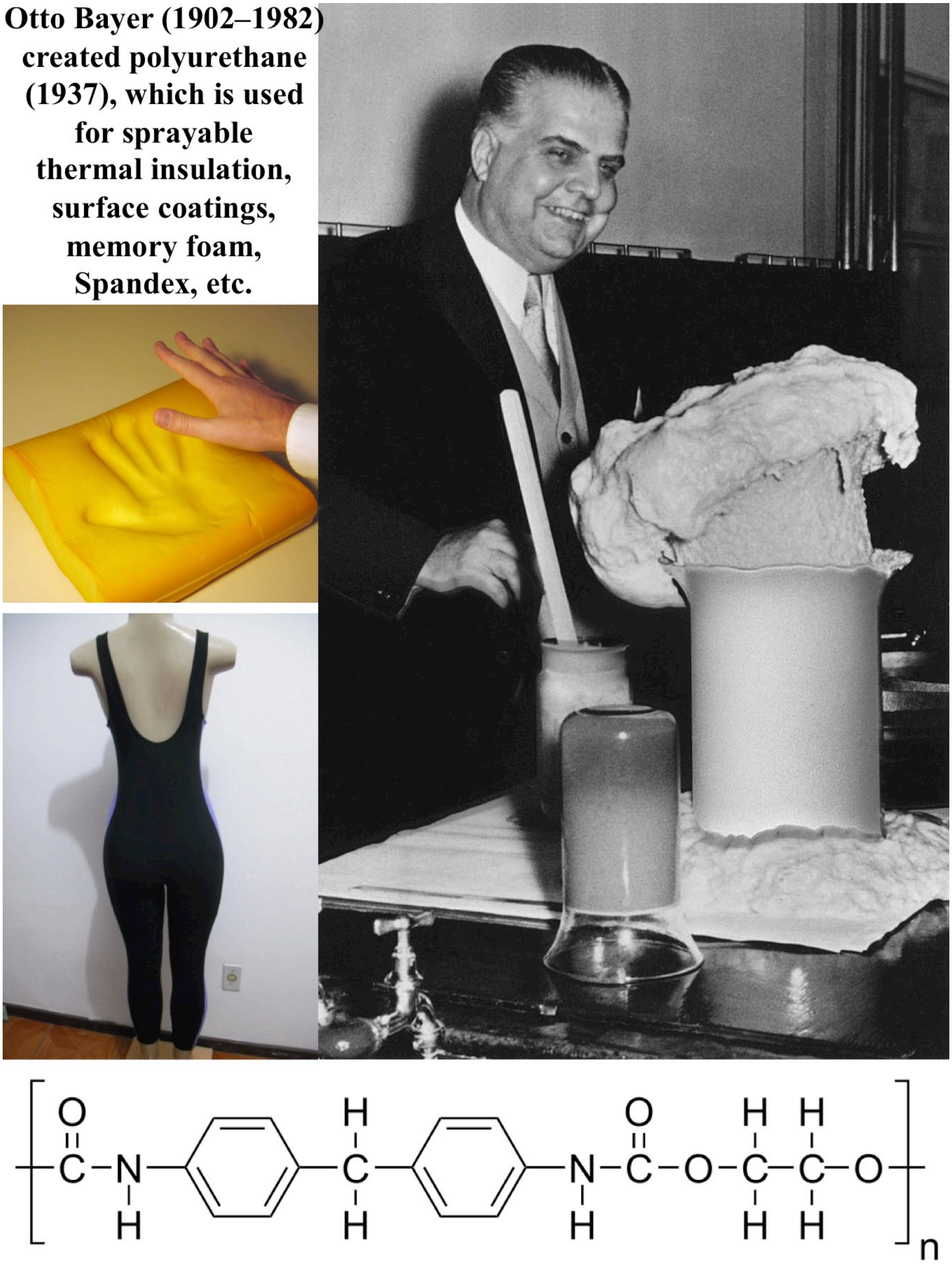


Figure 3.160: Otto Bayer created polyurethane in 1937. Polyurethane is now used for sprayable thermal insulation, surface coatings, memory foam, Spandex, and other products.

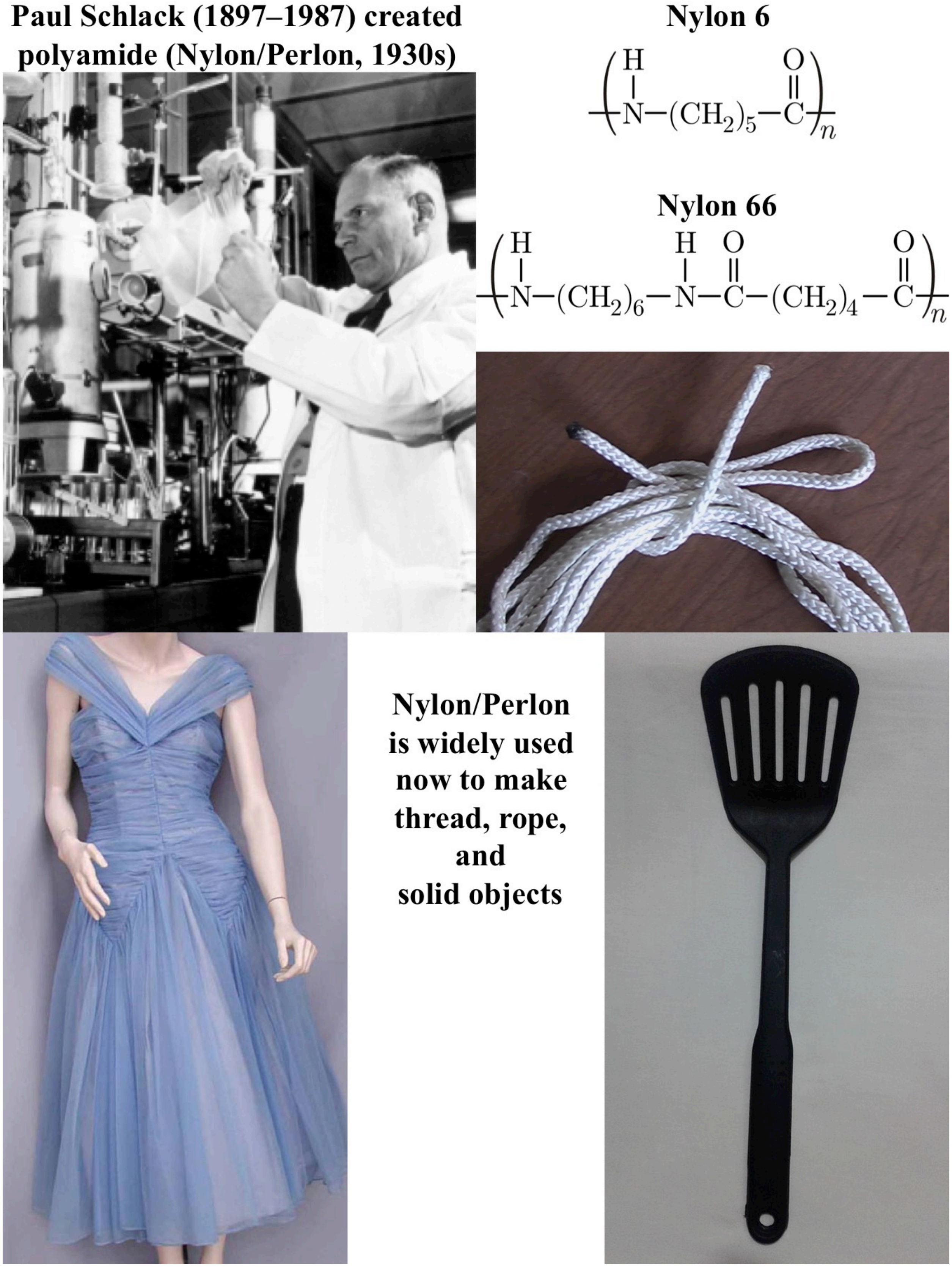


Figure 3.161: Paul Schlack created polyamide (Nylon/Perlon) in the 1930s. Nylon/Perlon is widely used now to make thread, rope, and solid objects.

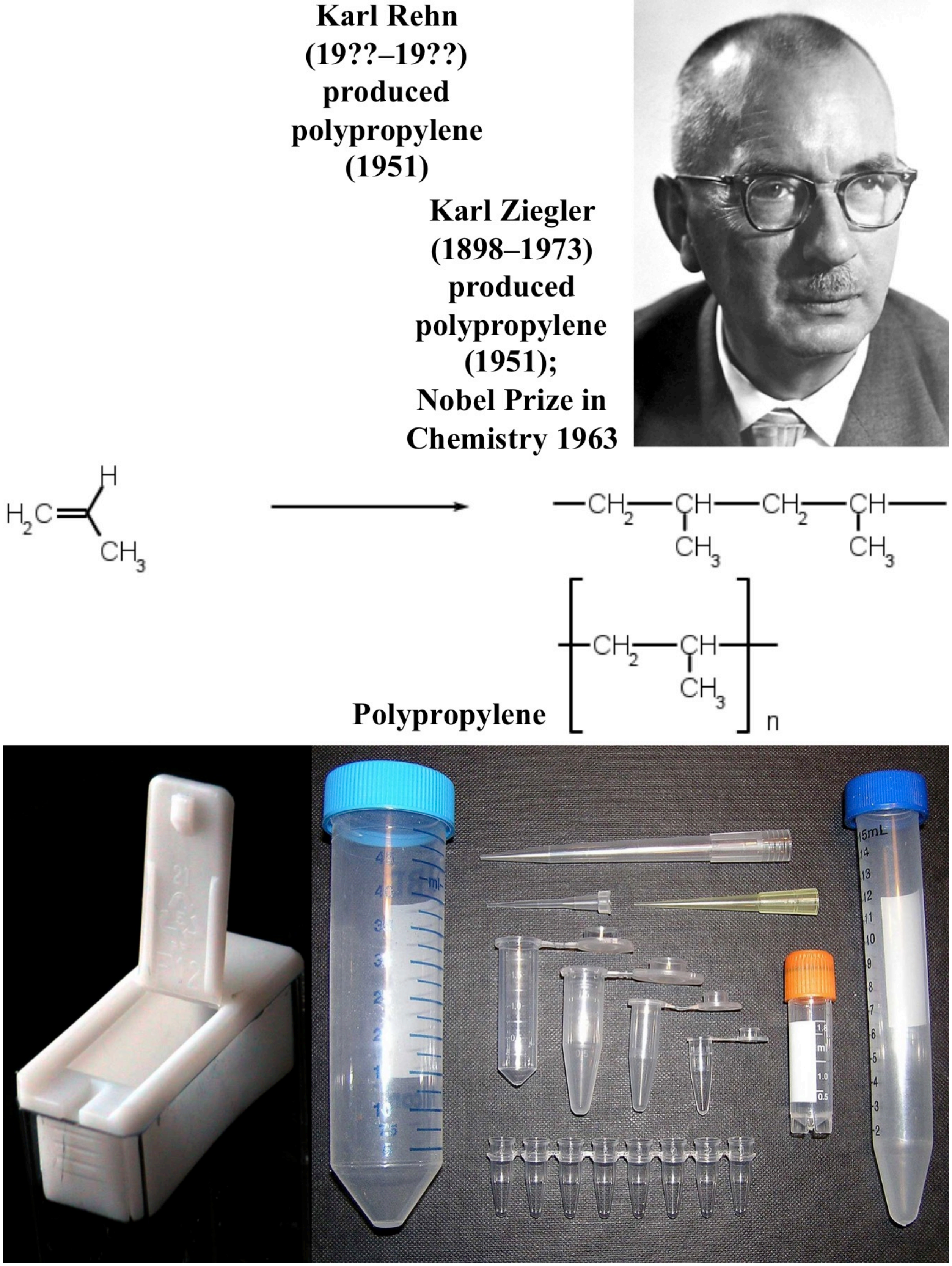
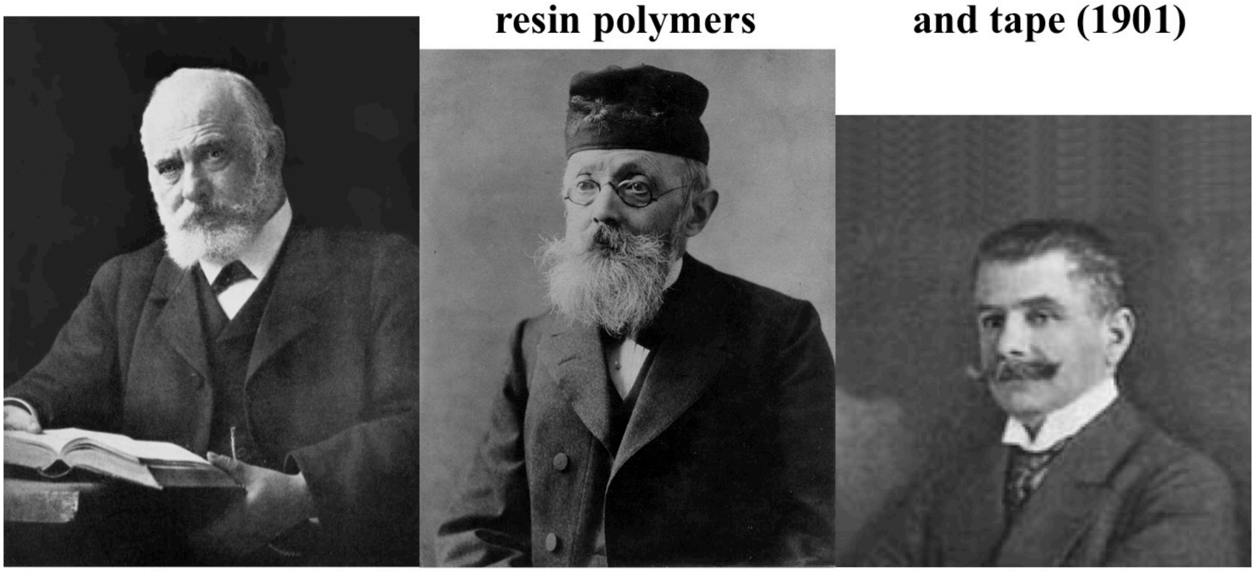


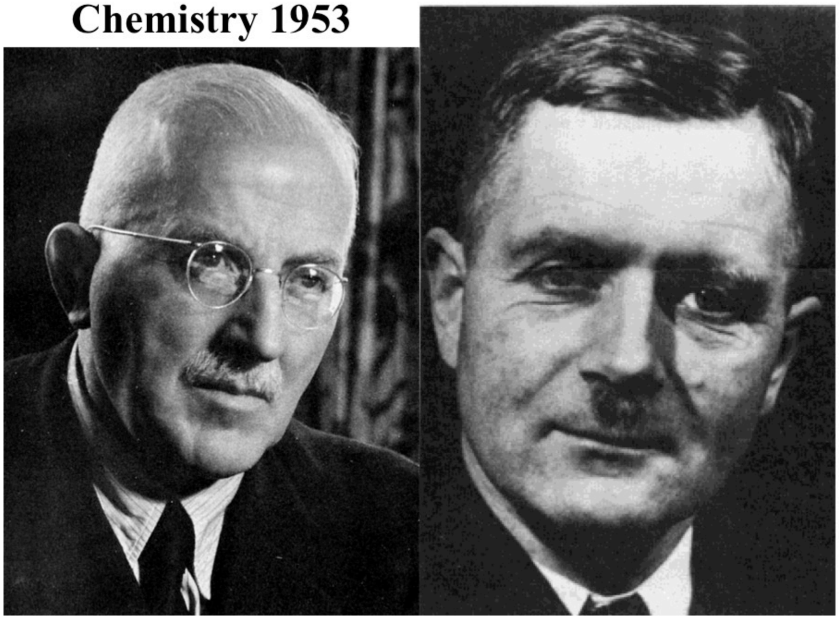
Figure 3.162: Karl Rehn and Karl Ziegler produced polypropylene in 1951. Ziegler won the Nobel Prize in Chemistry 1963. Polypropylene is widely used for products that must not crack even after repeated bending and stress, such as plastic hinges and centrifuge tubes.



Wilhelm Rudolph Fittig (1835–1910) Polymers

Bernhard Tollens (1841–1918) Urea-formaldehyde resin polymers

Oscar Troplowitz (1863–1918) Adhesive bandages and tape (1901)



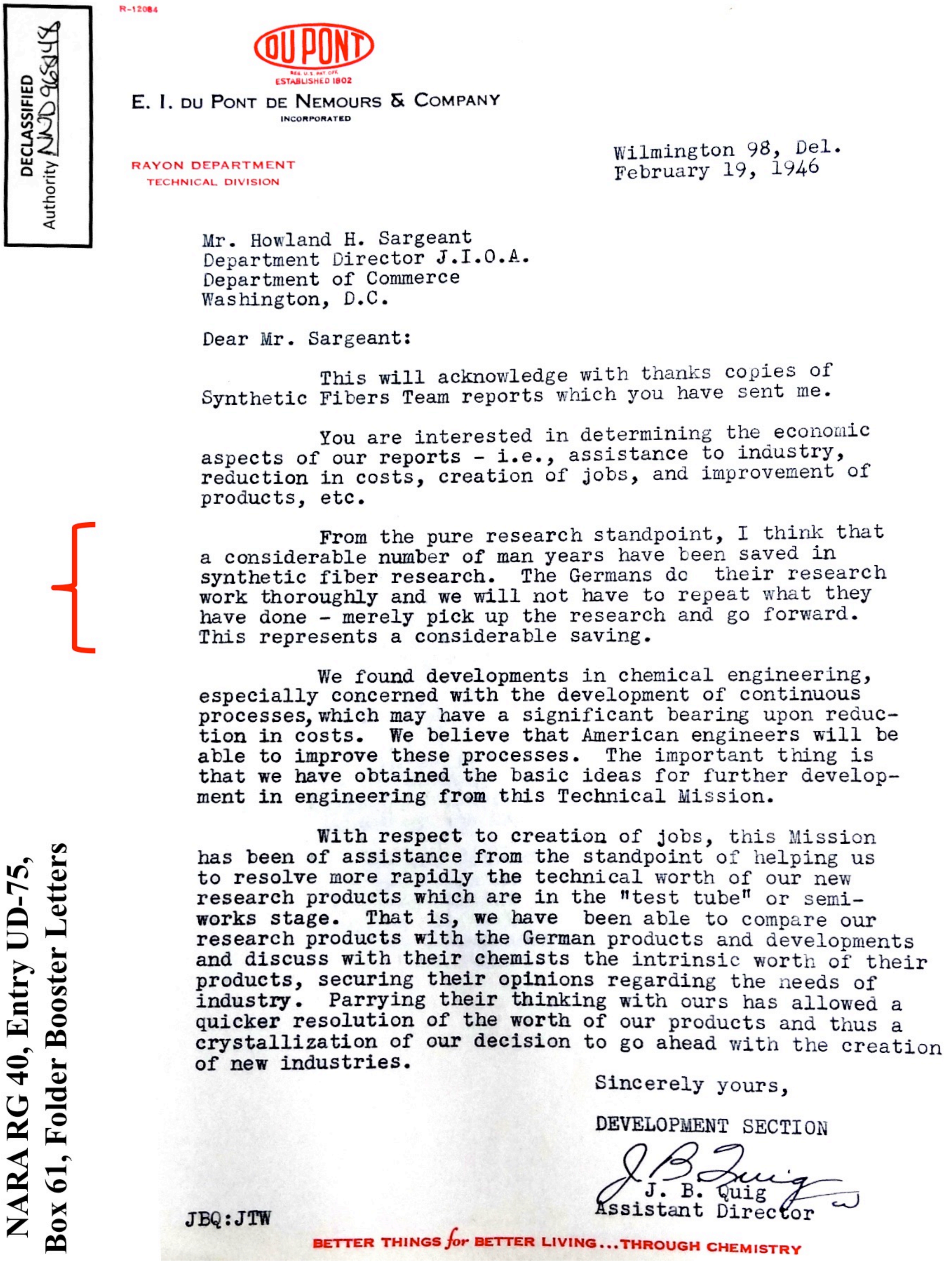
Hermann Staudinger (1881–1965) Polymer structures; Nobel Prize in Chemistry 1953

Werner Kuhn (1899–1963) Physical chemistry of polymers

Victor Garten (18??–19??) Electrically conducting polymers in Australia after the war (2000 Nobel Prize in Chemistry awarded to others for rediscovering that much later)

Figure 3.163: Other German-speaking scientists who made important contributions to polymers included Wilhelm Rudolph Fittig, Bernhard Tollens, Oscar Troplowitz, Hermann Staudinger, Werner Kuhn, and Victor Garten.

Figure 3.164: George de Mestral invented Velcro hook-and-loop fasteners in 1941. They were subsequently used in everything from the space program to sportswear.



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DU PONT
REG. U.S. PAT. OFF.
ESTABLISHED 1802

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

RAYON DEPARTMENT
TECHNICAL DIVISION

Wilmington 98, Del.
February 19, 1946

Mr. Howland H. Sargeant
Department Director J.I.O.A.
Department of Commerce
Washington, D.C.

Dear Mr. Sargeant:

This will acknowledge with thanks copies of Synthetic Fibers Team reports which you have sent me.

You are interested in determining the economic aspects of our reports - i.e., assistance to industry, reduction in costs, creation of jobs, and improvement of products, etc.

From the pure research standpoint, I think that a considerable number of man years have been saved in synthetic fiber research. The Germans do their research work thoroughly and we will not have to repeat what they have done - merely pick up the research and go forward. This represents a considerable saving.

We found developments in chemical engineering, especially concerned with the development of continuous processes, which may have a significant bearing upon reduction in costs. We believe that American engineers will be able to improve these processes. The important thing is that we have obtained the basic ideas for further development in engineering from this Technical Mission.

With respect to creation of jobs, this Mission has been of assistance from the standpoint of helping us to resolve more rapidly the technical worth of our new research products which are in the "test tube" or semi-works stage. That is, we have been able to compare our research products with the German products and developments and discuss with their chemists the intrinsic worth of their products, securing their opinions regarding the needs of industry. Parrying their thinking with ours has allowed a quicker resolution of the worth of our products and thus a crystallization of our decision to go ahead with the creation of new industries.

Sincerely yours,

DEVELOPMENT SECTION

J. B. Quig
Assistant Director

JBQ:JTW

BETTER THINGS for BETTER LIVING...THROUGH CHEMISTRY

NARA RG 40, Entry UD-75,
Box 61, Folder Booster Letters

Figure 3.165: The Assistant Director of the Development Section at the U.S. Du Pont company wrote that because of all of the information on polymers that his company acquired from Germany and Austria after the war, "a considerable number of man years have been saved in synthetic fiber research" at his company [NARA RG 40, Entry UD-75, Box 61, Folder Booster Letters].

3.8.2 Ceramics and Crystallography

Large numbers of German-speaking scientists played major roles in ceramics and crystallography. [16] Some examples are shown in Figs. 3.166–3.171 and briefly discussed below.

In the 1930s and 1940s, Eberhard Both (German, 1910–19??) conducted and led research at Vacuum Schmelze AG in Hanau on the development of new ceramic materials and metal alloys with improved high-temperature and/or magnetic properties. After the war, he moved to the U.S. Army's laboratory in Fort Monmouth, New Jersey, where he initiated and ran similar research programs. ?? Kolmar (German, 19??–19??) was also involved in the Vacuum Schmelze work at Hanau and may have moved to the United States after the war.

At Siemens at Neuhaus near Sonnenberg during World War II, Wilhelm Buessem (German, 1903–1992), ?? Koenig (German, 19??–19??), Hans Joachim Reusch (German, 19??–19??), and Berthold Weber (German, 19??–19??) developed alumina-based ceramics for electronic components and for turbojet engine blades. They also created new titanium-oxide-based dielectrics for capacitors. After the war, Buessem moved to the U.S. Army's Fort Monmouth laboratory, and Weber went to the Air Force's laboratory at Wright Field, Ohio.

Adolf Hugo Dietzel (German, 1902–1993) studied silicates and other ceramic materials at the Kaiser Wilhelm (later Max Planck) Institute for Silicate Research during the period 1930–1969.

Wilhelm Eitel (German, 1891–1979) was director of the Kaiser Wilhelm Institute for Silicate Research 1926–1945, and continued his work on silicates and other materials in the United States after the war.

Johann Hessel (German, 1796–1872) was one of the pioneers of classifying crystal shapes and describing them mathematically. He also studied the composition of feldspar and other minerals.

At Degussa's research facility at Stierstadt during World War II, Gustav Jaeger (German, 19??–19??) and Eugen Ryschkewitz (German, 19??–19??) developed ceramic materials based on alumina, other metal oxides, and silicon carbide for a variety of applications, including electronic components, turbojet engine blades, cutting tools. After the war, Ryschkewitz moved to Wright Field, Ohio to continue this work.

At the wartime Hescho facility at Hermsdorf near Jena, ?? Kaase (German, 19??–19??), Fritz Obenaus (German, 1904–1980), ?? Rath (German, 19??–19??), and ?? Scheid (German, 19??–19??) developed high-temperature ceramics for turbojet engine blades. They created and tested several different ceramic materials, including soapstone-based Calit, silicon-carbide-based Sicalit, and kaolin-based Ardostan. They also developed titanium-oxide-based dielectrics for capacitors.

---

[16] Brock 1993; Bugge 1955; Engels et al. 1989; Farber 1961; Ihde 1984; Johnson 1990; Kahlert 2002; Maier 2015; Neufeldt 2003; Partington 1935, 1957, 1964; Thurnauer 1946; Warde 1946; Werner 2017; BIOS 23; BIOS 30; BIOS 143; BIOS 465; BIOS 470; BIOS 785; BIOS 788; BIOS 1111; BIOS 1446; BIOS 1448; BIOS 1459; BIOS 1705; BIOS 1762; BIOS Overall 28; CIOS XXII-11; CIOS XXV-9; CIOS XXV-10; CIOS XXVI-27; CIOS XXVI-28; CIOS XXVI-29; CIOS XXVI-30; CIOS XXVII-20; CIOS XXIX-48; CIOS XXX-66; FIAT 78; FIAT 278; FIAT 617; FIAT 740; FIAT 746; FIAT 747; FIAT 748; FIAT 749; FIAT 794; FIAT 892; FIAT 924; FIAT 927; FIAT 1050; FIAT 1150; JIOA 78; NavTecMisEu 166-45; NavTecMisEu 275-45; NavTecMisEu 465-45.

Ralph Kronig (German, 1904–1995) developed detailed theoretical models of the behavior of X-rays and electrons in crystal lattices, thus helping to better understand the structures and properties of crystalline materials, including ceramics, metals, and semiconductors.

Max von Laue (German, 1879–1960) pioneered the use of X-rays to analyze the atomic arrangements in crystals and ceramic materials. He focused primarily on theoretical methods of analyzing the results, and the experiments were implemented by Walter Friedrich (German, 1883–1968) and Paul Knipping (German, 1883–1935). Max von Laue won the Nobel Prize in Physics in 1914 for this work. Professor G. Granqvist, Chairman of the Nobel Committee for Physics, explained the importance of the methods and discoveries of von Laue's group [https://www.nobelprize.org/prizes/physics/1914/press-release/]:

> This was the situation when von Laue placed a research medium of the highest import at the disposal of science by virtue of his epoch-making discovery of the interference of X-rays and, at the same time, proved that X-rays, as is the case with light rays, consist of progressive transversal waves.
>
> Previous research had indicated, as is mentioned in the foregoing, that it was highly probable that, if X-rays are wave motions of the same type as light rays, then their wavelengths would have to be of an order of 10^{-9} cm. In order to obtain clear interference phenomena of the same type as those which are caused when light rays pass a grating it was necessary for the distance between the grating slits to be of an order of 10^{-8} cm. But this is approximately the distance between the molecules of a solid body and it was in this manner that von Laue arrived at the idea of employing, as a diffraction grating, a solid body with regularly-arranged molecules, e.g. a crystal. As early as 1850 Bravais had introduced into crystallography the assumption that the atoms composing the various crystals are arranged in regular groups, so-called three-dimensional lattices or space-lattices, whose constants could be calculated with the aid of crystallographic data.
>
> However, the theoretical basis of a space-lattice was unknown and thus it was first necessary for von Laue to develop this theory if else the investigation were to have a value. This he did mainly according to the same approximations as those conventional to the science of optics as applied to normal one-dimensional lattices.
>
> Von Laue left the execution of the experimental work in the hands of W. Friedrich and P. Knipping. The apparatus which they employed consisted of a lead box into which they admitted a thin bundle of X-rays which they directed so as to fall upon a precisely oriented crystal. Sensitized film was positioned both behind and at the sides of the crystal. Already the preparatory tests showed that the intensity maxima which had been anticipated by von Laue became evident in the form of blackened spots on the film positioned behind the crystal. [...]
>
> As a result of von Laue's discovery of the diffraction of X-rays in crystals proof was thus established that these light waves are of very small wavelengths. However, this discovery also resulted in the most important discoveries in the field of crystallography. It is now possible to determine the position of atoms in crystals and much important knowledge has been gained in this connection. We can anticipate further discoveries of equal note

> in the future. It is thus rendered likely that experimental research into the influence of temperature upon diffraction will provide the solution to the question of a zero-point energy, or will at least be of some assistance in arriving at a solution to this problem, as the temperature factor assumes a different value according to whether a zero-point energy exists or not. However, the direct results of this discovery of diffraction are of no less importance: it is now possible to subject the X-ray spectra to direct examination, their line spectra can even be photographed, and science has thus been enriched by a method of research whose full implications can not yet be fully appreciated.

At Lutz & Co. at Lauf an der Pegnitz during World War II, Nikolaus Lutz (German, 19??–19??) and Franz Rother (German, 19??–19??) developed new ceramic materials for specialized electronic applications. Their ceramics included titanium-oxide-based dielectrics, iron-oxide-based magnetic ceramics, magnesium oxide-based ceramics, and other materials with semiconducting and/or magnetic properties.

Herman(n) Mark (Austrian, 1895–1992) primarily focused on polymer research, yet he carried out some important work with X-ray crystallography as well.

Friedrich Mayer (German, 19??–19??) developed metal-oxide coatings and other ceramic coatings to harden metal tool surfaces.

Eilhard Mitscherlich (German states, 1794–1863) made several important contributions to crystallography. He is especially remembered for his discovery of crystallographic isomorphism, or the ability of the same chemical composition to form crystals of somewhat different shapes depending on the alignment of the component atoms.

Friedrich Mohs (German states, 1773–1839) studied many aspects of crystallography. He is particularly famous for introducing his mineral hardness scale in 1812. The Mohs scale ranks minerals from softer (starting with 1 for talc) to harder (ending with 10 for diamond) based on which mineral receives scratches when two dissimilar minerals are rubbed together. It is still widely used today.

Paul Niggli (Swiss, 1888–1953) was another important pioneer of X-ray crystallography, and further developed the mathematical methods of describing crystal structures.

Hans Pulfrich (German, 19??–19??) developed ceramics for electrical applications at AEG and Telefunken from the 1920s to the 1960s.

Working at the Aerodynamische Versuchsanstalt (AVA) at Göttingen during World War II, L. Ritz (German, 19??–19??) designed and demonstrated high-temperature ceramic heat exchangers for turbojet engines and other applications.

At the Luftfahrtforschungsanstalt (LFA) in Brunswick during World War II, Ernst Schmidt (German, 19??–19??) and H. Söhngren (German, 19??–19??) developed high-temperature ceramics for turbojet engine blades.

Arthur Schoenflies (German, 1853–1928) applied advanced mathematical methods such as group theory to the analysis of crystal structures. "Schoenflies notation" is still widely utilized in crystallography and solid state physics.

Working at various German companies from the 1930s to the 1950s, Carl Schusterius (German, 19??–19??) developed and patented novel ceramics for a wide variety of electrical components, as well as for other applications such as dental prostheses.

At the Machinenfabrik Augsburg-Nürnberg A.G., D. Emil Sorensen (German, 19??–19??) developed high-temperature ceramics for turbojet engine blades during World War II.

Gustav Tschermak von Seysenegg (Austrian, 1836–1927) studied the crystallographic structures and chemical compositions of a wide variety of minerals and even meteorites.

Christian Samuel Weiss (German states, 1780–1856) was one of the pioneers of classifying crystal shapes and describing them mathematically.

F. Werther (German, 19??–19??) developed titanium-oxide-based ceramics for various applications.

For German-speaking creators and creations in the closely related fields of solid state physics, semiconductor devices, superconductivity, and piezoelectricity, see Section 6.5.

Large amounts of information, materials, and scientists involved in work on advanced ceramics were transferred to other countries after World War II (Fig. 3.172). See for example:

> Warde, John M. 1946. Status Report on the German Ceramic, Glass, and Refractories Industries in the U.S. Zone of Occupation. *American Ceramic Society Bulletin* (15 September 1946) 25:321-32.
>
> Thurnauer, Hans. 1946. Electrical Insulators. *Ceramic Industry* (June 1946) 46:55-56.
>
> BIOS 23. *High Temperature Ceramics in South Germany.*
>
> BIOS 30. *Telefunken Metal/Ceramic Radio Valves.*
>
> BIOS 143. *German Porous Ceramic Industry.*
>
> BIOS 465. *High Temperature Refractories and Ceramics.*
>
> BIOS 470. *Specialized Ceramic Materials with Particular Reference to Ceramic Gas Turbine Blades.* [High-temp ceramics]
>
> BIOS 788. *The German Vitreous Enamel Industry.* With Appendix.
>
> BIOS 1111. *Industrial Ceramics. Interrogation of Dr. Ungewiss of Steatit-Magnesia A.G. Berlin at Beltane Schools, Wimbledon, S.W.19.* [titanium oxide and other ceramics for dielectrics]
>
> BIOS 1446. *Some Targets of Ceramic Interest in the Berlin Area.* [Silicate research]
>
> BIOS 1448. *The German Industrial Diamond Industry.*
>
> BIOS 1705. *The German Ceramic Industry.*

BIOS 1762. *German Electro-Technical Ceramics.*

BIOS Overall 28. *Fine Ceramics.*

CIOS XXV-9. *Development of Ceramic Materials for Use in Gas Turbine Engines.*

CIOS XXV-10. *Research and Development on Gas Turbines Hermann Goering Institute Volkenrode.*

CIOS XXVI-27. *Research and Development of Engines at Hermann Goering Institute, Volkenrode.*

CIOS XXVI-28. *Research and Development on Gas Turbines at Hermann Goering Institute, Volkenrode.*

CIOS XXVI-29. *Research and Development on Gas Turbines at Junkers Motoren Werke, Dessau.*

CIOS XXVI-30. *Gas Turbine Development by B. M. W.*

CIOS XXVII-20. *Prof. Dr. Ing. Emil Sorensen, Maschinenfabrik Augsberg-Nurnberg AG, Augsberg.* [Ceramic gas turbine blades]

CIOS XXIX-48. *Ceramic Developments of Dr. Rother, Lutz and Co., Lauf/Pegnitz.*

CIOS XXX-66. *Information on Ceramic and Water-Cooled Turbine Blading for Gas Turbines.*

FIAT 78. *High Frequency Technical Ceramic Materials of Germany.*

FIAT 278. *Specialized Ceramic Products, Their Use in German Communication Equipment.* [Selenium rectifiers]

FIAT 617. *The Electrical and Technical Ceramic Industry of Germany.* [High temp zirconium ceramics]

FIAT 740. *Report on High Frequency Technical Ceramic Materials of Germany.*

FIAT 794. *The Porcelain Enamel and Ceramic Color Industry in Germany.* With two supplements. [Rare earths (Dr. Egon Ihwe)]

FIAT 892. *Ceramic Dielectrics for Condensers.*

FIAT 924. *Investigation of Pure Oxide Ceramic Materials Intended for High Temperature and High Stress Applications.* [Silicon carbide]

FIAT 927. *Production of High Alumina Slags in Blast Furnaces and Allied Processes for Recovering Alumina.*

FIAT 1150. *Further Advances of the German Ceramic Industry.*

JIOA 78. *High Frequency Technical Ceramic Materials of Germany.*

NavTecMisEu 166-45. *Turbine Ceramic Bucket and Wheel Development Project at M.A.N. Plant, Augsburg, Germany.*

NavTecMisEu 275-45. *Information on Ceramic and Water-Cooled Turbine Blading for Gas Turbines Obtained from Dr. E. Schmidt (LFA).*

NavTecMisEu 465-45. *Ceramic Fuses.*

While the postwar technology transfer involved a broad range of advanced ceramic materials, one especially important area was synthetic mica for electronics applications. Due to a shortage of real mica in wartime Germany, scientists invented synthetic mica-like ceramics that proved to be superior to the original material. After the war, large amounts of information, materials, and scientists involved in work on synthetic mica were transferred to other countries, as documented in reports such as:

BIOS 785. *The German Mica Industry.*

BIOS 1459. *German Radio Ceramics.*

CIOS XXII-11. *Synthetic Mica Process, Ostheim.*

FIAT 746. *Synthetic Mica Research.*

FIAT 747. *The Synthesis of Fluorine-Mica of the Phlogopite Group.*

FIAT 748. *Crystallochemical and Microscopic Investigations of Synthetic Phlogopites.*

FIAT 749. *Regular Intergrowth of Synthetic Phlogopite with Hydrous Mica.*

FIAT 1050. *Crucibles for Synthetic Mica Development.*

Ceramics and crystallography

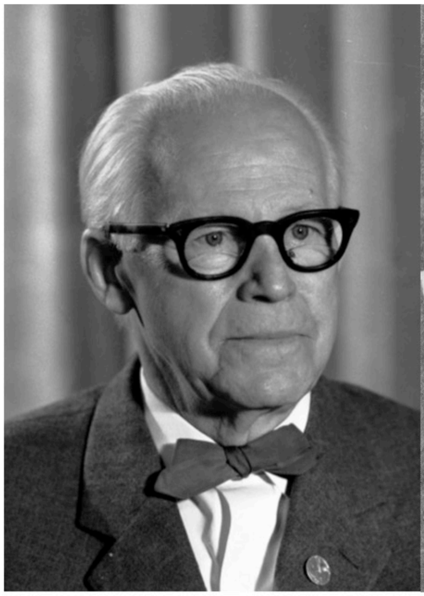
Eberhard Both
(1910–19??)

Wilhelm Buessem
(1903–1992)

Adolf Hugo Dietzel
(1902–1993)

Wilhelm Eitel
(1891–1979)

Walter Friedrich
(1883–1968)



Johann Hessel
(1796–1872)

Figure 3.166: Some creators who made important contributions to ceramics and crystallography included Eberhard Both, Wilhelm Buessem, Adolf Dietzel, Wilhelm Eitel, Walter Friedrich, and Johann Hessel.

Ceramics and crystallography

Gustav Jaeger
(19??–19??)

?? Kaase
(19??–19??)

Paul Knipping
(1883–1935)

?? Koenig
(19??–19??)

?? Kolmar
(19??–19??)

Ralph Kronig
(1904–1995)

Figure 3.167: Other creators who made important contributions to ceramics and crystallography included Gustav Jaeger, ?? Kaase, Paul Knipping, ?? Koenig, ?? Kolmar, and Ralph Kronig.

Ceramics and crystallography

Max von Laue
(1879–1960)

Nikolaus Lutz
(19??–19??)

Herman(n) Mark
(1895–1992)

Friedrich Mayer
(19??–19??)

Eilhard Mitscherlich
(1794–1863)

Friedrich Mohs
(1773–1839)

Figure 3.168: Other creators who made important contributions to ceramics and crystallography included Max von Laue, Nikolaus Lutz, Herman(n) Mark, Friedrich Mayer, Eilhard Mitscherlich, and Friedrich Mohs.

Ceramics and crystallography

Paul Niggli
(1888–1953)

Fritz Obenaus
(1904–1980)

Hans Pulfrich
(19??–19??)

?? Rath
(19??–19??)

Hans Reusch
(19??–19??)

L. Ritz
(19??–19??)

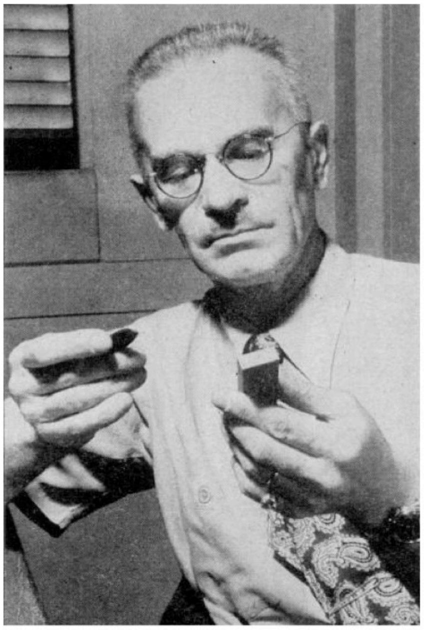
Figure 3.169: Other creators who made important contributions to ceramics and crystallography included Paul Niggli, Fritz Obenaus, Hans Pulfrich, ?? Rath, Hans Reusch, and L. Ritz.

Ceramics and crystallography

Franz Rother
(19??–19??)

Eugen Ryschkewitz
(19??–19??)

?? Scheid
(19??–19??)



Ernst Schmidt
(19??–19??)

Arthur Schoenflies
(1853–1928)

Carl Schusterius
(19??–19??)

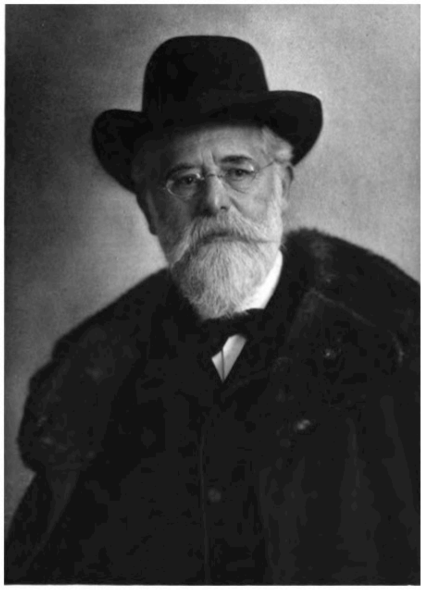
Figure 3.170: Other creators who made important contributions to ceramics and crystallography included Franz Rother, Eugen Ryschkewitz, ?? Scheid, Ernst Schmidt, Arthur Schoenflies, and Carl Schusterius.

Ceramics and crystallography

H. Söhngren
(19??–19??)

D. Emil Sorensen
(19??–19??)

Gustav Tschermak von Seysenegg
(1836–1927)

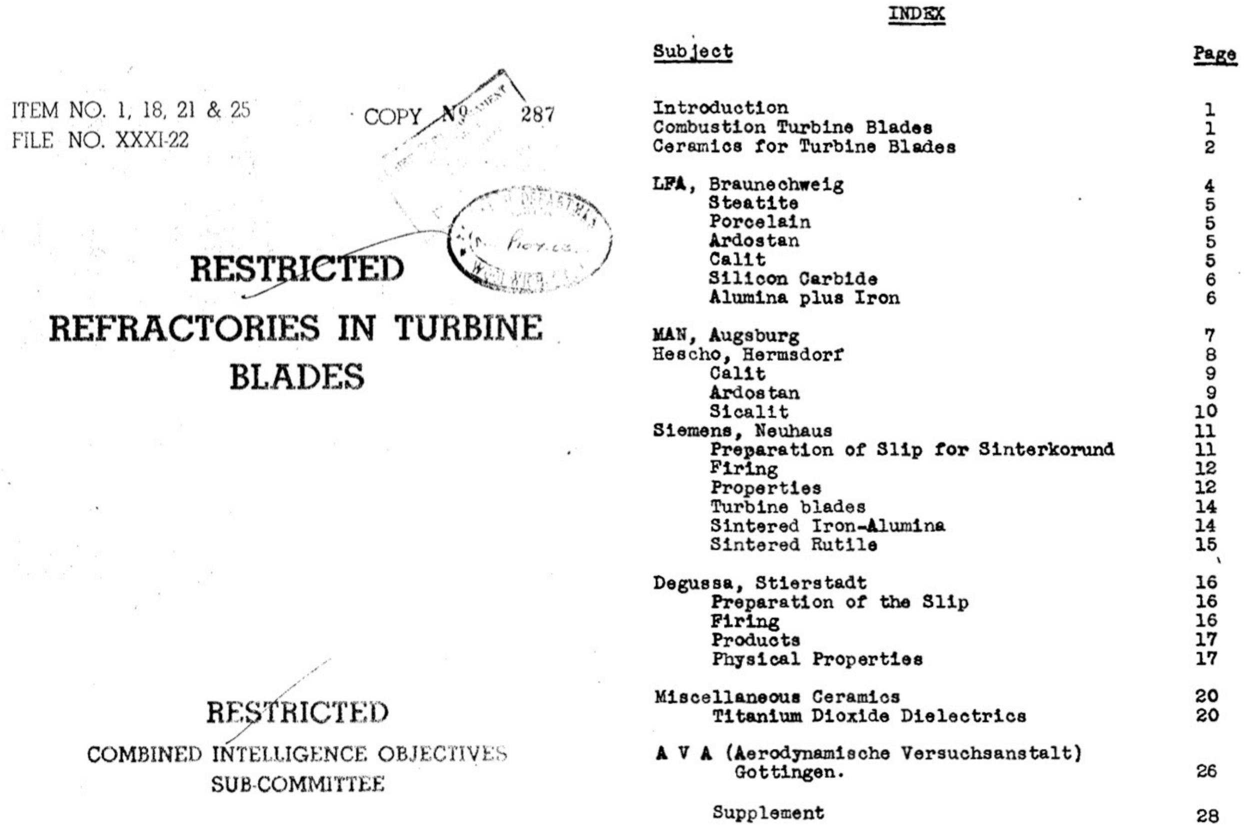


Berthold Weber
(19??–19??)

Christian Samuel Weiss
(1780–1856)

F. Werther
(19??–19)

Figure 3.171: Other creators who made important contributions to ceramics and crystallography included H. Söhngren, D. Emil Sorensen, Gustav Tschermak von Seysenegg, Berthold Weber, Christian Samuel Weiss, and F. Werther.



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COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE

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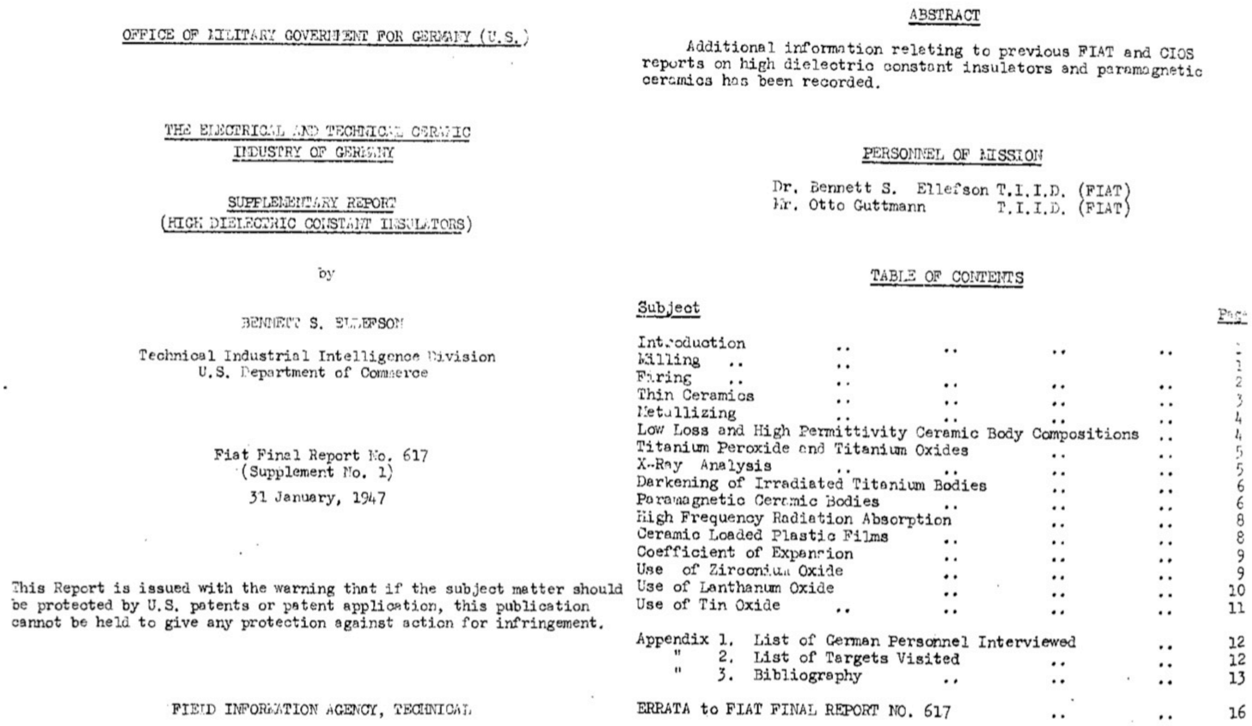
Ceramics and crystallography



OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)

THE ELECTRICAL AND TECHNICAL CERAMIC INDUSTRY OF GERMANY

SUPPLEMENTARY REPORT
(HIGH DIELECTRIC CONSTANT INSULATORS)

by

BENNETT S. ELLEFSON

Technical Industrial Intelligence Division
U.S. Department of Commerce

Fiat Final Report No. 617
(Supplement No. 1)
31 January, 1947

This Report is issued with the warning that if the subject matter should be protected by U.S. patents or patent application, this publication cannot be held to give any protection against action for infringement.

FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

Additional information relating to previous FIAT and CIOS reports on high dielectric constant insulators and paramagnetic ceramics has been recorded.

PERSONNEL OF MISSION

Dr. Bennett S. Ellefson	T.I.I.D.	(FIAT)
Mr. Otto Guttmann	T.I.I.D.	(FIAT)

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Figure 3.172: Large amounts of information, materials, and scientists involved in work on advanced ceramics were transferred to other countries after World War II [CIOS XXXI-22, FIAT 617].

3.8.3 Glass

Glass production has a history going back to ancient times, and has been practiced worldwide. The glassmaking industry was especially prominent and advanced in the German-speaking world, dating back many centuries in Thuringia, Bohemia, and other regions. As scientific research gained greater prominence in the German-speaking world around 1800, it was combined with the older traditions of glassmaking craftsmanship, resulting in a number of major technological advances in methods of producing and utilizing glass.

Joseph von Fraunhofer (German states, 1787–1826) made a number of early improvements in glass manufacturing processes for optics and other applications. He then used his glass elements to create new optical instruments such as spectroscopes (pp. 970 and 1269).

Other especially important early glassmakers who produced and used improved optical elements and optical instruments included:

- Simon Plössl (Austrian, 1794–1868, Fig. 6.229), who was particularly noted for producing achromatic (non-color-distorting) lenses for microscopes and telescopes.

- Georg Johann Oberhäuser (German states, 1798–1868) and Edmund Hartnack (German, 1826–1891), who also produced early microscopes. Hartnack invented liquid-immersion lenses to achieve higher resolution. See p. 1278.

- Carl Zeiss (German, 1816–1888) and Ernst Abbe (German, 1840–1905), who revolutionized the production of high-quality microscopes at the Zeiss optical company (p. 1279).

- Carl Kellner (German states, 1826–1855) and Ernst Leitz I (German, 1843–1920) at the Leitz optical company (p. 1284), another producer of high-quality microscopes and other optical instruments.

Arguably the most important glass scientist in the German optical industry, though, was Otto Schott (German, 1851–1935), who is shown in Fig. 3.173. In partnership with the Zeiss company, he founded the Schott glassworks in Jena and created a variety of special-purpose types of glass, including optical glass (1873, for Zeiss microscopes to achieve the maximum diffraction-limited resolution), lithium glass (1879), and borosilicate glass (1887). Borosilicate glass is resistant to thermal stress (when exposed to temperature changes, it expands and contracts less than normal glass, and therefore is much less likely to shatter when heated or cooled), so it is still widely used to make glassware containers for cooking and laboratory work.

One area of traditional German glassmaking craftsmanship, dating back before 1800, was producing long, flexible fibers of glass. The glass fibers were used for decoration and other applications.

Apparently drawing upon those German glass fiber methods, Hermann Hammesfahr (German, 1845–1914) moved to the United States and began producing and patenting fiberglass threads, cloth, and insulation. See Fig. 3.174. After a slow start, his work eventually prompted broader American industrial interest in fiberglass in the twentieth century.

Even as Hammesfahr took fiberglass technology to the United States, fiberglass production and applications continued to advance in the German-speaking world. For example, Ulrich Hütter (Austrian, 1910–1990, Fig. 3.175) produced glass-fiber-reinforced polymers in Germany during and after World War II for applications ranging from aircraft structures to wind turbine blades.

Similarly, Alfred Schmid (Swiss, 1899–1968) demonstrated how to make very strong yet very light composite materials by reinforcing processed wood and/or polymers with fiberglass. After the war, Schmid transferred that technology to Allied countries (Fig. 3.175). For example, BIOS 563, *The German Radio Component Industry*, p. 18, reported:

> A synthetic material composed of fibreglass coated with an artificial resin had been developed, and was used to coat articles made of a low-density homogeneous wood with a coating 0.02 mm thick. This resulted in an article of light weight but having great strength. It was claimed that both tensioned and compressional forces could be dealt with. Dr. Schmid envisaged the aircraft of the future as being made from glass coated homogeneous wood for light weight combined with great strength. He also claimed that repairs to the skin, if damaged, could be done simply by the application of more of the fibre-glass material.

As shown in Fig. 3.176, an 11 May 1945 document from the U.S. Army Air Forces stated [AFHRA A5729 electronic pp. 1650–1651]:

> Glass types which are not available in this country and which might be of considerable value to American manufacturers are known to have existed in Germany before the war and it is recommended that a survey be made[...]

Indeed, numerous BIOS, CIOS, and FIAT reports documented widespread production and use of advanced glass and fiberglass products in the German-speaking world, as well as the transfer of those technologies to Allied countries after World War II (Fig. 3.177). See for example:

> BIOS 403. [Glass fibers]
>
> BIOS 404. *German Asbestos Industry.*
>
> BIOS 563. *The German Radio Component Industry.* [fiberglass composite materials]
>
> BIOS 627. *The Worsted Spinning Industry in the British and U.S. Zones of Germany.* [glass fibers]
>
> BIOS 894. *Mineral Wool Plant, Gelsenkirchener Eisenwerk.*
>
> BIOS 1066. *German Glass Manufacturing Equipment.*
>
> BIOS 1118. *Final Report on the Investigation of the Use of Industrial Glassware for Chemical Plants in Germany.*
>
> BIOS 1183. *Anti-Reflection Surfaces on Glass, Optical Cements & Etching Resist for Fine Lines.*

BIOS 1340. *Report on Glass Fibre Industry in Germany.*

BIOS 1451. *Glass Jets. Interrogation of Bernhard Wempe at Coventry.*

BIOS 1664. *German Fibrous and Scientific Glass Industry.*

BIOS 1780. *Some Aspects of the German Glass Industry in 1946.*

BIOS Overall 4. *Glass and Industry.*

CIOS XXV-8. *Land and Air Service Fire Control Instruments, Carl Zeiss, Jena—Production of Optical Glass Schott and Genossen Lenses and Graduated Scales, Zeiss and Others.*

CIOS XXVII-43. *Manufacture of Glass Fabric Impregnated Fibre Used as a Substitute for Mica Insulation Between Commutator Segments in Motors and Generators.*

CIOS XXIX-41. *Production of Optical Glass in Germany and France. CIOS Target Nos. 9/1, 9/36 & 9/80. Physical and Optical Instruments and Devices.*

CIOS XXIX-42. *The Production of Binoculars by Zeiss. CIOS Target No. 9/1. Physical and Optical Instruments and Devices.*

CIOS XXIX-43. *Pots Used in Melting Optical Glass at Schott and Genossen.*

CIOS XXXII-22. *Optical Glass Manufacturing at Schott & Gen, Jena.*

CIOS XXXIII-23. *Investigation of German Plastics Plants, Part 2.* [Glass-like wire with cellulose acetate—fiber optics?]

CIOS XXXIII-50. [Synthetic fibers comprehensive survey]

CIOS XXXIII-69. *Schott and Genossen of Jena.* [Schott glass, mirrors]

FIAT 9. *Investigation of Scientific and Laboratory Glassware Area of Thuringia, Germany.*

FIAT 454. *Records of Wartime Improvements in Fiber Manufacture and in Fiber Processing. I.G. Farben (Badische Plant) Ludwigshafen.* [Synthetic fibers and fabric treatments]

FIAT 460. *The Asbestos Textile Industry in Germany.*

FIAT 461. *The Fibrous Glass Textile Industry in Germany.*

FIAT 552. *Fiberglass-Weaving by Rheydt Glass-Weaving Company, Walter Klevers, Rheydt Near München-Gladbach.*

FIAT 824. *The Miscellaneous Glass Industry of Central Europe.* [Neodymium glasses and other exotic glasses]

FIAT 981. *The Dyeing of Glass Fiber Textiles.*

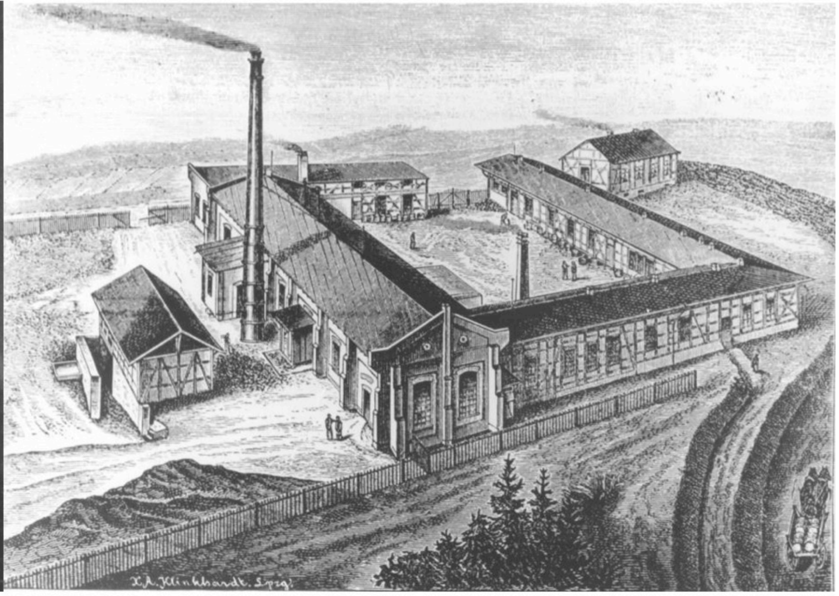
NavTecMisEu 519-45. *The Properties of Klieforth Infrared Transparent Glasses.*

During World War II, the Zeiss infrared Lichtsprechgerät was used for optical transmission of voice communications over distances up to several kilometers (pp. 1140, 1151). That device also would have been quite suitable for use with optical fibers instead of free-space transmission. Fiber optics would have given the signals far more privacy, which would have been an obvious advantage during wartime. More historical research is needed to determine if optical fibers (made of either glass or polymers) were indeed used in conjunction with optical data transmissions in wartime Germany.

In fact, further archival research on all aspects of the history, accomplishments, and global influence of the German-speaking world on glassmaking technologies and applications could be quite enlightening.

Otto Schott (1851–1935) created optical glass (1873), lithium glass (1879), borosilicate glass (1887)

Schott Glassworks Jena (1884)



Borosilicate glass is resistant to thermal stress and widely used for glassware containers for cooking and laboratory work

Figure 3.173: Otto Schott created optical glass, lithium glass, borosilicate glass. Borosilicate glass is resistant to thermal stress and widely used for glassware containers for cooking and laboratory work.

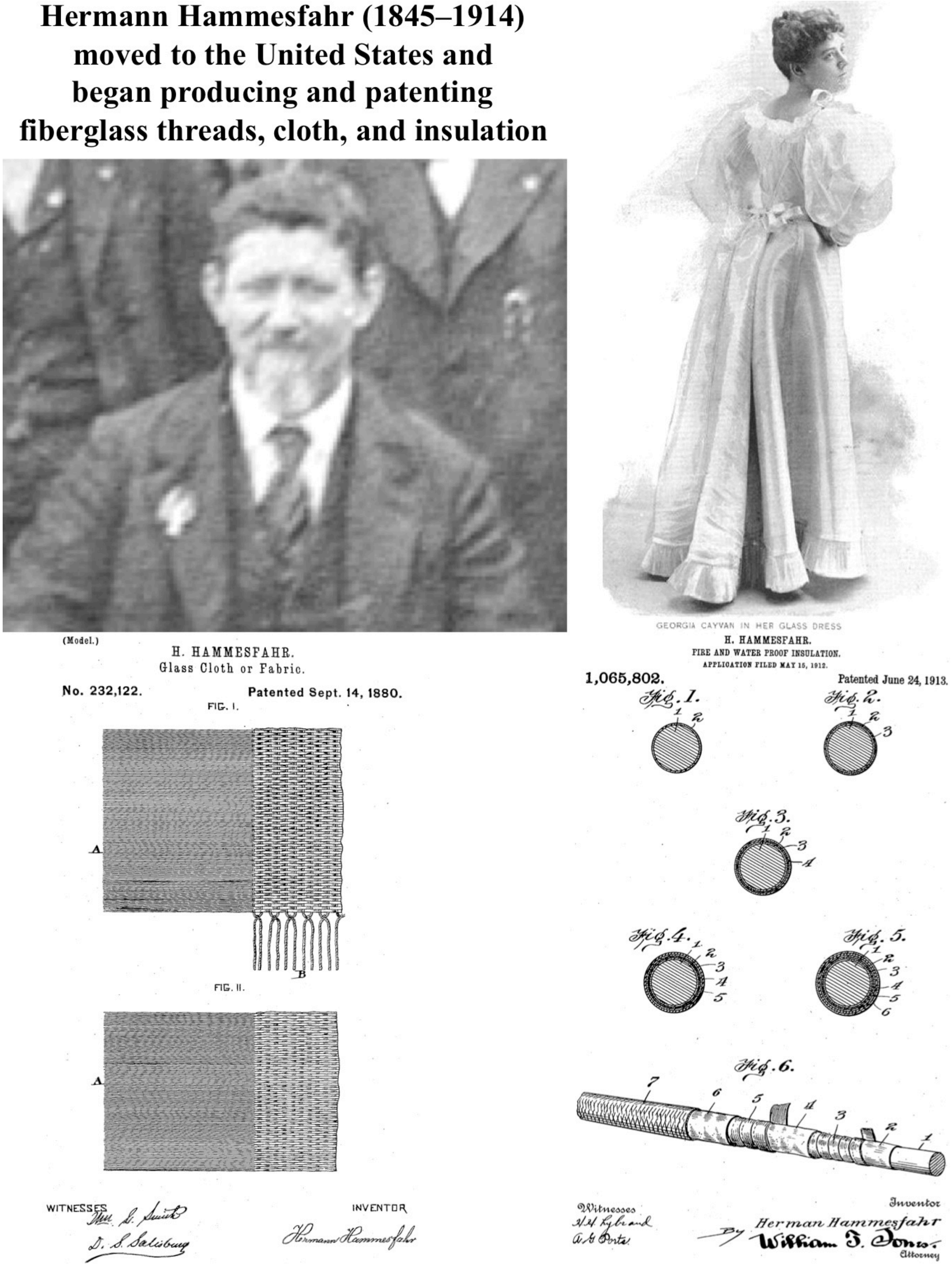
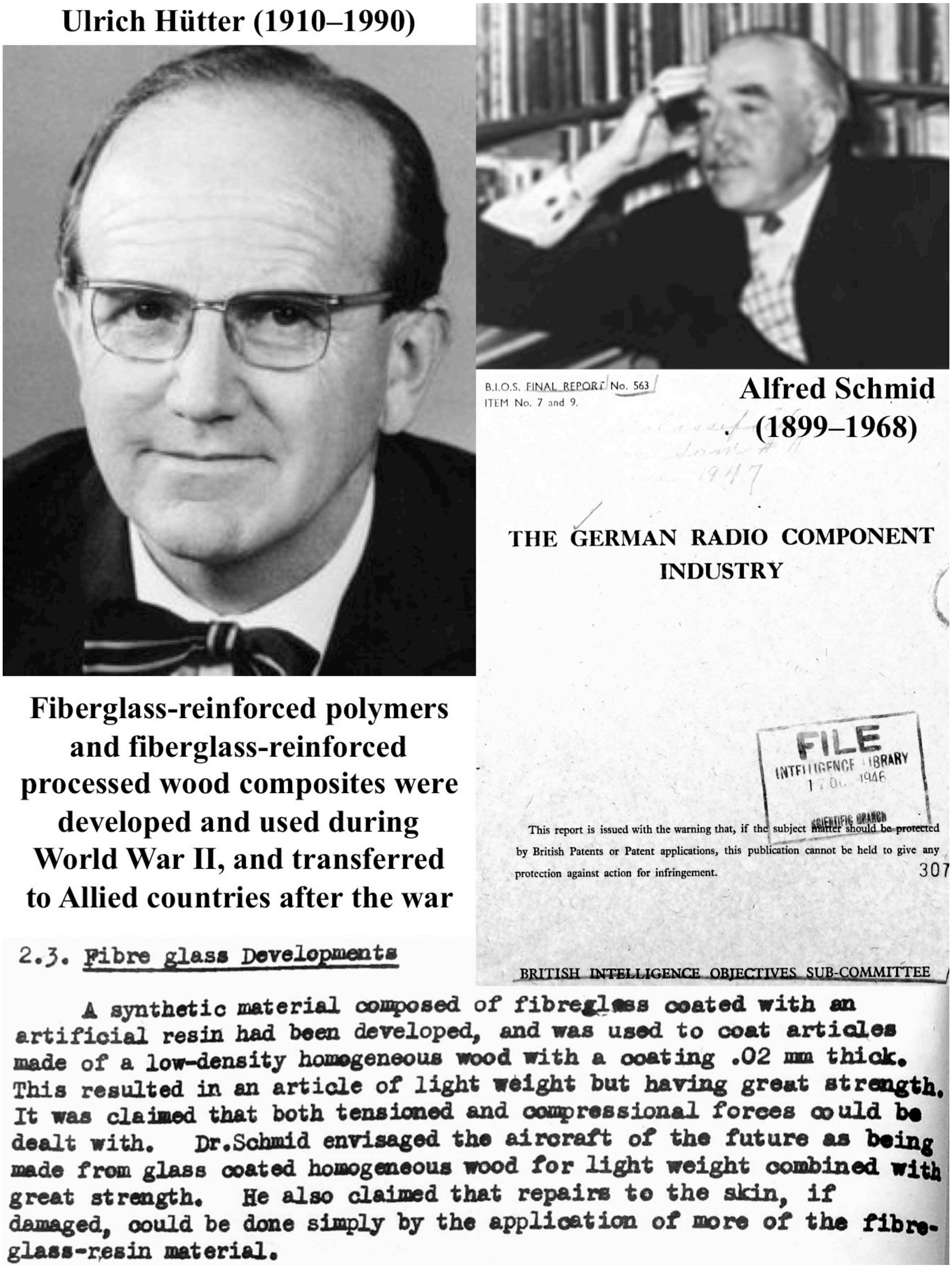


Figure 3.174: Hermann Hammesfahr moved to the United States and began producing and patenting fiberglass threads, cloth, and insulation.



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1947

THE GERMAN RADIO COMPONENT INDUSTRY

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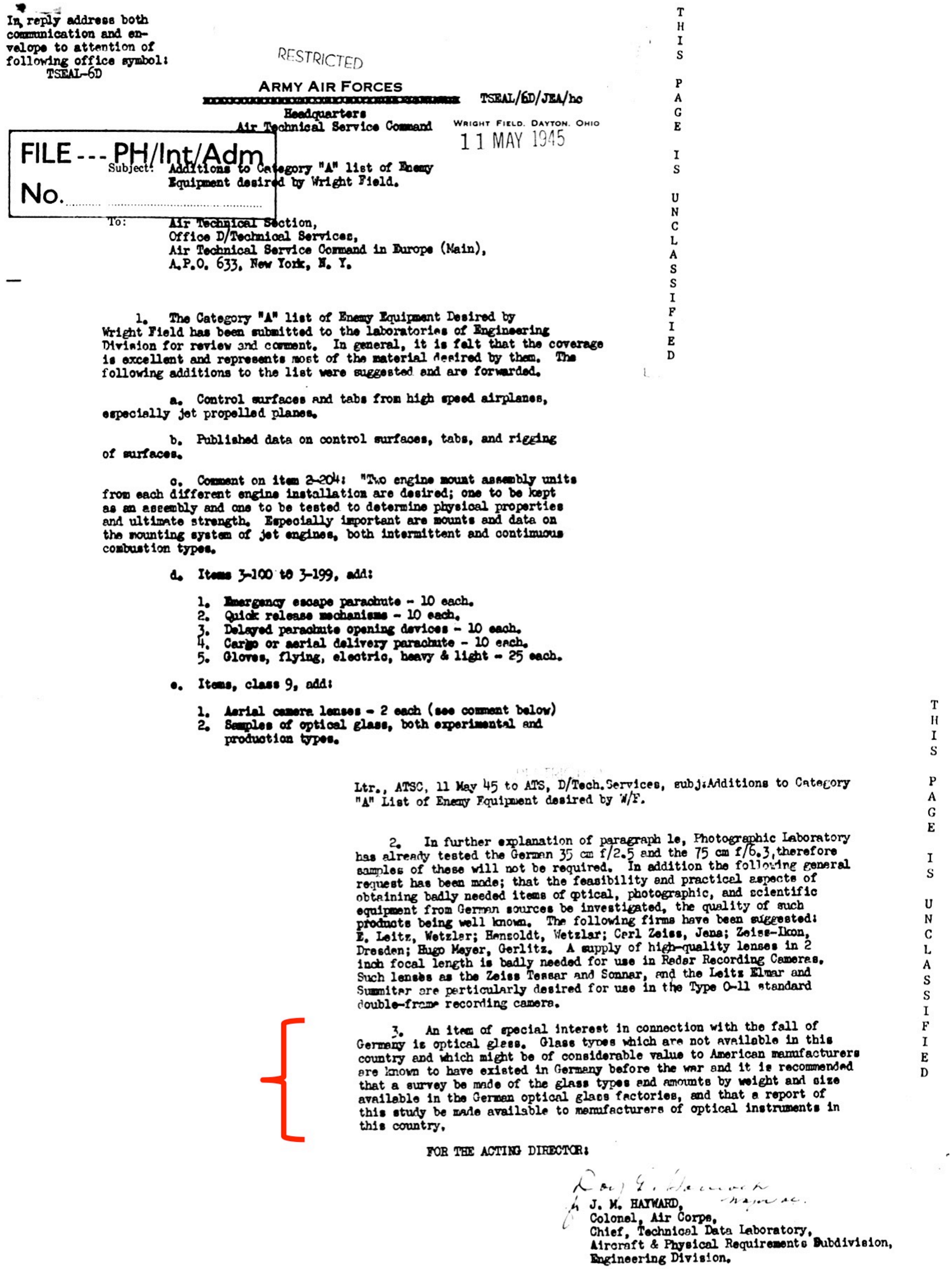
BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

2.3. Fibre glass Developments

A synthetic material composed of fibreglass coated with an artificial resin had been developed, and was used to coat articles made of a low-density homogeneous wood with a coating .02 mm thick. This resulted in an article of light weight but having great strength. It was claimed that both tensioned and compressional forces could be dealt with. Dr.Schmid envisaged the aircraft of the future as being made from glass coated homogeneous wood for light weight combined with great strength. He also claimed that repairs to the skin, if damaged, could be done simply by the application of more of the fibre-glass-resin material.

Figure 3.175: Ulrich Hütter and Alfred Schmid separately demonstrated fiberglass-reinforced polymers and fiberglass-reinforced processed wood composite materials during World War II, then transferred that technology to Allied countries after the war [BIOS 563].



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ARMY AIR FORCES
Headquarters
Air Technical Service Command

TSEAL/6D/JEA/hc

WRIGHT FIELD, DAYTON, OHIO
11 MAY 1945

FILE --- PH/Int/Adm
No. ....

Subject: Additions to Category "A" list of Enemy Equipment desired by Wright Field.

To: Air Technical Section,
Office D/Technical Services,
Air Technical Service Command in Europe (Main),
A.P.O. 633, New York, N. Y.

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1. The Category "A" list of Enemy Equipment Desired by Wright Field has been submitted to the laboratories of Engineering Division for review and comment. In general, it is felt that the coverage is excellent and represents most of the material desired by them. The following additions to the list were suggested and are forwarded.

a. Control surfaces and tabs from high speed airplanes, especially jet propelled planes.

b. Published data on control surfaces, tabs, and rigging of surfaces.

c. Comment on item 2-204: "Two engine mount assembly units from each different engine installation are desired; one to be kept as an assembly and one to be tested to determine physical properties and ultimate strength. Especially important are mounts and data on the mounting system of jet engines, both intermittent and continuous combustion types.

d. Items 3-100 to 3-199, add:

1. Emergency escape parachute - 10 each.
2. Quick release mechanisms - 10 each.
3. Delayed parachute opening devices - 10 each.
4. Cargo or aerial delivery parachute - 10 each.
5. Gloves, flying, electric, heavy & light - 25 each.

e. Items, class 9, add:

1. Aerial camera lenses - 2 each (see comment below)
2. Samples of optical glass, both experimental and production types.

Ltr., ATSC, 11 May 45 to ATS, D/Tech.Services, subj:Additions to Category "A" List of Enemy Equipment desired by W/F.

2. In further explanation of paragraph 1e, Photographic Laboratory has already tested the German 35 cm f/2.5 and the 75 cm f/6.3, therefore samples of these will not be required. In addition the following general request has been made; that the feasibility and practical aspects of obtaining badly needed items of optical, photographic, and scientific equipment from German sources be investigated, the quality of such products being well known. The following firms have been suggested: E. Leitz, Wetzlar; Hensoldt, Wetzlar; Carl Zeiss, Jena; Zeiss-Ikon, Dresden; Hugo Meyer, Gerlitz. A supply of high-quality lenses in 2 inch focal length is badly needed for use in Radar Recording Cameras. Such lenses as the Zeiss Tessar and Sonnar, and the Leitz Elmar and Summitar are particularly desired for use in the Type O-11 standard double-frame recording camera.

3. An item of special interest in connection with the fall of Germany is optical glass. Glass types which are not available in this country and which might be of considerable value to American manufacturers are known to have existed in Germany before the war and it is recommended that a survey be made of the glass types and amounts by weight and size available in the German optical glass factories, and that a report of this study be made available to manufacturers of optical instruments in this country.

FOR THE ACTING DIRECTOR:

J. M. HAYWARD,
Colonel, Air Corps,
Chief, Technical Data Laboratory,
Aircraft & Physical Requirements Subdivision,
Engineering Division.

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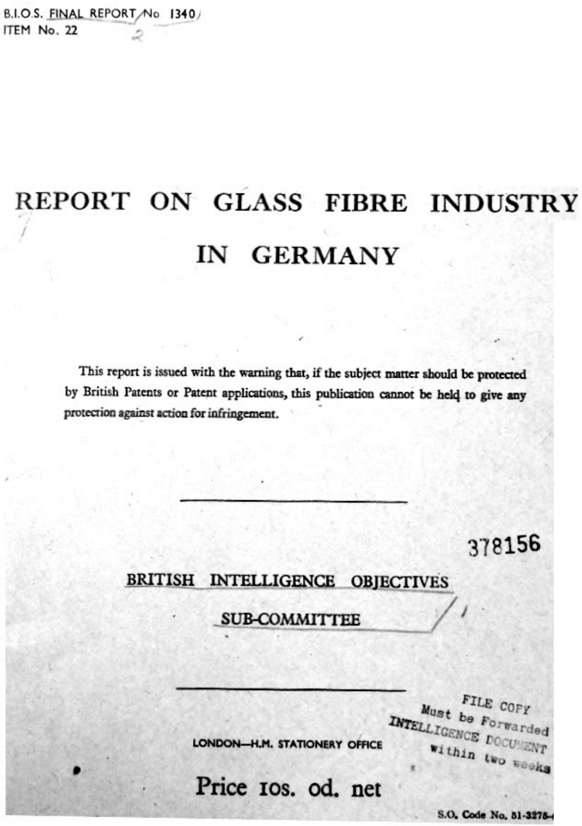
Figure 3.176: An 11 May 1945 document from the U.S. Army Air Forces stated: "Glass types which are not available in this country and which might be of considerable value to American manufacturers are known to have existed in Germany before the war and it is recommended that a survey be made..." [AFHRA A5729 electronic pp. 1650–1651].

Numerous BIOS, CIOS, and FIAT reports documented widespread production and use of glass fiber products in the German-speaking world, as well as the transfer of those technologies to Allied countries after World War II



B.I.O.S. FINAL REPORT No 1340
ITEM No. 22

REPORT ON GLASS FIBRE INDUSTRY
IN GERMANY

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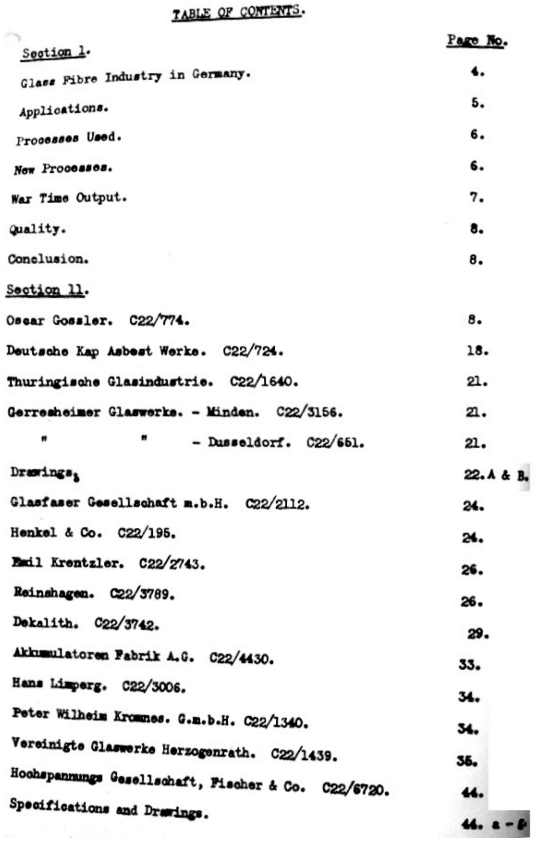

TABLE OF CONTENTS.

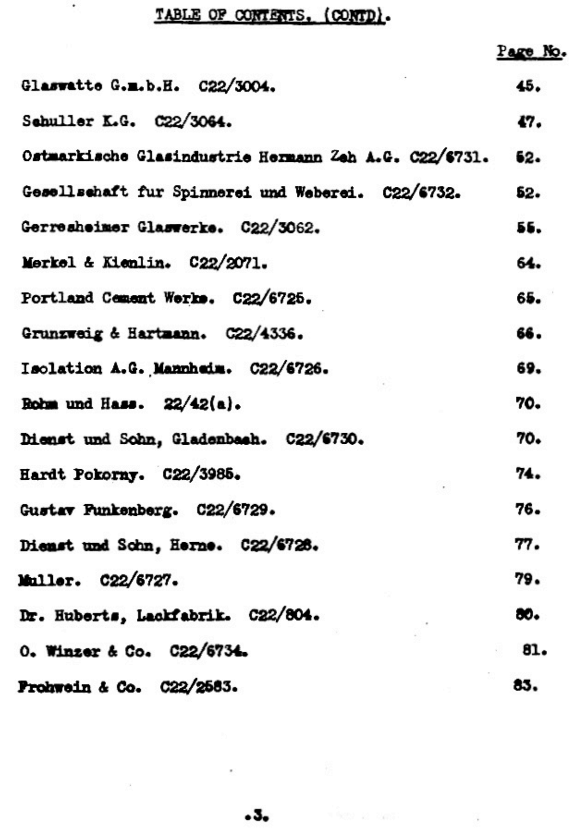

TABLE OF CONTENTS. (CONTD).

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Figure 3.177: Numerous BIOS, CIOS, and FIAT reports documented widespread production and use of advanced glass and fiberglass products in the German-speaking world, as well as the transfer of those technologies to Allied countries after World War II [BIOS 1340].

3.8.4 Metals

A common view is that by 1945, metallurgy was less advanced in the German-speaking world than elsewhere, due to the scarcity of some types of metal ores in German-speaking areas and the international blockade of metal imports during the wars. In fact, a huge number of German-speaking scientists made major contributions to metallurgy from the nineteenth century through WWII, and then many of these creators and their creations were transferred to the United States and other countries [Maier 2007]. Just a few illustrative examples are shown in Figs. 3.178–3.186 and discussed below in alphabetical order.

Heinrich Adenstedt (German, 1910–1991) was an expert on titanium and other metal alloys who came to the United States after the war [Figs. 3.178–3.179]. Both in Germany during the war and in the United States after the war, he worked very closely with jet/helicopter/tank engine designer Anselm Franz (pp. 1391 and 1751–1752). In a 1948 article [Adenstedt 1948], Adenstedt listed several advanced iron-based (steel) alloys that were developed and used in Germany before and during WWII, including Tinidur (Titanium Nickel Durable alloy), Cromadur (Chromium Manganese Durable alloy), FKDM 10 (V, Cr, W, Mo), FKM 10 (V, Cr, Mo), and MC 120 (Mo, Cr). Some of the related alloys that were also developed and used then included Vanidur (Vanadium Nickel Durable alloy) and Sinidur (Silver Nickel Durable alloy). Most of those advanced alloys were produced by Krupp and were intended for jet engine components, due to their heat resistance and good structural properties. They are still used for that purpose even today.

Georgius Agricola, or Georg Bauer (German states, 1494–1555, Fig. 3.10), discovered bismuth around 1540 and conducted extensive work on metallurgy.

Kurt Anderko (German, 19??–19??) was another expert on titanium and advanced metal alloys in Germany during World War II. After the war, he came to the United States as part of the Paperclip program.

Carl Josef Bayer (Austrian, 1847–1904) developed a practical industrial process for extracting aluminum metal from the mineral bauxite.

A. Beerwald (German, 19??–19??) developed very lightweight magnesium alloys for aerospace vehicles in Germany during World War II.

?? Berblinger (German, 19??–19??) was a metallurgy expert in Germany during World War II, and was employed or at least sought by the U.S. Army's Fort Monmouth, New Jersey laboratory after the war.

Carl Berg (German, 1851–1906) developed and supplied aluminum alloys for the first rigid airships that were made by David Schwarz and Ferdinand von Zeppelin (pp. 1656–1657).

Franz Bollenrath (German, 1898–1981) was an expert on metallic materials and structures who worked at the Technische Hochschule Berlin before World War II, Sonthofen on secret military work during the war, and the Technische Hochschule Aachen after the war.

August Borsig (German states, 1804–1854) was a metal manufacturer and industrialist who founded the Borsig company, which later became Rheinmetall-Borsig.

Hermann Bottenhorn (German, 19??–19??) was an expert on aircraft metallurgy in Germany during World War II, and continued his work at Wright Field, Ohio, after the war.

?? Bruche (German, 19??–19??) conducted work on metallurgy during World War II. After the war, he either worked for or at least was actively sought by the U.S. Army's Fort Monmouth laboratory.

Robert Bunsen (German, 1811–1899, p. 439) discovered that pure aluminum could be produced using electrolysis.

Otto Dahl (German, 19??–19??) developed metal alloys at Siemens & Halske during World War II.

Walter Dawihl (German, 1904–19??), the head of Osram's research department, developed novel hard metal alloys and hard coatings for metal tools during World War II. After the war, he was extensively interrogated by Allied investigators, and he wrote a widely used handbook on hard metal alloys and coatings.

Ulrich Dehlinger (German, 1901–1981) developed the theory of dislocations in metals at the University of Stuttgart, where he worked from the 1920s to the end of his career.

Bernard Dirksen (German, 19??–19??) conducted research on metallic materials and structures in Germany during World War II and at Wright Field, Ohio, after the war.

Hans Fischer (German, 19??–19??) was an expert on the cold processing of steel in Germany during World War II. After the war, he continued his work at the Aberdeen Proving Ground in Maryland, along with Heinrich Kopp and Ludwig Schuster.

Richard Glocker (German, 19??–19??) was a metallurgist in Stuttgart during World War II and worked at the U.S. Army's Fort Monmouth laboratory after the war.

Max Hansen (German, 1901–1978) was another expert on titanium and other metal alloys who came to the United States after the war, before eventually returning to (West) Germany. In her history of titanium research, Kathleen Housley wrote [Housley 2007]:

> The research at Armour [Research Foundation in Chicago] was led by Max Hansen, a German metallurgist and world-renowned expert on phase diagrams whose doctoral work had been paid for by Kroll, who considered Hansen's intelligence to be worth the gift of tuition. Hansen had taken the position of professor of metallurgy at Illinois Institute of Technology after the war. Harold Kessler, who worked with Hansen at Armour, recalled the circumstances of his appointment. "As the war was coming to an end, the British were aware of Max, for he had published many important papers on aluminum alloy development as well as his pioneering work on binary alloy phase diagrams. They smuggled him out of Germany to England just as the Russians were coming to get him with the intention of smuggling him to the U.S.S.R. Then the position at Armour opened up and he came to the States." Like his mentor Kroll, Hansen was a gentle, soft-spoken man venerated by his co-workers who included besides Kessler, Donald McPherson, William Rostocker, Frank Crossley, Raymond van Thyne, and C. Robert Lillie. "He set a personal example of professional excellence and integrity," remembered Kessler. "He taught, counseled, and cajoled his students and colleagues toward better, more productive careers, and inspired an esprit de corps in all those with whom he

> worked." According to Margolin, the esteem in which Hansen was held bordered on awe. "On phase diagrams, Hansen was the authority. With a phase diagram, you do it, but a lot of times, there are things wrong because you don't fully understand what you are doing, and you have to guess. It is a very time-consuming process. I remember that Hansen did the titanium-aluminum diagram in three months. I was absolutely amazed." [...] Armour had several contracts with industry and branches of the Armed Forces, particularly with Wright-Patterson Air Force Base where metallurgical research was under the direction of Dr. H. K. Adenstedt. A close friend of Hansen's, Adenstedt had worked with him in the German aluminum industry and had come to the United States as part of the round-up of German scientists.

F. Heimes (German, 19??–19??) conducted metallurgy research at Neckersulm during World War II. After the war, he either worked for or was sought by the U.S. Army's Fort Monmouth lab.

Wilhelm Carl Heraeus (German, 1827–1904), who came from a generations-long family pharmacy, developed a high-temperature smelting process to produce pure platinum in 1856. To make use of that process, he founded and managed the Heraeus metallurgy company in Hanau. The company was subsequently run, and its metallurgical processes improved, by this founder's son Wilhelm Heraeus (German, 1860–1948) and then grandson Wilhelm Heinrich Heraeus (German, 1900–1985), both of whom were Ph.D. scientists.[17]

Albrecht Herzog (German, 19??–19??) worked on metallic materials and structures in Germany during World War II and at Wright Field, Ohio, after the war.

Albert Kochendörfer (German, 19??–19??) and Werner Köster (German, 1896–1989) conducted metallurgy research at Stuttgart during World War II. After the war, they either worked for or were sought by the U.S. Army's Fort Monmouth lab.

Heinrich Anton Karl Kopp (German, 19??–19??) was another expert on the cold processing of steel in Germany during World War II. After the war, he continued his work at the Aberdeen Proving Ground in Maryland, along with Hans Fischer and Ludwig Schuster.

?? Kornetzke (German, 19??–19??) conducted metallurgy research at Heidenheim during World War II. After the war, he either worked for or was sought by the U.S. Army's Fort Monmouth lab.

A. Krisch (German, 19??–19??) developed new processes for manufacturing and fabricating steel stock and components during World War II. He appears to have worked for the United States after the war.

William Kroll (1889–1973) was born in Luxembourg but was educated and worked in Germany. Like Anderko, Adenstedt, and Hansen, he developed titanium and other advanced metal alloys in Germany during World War II and in the United States after the war.

Friedrich Krupp (German states, 1787–1826) founded the Krupp steel company and developed new casting techniques. Alfred Krupp (German, 1812–1887) inherited and expanded the Krupp steel company. He and others at the company developed greatly improved methods of fabricating steel components ranging from train wheels to cannon barrels.

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[17] https://www.heraeus.com/en/group/about_heraeus/corporate_history/corporate_history.html

Richard Küch (German, 1860–1915) was the head scientist at Heraeus in the years around 1900. Küch developed alloys and processes for producing them, as well as a high-temperature process to produce quartz of exceptionally high purity and quality.

Ernest Kugel (German, 19??–19??) was an expert on aircraft metallurgy in Germany during World War II, and continued his work at Wright Field, Ohio, after the war.

Reinhard Mannesmann (German, 1856–1922) inherited and expanded the Reinhard Mannesmann steel company along with his brothers. He developed a number of new methods of fabricating steel stock and steel components.

Günther Möhling (German, 19??–19??) obtained his Ph.D. in Germany in 1928 with a thesis "Über Optisch Aktive Arsenverbindungen" ("On Optically Active Arsenic Compounds"). He appears to have moved to the United States in the 1930s. He ended up in charge of metallurgical development at the Allegheny Ludlum Steel Corporation, where he introduced German metallurgical methods and alloys and began receiving U.S. government funding.[18] He also appears to have reaped a windfall of additional metallurgical information from Germany when World War II ended. At Allegheny Ludlum, Möhling copied Tinidur (renamed A-286), Cromadur (renamed AF-71), and other German alloys, as well as German metallurgical methods such as vacuum melting. Metallurgist Art Kracke briefly alluded to the early history of these technologies in Germany and their transfer to the United States during and after World War II [Kracke 2010]:

> Breakthrough Events in Superalloy Processing
>
> - 1905: W. von Bolton consumable electrode arc melted tantalum in a cooled copper crucible under a low pressure of argon. [See p. 976.]
> - 1917: W. Rohn first melted nickel alloy in a vacuum resistance heated furnace.
> - 1923: Heraeus Vacuumschmelze A.G. founded to operate vacuum furnaces.
> - 1926: Two VIM furnaces in operation melting 80 Ni 20 Cr and 65 Ni 15Fe 20 Cr for thermocouples and denture alloys.
> - 1950: Dr. Möhling melts first large heat, ten tons, vacuum induction melt of aluminum and titanium containing strengthened superalloy at Allegheny Ludlum Steel laboratory in Watervliet, NY.
> - 1952: Special Metals Co., New Hartford, N.Y. produces the first production heat of Waspaloy in a 6-lb furnace for Pratt & Whitney J48 turbine engine blades
> - 1953: First production vacuum arc remelting of superalloys by Allegheny Ludlum Steel in their Watervliet, NY laboratory.
>
> [...] Vacuum melting was first performed in 1916 in Hanau, Germany by Dr. Wilhelm Rohn and W. C. Heraeus in a vacuum induction furnace of their design. Their work,

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[18] *Automotive News*, 30 April 1945, p. 57, cols. 3–4. https://chroniclingamerica.loc.gov/lccn/77618337/1945-04-30/ed-1/seq-57/

> focused on steels, led to the development of clean steels that enabled aircraft engine technology including the development of turbine engines for military aircraft used in WWII.
>
> In 1945 a small vacuum furnace was built at NACA to melt high temperature alloy samples for evaluation. [...]
>
> The following comment made by Rudolph Thielemann in 1967 in a presentation to the European Investment Casters Federation is a testimonial to the role vacuum melting played in the success of superalloys and their role in gas turbines. “Since the early work on the exhaust gas driven turbosuperchargers, a great deal of progress has been made in developing high temperature alloys for critical gas turbine applications. In this effort, the development of new processes and techniques for melting, consolidating and casting the alloys has been very important. The introduction of the (vacuum) melting furnace has furthered the metallurgical progress in the alloy development more than any other single factor.”

Hermann Nehlsen (German, 19??–19??) was an expert on aircraft metallurgy in Germany during World War II, and continued his work at Wright Field, Ohio, after the war.

Wilhelm Rohn (German, 1887–1943) was the head scientist at Heraeus after Richard Küch. In 1913 he invented vacuum melting, a technique that enabled the production of advanced, high-temperature alloys. Rohn and Heraeus developed and used the technique for commercial applications from then through World War II.[19]

Franz Sauerwald (German, 1894–1979) developed very lightweight magnesium alloys for aerospace vehicles in Breslau during World War II.

Ludwig Schuster (German, 19??–19??) was another expert on the cold processing of steel in Germany during World War II. After the war, he continued his work at the Aberdeen Proving Ground in Maryland, along with Hans Fischer and Heinrich Kopp.

Hugo Stinnes (German, 1870–1924) ran the Stinnes steel company, which developed new metal alloys and custom metal components for new technological applications.

Fritz Thyssen (German, 1873–1951) was a metallurgist who inherited, expanded, and ran the Thyssen steel company, which developed a variety of new alloys in the early twentieth century.

Carl Auer von Welsbach (Austrian, 1858–1929, pp. 441 and 975) discovered praseodymium (1885), neodymium (1885), ytterbium (1905), and lutetium (1905). He also invented the gaslight mantle (1885), osmium wire (1890), metal filament incandescent lamps (1898), and the flint metal lighter (1903). In order to commercialize his discoveries and inventions, he founded the companies of Auergesellschaft, Treibacher Industrie, and Osram.

In 1906, Alfred Wilm (German, 1869–1937) invented the Duralumin aluminum alloy (aluminum with small amounts of copper, magnesium, manganese), which has been widely used in the aerospace industry ever since. He also discovered age hardening for aluminum alloys and other metals in 1901.

---

[19] https://vacuumschmelze.de/unternehmen/firmenhistorie

Friedrich Wöhler (German, 1800–1882, p. 438) discovered and purified aluminum.

Despite the wartime shortages, by 1945 metallurgy was so advanced in the German-speaking world that Allied countries seized large quantities of information and scientists, and even complete factories, to improve the state of metallurgy in their own countries (Figs. 3.187–3.188).

For example, in September 1945, R. P. Linstead and T. J. Betts, the British and American chairs of the Combined Intelligence Objectives Subcommittee (CIOS), listed a number of important German innovations in metallurgy [AFHRA A5186 electronic version pp. 904–1026, Ch. 4, pp. 52–53]:

> In the field of ferrous and nonferrous metallurgy the following discoveries are worth recording:
>
> 1. A new flux for welding magnesium.
>
> 2. A hard magnesium coating obtained by anodizing aluminum oxide which had many industrial and armament applications.
>
> 3. Refinements in the process of continuous casting. This casting was done into a tank of water rather than an open pit. The method employed a small mould which resulted in many economies of production.
>
> 4. The use of chemicals in the grain refining process in heating magnesium for casting. This process, used in the production of high quality magnesium, permitted achievement of equal quality by using a temperature 100^oC below that employed in the conventional process.
>
> 5. The electric smelting furnace developed by Siemens and Halske. This resulted in the production of pig iron with little coke, a process with distinct advantages when coke supplies are limited and cheap hydro-electric power abundant. A further advantage is the reduction of the sulphur content in pig iron.
>
> 6. Improved hard cemented carbide for use in cutting tools.
>
> 7. German development and use of drawn steel cartridge cases. Steel cartridge cases were designed for a wide range of calibers ranging from small arms to large artillery pieces. Steel cartridge cases have the obvious advantages of saving critical materials.

As a more focused example, BIOS 925, *Tungsten Carbide Research in Germany*, p. 3, discussed German innovations in metal hardening that Allied countries wanted to copy (see also BIOS 1076):

> This report contains the results of a detailed interrogation of Dr. [Walter] Dawihl who was head of Osram's Research Department. By agreement with Krupps this Laboratory carried out all hard metal research on behalf of the Widia organisation and as such was the most important Hard Metal Research Laboratory in Germany.
>
> The report gives a general survey of the Research Programme of the Laboratory during the war years and traverses the latest theories on the fundamental metallurgy of hard metal as developed by Dr. Dawihl.

> It describes his experiments to relate the practical performance of hard metal with metallurgy and discusses the effect of crystal formation and shape on the physical properties.
>
> A technique of coating steel with a thin hard metal skin is described and the composition of the metal is given.
>
> Descriptions of the processes of making boron carbide and titanium boride are given and a very brief resume of the work done on sintered iron and steel.
>
> Part III deals with the practical application of Laboratory Research to commercial practice and gives brief descriptions of methods of manufacture, specifications and a detailed costing of each operation.
>
> Appendix I is probably the most valuable portion of the report as it contains a list of Reports issued by the laboratory, copies of which are in our hands. They are listed by H.E.C. numbers, title and number of pages and diagrams.
>
> Appendix II is a description of making tungsten carbide in an electric arc furnace of novel design by D.E.W., Krefeld.
>
> Appendix III is a drawing of a continuous rotary tube furnace for carburising.

For further examples of how advanced German and Austrian metallurgy technologies were transferred to Allied countries after the war, see pp. 4128– 4190. See also the large number of metallurgy-related BIOS ER, BIOS, BIOS Misc., BIOS Overall, CIOS ER, CIOS, FIAT, *FIAT Review*, JIOA, NavTecMisEu LR, and NavTecMisEu reports in the Bibliography.

American metallurgists Charles R. Simcoe and Frances Richards provided a glimpse of how German-speaking scientists and methods were utilized to create advanced metal alloys in the postwar United States [Simcoe and Richards 2018 pp. 145, 147–148]:

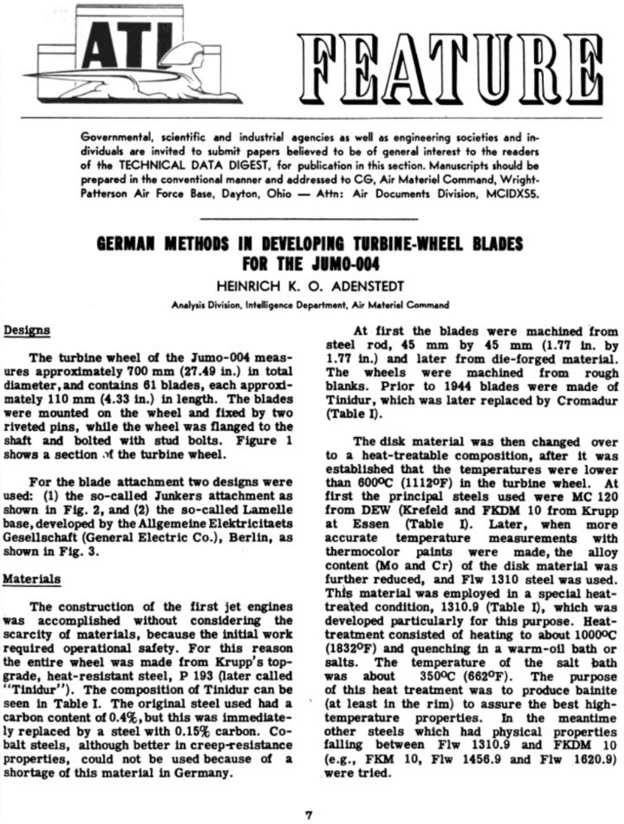
> Titanium was on its way to becoming the aerospace metal that its promoters had hoped it would be. Then an earthquake shook both the aerospace industry and titanium. The Secretary of Defense, Charles Wilson, formerly of General Motors Corporation, announced a decision to base the defense of the country on missiles rather than on manned aircraft. The accompanying reductions and cancellations of contracts rocked the industry. [...] The reduction in aircraft and engine production caused a near-total collapse of the titanium market. This most promising of metals for the postwar era, which had received an estimated $200 million in government support, was in serious danger of extinction by the very DOD that had brought it into being. [...]
>
> The changes in the titanium industry had changed the career paths of many of the individuals selected as founders. William Kroll returned to Europe to enjoy his retirement years in Brussels. Max Hansen left ARF to accept a high-level post in the metals industry in Germany. In 1958, Hansen and Kurt Anderko, another German who worked with Hansen at ARF and who had returned to Germany with him, published a monumental second edition of the "Constitution of Binary Alloys." [...]

> By the late 1950s and early 1960s, the major research and development support for titanium by the government had ceased. The founders, as well as the younger researchers, were forced to find other areas of research or move on to other employment. [...]
>
> One significant development in the 1960s was the building of the SR-71 Blackbird military reconnaissance plane with a speed capability of Mach 3. The SR-71 was an all-titanium aircraft manufactured with Ti-6Al-4V and a new alloy, Ti-13V-11Cr-3Al. Another early 1960s attraction was the interest in a supersonic transport plane. It would have been an all-titanium aircraft that was planned to compete with the European-made Concorde. It was planned to fly at nearly Mach 3 and would have used large amounts of titanium per plane for a planned 200-plane fleet. The program was cancelled by Congress in 1971.

Thus German-speaking scientists were apparently responsible for the heat-resistant, strong, lightweight titanium alloys that made the SR-71 Blackbird spy plane and the XB-70 Valkyrie bomber (pp. 1762, 1766–1767) possible, and that would have made possible a fleet of Mach-3 passenger aircraft. Unfortunately the United States lost interest in such technologies, and those German-speaking scientists retired or found employment in other areas.

Much more archival research should be conducted to clarify the direct (via invention and development) and indirect (via technology transfer) contributions of German-speaking scientists to the methods and applications of metallurgy.

Heinrich Adenstedt (1910–1991)



ATI FEATURE

Governmental, scientific and industrial agencies as well as engineering societies and individuals are invited to submit papers believed to be of general interest to the readers of the TECHNICAL DATA DIGEST, for publication in this section. Manuscripts should be prepared in the conventional manner and addressed to CG, Air Materiel Command, Wright-Patterson Air Force Base, Dayton, Ohio — Attn: Air Documents Division, MCIDXS5.

GERMAN METHODS IN DEVELOPING TURBINE-WHEEL BLADES FOR THE JUMO-004

HEINRICH K. O. ADENSTEDT

Analysis Division, Intelligence Department, Air Materiel Command

Designs

The turbine wheel of the Jumo-004 measures approximately 700 mm (27.49 in.) in total diameter, and contains 61 blades, each approximately 110 mm (4.33 in.) in length. The blades were mounted on the wheel and fixed by two riveted pins, while the wheel was flanged to the shaft and bolted with stud bolts. Figure 1 shows a section of the turbine wheel.

For the blade attachment two designs were used: (1) the so-called Junkers attachment as shown in Fig. 2, and (2) the so-called Lamelle base, developed by the Allgemeine Elektricitaets Gesellschaft (General Electric Co.), Berlin, as shown in Fig. 3.

Materials

The construction of the first jet engines was accomplished without considering the scarcity of materials, because the initial work required operational safety. For this reason the entire wheel was made from Krupp's top-grade, heat-resistant steel, P 193 (later called "Tinidur"). The composition of Tinidur can be seen in Table I. The original steel used had a carbon content of 0.4%, but this was immediately replaced by a steel with 0.15% carbon. Cobalt steels, although better in creep-resistance properties, could not be used because of a shortage of this material in Germany.

At first the blades were machined from steel rod, 45 mm by 45 mm (1.77 in. by 1.77 in.) and later from die-forged material. The wheels were machined from rough blanks. Prior to 1944 blades were made of Tinidur, which was later replaced by Cromadur (Table I).

The disk material was then changed over to a heat-treatable composition, after it was established that the temperatures were lower than 600°C (1112°F) in the turbine wheel. At first the principal steels used were MC 120 from DEW (Krefeld and FKDM 10 from Krupp at Essen (Table I). Later, when more accurate temperature measurements with thermocolor paints were made, the alloy content (Mo and Cr) of the disk material was further reduced, and Flw 1310 steel was used. This material was employed in a special heat-treated condition, 1310.9 (Table I), which was developed particularly for this purpose. Heat-treatment consisted of heating to about 1000°C (1832°F) and quenching in a warm-oil bath or salts. The temperature of the salt bath was about 350°C (662°F). The purpose of this heat treatment was to produce bainite (at least in the rim) to assure the best high-temperature properties. In the meantime other steels which had physical properties falling between Flw 1310.9 and FKDM 10 (e.g., FKM 10, Flw 1456.9 and Flw 1620.9) were tried.

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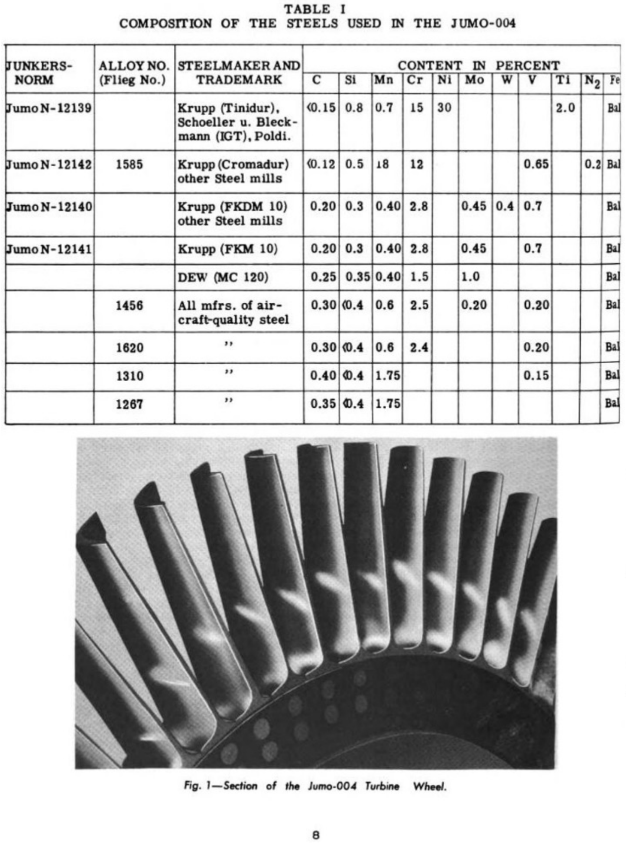

TABLE I
COMPOSITION OF THE STEELS USED IN THE JUMO-004

JUNKERS-NORM	ALLOY NO. (Flieg No.)	STEELMAKER AND TRADEMARK	CONTENT IN PERCENT										
			C	Si	Mn	Cr	Ni	Mo	W	V	Ti	N_2	Fe
Jumo N-12139		Krupp (Tinidur), Schoeller u. Bleckmann (IGT), Poldi.	<0.15	0.8	0.7	15	30				2.0		Bal
Jumo N-12142	1585	Krupp (Cromadur) other Steel mills	<0.12	0.5	18	12				0.65		0.2	Bal
Jumo N-12140		Krupp (FKDM 10) other Steel mills	0.20	0.3	0.40	2.8		0.45	0.4	0.7			Bal
Jumo N-12141		Krupp (FKM 10)	0.20	0.3	0.40	2.8		0.45		0.7			Bal
		DEW (MC 120)	0.25	0.35	0.40	1.5		1.0					Bal
	1456	All mfrs. of aircraft-quality steel	0.30	<0.4	0.6	2.5		0.20		0.20			Bal
	1620	”	0.30	<0.4	0.6	2.4				0.20			Bal
	1310	”	0.40	<0.4	1.75					0.15			Bal
	1267	”	0.35	<0.4	1.75								Bal

Fig. 1—Section of the Jumo-004 Turbine Wheel.

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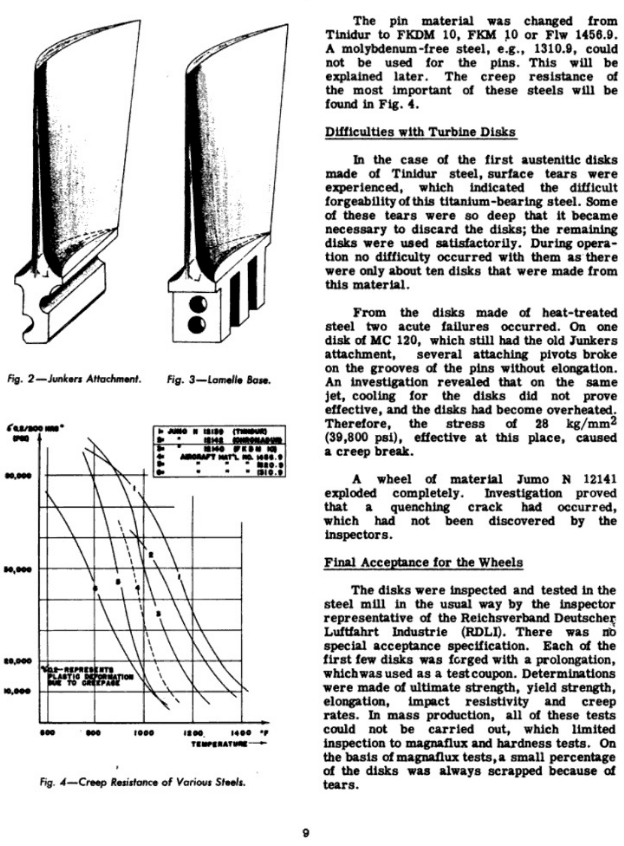

Fig. 2—Junkers Attachment. Fig. 3—Lamelle Base.

Fig. 4—Creep Resistance of Various Steels.

The pin material was changed from Tinidur to FKDM 10, FKM 10 or Flw 1456.9. A molybdenum-free steel, e.g., 1310.9, could not be used for the pins. This will be explained later. The creep resistance of the most important of these steels will be found in Fig. 4.

Difficulties with Turbine Disks

In the case of the first austenitic disks made of Tinidur steel, surface tears were experienced, which indicated the difficult forgeability of this titanium-bearing steel. Some of these tears were so deep that it became necessary to discard the disks; the remaining disks were used satisfactorily. During operation no difficulty occurred with them as there were only about ten disks that were made from this material.

From the disks made of heat-treated steel two acute failures occurred. On one disk of MC 120, which still had the old Junkers attachment, several attaching pivots broke on the grooves of the pins without elongation. An investigation revealed that on the same jet, cooling for the disks did not prove effective, and the disks had become overheated. Therefore, the stress of 28 kg/mm^2 (39,800 psi), effective at this place, caused a creep break.

A wheel of material Jumo N 12141 exploded completely. Investigation proved that a quenching crack had occurred, which had not been discovered by the inspectors.

Final Acceptance for the Wheels

The disks were inspected and tested in the steel mill in the usual way by the inspector representative of the Reichsverband Deutscher Luftfahrt Industrie (RDLI). There was no special acceptance specification. Each of the first few disks was forged with a prolongation, which was used as a test coupon. Determinations were made of ultimate strength, yield strength, elongation, impact resistivity and creep rates. In mass production, all of these tests could not be carried out, which limited inspection to magnaflux and hardness tests. On the basis of magnaflux tests, a small percentage of the disks was always scrapped because of tears.

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Figure 3.178: Heinrich Adenstedt developed and used advanced metal alloys in Germany during the war and in the United States after the war [Adenstedt 1948]. Throughout his career, he worked very closely with jet/helicopter/tank engine designer Anselm Franz (pp. 1391, 1751–1752).

Temperature Measurements of the Disks

At first, temperature measurements were made with thermocouples. In using these measurements, the wheel was made stationary and the blades were heated to the correct temperature by means of a ring burner, while the other testing apparatus cooled the disk to a ratio as if it were in operation. These tests could give only approximate results, and were later replaced by thermocolor paints which determined the temperature of the wheel during operation. This test was made as follows: Several small strips along different radius vectors of the disk were sand blasted and then sprayed with aluminum by the Schoop procedure. Onto the white rough aluminum surface a suitable thermocolor paint was applied by brush. On this prepared surface a strip of asbestos and a sheet-metal strip of 18-8 steel were screwed tightly against the disk. This arrangement, which proved satisfactory, can be seen in Fig. 5. The asbestos covering prevented the thermocolor paint from being affected by external heat conditions caused by surrounding air. This insured accurate wheel temperature determinations by the thermocolor paints. On the white aluminum surface the change of color was easily visible and the few isolated strips affected very little the cooling of the disk through the surface. (Only 10% of the disk surface was covered by the strips). These investigations proved an operational temperature of 400°C (752°F) at the lower end of the blade base and 220°C (428°F) in the center of the disk. These values gave the basis for the material change to Flw 1310.9. Later the temperature measurements were repeated on hollow-blade wheels in a somewhat different manner. The thermocolor paints were placed inside of hollow drilled screws of 18-8 steel; the hole was then closed with a piece of sheet metal. The screw prepared in this way was driven into the disk at the desired place for temperature measurement. After the test the screw was opened, the paint was sifted on paper and spread out with a knife; the color change was easily visible.

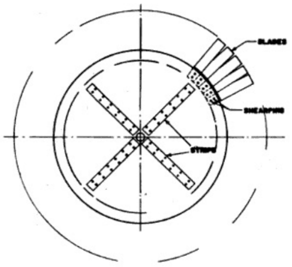


Fig. 5—Location of Strips for Temperature Measurement on the Wheel.

Difficulties with Shear Pins

During mass production, no pin failures were caused by shear. Two test wheels were constructed with pins of steel Flw 1267.9 (Table I). In the case of one wheel, after 92-hr operation the pins sheared off, and one blade flew off. Because of this failure, the pins were then made of a molybdenum steel (Flw 1456.9, Jumo N 12140 or 12141). Flw 1310.9, which has a higher creep resistance than 1267.9 by about 30°C, was not used for the pins, because the 30°C advantage was considered insufficient. Special final acceptance was not prescribed for the pins.

Difficulties with the Blades

The observed blade breaks can be placed into two categories: (1) fatigue breaks and (2) creep breaks. These are discussed specifically below.

1. **Fatigue Breaks**

This type of break was observed almost exclusively at the beginning of turbine-blade development, with fractures occurring at different points in the lower part of the blades. Using the old Junkers attachment (Fig. 2), the weak place proved to be the upper shear-pin hole. Fatigue fractures were experienced in a number of blades at this particular place. This condition was improved by employing a different method of fastening. The diameter of the upper pin was decreased, and the outer radius (R) on the wheel base and on the pivots was decreased as shown in Fig. 2. Also on the lamelle base (Fig. 3) several fatigue breaks were recognized - in the lamelles themselves and in the base plate. This necessitated a heavier base plate. The fatigue breaks in the blades themselves occurred mostly at the lower part of the blade length.

The temperature and velocity distribution behind the nozzle diaphragm were found to be not uniform, which led to excitations of the blades, causing the fatigue breaks. At full power there are 145 rps x 6 (combustion chambers) = 870 stress cps. This figure corresponded to nearly fundamental natural frequency of the blades during operation. When cold, the latter was 900 - 950 cps, but this value is increased during the operation by centrifugal force, and decreased by modification of the material (change of modulus of elasticity). In all, a decrease of 8% was calculated.

The breaks appeared partially after operation of 50 hours or more, which corresponds to over 10^8 c of load, and therefore means a very long working time. After the lapse of such a long time, no breaks should be expected if we consider a Woehler curve. The explanation is the very sharp natural frequency of the blades, effected by a small degree of damping. Therefore a small rpm fluctuation gives a great reduction of the stresses in the critical blades. All these cycles with reduced stresses do not count in our consideration of the Woehler curve.

As a remedy, the natural frequency was increased about 100 cps by more acutely conical forming of the blades, and by a 1-mm reduction of the length. Further, a 100% frequency test was prescribed, whereby the natural frequency was required to be over 1000 cps. Blades with too low natural frequencies were saved by reworking (material machining of the inner side of the blade in the upper quarter of the length).

The frequency test of the finished wheel was carried out by an acoustical method. The 61 blades were agitated at the head end with a violin bow, and the arising tone was compared with a normal known tone. The normal tone was created by a set of tuning forks consisting of prongs with a natural frequency (with an interval of 25) of between 950 and 1150 cps. The forks were agitated by means of an eccentric, and the tone was reproduced by means of a coil, an amplifier, and a loud speaker. All forks could be simultaneously agitated, and the desired tone could be heard by pressing the proper button. Figure 6 shows the arrangement schematically. In this way it was possible to test a wheel in a few minutes, and the natural frequencies of the different blades could be determined within limits of less than 25 cps.

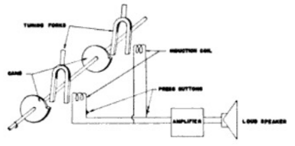


Fig. 6—Schematic Diagram of Frequency Generator.

After the increase of the blade frequencies and after the introduction of the preceding acceptance test, practically no fatigue breaks occurred.

2. **Creep Breaks**

Creep breaks occurred particularly in the upper part of the blades. These were mostly intergranular and without deformation. As such breaks practically marked the life limit of the wheel, great effort was made to avert them as long as possible. This was done in collaboration with the factory of Krupp, the AEG turbine factory, and the branches of the Junkers concern.

From the breaks which occurred and from the creep-rupture tests, it was concluded that Tinidur is not very ductile at elevated temperatures when subjected to creep conditions; that when creep progresses to about 1.5%, a brittle fracture will occur, and that the ultimate elongation caused by creep is further reduced by: (1) large grains, (2) notches (grinding marks, too sharp edges, etc.), (3) inclusions which cause notch effects (oxides, segregations, etc.), and (4) melting influences, which could not be explained in detail (gas content, melting procedure, etc.).

If these irregularities occur, premature failures are to be expected, especially if, by the tilting of the blade (caused by manufacturing inaccuracy) or by thermal shock, a stress raiser occurs locally. The stress raiser, caused by tilting of the blade, is dependent upon the direction of the inclination of the blade outwards of its gravity line. This stress increase can be very important. Numerical values can be given only when exact drawings of the blades are available. A thermal shock (caused by sudden heating or cooling of the blades during starting or stopping) may overstress the extreme edges of the blades. It was found that the number of cycles of starting and stopping is very important for the life of the blades. In particular, coarse-grain blades were very sensitive to thermal shock. In the Jumo-004 a more elastic type of controller system minimized excessive thermal shock.

Control of the Blades

The specifications prescribed for the control of the blades were:

1. Control of the Melt - The chemical composition had to be as prescribed in the standard Jumo N 12139; especially the titanium content had to be precise. Difficulties in the chemical-analysis procedure which existed at first in the titanium determination were removed. In the steel mill, the basic suitability of the melt was proved (RDLI Control, quality test, precipitated hardening).

2. Forging Procedure - The forging was inspected at each place in order to facilitate the procedure. Between the various steps of forging, macro-etchings were made. Rod sections with center segregation were rejected; half-finished rough forgings with surface tears were ground out or rejected. Figure 7 depicts in both views A and B two characteristic troubles of Tinidur. View A shows a surface crack caused by titanium oxide aggregation, and View B a preforged sample with opened head due to central segregations. The forging furnaces were temperature-controlled and the various forging dies were adapted in such a way that the end deformation was greater than 15%. By this procedure at 1080°C (1976°F) end forging temperature, good rough forgings with suitably small grains were obtained. The rough forgings were random tested for grain size by surface grinding the head of the blade (Krupp Company's system).

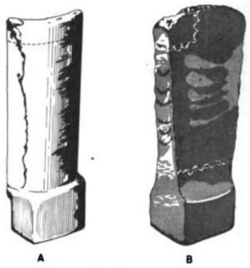


Fig. 7
A—Forging with a Surface Crack.
B—Preforged Sample with a Center Crack.

3. Testing the Finished Blades - The finished blades were all macro-etched before the end polishing, and then, by means of a magnifying glass, inspected by experienced workers for surface tears, large grains, segregations, and aggregation of titanium oxides. Acceptance specifications were determined by reference to photos and standard parts. By means of a special marking procedure which made it possible to recognize the particular steel mill, the melt number, and the forging manufacturer of the respective blade, it was possible to publish a monthly reject report from Dessau. This report was important for the steel mills and for the forges, because especially bad melts and bad forgings could immediately be traced. Ultimately 80 percent of the blades were found to be good.

4. Length Polishing - The surface of the blades was length ground and length polished in order to erase all transverse grinding marks.

5. Control of Tilting - After the blades were mounted, a special measuring procedure was provided for keeping the blades erect and for preventing tilting.

6. Frequency Control - Finally, the frequency test was made as described above.

7. Operating Life - The wheels were permitted to run 25 hours; then the blades were tested at random for hardness on the small phase, which is on the exhaust side of the blades. If the hardness of the entire length of the blade was higher than 200 Brinell, the blades were again length ground, and eventually notches were removed. The wheel was then operated for another 25 hours. The total time of operation was inscribed on the wheel by means of number stamps. It was the intention to continue this service to 100-hr total operation time, and then to replace the blades.

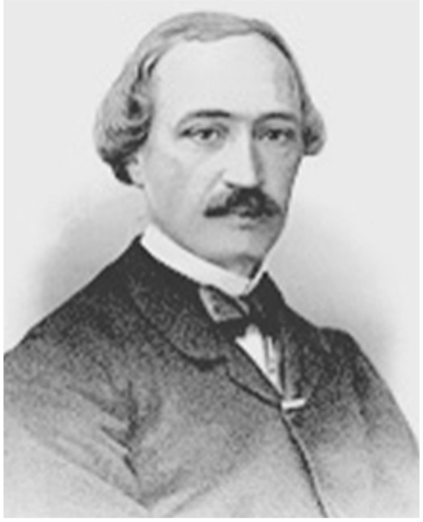
Up until the end of the war, only a few solid-blade wheels had reached this total operation time. Since 1944, the hollow blade has replaced the solid blade.

Figure 3.179: Heinrich Adenstedt developed and used advanced metal alloys in Germany during the war and in the United States after the war [Adenstedt 1948]. Throughout his career, he worked very closely with jet/helicopter/tank engine designer Anselm Franz (pp. 1391, 1751–1752).

Metallurgy

Kurt Anderko
(19??–19??)

Carl Josef Bayer
(1847–1904)



A. Beerwald
(19??–19??)

?? Berblinger
(19??–19??)

Carl Berg
(1851–1906)

Franz Bollenrath
(1898–1981)

Figure 3.180: Some creators who made important contributions to metallurgy included Kurt Anderko, Carl Josef Bayer, A. Beerwald, ?? Berblinger, Carl Berg, and Franz Bollenrath.

Metallurgy

August Borsig
(1804–1854)

Hermann Bottenhorn
(19??–19??)

?? Bruche
(19??–19??)

Otto Dahl
(19??–19??)

Walter Dawihl
(1904–19??)

Ulrich Dehlinger
(1901–1981)

Figure 3.181: Other creators who made important contributions to metallurgy included August Borsig, Hermann Bottenhorn, ?? Bruche, Otto Dahl, Walter Dawihl, and Ulrich Dehlinger.

Metallurgy

Bernard Dirksen
(19??–19??)

Hans Fischer
(19??–19??)

Richard Glocker
(19??–19??)

Max Hansen
(1901–1978)

F. Heimes
(19??–19??)

Wilhelm Carl Heraeus
(1827–1904)

Figure 3.182: Other creators who made important contributions to metallurgy included Bernard Dirksen, Hans Fischer, Richard Glocker, Max Hansen, F. Heimes, and Wilhelm Carl Heraeus.

Metallurgy

Wilhelm Heraeus (1860–1948)

Wilhelm Heinrich Heraeus (1900–1985)

Albrecht Herzog (19??–19??)

Albert Kochendörfer (19??–19??)

Heinrich Anton Karl Kopp (19??–19??)

?? Kornetzke (19??–19??)

Figure 3.183: Other creators who made important contributions to metallurgy included Wilhelm Heraeus, Wilhelm Heinrich Heraeus, Albrecht Herzog, Albert Kochendörfer, Heinrich Anton Karl Kopp, and ?? Kornetzke.

Metallurgy

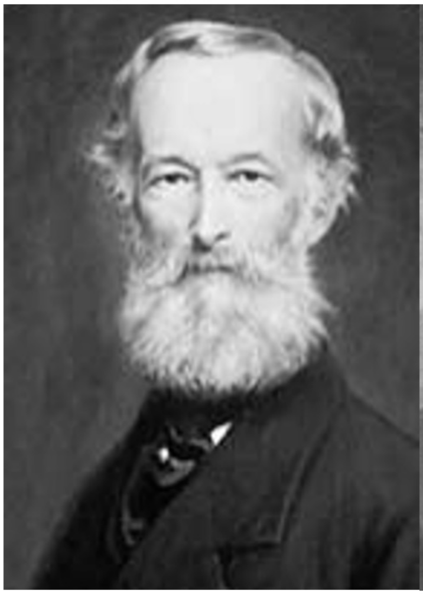
Werner Köster
(1896–1989)

A. Krisch
(19??–19??)

William Kroll
(1889–1973)

Friedrich Krupp
(1787–1826)

Alfred Krupp
(1812–1887)



Richard Küch
(1860–1915)

Figure 3.184: Other creators who made important contributions to metallurgy included Werner Köster, A. Krisch, William Kroll, Friedrich Krupp, Alfred Krupp, and Richard Küch.

Metallurgy

Ernest Kugel
(19??–19??)

Reinhard Mannesmann
(1856–1922)

Günther Möhling
(19??–19??)

Hermann Nehlsen
(19??–19??)

Wilhelm Rohn
(1887–1943)

Franz Sauerwald
(1894–1979)

Figure 3.185: Other creators who made important contributions to metallurgy included Ernest Kugel, Reinhard Mannesmann, Günther Möhling, Hermann Nehlsen, Wilhelm Rohn, and Franz Sauerwald.

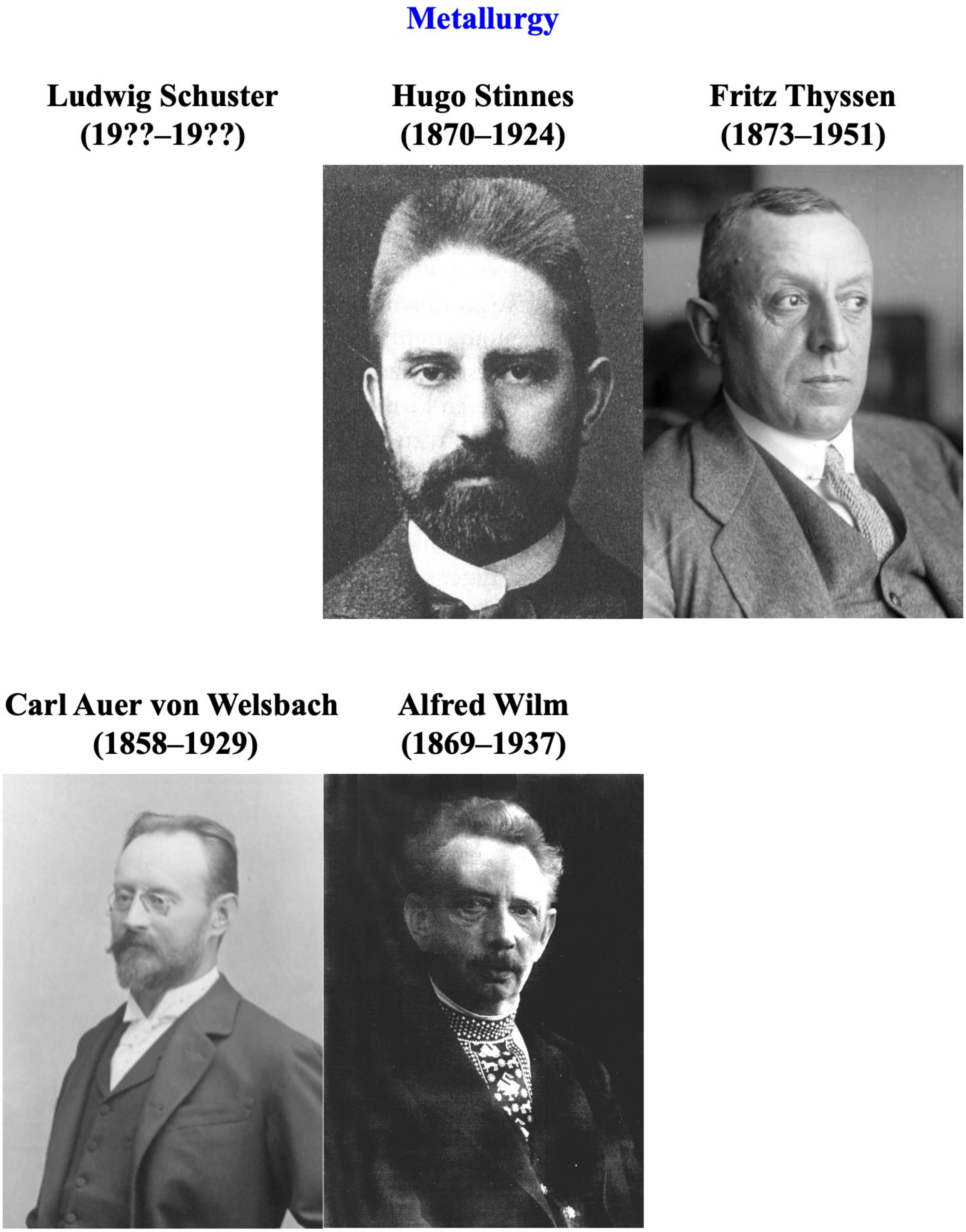
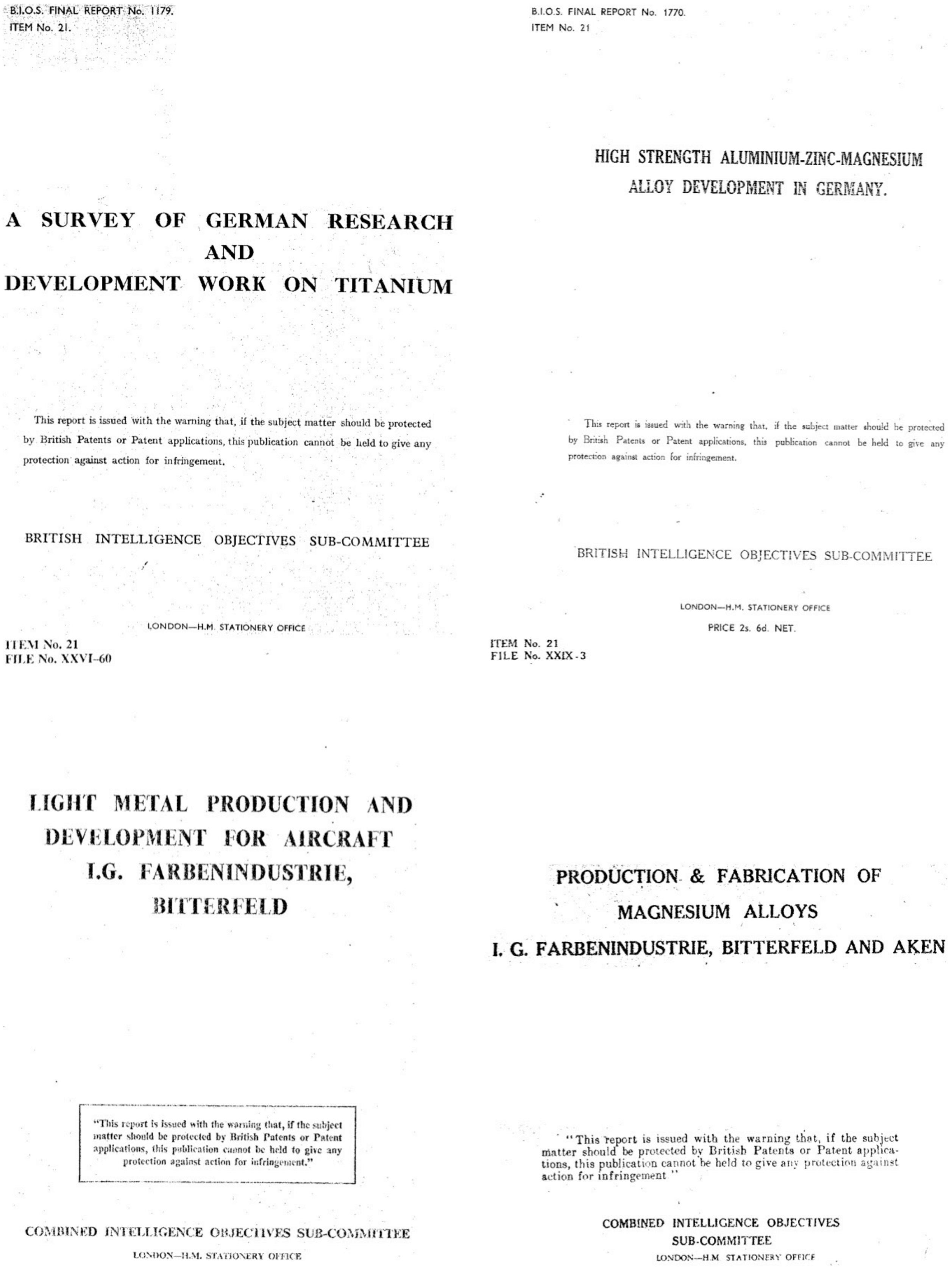


Figure 3.186: Other creators who made important contributions to metallurgy included Ludwig Schuster, Hugo Stinnes, Fritz Thyssen, Carl Auer von Welsbach, and Alfred Wilm.



B.I.O.S. FINAL REPORT No. 1179.
ITEM No. 21.

A SURVEY OF GERMAN RESEARCH
AND
DEVELOPMENT WORK ON TITANIUM

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LONDON—H.M. STATIONERY OFFICE

ITEM No. 21
FILE No. XXVI-60

B.I.O.S. FINAL REPORT No. 1770.
ITEM No. 21

HIGH STRENGTH ALUMINIUM-ZINC-MAGNESIUM
ALLOY DEVELOPMENT IN GERMANY.

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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE
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ITEM No. 21
FILE No. XXIX-3

LIGHT METAL PRODUCTION AND
DEVELOPMENT FOR AIRCRAFT
I.G. FARBENINDUSTRIE,
BITTERFELD

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COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

PRODUCTION & FABRICATION OF
MAGNESIUM ALLOYS
I. G. FARBENINDUSTRIE, BITTERFELD AND AKEN

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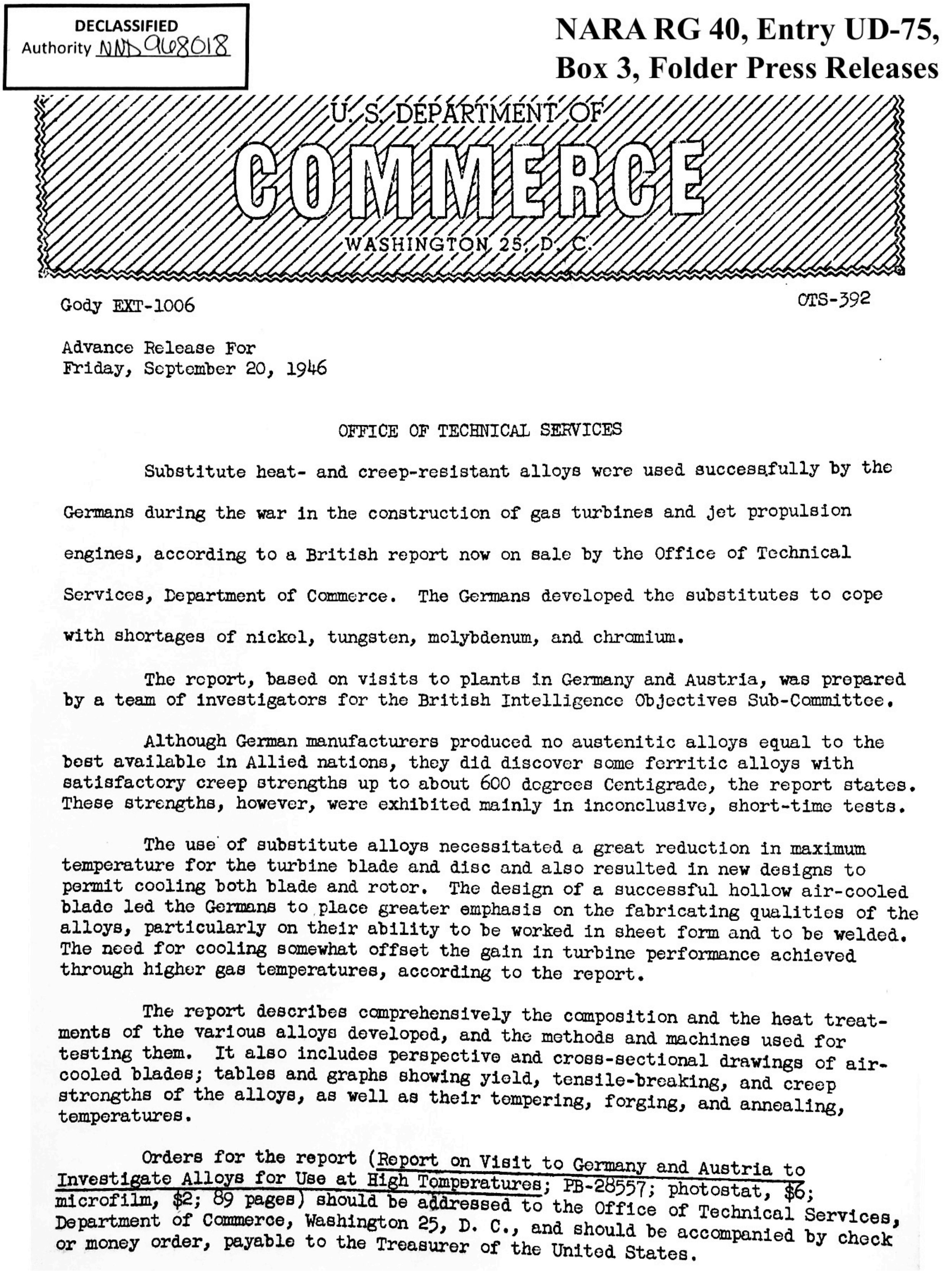
COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE
LONDON—H.M. STATIONERY OFFICE

Figure 3.187: Large amounts of information, materials, and scientists involved in work on advanced metallurgy were transferred to other countries after World War II [BIOS 1179; BIOS 1770; CIOS XXVI-60; CIOS XXIX-3].



DECLASSIFIED
Authority NND968018

NARA RG 40, Entry UD-75, Box 3, Folder Press Releases

U.S. DEPARTMENT OF
COMMERCE
WASHINGTON 25, D.C.

Gody EXT-1006

OTS-392

Advance Release For
Friday, September 20, 1946

OFFICE OF TECHNICAL SERVICES

Substitute heat- and creep-resistant alloys were used successfully by the Germans during the war in the construction of gas turbines and jet propulsion engines, according to a British report now on sale by the Office of Technical Services, Department of Commerce. The Germans developed the substitutes to cope with shortages of nickel, tungsten, molybdenum, and chromium.

The report, based on visits to plants in Germany and Austria, was prepared by a team of investigators for the British Intelligence Objectives Sub-Committee.

Although German manufacturers produced no austenitic alloys equal to the best available in Allied nations, they did discover some ferritic alloys with satisfactory creep strengths up to about 600 degrees Centigrade, the report states. These strengths, however, were exhibited mainly in inconclusive, short-time tests.

The use of substitute alloys necessitated a great reduction in maximum temperature for the turbine blade and disc and also resulted in new designs to permit cooling both blade and rotor. The design of a successful hollow air-cooled blade led the Germans to place greater emphasis on the fabricating qualities of the alloys, particularly on their ability to be worked in sheet form and to be welded. The need for cooling somewhat offset the gain in turbine performance achieved through higher gas temperatures, according to the report.

The report describes comprehensively the composition and the heat treatments of the various alloys developed, and the methods and machines used for testing them. It also includes perspective and cross-sectional drawings of air-cooled blades; tables and graphs showing yield, tensile-breaking, and creep strengths of the alloys, as well as their tempering, forging, and annealing, temperatures.

Orders for the report (Report on Visit to Germany and Austria to Investigate Alloys for Use at High Temperatures; PB-28557; photostat, $6; microfilm, $2; 89 pages) should be addressed to the Office of Technical Services, Department of Commerce, Washington 25, D. C., and should be accompanied by check or money order, payable to the Treasurer of the United States.

Figure 3.188: Large amounts of information, materials, and scientists involved in work on advanced metallurgy were transferred to other countries after World War II [NARA RG 40, Entry UD-75, Box 3, Folder Press Releases].

3.9 Other Creations in Chemistry

German-speaking scientists made many other important discoveries and inventions in chemistry. This section covers just a few examples, including:

3.9.1. Chromatography

3.9.2. Colloids

3.9.3. Synthetic lubricating oils

3.9.4. Synthetic detergents and paper recycling

3.9.5. Chemical treatments to make fabrics resistant to fire, water, stains, and wrinkling

3.9.6. Firefighting chemicals

3.9.7. "Superglue"

3.9.1 Chromatography

Chromatography is a technique for separating molecules of different sizes that are initially mixed together, based on the fact that they will diffuse at different rates through wet paper, capillary tubes, or other solid, liquid, or gaseous materials. German-speaking scientists developed the general approach of chromatography as well as most of its specific implementations [Ettre 2001; Goppelsröder 1861, 1901; Runge 1850; Schönbein 1861].

Friedlieb Ferdinand Runge (German, 1795–1867) developed chemical spot tests on filter paper in the 1840s and first published his results in 1850, as shown in Fig. 3.189 [Runge 1850]. Runge's tests were essentially two-dimensional chromatography for separating a pool of molecules placed in the central spot into concentric rings of different types of molecules. (In 1820, Runge was also the first scientist to extract and identify caffeine.)

By exploring and harnessing that initial technique, Christian Schönbein (German states, 1799–1868) and his student Friedrich Goppelsröder (Swiss, 1837–1919) demonstrated one-dimensional chromatography methods both in filter paper and in capillary tubes in 1861 [Schönbein 1861; Goppelsröder 1861]. See Fig. 3.190.

Goppelsröder continued working to improve and to apply capillary-based chromatography for several decades, including using it to separate and analyze the colored pigments from plant leaves [Goppelsröder 1901]. See Figs. 3.191–3.193.

Raphael Eduard Liesegang (German, 1869–1947, Fig. 3.194) also developed and used improved methods of capillary and paper chromatography [Ettre 2001].

Building on the earlier work of Goppelsröder with the chromatography of plant pigments, Richard Willstätter (German, 1872–1942) developed improved methods for chromatography and used those to identify in detail the molecular structures of different types of chlorophyll and other plant pigment molecules (Fig. 3.194). For that work, he won the Nobel Prize in Chemistry in 1915 (p. 411).

Gustav Hertz (German, 1887–1975) invented gaseous diffusion enrichment and gas chromatography; he filed detailed patent applications on his methods in 1923 (Fig. 3.195). He continued to work on gas chromatography (as well as other projects) in Germany until 1945, and in the Soviet Union during the period 1945–1955. It seems likely that his work for those two countries involved using gaseous diffusion methods to separate uranium isotopes for nuclear weapons programs, although currently very little documentation from that work is publicly available.

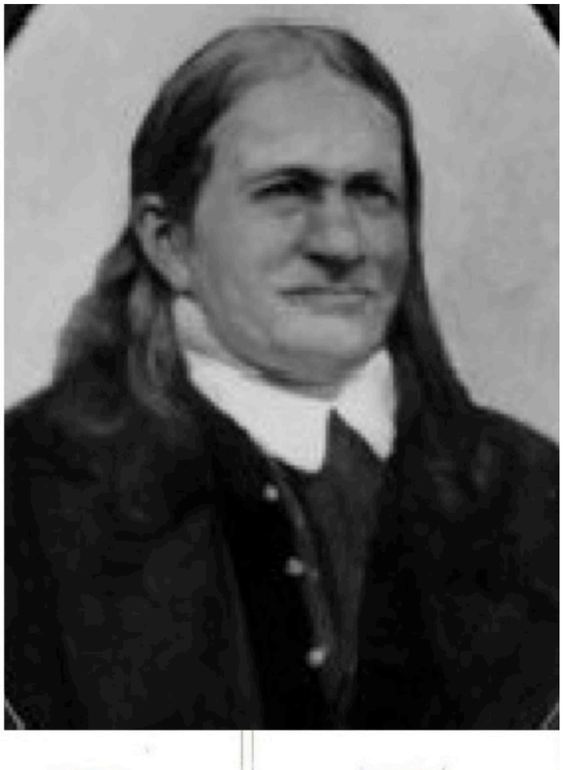
Inspired by the pioneering work by Hertz, Erika Cremer (German, 1900–1996) began developing improved methods of gaseous diffusion and gas chromatography in the late 1930s and continued throughout World War II (Fig. 3.195). As with Hertz, it seems likely that her work involved using gaseous diffusion methods to separate uranium isotopes for the German nuclear program, though little documentation is currently available. Cremer continued to work on gas chromatography after the war, and is best known for her postwar demonstrations and publications on gas chromatography, including those with her student Fritz Prior (Austrian, 1921–1996) [Bobleter 1997].

See also pp. 3512–3674 for other work related to gaseous separation and gas chromatography.

Two-dimensional paper chromatography

Friedlieb Ferdinand Runge (1795–1867)

Chemical spot tests on filter paper (1850)



Zur Farben-Chemie.

MUSTERBILDER

für

Freunde des Schönen

und zum Gebrauch

für

Zeichner, Maler, Verzierer und Zeugdrucker.

1ste LIEFERUNG.

Dargeſtellt

durch chemiſche Wechſelwirkung

von

Dr F. F. RUNGE

Profeſſor an der Hochſchule zu Breslau.

Berlin 1850.

Verlag von E. S. Mittler & Sohn.

[Zimmerstraſse No 84. 85.]

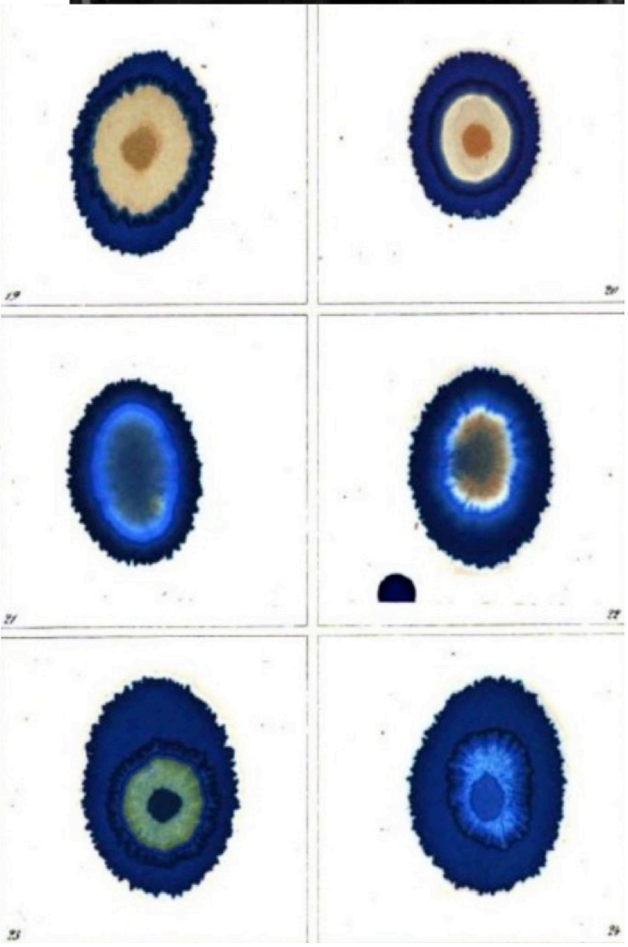
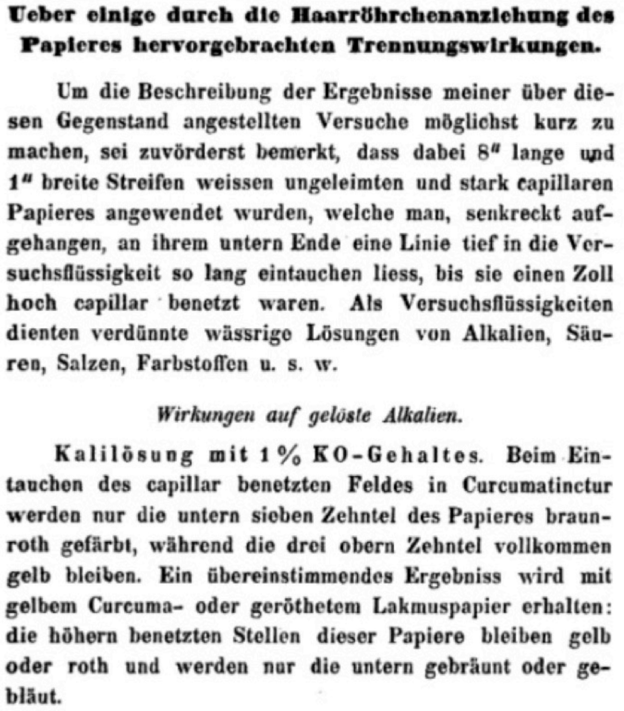


Figure 3.189: Friedlieb Ferdinand Runge developed chemical spot tests or two-dimensional chromatography on filter paper in 1850 [Runge 1850].

Chromatography in filter paper and in capillary tubes (1861)

Christian Friedrich Schönbein (1799–1868)



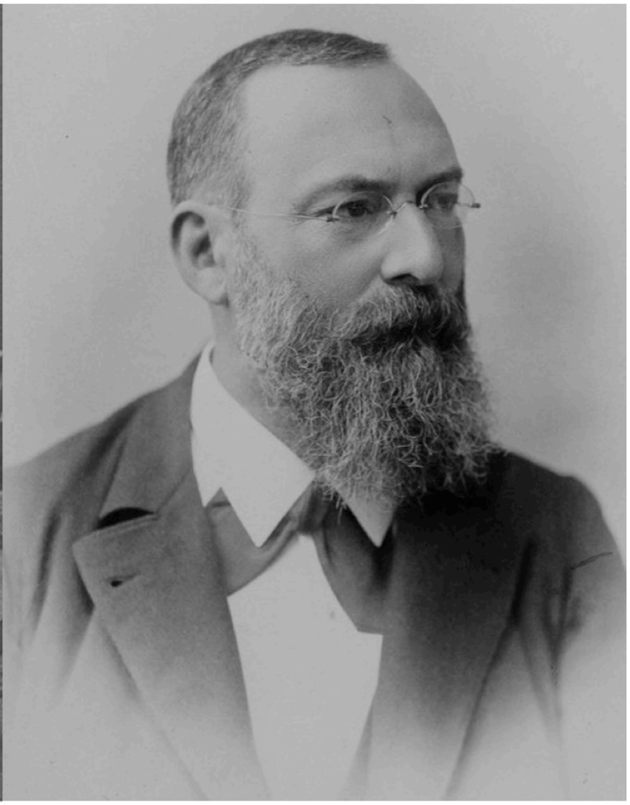
Ueber einige durch die Haarröhrchenanziehung des Papieres hervorgebrachten Trennungswirkungen.

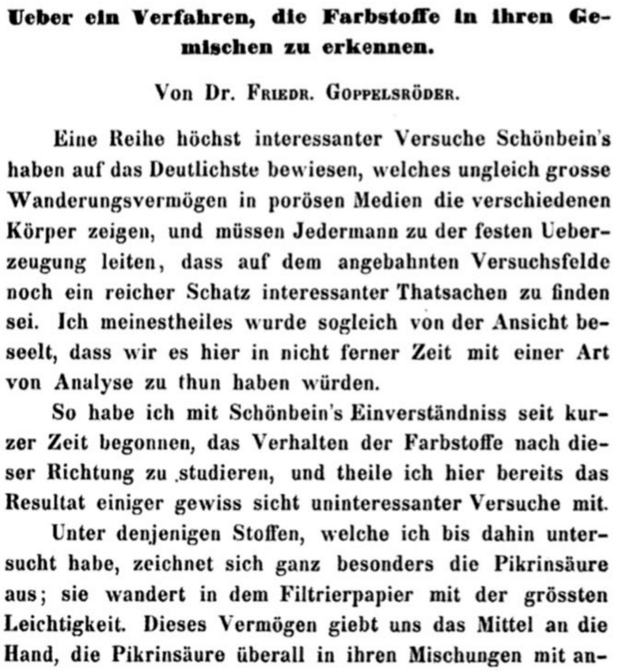
Um die Beschreibung der Ergebnisse meiner über diesen Gegenstand angestellten Versuche möglichst kurz zu machen, sei zuvörderst bemerkt, dass dabei 8" lange und 1" breite Streifen weissen ungeleimten und stark capillaren Papieres angewendet wurden, welche man, senkrecht aufgehangen, an ihrem untern Ende eine Linie tief in die Versuchsflüssigkeit so lang eintauchen liess, bis sie einen Zoll hoch capillar benetzt waren. Als Versuchsflüssigkeiten dienten verdünnte wässrige Lösungen von Alkalien, Säuren, Salzen, Farbstoffen u. s. w.

Wirkungen auf gelöste Alkalien.

Kalilösung mit 1 % KO-Gehaltes. Beim Eintauchen des capillar benetzten Feldes in Curcumatinctur werden nur die untern sieben Zehntel des Papieres braunroth gefärbt, während die drei obern Zehntel vollkommen gelb bleiben. Ein übereinstimmendes Ergebniss wird mit gelbem Curcuma- oder geröthetem Lakmuspapier erhalten: die höhern benetzten Stellen dieser Papiere bleiben gelb oder roth und werden nur die untern gebräunt oder gebläut.

Friedrich Goppelsröder (1837–1919)





Ueber ein Verfahren, die Farbstoffe in ihren Gemischen zu erkennen.

Von Dr. Friedr. Goppelsröder.

Eine Reihe höchst interessanter Versuche Schönbein's haben auf das Deutlichste bewiesen, welches ungleich grosse Wanderungsvermögen in porösen Medien die verschiedenen Körper zeigen, und müssen Jedermann zu der festen Ueberzeugung leiten, dass auf dem angebahnten Versuchsfelde noch ein reicher Schatz interessanter Thatsachen zu finden sei. Ich meinestheiles wurde sogleich von der Ansicht beseelt, dass wir es hier in nicht ferner Zeit mit einer Art von Analyse zu thun haben würden.

So habe ich mit Schönbein's Einverständniss seit kurzer Zeit begonnen, das Verhalten der Farbstoffe nach dieser Richtung zu studieren, und theile ich hier bereits das Resultat einiger gewiss sicht uninteressanter Versuche mit.

Unter denjenigen Stoffen, welche ich bis dahin untersucht habe, zeichnet sich ganz besonders die Pikrinsäure aus; sie wandert in dem Filtrierpapier mit der grössten Leichtigkeit. Dieses Vermögen giebt uns das Mittel an die Hand, die Pikrinsäure überall in ihren Mischungen mit an-

Figure 3.190: Christian Schönbein and Friedrich Goppelsröder developed one-dimensional chromatography in filter paper and in capillary tubes in 1861 [Schönbein 1861; Goppelsröder 1861].

Ueberreicht vom Autor Prof Dr. F. Goppelsroeder
Dec 12, 01

Capillaranalyse

Beruhend auf Capillaritäts- und Adsorptionserscheinungen

mit dem Schlusskapitel:

das Emporsteigen der Farbstoffe in den Pflanzen

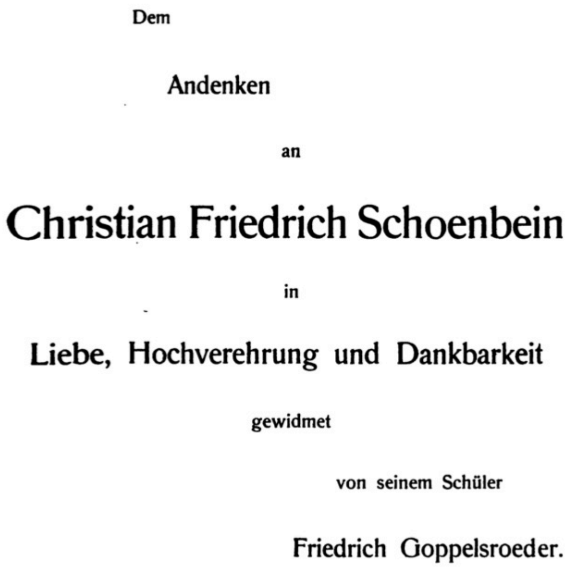
von

FRIEDRICH GOPPELSROEDER

Mit 59 Tafeln.

Separatabdruck aus den Verhandlungen der Naturforschenden Gesellschaft in Basel, Band XIV.

BASEL
Buchdruckerei Emil Birkhäuser
1901



Dem

Andenken

an

Christian Friedrich Schoenbein

in

Liebe, Hochverehrung und Dankbarkeit

gewidmet

von seinem Schüler

Friedrich Goppelsroeder.

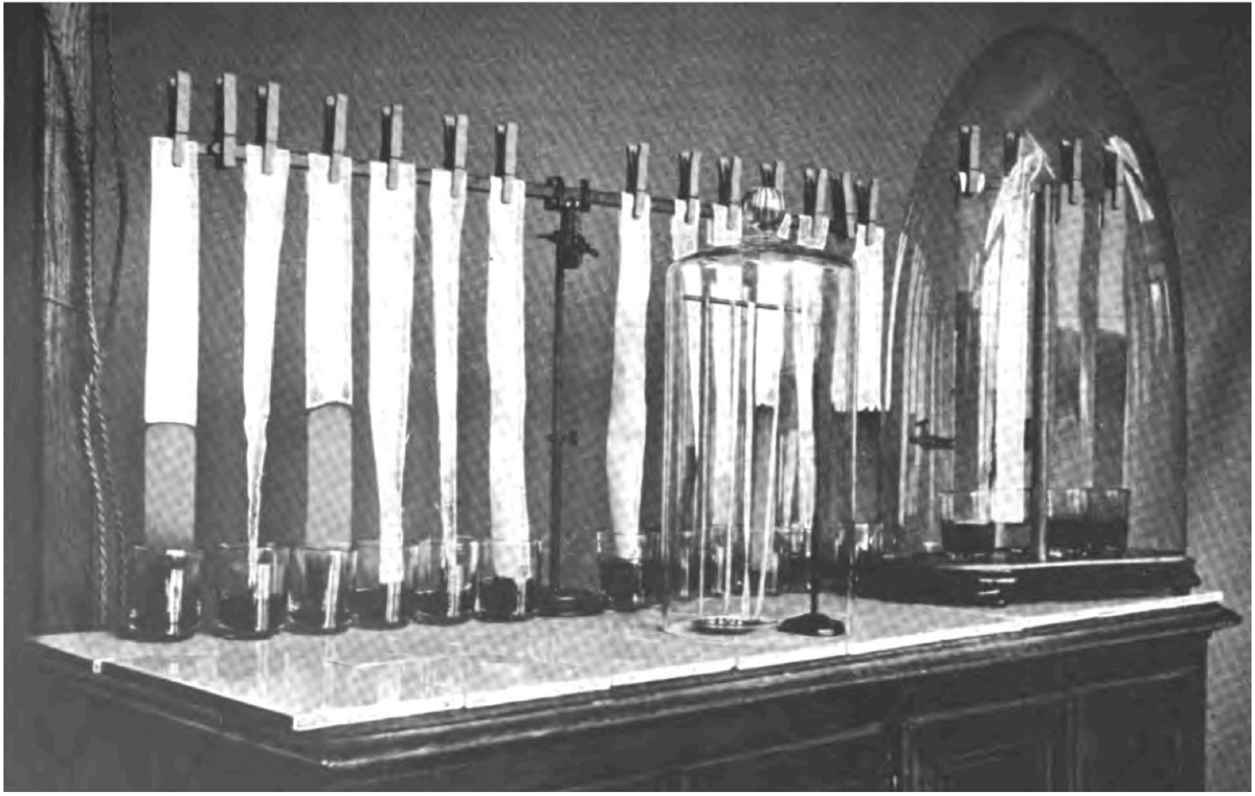


Figure 3.191: Friedrich Goppelsröder continued working to improve and to apply capillary-based chromatography for several decades, including using it to separate and analyze the colored pigments from plant leaves [Goppelsröder 1901].

Chromatography

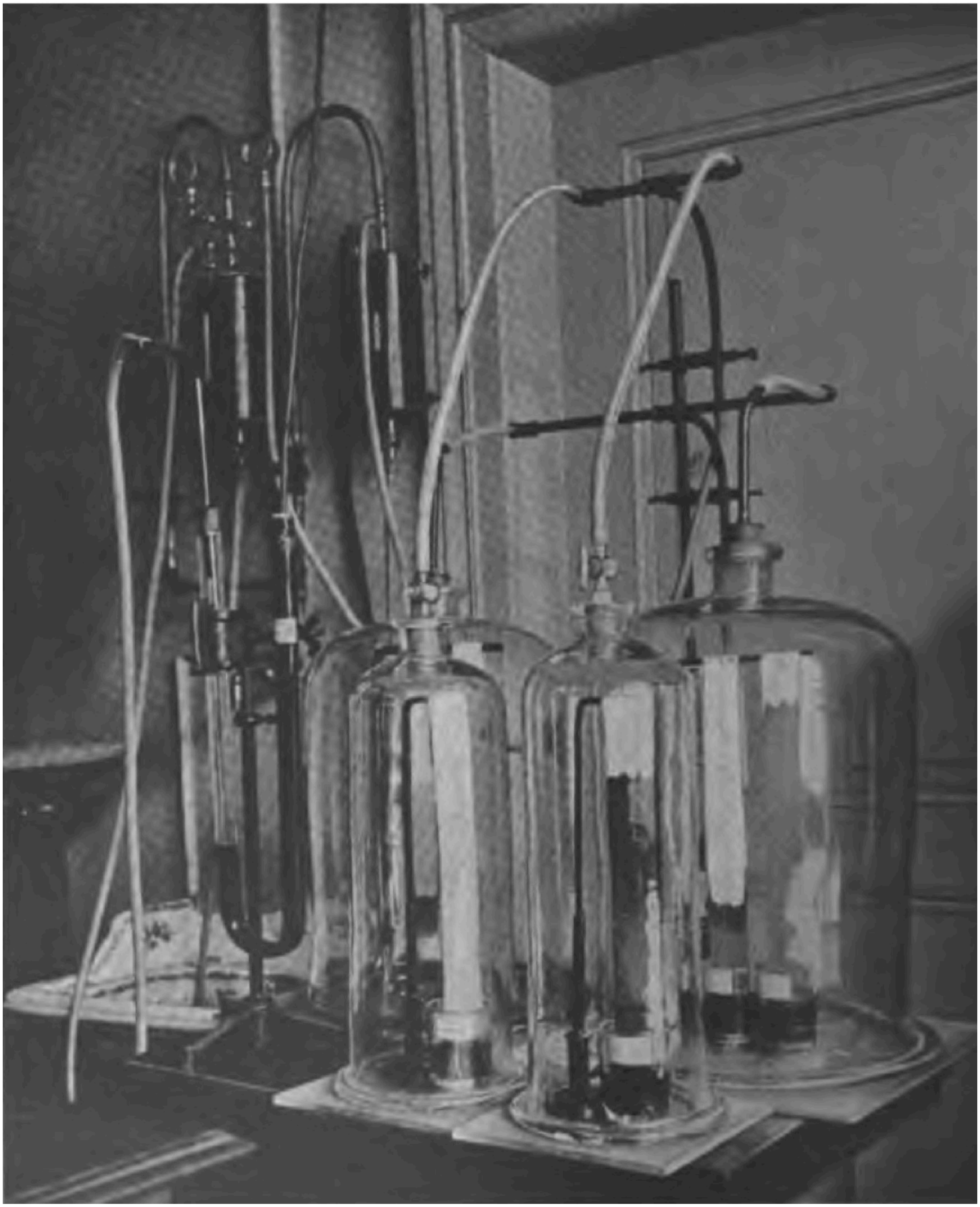


Figure 3.192: Friedrich Goppelsröder continued working to improve and to apply capillary-based chromatography for several decades, including using it to separate and analyze the colored pigments from plant leaves [Goppelsröder 1901].

Chromatography

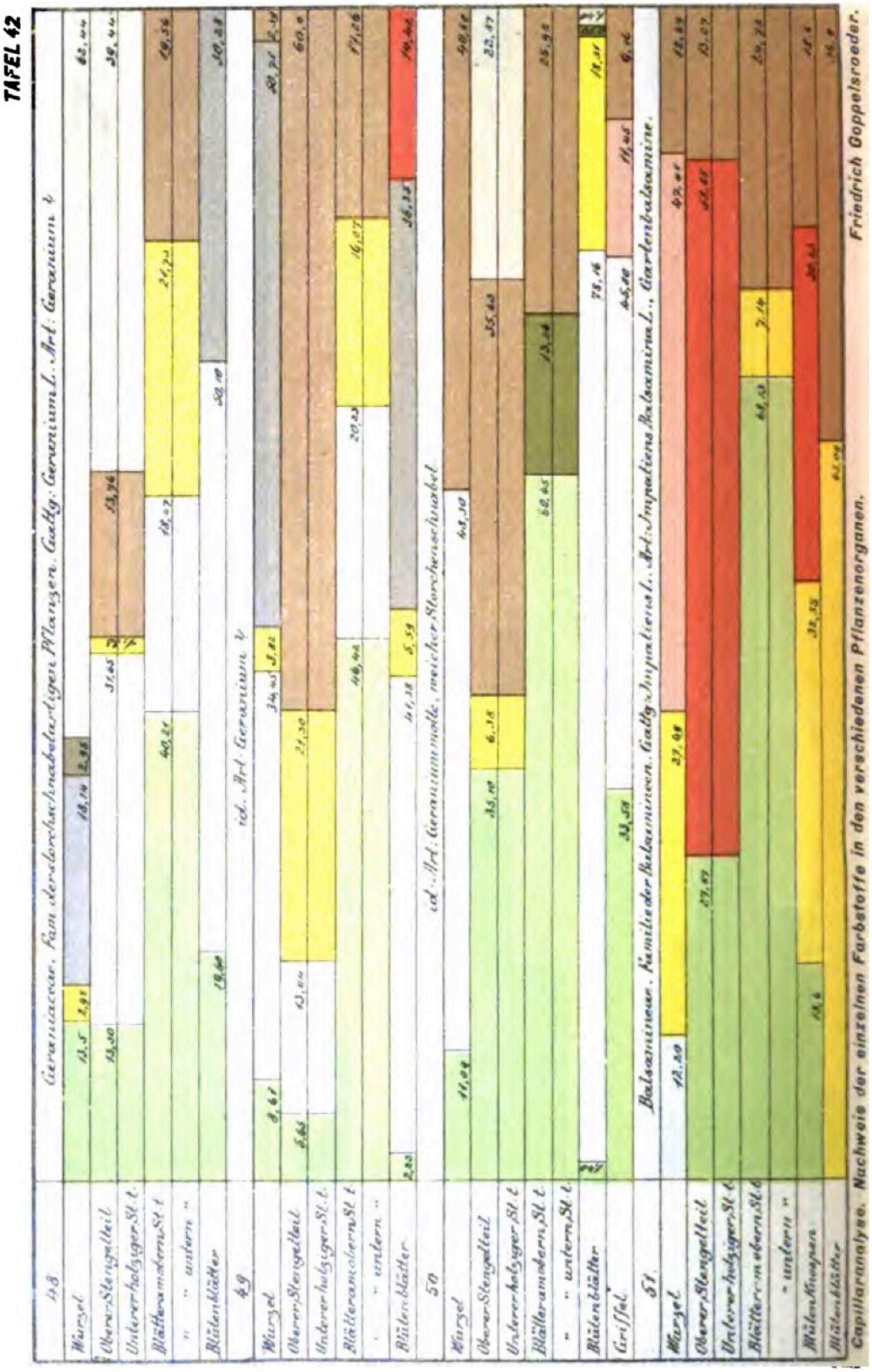


Figure 3.193: Friedrich Goppelsröder continued working to improve and to apply capillary-based chromatography for several decades, including using it to separate and analyze the colored pigments from plant leaves [Goppelsröder 1901].

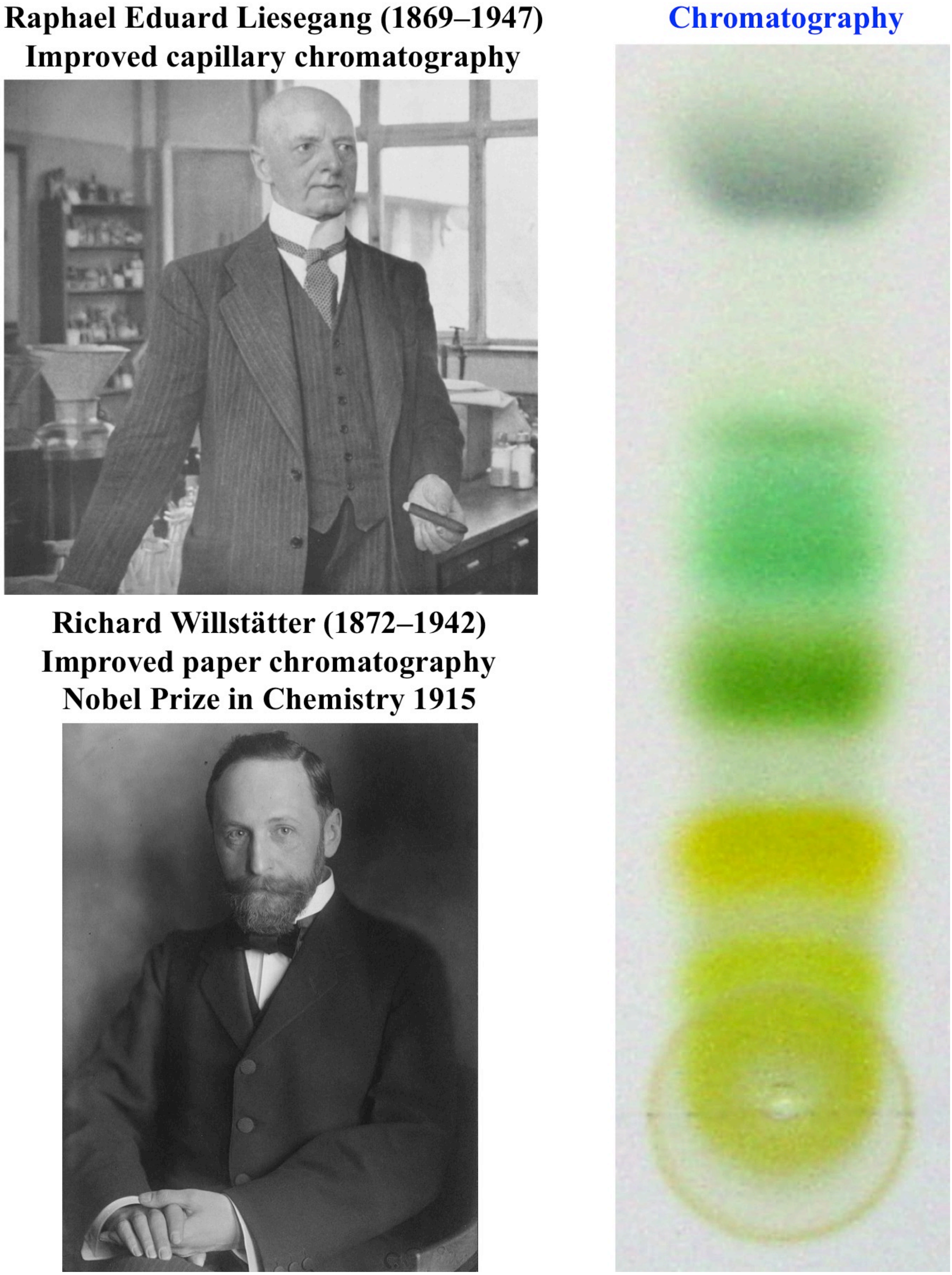
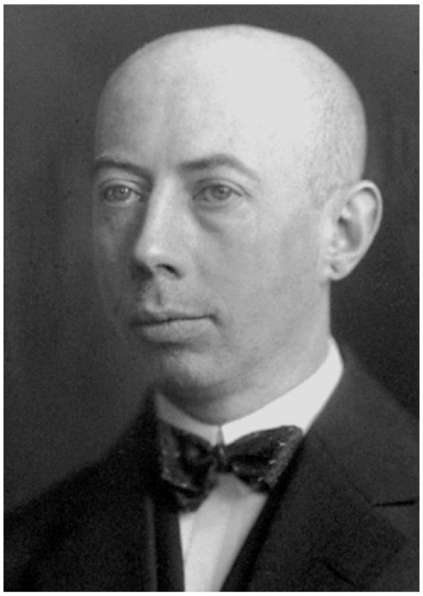
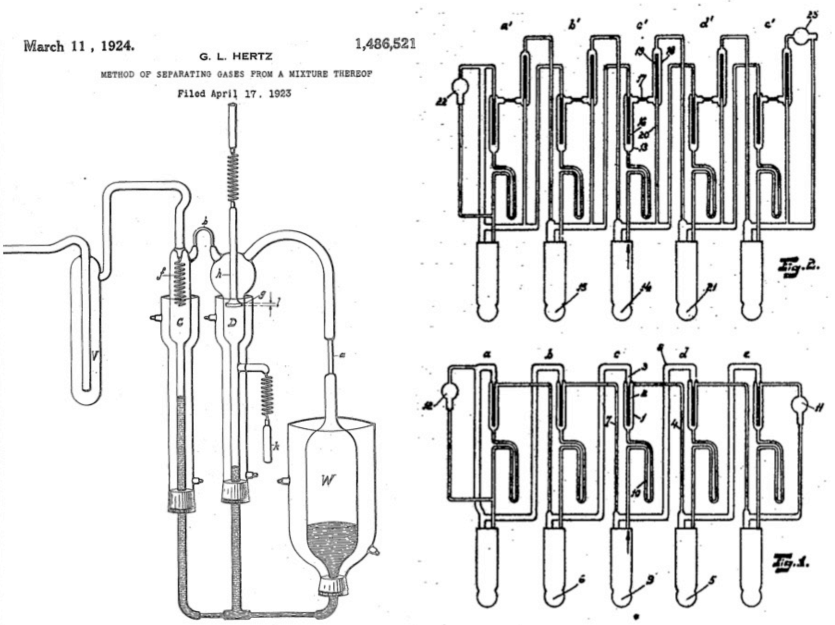


Figure 3.194: Raphael Eduard Liesegang and Richard Willstätter developed and applied improved methods for capillary and paper chromatography.

Gaseous diffusion separation and gas chromatography

Gustav Hertz
(1887–1975)





Erika Cremer (1900–1996)

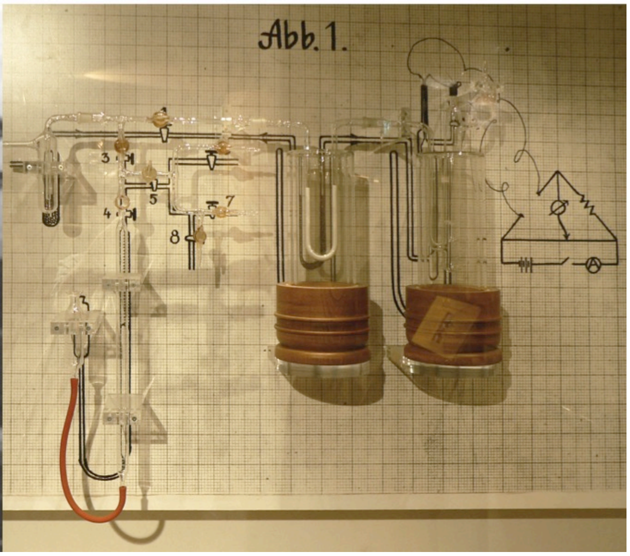


Figure 3.195: Gustav Hertz and Erika Cremer invented the methods of gaseous diffusion separation and gas chromatography.

3.9.2 Colloids

Figure 3.196 illustrates what a colloid is. As opposed to solutions of tiny particles that remain dissolved permanently (such as salt in water), or suspensions of large particles that eventually settle out (such as sand in water), colloids have medium-sized particles that can remain suspended indefinitely within a material (such as fat particles suspended in water as in milk). Some German-speaking scientists who made important contributions to the understanding and application of colloids are shown in Figs. 3.196–3.197.

Georg Bredig (German, 1868–1944) developed colloidal solutions of metals as catalysts.

Herbert Freundlich (German, 1880–1941) studied colloidal stability and coagulation.

Franz Kolb (German, 18??–19??) worked with colloids and invented plasticine modeling clay in 1890.

Robert Havemann (German, 1910–1982) conducted research on colloids. In 1936, he also invented the spectrophotometer, which is now a widely used instrument in biology and chemistry laboratories (p. 2319).

Carl Wilhelm Wolfgang Ostwald (German, 1883–1943) also did important work on colloids.

Hermann Staudinger (German, 1881–1965) studied colloids, macromolecules, and polymers. He found that many substances that had been regarded as colloidal clumps of small molecules were actually composed of macromolecules or polymers. For his discoveries, he won the Nobel Prize in Chemistry in 1953 (p. 480).

Richard Zsigmondy (Austrian, 1865–1929) made a number of important discoveries regarding colloids, and also developed synthetic food products. He won the Nobel Prize in Chemistry 1925 for his work on colloids. Professor H.G. Söderbaum, Secretary of the Royal Swedish Academy of Sciences, stated [https://www.nobelprize.org/prizes/chemistry/1925/ceremony-speech/]:

> Zsigmondy's work has quite simply been pioneering as regards the explanation of the mechanism of the coagulation phenomenon and also as regards the study of the structure of gels. [...]
>
> The brief review given here of some of the most important work of Zsigmondy is necessarily highly incomplete, if not to say fragmentary, but should surely suffice to show how it pioneered the way and opened up new regions in a field of research which had so far been difficult of access, a field which must be recognized as having the very greatest importance for human knowledge. Let us only remember in this connection that all manifestations of organic life are finally bound to the colloidal media of the protoplasm.
>
> This by way of motivation for the decision of the Academy of Sciences to award the Chemistry Nobel Prize for 1925 to Dr. Richard Zsigmondy, Professor of Chemistry at the University of Göttingen, for proving the heterogeneous nature of colloidal solutions and for the methods used which have laid the foundation of modern colloid chemistry.

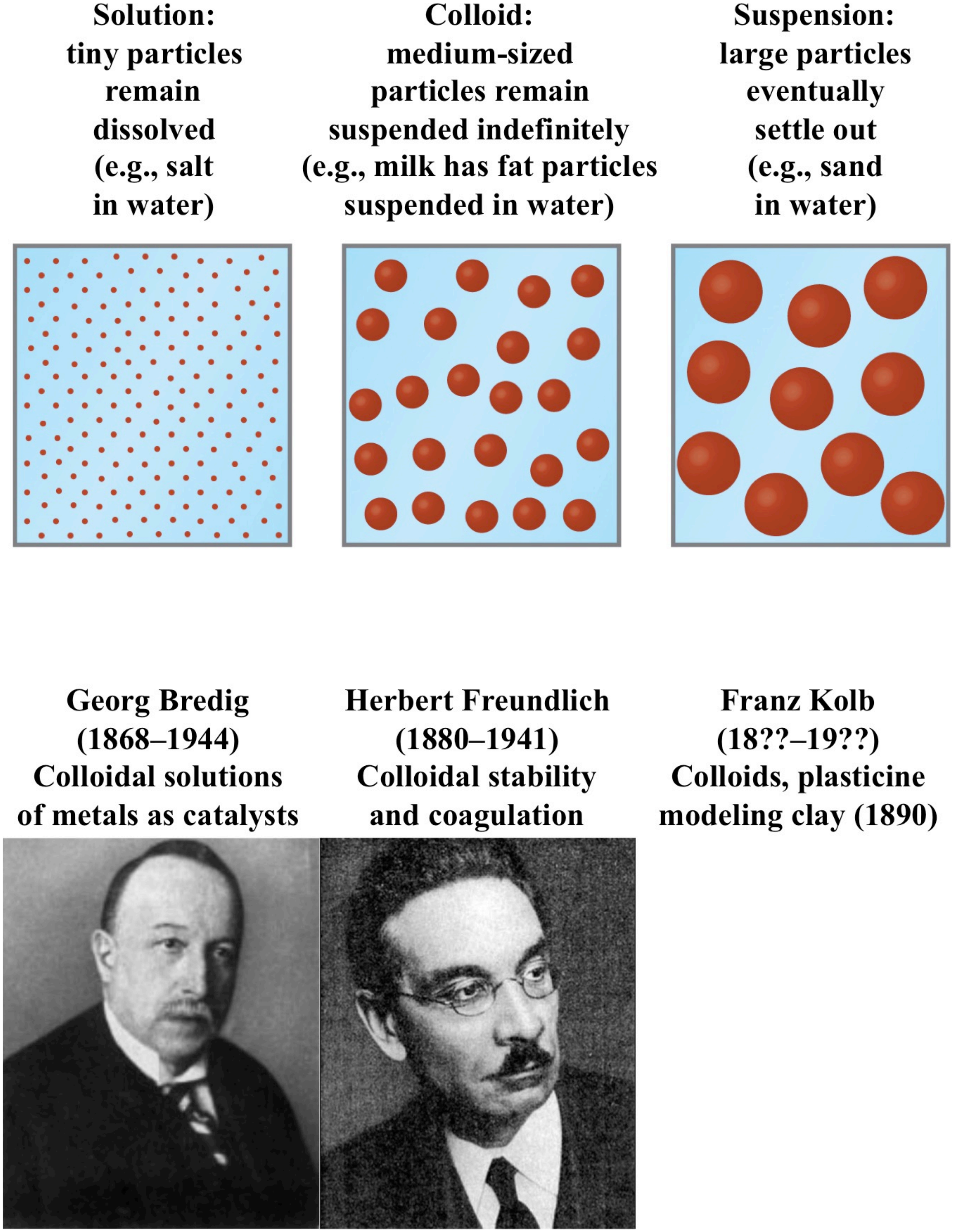
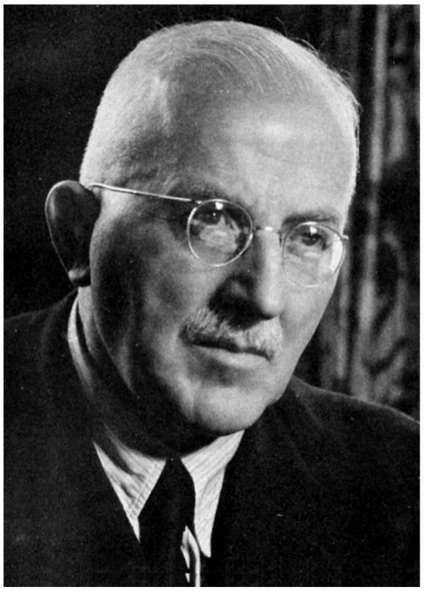


Figure 3.196: Colloids have medium-sized particles that can remain suspended indefinitely in a medium, such as the fat particles in milk. Some German-speaking scientists who made important contributions to the understanding and application of colloids included Georg Bredig, Herbert Freundlich, and Franz Kolb.

Robert Havemann (1910–1982) Colloids, spectrophotometer (1936)

Carl Wolfgang Ostwald (1883–1943) Colloids

Hermann Staudinger (1881–1965) Colloids and macromolecules Nobel Prize in Chemistry 1953



Richard Zsigmondy (1865–1929) Colloids, synthetic food products, Nobel Prize in Chemistry 1925

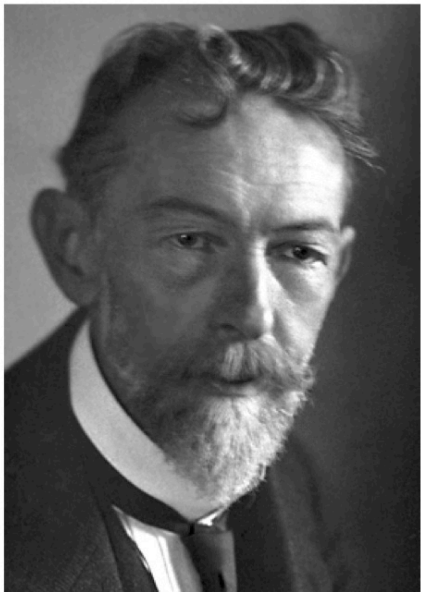


Figure 3.197: Other German-speaking scientists who made important contributions to the understanding and application of colloids included Robert Havemann, Carl Wolfgang Ostwald, Hermann Staudinger, and Richard Zsigmondy.

3.9.3 Synthetic Lubricating Oils

During the period 1927–1945, Hermann Zorn (German, 1896–1983) led a large group at I.G. Farben Ludwigshafen that invented and mass-produced synthetic lubricating oils and additives [Jantzen 1996a, 1996b]. As a result of their work, Zorn and his coworkers filed a large number of patents worldwide; see Figs. 3.198–3.199 for some examples. Some of their patents were approved and issued in the 1930s, but many were not finally approved and issued until after World War II.

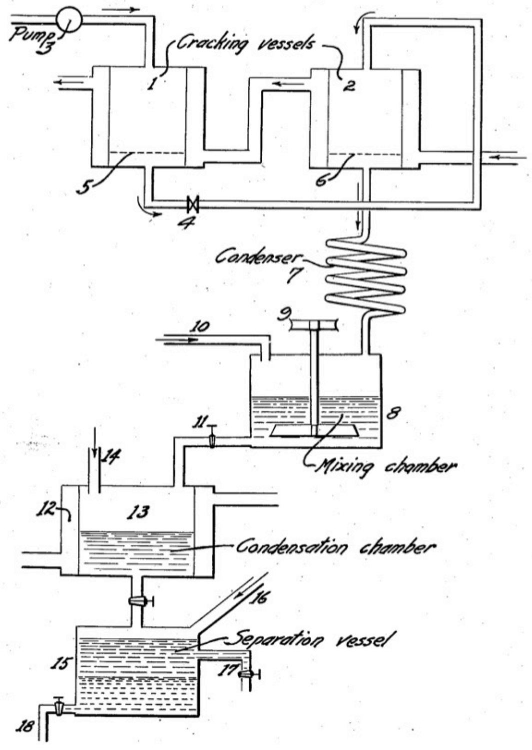
In addition to Zorn's group, several other groups of German-speaking scientists developed various types of synthetic lubricating oils during the same time period, as documented in BIOS 1611, *Major Developments in Synthetic Lubricants and Additives in Germany*, pp. 92–93 and 99–100:

> In the investigation of the German oil industry and interrogation of the leading personnel, certain facts have come to light which show that Germany had a well-developed synthetic lubricating oil industry already in being, and undergoing rapid expansion. Although from a quantity basis the products obtained from natural petroleum resources predominated, it would appear that from the quality standpoint the synthetic production was of most importance. [...]
>
> As would be expected, the outstanding developments were made under the auspices of the I.G. Farbenindustrie. It would appear that as early as 1927 a department under Dr. Zorn at Ludwigshafen commenced research on the polymerisation of olefines for the production of lubricants, this work being coupled with an investigation of the possible constituents of lubricating oils by synthesis of likely hydrocarbons; this work was similar to but apparently much wider in scope than that of Mikeska.
>
> By 1936 the process based on the polymerisation of ethylene was developed and production started in 1937 at Leuna, and later at Schkopau. By Government order this development was kept secret. Similar processes but based on the production of olefines by wax cracking were developed and operated by the I.G. and Vakuum at Pölitz and Rhenania Ossag (Shell) at Harburg. [...]
>
> Besides the above developments, Ruhrchemie produced about 1500 tons/month of a synthetic automotive engine oil (based on Fischer-Tropsch products) of a rather unsaturated, easily oxidisable character, which was used by the Army[...] [...] Rheinpreussen A.G., Homberg produced spindle oil, machine oil and steam cylinder oil, each of which found application in the various Services, particularly the Navy, where the aromatic character of the products was found beneficial in diesel engine lubricants. Other low pour steam cylinder oils were produced at Pölitz and Ludwigshafen, the latter by the Paraflow synthesis. [...]
>
> Reviewing the above topics as a whole it is apparent that in the synthetic field particularly, the Germans were ahead of the Allied developments, especially in their widespread application of the adipic ester type of lubricant. [...] Certainly some of the uses already explored experimentally open up very interesting fields for development, particularly in the lubrication of internal combustion engines.

The synthetic lubricating oils and additives that were invented by Zorn and other German-speaking scientists were extensively studied by Allied countries [e.g., BIOS 373; BIOS 1611; CIOS XXXII-68; CIOS XXXII-94; CIOS XXXII-107.] Now they are widely used around the world.

**Hermann Zorn
(1896–1983)
led a group at
I.G. Farben
Ludwigshafen
that invented and
mass-produced
synthetic
lubricating oils
and additives
(1927–1945)**

Dec. 5, 1933. W. PUNGS ET AL 1,938,088
PRODUCTION OF HIGH QUALITY LUBRICATING OILS
Filed Jan. 30, 1931



July 10, 1934. H. ZORN ET AL 1,965,952
PRODUCTION OF HIGH QUALITY LUBRICATING OILS
Filed Feb. 28, 1931

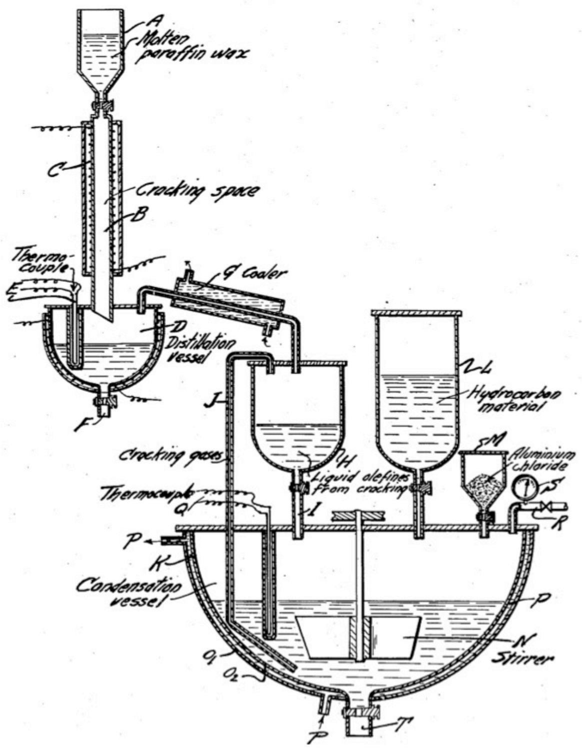
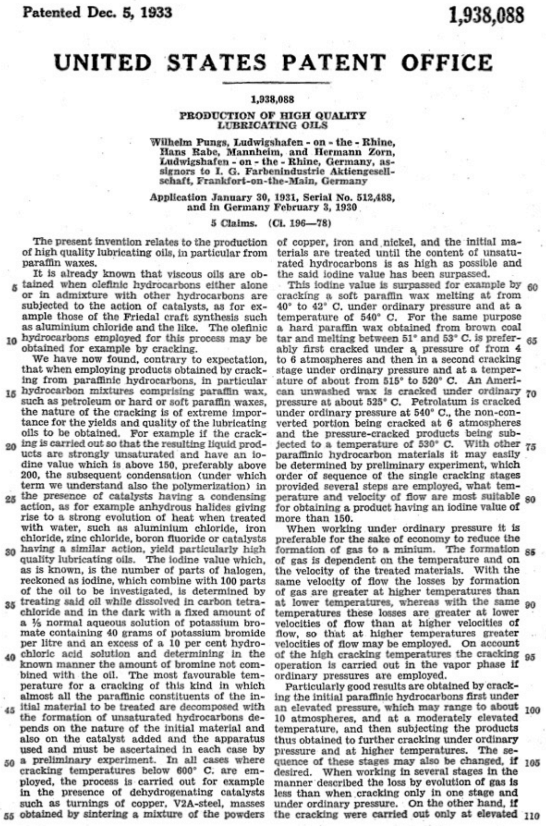


Figure 3.198: Hermann Zorn led a group at I.G. Farben Ludwigshafen that invented and mass-produced synthetic lubricating oils and additives during the period 1927–1945.



Patented Dec. 5, 1933 **1,938,088**

UNITED STATES PATENT OFFICE

1,938,088

PRODUCTION OF HIGH QUALITY LUBRICATING OILS

Wilhelm Pungs, Ludwigshafen - on - the - Rhine,
Hans Rabe, Mannheim, and Hermann Zorn,
Ludwigshafen - on - the - Rhine, Germany, assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany

Application January 30, 1931, Serial No. 512,488,
and in Germany February 3, 1930

5 Claims. (Cl. 196—78)

The present invention relates to the production of high quality lubricating oils, in particular from paraffin waxes.

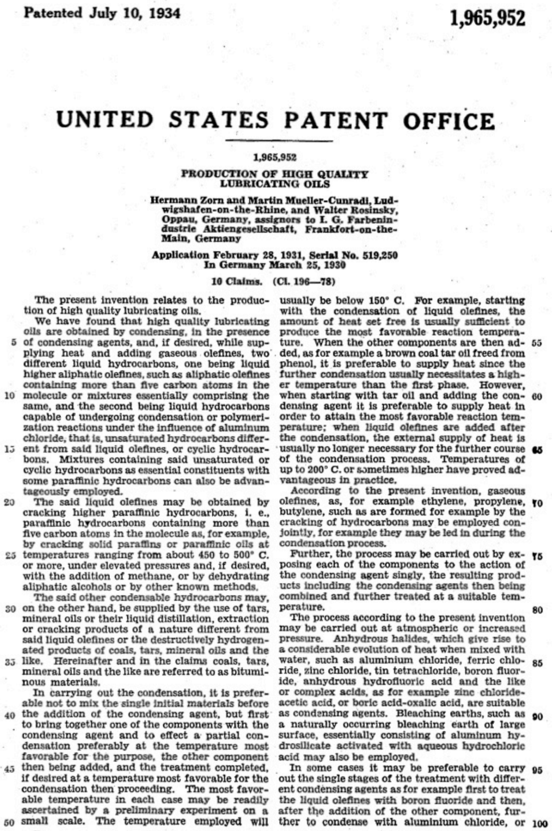
It is already known that viscous oils are obtained when olefinic hydrocarbons either alone or in admixture with other hydrocarbons are subjected to the action of catalysts, as for example those of the Friedal craft synthesis such as aluminium chloride and the like. The olefinic hydrocarbons employed for this process may be obtained for example by cracking.

We have now found, contrary to expectation, that when employing products obtained by cracking from paraffinic hydrocarbons, in particular hydrocarbon mixtures comprising paraffin wax, such as petroleum or hard or soft paraffin waxes, the nature of the cracking is of extreme importance for the yields and quality of the lubricating oils to be obtained. For example if the cracking is carried out so that the resulting liquid products are strongly unsaturated and have an iodine value which is above 150, preferably above 200, the subsequent condensation (under which term we understand also the polymerization) in the presence of catalysts having a condensing action, as for example anhydrous halides giving rise to a strong evolution of heat when treated with water, such as aluminium chloride, iron chloride, zinc chloride, boron fluoride or catalysts having a similar action, yield particularly high quality lubricating oils. The iodine value which, as is known, is the number of parts of halogen, reckoned as iodine, which combine with 100 parts of the oil to be investigated, is determined by treating said oil while dissolved in carbon tetrachloride and in the dark with a fixed amount of a ⅕ normal aqueous solution of potassium bromate containing 40 grams of potassium bromide per litre and an excess of a 10 per cent hydrochloric acid solution and determining in the known manner the amount of bromine not combined with the oil. The most favourable temperature for a cracking of this kind in which almost all the paraffinic constituents of the initial material to be treated are decomposed with the formation of unsaturated hydrocarbons depends on the nature of the initial material and also on the catalyst added and the apparatus used and must be ascertained in each case by a preliminary experiment. In all cases where cracking temperatures below 600° C. are employed, the process is carried out for example in the presence of dehydrogenating catalysts such as turnings of copper, V2A-steel, masses obtained by sintering a mixture of the powders of copper, iron and nickel, and the initial materials are treated until the content of unsaturated hydrocarbons is as high as possible and the said iodine value has been surpassed.

This iodine value is surpassed for example by cracking a soft paraffin wax melting at from 40° to 42° C. under ordinary pressure and at a temperature of 540° C. For the same purpose a hard paraffin wax obtained from brown coal tar and melting between 51° and 53° C. is preferably first cracked under a pressure of from 4 to 6 atmospheres and then in a second cracking stage under ordinary pressure and at a temperature of about from 515° to 520° C. An American unwashed wax is cracked under ordinary pressure at about 525° C. Petrolatum is cracked under ordinary pressure at 540° C., the non-converted portion being cracked at 6 atmospheres and the pressure-cracked products being subjected to a temperature of 530° C. With other paraffinic hydrocarbon materials it may easily be determined by preliminary experiment, which order of sequence of the single cracking stages provided several steps are employed, what temperature and velocity of flow are most suitable for obtaining a product having an iodine value of more than 150.

When working under ordinary pressure it is preferable for the sake of economy to reduce the formation of gas to a minium. The formation of gas is dependent on the temperature and on the velocity of the treated materials. With the same velocity of flow the losses by formation of gas are greater at higher temperatures than at lower temperatures, whereas with the same temperatures these losses are greater at lower velocities of flow than at higher velocities of flow, so that at higher temperatures greater velocities of flow may be employed. On account of the high cracking temperatures the cracking operation is carried out in the vapor phase if ordinary pressures are employed.

Particularly good results are obtained by cracking the initial paraffinic hydrocarbons first under an elevated pressure, which may range to about 10 atmospheres, and at a moderately elevated temperature, and then subjecting the products thus obtained to further cracking under ordinary pressure and at higher temperatures. The sequence of these stages may also be changed, if desired. When working in several stages in the manner described the loss by evolution of gas is less than when cracking only in one stage and under ordinary pressure. On the other hand, if the cracking were carried out only at elevated



Patented July 10, 1934 **1,965,952**

UNITED STATES PATENT OFFICE

1,965,952

PRODUCTION OF HIGH QUALITY LUBRICATING OILS

Hermann Zorn and Martin Mueller-Cunradi, Ludwigshafen-on-the-Rhine, and Walter Rosinsky, Oppau, Germany, assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany

Application February 28, 1931, Serial No. 519,250
In Germany March 25, 1930

10 Claims. (Cl. 196—78)

The present invention relates to the production of high quality lubricating oils.

We have found that high quality lubricating oils are obtained by condensing, in the presence of condensing agents, and, if desired, while supplying heat and adding gaseous olefines, two different liquid hydrocarbons, one being liquid higher aliphatic olefines, such as aliphatic olefines containing more than five carbon atoms in the molecule or mixtures essentially comprising the same, and the second being liquid hydrocarbons capable of undergoing condensation or polymerization reactions under the influence of aluminum chloride, that is, unsaturated hydrocarbons different from said liquid olefines, or cyclic hydrocarbons. Mixtures containing said unsaturated or cyclic hydrocarbons as essential constituents with some paraffinic hydrocarbons can also be advantageously employed.

The said liquid olefines may be obtained by cracking higher paraffinic hydrocarbons, i. e., paraffinic hydrocarbons containing more than five carbon atoms in the molecule as, for example, by cracking solid paraffins or paraffinic oils at temperatures ranging from about 450 to 500° C. or more, under elevated pressures and, if desired, with the addition of methane, or by dehydrating aliphatic alcohols or by other known methods.

The said other condensable hydrocarbons may, on the other hand, be supplied by the use of tars, mineral oils or their liquid distillation, extraction or cracking products of a nature different from said liquid olefines or the destructively hydrogenated products of coals, tars, mineral oils and the like. Hereinafter and in the claims coals, tars, mineral oils and the like are referred to as bituminous materials.

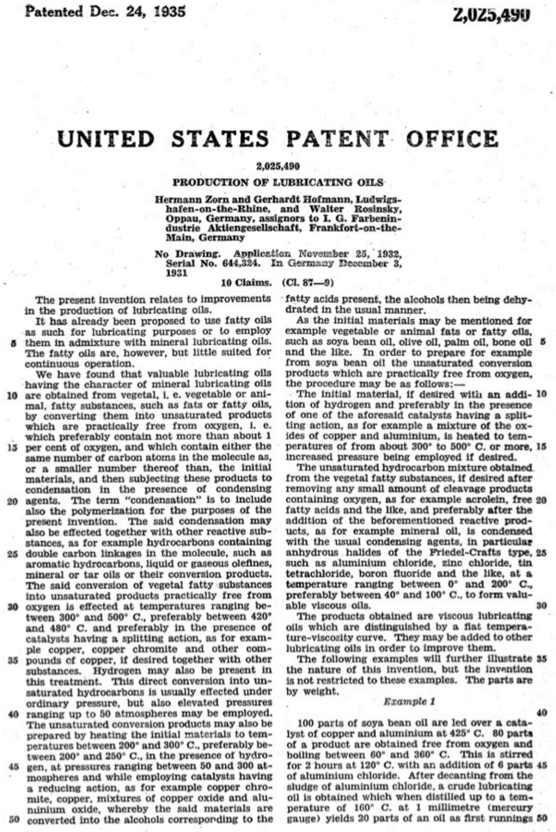
In carrying out the condensation, it is preferable not to mix the single initial materials before the addition of the condensing agent, but first to bring together one of the components with the condensing agent and to effect a partial condensation preferably at the temperature most favorable for the purpose, the other component then being added, and the treatment completed, if desired at a temperature most favorable for the condensation then proceeding. The most favorable temperature in each case may be readily ascertained by a preliminary experiment on a small scale. The temperature employed will usually be below 150° C. For example, starting with the condensation of liquid olefines, the amount of heat set free is usually sufficient to produce the most favorable reaction temperature. When the other components are then added, as for example a brown coal tar oil freed from phenol, it is preferable to supply heat since the further condensation usually necessitates a higher temperature than the first phase. However, when starting with tar oil and adding the condensing agent it is preferable to supply heat in order to attain the most favorable reaction temperature; when liquid olefines are added after the condensation, the external supply of heat is usually no longer necessary for the further course of the condensation process. Temperatures of up to 200° C. or sometimes higher have proved advantageous in practice.

According to the present invention, gaseous olefines, as, for example ethylene, propylene, butylene, such as are formed for example by the cracking of hydrocarbons may be employed conjointly, for example they may be led in during the condensation process.

Further, the process may be carried out by exposing each of the components to the action of the condensing agent singly, the resulting products including the condensing agents then being combined and further treated at a suitable temperature.

The process according to the present invention may be carried out at atmospheric or increased pressure. Anhydrous halides, which give rise to a considerable evolution of heat when mixed with water, such as aluminium chloride, ferric chloride, zinc chloride, tin tetrachloride, boron fluoride, anhydrous hydrofluoric acid and the like or complex acids, as for example zinc chloride-acetic acid, or boric acid-oxalic acid, are suitable as condensing agents. Bleaching earths, such as a naturally occurring bleaching earth of large surface, essentially consisting of aluminum hydrosilicate activated with aqueous hydrochloric acid may also be employed.

In some cases it may be preferable to carry out the single stages of the treatment with different condensing agents as for example first to treat the liquid olefines with boron fluoride and then, after the addition of the other component, further to condense with aluminium chloride, or



Patented Dec. 24, 1935 **2,025,490**

UNITED STATES PATENT OFFICE

2,025,490

PRODUCTION OF LUBRICATING OILS

Hermann Zorn and Gerhardt Hofmann, Ludwigshafen-on-the-Rhine, and Walter Rosinsky, Oppau, Germany, assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany

No Drawing. Application November 25, 1932,
Serial No. 644,324. In Germany December 3,
1931

10 Claims. (Cl. 87—9)

The present invention relates to improvements in the production of lubricating oils.

It has already been proposed to use fatty oils as such for lubricating purposes or to employ them in admixture with mineral lubricating oils. The fatty oils are, however, but little suited for continuous operation.

We have found that valuable lubricating oils having the character of mineral lubricating oils are obtained from vegetal, i. e. vegetable or animal, fatty substances, such as fats or fatty oils, by converting them into unsaturated products which are practically free from oxygen, i. e. which preferably contain not more than about 1 per cent of oxygen, and which contain either the same number of carbon atoms in the molecule as, or a smaller number thereof than, the initial materials, and then subjecting these products to condensation in the presence of condensing agents. The term "condensation" is to include also the polymerization for the purposes of the present invention. The said condensation may also be effected together with other reactive substances, as for example hydrocarbons containing double carbon linkages in the molecule, such as aromatic hydrocarbons, liquid or gaseous olefines, mineral or tar oils or their conversion products. The said conversion of vegetal fatty substances into unsaturated products practically free from oxygen is effected at temperatures ranging between 300° and 500° C., preferably between 420° and 480° C. and preferably in the presence of catalysts having a splitting action, as for example copper, copper chromite and other compounds of copper, if desired together with other substances. Hydrogen may also be present in this treatment. This direct conversion into unsaturated hydrocarbons is usually effected under ordinary pressure, but also elevated pressures ranging up to 50 atmospheres may be employed. The unsaturated conversion products may also be prepared by heating the initial materials to temperatures between 200° and 300° C., preferably between 200° and 250° C., in the presence of hydrogen, at pressures ranging between 50 and 300 atmospheres and while employing catalysts having a reducing action, as for example copper chromite, copper, mixtures of copper oxide and aluminium oxide, whereby the said materials are converted into the alcohols corresponding to the fatty acids present, the alcohols then being dehydrated in the usual manner.

As the initial materials may be mentioned for example vegetable or animal fats or fatty oils, such as soya bean oil, olive oil, palm oil, bone oil and the like. In order to prepare for example from soya bean oil the unsaturated conversion products which are practically free from oxygen, the procedure may be as follows:—

The initial material, if desired with an addition of hydrogen and preferably in the presence of one of the aforesaid catalysts having a splitting action, as for example a mixture of the oxides of copper and aluminium, is heated to temperatures of from about 300° to 500° C. or more, increased pressure being employed if desired.

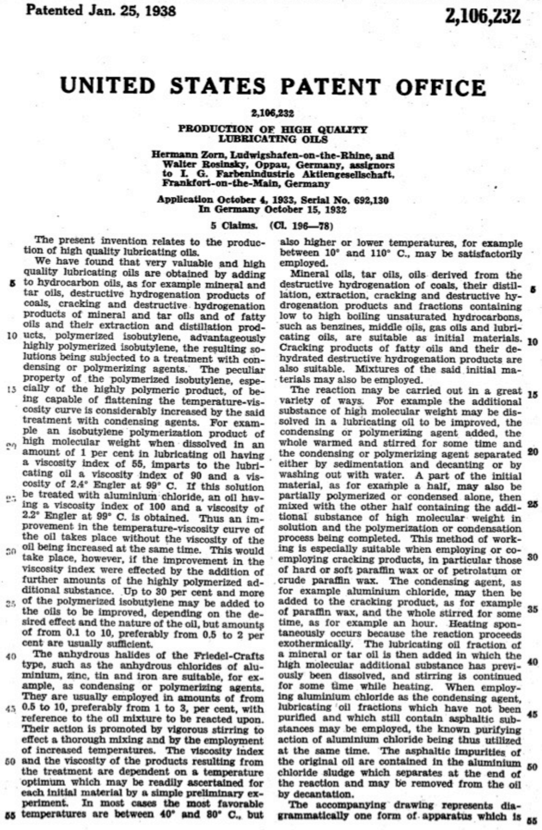
The unsaturated hydrocarbon mixture obtained from the vegetal fatty substances, if desired after removing any small amount of cleavage products containing oxygen, as for example acrolein, free fatty acids and the like, and preferably after the addition of the beforementioned reactive products, as for example mineral oil, is condensed with the usual condensing agents, in particular anhydrous halides of the Friedel-Crafts type, such as aluminium chloride, zinc chloride, tin tetrachloride, boron fluoride and the like, at a temperature ranging between 0° and 200° C., preferably between 40° and 100° C., to form valuable viscous oils.

The products obtained are viscous lubricating oils which are distinguished by a flat temperature-viscosity curve. They may be added to other lubricating oils in order to improve them.

The following examples will further illustrate the nature of this invention, but the invention is not restricted to these examples. The parts are by weight.

Example 1

100 parts of soya bean oil are led over a catalyst of copper and aluminium at 425° C. 80 parts of a product are obtained free from oxygen and boiling between 60° and 360° C. This is stirred for 2 hours at 120° C. with an addition of 6 parts of aluminium chloride. After decanting from the sludge of aluminium chloride, a crude lubricating oil is obtained which when distilled up to a temperature of 160° C. at 1 millimetre (mercury gauge) yields 20 parts of an oil as first runnings



Patented Jan. 25, 1938 **2,106,232**

UNITED STATES PATENT OFFICE

2,106,232

PRODUCTION OF HIGH QUALITY LUBRICATING OILS

Hermann Zorn, Ludwigshafen-on-the-Rhine, and Walter Rosinsky, Oppau, Germany, assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany

Application October 4, 1933, Serial No. 692,130
In Germany October 15, 1932

5 Claims. (Cl. 196—78)

The present invention relates to the production of high quality lubricating oils.

We have found that very valuable and high quality lubricating oils are obtained by adding to hydrocarbon oils, as for example mineral and tar oils, destructive hydrogenation products of coals, cracking and destructive hydrogenation products of mineral and tar oils and of fatty oils and their extraction and distillation products, polymerized isobutylene, advantageously highly polymerized isobutylene, the resulting solutions being subjected to a treatment with condensing or polymerizing agents. The peculiar property of the polymerized isobutylene, especially of the highly polymeric product, of being capable of flattening the temperature-viscosity curve is considerably increased by the said treatment with condensing agents. For example an isobutylene polymerization product of high molecular weight when dissolved in an amount of 1 per cent in lubricating oil having a viscosity index of 55, imparts to the lubricating oil a viscosity index of 90 and a viscosity of 2.4° Engler at 99° C. If this solution be treated with aluminium chloride, an oil having a viscosity index of 100 and a viscosity of 2.2° Engler at 99° C. is obtained. Thus an improvement in the temperature-viscosity curve of the oil takes place without the viscosity of the oil being increased at the same time. This would take place, however, if the improvement in the viscosity index were effected by the addition of further amounts of the highly polymerized additional substance. Up to 30 per cent and more of the polymerized isobutylene may be added to the oils to be improved, depending on the desired effect and the nature of the oil, but amounts of from 0.1 to 10, preferably from 0.5 to 2 per cent are usually sufficient.

The anhydrous halides of the Friedel-Crafts type, such as the anhydrous chlorides of aluminium, zinc, tin and iron are suitable, for example, as condensing or polymerizing agents. They are usually employed in amounts of from 0.5 to 10, preferably from 1 to 3, per cent, with reference to the oil mixture to be reacted upon. Their action is promoted by vigorous stirring to effect a thorough mixing and by the employment of increased temperatures. The viscosity index and the viscosity of the products resulting from the treatment are dependent on a temperature optimum which may be readily ascertained for each initial material by a simple preliminary experiment. In most cases the most favorable temperatures are between 40° and 80° C., but also higher or lower temperatures, for example between 10° and 110° C., may be satisfactorily employed.

Mineral oils, tar oils, oils derived from the destructive hydrogenation of coals, their distillation, extraction, cracking and destructive hydrogenation products and fractions containing low to high boiling unsaturated hydrocarbons, such as benzines, middle oils, gas oils and lubricating oils, are suitable as initial materials. Cracking products of fatty oils and their dehydrated destructive hydrogenation products are also suitable. Mixtures of the said initial materials may also be employed.

The reaction may be carried out in a great variety of ways. For example the additional substance of high molecular weight may be dissolved in a lubricating oil to be improved, the condensing or polymerizing agent added, the whole warmed and stirred for some time and the condensing or polymerizing agent separated either by sedimentation and decanting or by washing out with water. A part of the initial material, as for example a half, may also be partially polymerized or condensed alone, then mixed with the other half containing the additional substance of high molecular weight in solution and the polymerization or condensation process being completed. This method of working is especially suitable when employing or co-employing cracking products, in particular those of hard or soft paraffin wax or of petrolatum or crude paraffin wax. The condensing agent, as for example aluminium chloride, may then be added to the cracking product, as for example of paraffin wax, and the whole stirred for some time, as for example an hour. Heating spontaneously occurs because the reaction proceeds exothermically. The lubricating oil fraction of a mineral or tar oil is then added in which the high molecular additional substance has previously been dissolved, and stirring is continued for some time while heating. When employing aluminium chloride as the condensing agent, lubricating oil fractions which have not been purified and which still contain asphaltic substances may be employed, the known purifying action of aluminium chloride being thus utilized at the same time. The asphaltic impurities of the original oil are contained in the aluminium chloride sludge which separates at the end of the reaction and may be removed from the oil by decantation.

The accompanying drawing represents diagrammatically one form of apparatus which is

Figure 3.199: Hermann Zorn led a group at I.G. Farben Ludwigshafen that invented and mass-produced synthetic lubricating oils and additives during the period 1927–1945.

3.9.4 Synthetic Detergents and Paper Recycling

Traditional soap-making requires animal fat. Even during peacetime and certainly during wartime, most animal fat in the German-speaking world was needed for cooking purposes. Therefore it was in short supply for soap, and there was a strong incentive to find synthetic chemical alternatives. German-speaking chemists developed both inorganic and organic detergents using methods of direct chemical synthesis.[20] Such synthetic detergents are now used worldwide, since they proved to have superior properties and lower production costs compared to traditional soaps.

In 1876, Friedrich (Fritz) Henkel (German, 1848–1930) founded the Henkel & Cie. soap company and began producing the first synthetic inorganic detergent powder, a mixture of sodium carbonate for bleaching and sodium silicate for abrasive cleaning. See Fig. 3.200. Later Henkel's sons joined the company; in particular, his third son, Hugo Henkel (German, 1881–1952), obtained a Ph.D. in chemistry and became the head chemist for the Henkel company. In 1907, Hugo Henkel invented and began selling an improved inorganic detergent powder, using sodium perborate for bleaching and sodium silicate for abrasive cleaning, that was dubbed Persil for those two components. Hugo Henkel and Otto Gessler (German, 18??–19??) also invented the first successful methods of recycling printed paper by using similar bleaching and cleaning compounds. Along the way, the Henkels and several other chemists in their company developed a variety of other chemical products, including new adhesives (and later the first glue stick, Pritt).

In contrast to inorganic detergents, organic detergents such as those made from animal fat contain long hydrocarbon molecules that are better able to interact with and remove hydrocarbon stains such as grease. Thus there was a strong need to develop synthetic organic detergents.

Perhaps the most important chemist in the development of synthetic organic detergents was Fritz Günther (German, 1877–1957), who led a large research group devoted to that topic at BASF in Ludwigshafen (which became I.G. Farben Ludwigshafen). Günther and his group began working on the problem during World War I and produced their first commercial synthetic organic detergent, called Nekal, in 1916.

Günther and his group developed a wide range of other synthetic organic detergents over the following decades: Nekalin, alkylbenzene sulfonates (ABS) such as sodium dodecyl benzene sulfonate, and others. See Fig. 3.201. Günther retired in 1938 due to failing eyesight (possibly caused by prolonged chemical exposure), yet his group at Ludwigshafen remained highly active until at least 1945.

At I.G. Farben Höchst, Hermann Ludwig Orthner (German, 1897–1971) ran another important group that developed and mass-produced synthetic organic detergents such as Igepon/Hostapon and Mersol until at least 1945 (Fig. 3.202). For example, BIOS 1222, *Mersol and Hostapon Processes, I.G. Farbenindustrie, Höchst*, p. 1, reported:

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[20] Baird 1955; Gritz 2013, 2014; BIOS 518; BIOS 1222; FIAT 913.

> During the war the I.G. Farbenindustrie manufactured large quantities of Mersol type products from a hydrogenated Fischer Tropsch cut, Mepasin. Large scale manufacture of this product was carried out at Leuna and Wolfen, but the development work was done at Höchst under Professor Orthner. Höchst laboratories also developed two further processes for detergents (Hostapon) of the same type from Mepasin.

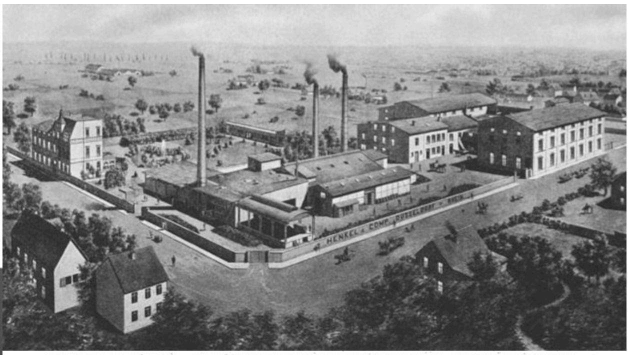
German-speaking scientists also invented methods of mass-producing and purifying enzymes (such as proteases that degrade proteins and lipases that degrade fats) and adding them to commercial detergents to improve their cleaning power (see for example p. 2365).

Many of these German developments were patented and known through those patents to other countries from the early 1900s onward. Others were not adopted by other countries until Allied investigators interrogated German scientists and visited plants after World War II. Synthetic detergents and detergents incorporating cleaning enzymes are now commonly used worldwide. Recycling of printed paper, as first developed by Hugo Henkel and Otto Gessler, is also used worldwide.

Persil synthetic detergents and paper recycling

Friedrich Henkel (1848–1930)

Hugo Henkel (1881–1952)



SCHWEIZERISCHE EIDGENOSSENSCHAFT

EIDGEN. AMT FÜR GEISTIGES EIGENTUM

PATENTSCHRIFT

Nr. 57536 28. Oktober 1911, 8 Uhr p. Klasse 36 i

HAUPTPATENT

HENKEL & Cie., Düsseldorf (Deutschland).

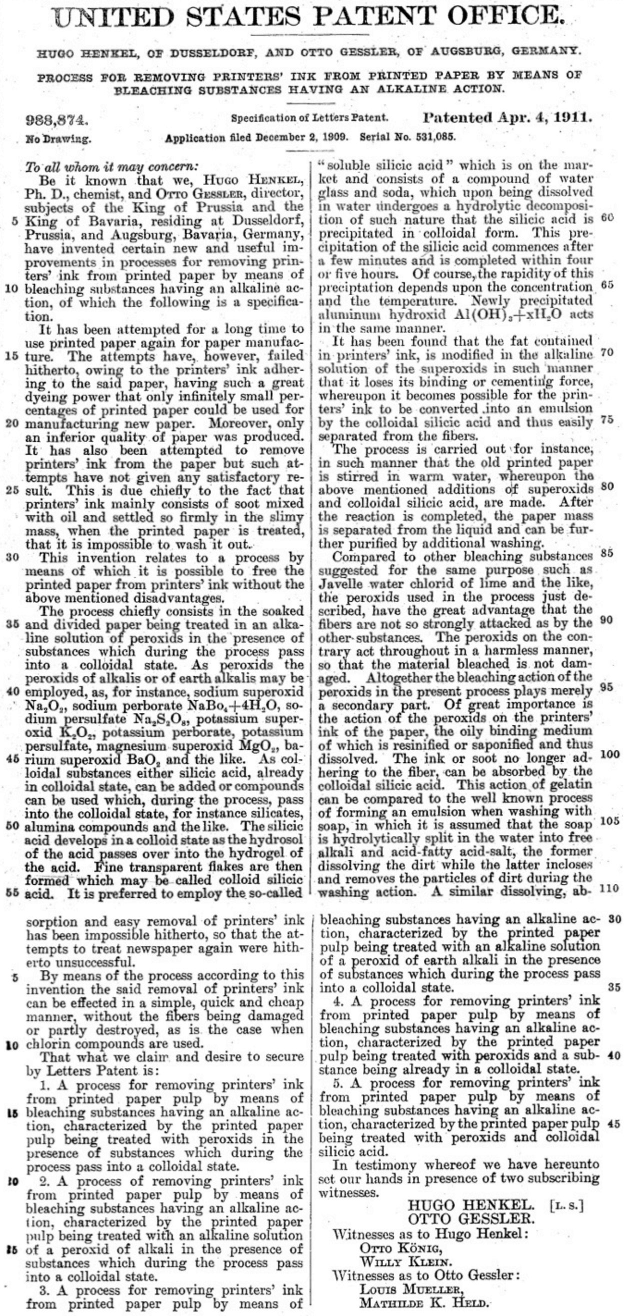
Verfahren zur Überführung von Alkalisilikatlösungen in trockene, leicht lösliche Pulver.

Es besteht schon seit langem in der Industrie das Bedürfnis nach einem pulverförmigen, leicht löslichen Alkalisilikat, da ein solches handlicher ist als die üblichen Lösungen, deren Verwendung für manche Zwecke, so z. B. für pulverförmige Farben und dergleichen, überhaupt ausgeschlossen ist. Die bisher vorgeschlagenen Wege zur Überführung z. B. von Wasserglas haben aber nur ein in kochendem oder heißem Wasser lösliches Produkt ergeben.

Die vorliegende Erfindung betrifft nun ein Verfahren zur Überführung von Alkalisilikatlösungen in trockene, leicht lösliche Pulver. Das Verfahren beruht darauf, daß man unter hohem Druck stehende, bei hoher Temperatur konzentrierte, heiße, zähflüssige Alkalisilikatlösungen durch plötzliche Druckentlastung in Form eines feinen Staubes mit kalter Luft in Berührung bringt.

Beispiel:

Man löst zunächst in einem rotierenden Wasserglas-Autoklaven, der unter hohem Druck, etwa 6—8 Atmosphären, steht, die übliche Ausgangssubstanz für die Herstellung von Wasserglaslösungen in Wasser auf. Das Auflösen wird bei höherer Temperatur vorgenommen, bis die dickflüssige Lösung ein spezifisches Gewicht von 1,44 besitzt. Die so erhaltene Lösung ist in heißem Zustand zähflüssig und nimmt beim Erkalten die Form einer zähen, unbeweglichen Gallerte an. Die heiße Lösung wird nun unter hohem Druck von 8 Atmosphären, der beständig aufrecht erhalten wird, durch eine Streudüse mit Öffnungen von etwa anderthalb Millimeter Durchmesser aus dem Autoklaven austreten gelassen. Die staubförmige Lösung wird unter der Einwirkung kalter Luft sofort in eine feste, trockene Form übergeführt. Diesen Vorgang unterstützt man dadurch, daß man mit einem kalte Luft zuführenden Ventilator das staubförmige Material durch einen Holzschacht etwa 4 Meter hoch in die Höhe führt, um es dann allmählich als vollkommen trockenes Pulver auf den Boden sinken zu lassen. Das auf den Boden sinkende, staubförmige Material enthält 10 bis 15 % weniger Wasser als die heiße Lösung. Durch die in der Luft enthaltene Kohlensäure wird die Oberfläche der Wasserglasstäubchen mit einer feinen Haut umgeben, wie dies stets



UNITED STATES PATENT OFFICE.

HUGO HENKEL, OF DUSSELDORF, AND OTTO GESSLER, OF AUGSBURG, GERMANY.

PROCESS FOR REMOVING PRINTERS' INK FROM PRINTED PAPER BY MEANS OF BLEACHING SUBSTANCES HAVING AN ALKALINE ACTION.

988,874. Specification of Letters Patent. Patented Apr. 4, 1911.

No Drawing. Application filed December 2, 1909. Serial No. 531,085.

To all whom it may concern:

Be it known that we, Hugo Henkel, Ph. D., chemist, and Otto Gessler, director, subjects of the King of Prussia and the King of Bavaria, residing at Dusseldorf, Prussia, and Augsburg, Bavaria, Germany, have invented certain new and useful improvements in processes for removing printers' ink from printed paper by means of bleaching substances having an alkaline action, of which the following is a specification.

It has been attempted for a long time to use printed paper again for paper manufacture. The attempts have, however, failed hitherto, owing to the printers' ink adhering to the said paper, having such a great dyeing power that only infinitely small percentages of printed paper could be used for manufacturing new paper. Moreover, only an inferior quality of paper was produced. It has also been attempted to remove printers' ink from the paper but such attempts have not given any satisfactory result. This is due chiefly to the fact that printers' ink mainly consists of soot mixed with oil and settled so firmly in the slimy mass, when the printed paper is treated, that it is impossible to wash it out.

This invention relates to a process by means of which it is possible to free the printed paper from printers' ink without the above mentioned disadvantages.

The process chiefly consists in the soaked and divided paper being treated in an alkaline solution of peroxids in the presence of substances which during the process pass into a colloidal state. As peroxids the peroxids of alkalis or of earth alkalis may be employed, as, for instance, sodium superoxid Na_2O_2, sodium perborate $NaBo_4 + 4H_2O$, sodium persulfate $Na_2S_2O_8$, potassium superoxid K_2O_2, potassium perborate, potassium persulfate, magnesium superoxid MgO_2, barium superoxid BaO_2 and the like. As colloidal substances either silicic acid, already in colloidal state, can be added or compounds can be used which, during the process, pass into the colloidal state, for instance silicates, alumina compounds and the like. The silicic acid develops in a colloid state as the hydrosol of the acid passes over into the hydrogel of the acid. Fine transparent flakes are then formed which may be called colloid silicic acid. It is preferred to employ the so-called "soluble silicic acid" which is on the market and consists of a compound of water glass and soda, which upon being dissolved in water undergoes a hydrolytic decomposition of such nature that the silicic acid is precipitated in colloidal form. This precipitation of the silicic acid commences after a few minutes and is completed within four or five hours. Of course, the rapidity of this preciptation depends upon the concentration and the temperature. Newly precipitated aluminum hydroxid $Al(OH)_3 + xH_2O$ acts in the same manner.

It has been found that the fat contained in printers' ink, is modified in the alkaline solution of the superoxids in such manner that it loses its binding or cementing force, whereupon it becomes possible for the printers' ink to be converted into an emulsion by the colloidal silicic acid and thus easily separated from the fibers.

The process is carried out for instance, in such manner that the old printed paper is stirred in warm water, whereupon the above mentioned additions of superoxids and colloidal silicic acid, are made. After the reaction is completed, the paper mass is separated from the liquid and can be further purified by additional washing.

Compared to other bleaching substances suggested for the same purpose such as Javelle water chlorid of lime and the like, the peroxids used in the process just described, have the great advantage that the fibers are not so strongly attacked as by the other substances. The peroxids on the contrary act throughout in a harmless manner, so that the material bleached is not damaged. Altogether the bleaching action of the peroxids in the present process plays merely a secondary part. Of great importance is the action of the peroxids on the printers' ink of the paper, the oily binding medium of which is resinified or saponified and thus dissolved. The ink or soot no longer adhering to the fiber, can be absorbed by the colloidal silicic acid. This action of gelatin can be compared to the well known process of forming an emulsion when washing with soap, in which it is assumed that the soap is hydrolytically split in the water into free alkali and acid-fatty acid-salt, the former dissolving the dirt while the latter incloses and removes the particles of dirt during the washing action. A similar dissolving, ab-

sorption and easy removal of printers' ink has been impossible hitherto, so that the attempts to treat newspaper again were hitherto unsuccessful.

By means of the process according to this invention the said removal of printers' ink can be effected in a simple, quick and cheap manner, without the fibers being damaged or partly destroyed, as is the case when chlorin compounds are used.

That what we claim and desire to secure by Letters Patent is:

1. A process for removing printers' ink from printed paper pulp by means of bleaching substances having an alkaline action, characterized by the printed paper pulp being treated with peroxids in the presence of substances which during the process pass into a colloidal state.

2. A process of removing printers' ink from printed paper pulp by means of bleaching substances having an alkaline action, characterized by the printed paper pulp being treated with an alkaline solution of a peroxid of alkali in the presence of substances which during the process pass into a colloidal state.

3. A process for removing printers' ink from printed paper pulp by means of

bleaching substances having an alkaline action, characterized by the printed paper pulp being treated with an alkaline solution of a peroxid of earth alkali in the presence of substances which during the process pass into a colloidal state.

4. A process for removing printers' ink from printed paper pulp by means of bleaching substances having an alkaline action, characterized by the printed paper pulp being treated with peroxids and a substance being already in a colloidal state.

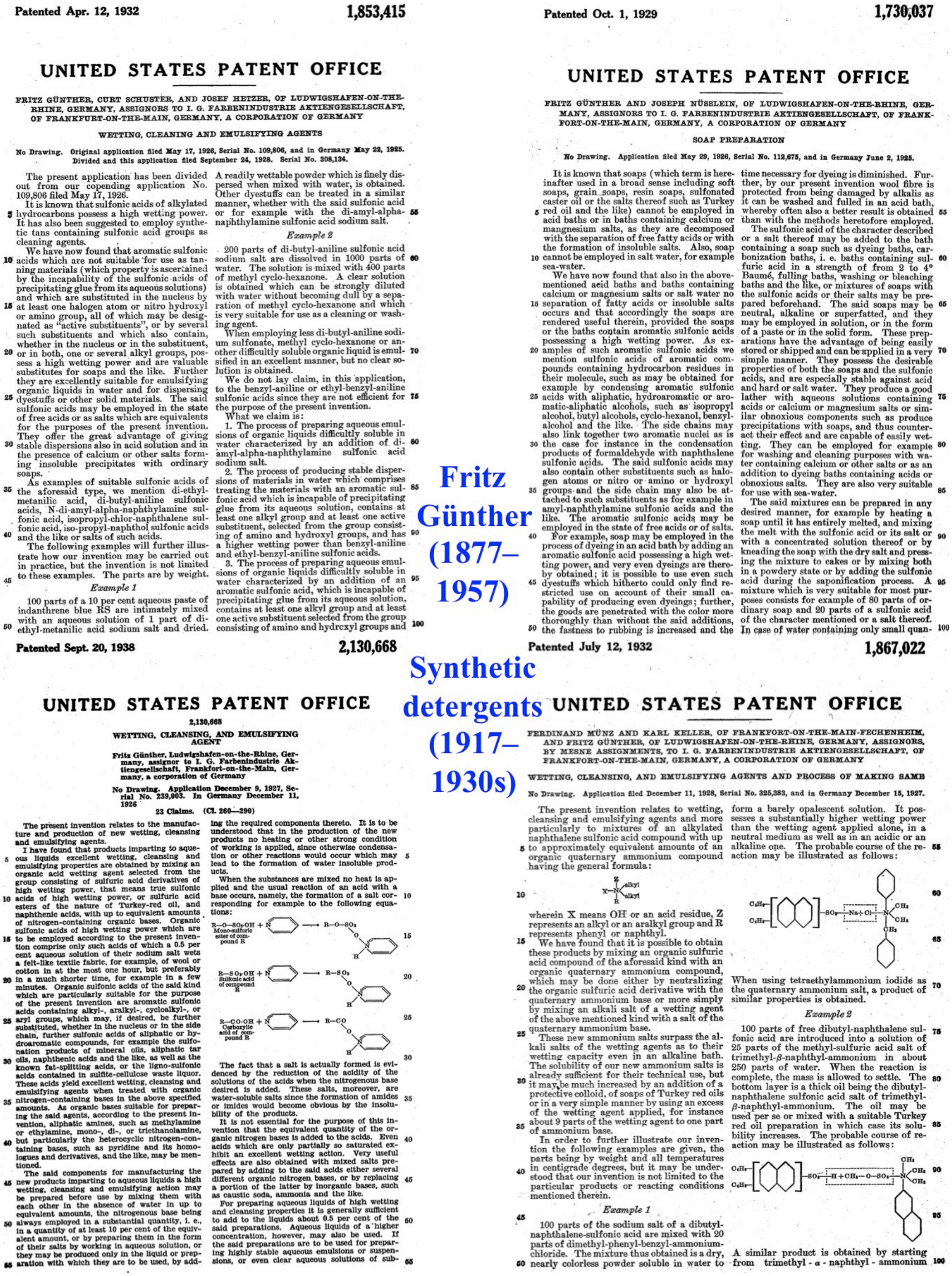
5. A process for removing printers' ink from printed paper pulp by means of bleaching substances having an alkaline action, characterized by the printed paper pulp being treated with peroxids and colloidal silicic acid.

In testimony whereof we have hereunto set our hands in presence of two subscribing witnesses.

HUGO HENKEL. [L. S.]
OTTO GESSLER.

Witnesses as to Hugo Henkel:
Otto König,
Willy Klein.
Witnesses as to Otto Gessler:
Louis Mueller,
Mathilde K. Held.

Figure 3.200: Friedrich (Fritz) Henkel and his sons, especially Hugo Henkel, as well as other chemists at their company, developed synthetic inorganic detergents such as Persil, as well as the first successful methods of recycling printed paper.



Patented Apr. 12, 1932 **1,853,415**

UNITED STATES PATENT OFFICE

FRITZ GÜNTHER, CURT SCHUSTER, AND JOSEF HETZER, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNORS TO I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, OF FRANKFURT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY

WETTING, CLEANING AND EMULSIFYING AGENTS

No Drawing. Original application filed May 17, 1926, Serial No. 109,806, and in Germany May 22, 1925. Divided and this application filed September 24, 1928. Serial No. 308,134.

The present application has been divided out from our copending application No. 109,806 filed May 17, 1926.

It is known that sulfonic acids of alkylated hydrocarbons possess a high wetting power. It has also been suggested to employ synthetic tans containing sulfonic acid groups as cleaning agents.

We have now found that aromatic sulfonic acids which are not suitable for use as tanning materials (which property is ascertained by the incapability of the sulfonic acids of precipitating glue from its aqueous solutions) and which are substituted in the nucleus by at least one halogen atom or nitro hydroxyl or amino group, all of which may be designated as "active substituents", or by several such substituents and which also contain, whether in the nucleus or in the substituent, or in both, one or several alkyl groups, possess a high wetting power and are valuable substitutes for soaps and the like. Further they are excellently suitable for emulsifying organic liquids in water and for dispersing dyestuffs or other solid materials. The said sulfonic acids may be employed in the state of free acids or as salts which are equivalents for the purposes of the present invention. They offer the great advantage of giving stable dispersions also in acid solution and in the presence of calcium or other salts forming insoluble precipitates with ordinary soaps.

As examples of suitable sulfonic acids of the aforesaid type, we mention di-ethyl-metanilic acid, di-butyl-aniline sulfonic acids, N-di-amyl-alpha-naphthylamine sulfonic acid, isopropyl-chlor-naphthalene sulfonic acid, iso-propyl-naphthol sulfonic acids and the like or salts of such acids.

The following examples will further illustrate how our invention may be carried out in practice, but the invention is not limited to these examples. The parts are by weight.

Example 1

100 parts of a 10 per cent aqueous paste of indanthrene blue RS are intimately mixed with an aqueous solution of 1 part of di-ethyl-metanilic acid sodium salt and dried. A readily wettable powder which is finely dispersed when mixed with water, is obtained. Other dyestuffs can be treated in a similar manner, whether with the said sulfonic acid or for example with the di-amyl-alpha-naphthylamine sulfonic acid sodium salt.

Example 2

200 parts of di-butyl-aniline sulfonic acid sodium salt are dissolved in 1000 parts of water. The solution is mixed with 400 parts of methyl cyclo-hexanone. A clear solution is obtained which can be strongly diluted with water without becoming dull by a separation of methyl cyclo-hexanone and which is very suitable for use as a cleaning or washing agent.

When employing less di-butyl-aniline sodium sulfonate, methyl cyclo-hexanone or another difficultly soluble organic liquid is emulsified in an excellent manner, but no clear solution is obtained.

We do not lay claim, in this application, to the benzyl-aniline or ethyl-benzyl-aniline sulfonic acids since they are not efficient for the purpose of the present invention.

What we claim is:

1. The process of preparing aqueous emulsions of organic liquids difficultly soluble in water characterized by an addition of di-amyl-alpha-naphthylamine sulfonic acid sodium salt.

2. The process of producing stable dispersions of materials in water which comprises treating the materials with an aromatic sulfonic acid which is incapable of precipitating glue from its aqueous solution, contains at least one alkyl group and at least one active substituent, selected from the group consisting of amino and hydroxyl groups, and has a higher wetting power than benzyl-aniline and ethyl-benzyl-aniline sulfonic acids.

3. The process of preparing aqueous emulsions of organic liquids difficultly soluble in water characterized by an addition of an aromatic sulfonic acid, which is incapable of precipitating glue from its aqueous solution, contains at least one alkyl group and at least one active substituent selected from the group consisting of amino and hydrcxyl groups and

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Patented Oct. 1, 1929 **1,730,037**

UNITED STATES PATENT OFFICE

FRITZ GÜNTHER AND JOSEPH NÜSSLEIN, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNORS TO I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, OF FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY

SOAP PREPARATION

No Drawing. Application filed May 29, 1926, Serial No. 112,675, and in Germany June 2, 1925.

It is known that soaps (which term is hereinafter used in a broad sense including soft soaps, grain soaps, resin soaps, sulfonated caster oil or the salts thereof such as Turkey red oil and the like) cannot be employed in acid baths or in baths containing calcium or mangnesium salts, as they are decomposed with the separation of free fatty acids or with the formation of insoluble salts. Also, soap cannot be employed in salt water, for example sea-water.

We have now found that also in the above-mentioned acid baths and baths containing calcium or magnesium salts or salt water no separation of fatty acids or insoluble salts occurs and that accordingly the soaps are rendered useful therein, provided the soaps or the baths contain aromatic sulfonic acids possessing a high wetting power. As examples of such aromatic sulfonic acids we mention sulfonic acids of aromatic compounds containing hydrocarbon residues in their molecule, such as may be obtained for example by condensing aromatic sulfonic acids with aliphatic, hydroaromatic or aromatic-aliphatic alcohols, such as isopropyl alcohol, butyl alcohols, cyclo-hexanol, benzyl-alcohol and the like. The side chains may also link together two aromatic nuclei as is the case for instance in the condensation products of formaldehyde with naphthalene sulfonic acids. The said sulfonic acids may also contain other substituents such as halogen atoms or nitro or amino or hydroxyl groups and the side chain may also be attached to such substituents as for example in amyl-naphthylamine sulfonic acids and the like. The aromatic sulfonic acids may be employed in the state of free acids or of salts.

For example, soap may be employed in the process of dyeing in an acid bath by adding an aromatic sulfonic acid possessing a high wetting power, and very even dyeings are thereby obtained; it is possible to use even such dyestuffs which hitherto could only find restricted use on account of their small capability of producing even dyeings; further, the goods are penetrated with the color more thoroughly than without the said additions, the fastness to rubbing is increased and the time necessary for dyeing is diminished. Further, by our present invention wool fibre is protected from being damaged by alkalis as it can be washed and fulled in an acid bath, whereby often also a better result is obtained than with the methods heretofore employed.

The sulfonic acid of the character described or a salt thereof may be added to the bath containing a soap such as dyeing baths, carbonization baths, i. e. baths containing sulfuric acid in a strength of from 2 to 4° Baumé, fulling baths, washing or bleaching baths and the like, or mixtures of soaps with the sulfonic acids or their salts may be prepared beforehand. The said soaps may be neutral, alkaline or superfatted, and they may be employed in solution, or in the form of a paste or in the solid form. These preparations have the advantage of being easily stored or shipped and can be applied in a very simple manner. They possess the desirable properties of both the soaps and the sulfonic acids, and are especially stable against acid and hard or salt water. They produce a good lather with aqueous solutions containing acids or calcium or magnesium salts or similar obnoxious components such as produce precipitations with soaps, and thus counteract their effect and are capable of easily wetting. They can be employed for example for washing and cleaning purposes with water containing calcium or other salts or as an addition to dyeing baths containing acids or obnoxious salts. They are also very suitable for use with sea-water.

The said mixtures can be prepared in any desired manner, for example by heating a soap until it has entirely melted, and mixing the melt with the sulfonic acid or its salt or with a concentrated solution thereof or by kneading the soap with the dry salt and pressing the mixture to cakes or by mixing both in a powdery state or by adding the sulfonic acid during the saponification process. A mixture which is very suitable for most purposes consists for example of 80 parts of ordinary soap and 20 parts of a sulfonic acid of the character mentioned or a salt thereof. In case of water containing only small quan-

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Patented Sept. 20, 1938 **2,130,668**

UNITED STATES PATENT OFFICE

2,130,668

WETTING, CLEANSING, AND EMULSIFYING AGENT

Fritz Günther, Ludwigshafen-on-the-Rhine, Germany, assignor to I. G. Farbenindustrie Aktiengesellschaft, Frankfort-on-the-Main, Germany, a corporation of Germany

No Drawing. Application December 9, 1927, Serial No. 239,003. In Germany December 11, 1926

23 Claims. (Cl. 260—290)

The present invention relates to the manufacture and production of new wetting, cleansing and emulsifying agents.

I have found that products imparting to aqueous liquids excellent wetting, cleansing and emulsifying properties are obtained by mixing an organic acid wetting agent selected from the group consisting of sulfuric acid derivatives of high wetting power, that means true sulfonic acids of high wetting power, or sulfuric acid esters of the nature of Turkey-red oil, and naphthenic acids, with up to equivalent amounts of nitrogen-containing organic bases. Organic sulfonic acids of high wetting power which are to be employed according to the present invention comprise only such acids of which a 0.5 per cent aqueous solution of their sodium salt wets a felt-like textile fabric, for example, of wool or cotton in at the most one hour, but preferably in a much shorter time, for example in a few minutes. Organic sulfonic acids of the said kind which are particularly suitable for the purpose of the present invention are aromatic sulfonic acids containing alkyl-, aralkyl-, cycloalkyl-, or aryl groups, which may, if desired, be further substituted, whether in the nucleus or in the side chain, further sulfonic acids of aliphatic or hydroaromatic compounds, for example the sulfonation products of mineral oils, aliphatic tar oils, naphthenic acids and the like, as well as the known fat-splitting acids, or the ligno-sulfonic acids contained in sulfite-cellulose waste liquor. These acids yield excellent wetting, cleansing and emulsifying agents when treated with organic nitrogen-containing bases in the above specified amounts. As organic bases suitable for preparing the said agents, according to the present invention, aliphatic amines, such as methylamine or ethylamine, mono-, di-, or triethanolamine, but particularly the heterocyclic nitrogen-containing bases, such as pyridine and its homologues and derivatives, and the like, may be mentioned.

The said components for manufacturing the new products imparting to aqueous liquids a high wetting, cleansing and emulsifying action may be prepared before use by mixing them with each other in the absence of water in up to equivalent amounts, the nitrogenous base being always employed in a substantial quantity, i. e., in a quantity of at least 10 per cent of the equivalent amount, or by preparing them in the form of their salts by working in aqueous solution, or they may be produced only in the liquid or preparation with which they are to be used, by adding the required components thereto. It is to be understood that in the production of the new products no heating or other strong condition of working is applied, since otherwise condensation or other reactions would occur which may lead to the formation of water insoluble products.

When the substances are mixed no heat is applied and the usual reaction of an acid with a base occurs, namely, the formation of a salt corresponding for example to the following equations:

The fact that a salt is actually formed is evidenced by the reduction of the acidity of the solutions of the acids when the nitrogenous base desired is added. These salts, moreover, are water-soluble salts since the formation of amides or imides would become obvious by the insolubility of the products.

It is not essential for the purpose of this invention that the equivalent quantity of the organic nitrogen bases is added to the acids. Even acids which are only partially so saturated exhibit an excellent wetting action. Very useful effects are also obtained with mixed salts prepared by adding to the said acids either several different organic nitrogen bases, or by replacing a portion of the latter by inorganic bases, such as caustic soda, ammonia and the like.

For preparing aqueous liquids of high wetting and cleansing properties it is generally sufficient to add to the liquids about 0.5 per cent of the said preparations. Aqueous liquids of a higher concentration, however, may also be used. If the said preparations are to be used for preparing highly stable aqueous emulsions or suspensions, or even clear aqueous solutions of sub-

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Patented July 12, 1932 **1,867,022**

UNITED STATES PATENT OFFICE

FERDINAND MÜNZ AND KARL KELLER, OF FRANKFORT-ON-THE-MAIN-FECHENHEIM, AND FRITZ GÜNTHER, OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY, ASSIGNORS, BY MESNE ASSIGNMENTS, TO I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, OF FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY

WETTING, CLEANSING, AND EMULSIFYING AGENTS AND PROCESS OF MAKING SAME

No Drawing. Application filed December 11, 1928, Serial No. 325,383, and in Germany December 15, 1927.

The present invention relates to wetting, cleansing and emulsifying agents and more particularly to mixtures of an alkylated naphthalene sulfonic acid compound with up to approximately equivalent amounts of an organic quaternary ammonium compound having the general formula:

wherein X means OH or an acid residue, Z represents an alkyl or an aralkyl group and R represents phenyl or naphthyl.

We have found that it is possible to obtain these products by mixing an organic sulfuric acid compound of the aforesaid kind with an organic quaternary ammonium compound, which may be done either by neutralizing the organic sulfuric acid derivative with the quaternary ammonium base or more simply by mixing an alkali salt of a wetting agent of the above mentioned kind with a salt of the quaternary ammonium base.

These new ammonium salts surpass the alkali salts of the wetting agents as to their wetting capacity even in an alkaline bath. The solubility of our new ammonium salts is already sufficient for their technical use, but it may be much increased by an addition of a protective colloid, of soaps of Turkey red oils or in a very simple manner by using an excess of the wetting agent applied, for instance about 9 parts of the wetting agent to one part of ammonium base.

In order to further illustrate our invention the following examples are given, the parts being by weight and all temperatures in centigrade degrees, but it may be understood that our invention is not limited to the particular products or reacting conditions mentioned therein.

Example 1

100 parts of the sodium salt of a dibutyl-naphthalene-sulfonic acid are mixed with 20 parts of dimethyl-phenyl-benzyl-ammonium-chloride. The mixture thus obtained is a dry, nearly colorless powder soluble in water to form a barely opalescent solution. It possesses a substantially higher wetting power than the wetting agent applied alone, in a neutral medium as well as in an acidic or an alkaline one. The probable course of the reaction may be illustrated as follows:

When using tetraethylammonium iodide as the quaternary ammonium salt, a product of similar properties is obtained.

Example 2

100 parts of free dibutyl-naphthalene sulfonic acid are introduced into a solution of 25 parts of the methyl-sulfuric acid salt of trimethyl-β-naphthyl-ammonium in about 250 parts of water. When the reaction is complete, the mass is allowed to settle. The bottom layer is a thick oil being the dibutyl-naphthalene sulfonic acid salt of trimethyl-β-naphthyl-ammonium. The oil may be used per se or mixed with a suitable Turkey red oil preparation in which case its solubility increases. The probable course of reaction may be illustrated as follows:

A similar product is obtained by starting from trimethyl-α-naphthyl-ammonium

Figure 3.201: Fritz Günther developed synthetic organic detergents from 1916 to the 1930s.

DEUTSCHES REICH

AUSGEGEBEN AM
11. OKTOBER 1940

REICHSPATENTAMT
PATENTSCHRIFT
№ 697 324
KLASSE 8o
I 49080 IVd/8 o

I. G. Farbenindustrie Akt.-Ges. in Frankfurt, Main*)
Wasch- und Netzmittel

Patentiert im Deutschen Reiche vom 25. März 1933 ab
Patenterteilung bekanntgemacht am 12. September 1940

Es wurde gefunden, daß säureamidartige Kondensationsprodukte aus höhermolekularen Carbonsäuren und wasserlöslichen, durch Abbau von Eiweißstoffen erhaltenen Peptidgemischen sich besonders gut als Wasch- und Netzmittel eignen.

Es wurde schon vorgeschlagen, bei der Behandlung von Textilien u. dgl. Kondensationsprodukte von höhermolekularen Carbonsäuren einerseits mit einfachen einheitlichen Aminocarbonsäuren vom Typ des Glykokolls, anderseits mit hochmolekularen Eiweißspaltprodukten vom Typ der Lysalbin- und Protalbinsäure zu verwenden. Diesen bekannten Produkten gegenüber zeichnen sich die vorliegenden neuen Hilfsmittel aus durch ihre überlegene Waschwirkung, beispielsweise in der alkalischen Wollwäsche, und ihr erhöhtes Netzvermögen, besonders bei höherer Temperatur; sie übertreffen außerdem die Kondensationsprodukte einfacher einheitlicher Aminocarbonsäuren weit hinsichtlich der Säurebeständigkeit und des Kalkseifendispergiervermögens.

Die neuen Hilfsmittel sind durch in an sich bekannter Weise erfolgende amidartige Verknüpfung von Resten höhermolekularer Carbonsäuren mit wasserlöslichen Peptidgemischen, wie sie bei der weitgehenden Hydrolyse von Eiweißstoffen aller Art, wie Leder-, Haut-, Horn- oder Haarabfällen, Streckfleisch oder Schlachthofabfällen, Wollabfällen u. dgl., entstehen, erhältlich. Als Carbonsäurekomponente enthalten sie solche Säuren, die einen organischen Rest mit mindestens acht Kohlenstoffatomen besitzen, z. B. Undecylen-, Laurin-, Palmitin-, Stearin-, Öl- und Ricinolsäure sowie die aus Kokosöl, Palmkernöl, Baumwollsaatöl, Leinöl, Sojaöl, Holzöl, Rüböl, Tran u. dgl. erhältlichen Fettsäuregemische, sowie Fettsäuregemische aus der Oxydation von Kohlenwasserstoffen, wie Paraffin, oder von Rückständen der Verarbeitung von Fetten, Ölen oder Fettsäuren derselben; ferner Härtungsprodukte der genannten ungesättigten Säuren oder ihrer Gemische sowie Naphthensäuren, Harzsäuren, wie diejenigen des Tallöls, des natürlichen oder hydrierten Kolophoniums, aromatische, cycloaliphatische und hydroaromatische Carbonsäuren, z. B. Naphthoe-, Oxynaphthoesäuren oder Tetrahydronaphthalincarbonsäure.

Die Produkte lassen sich als Wasch- und Netzmittel bei den verschiedenartigsten Ver-

*) *Von dem Patentsucher sind als die Erfinder angegeben worden:*
Dr. Ludwig Orthner in Frankfurt, Main, und Dr. Georg Meyer in Leverkusen-I. G. Werk.

Erteilt auf Grund der Verordnung vom 12. Mai 1943
(RGBl. II S. 150)

DEUTSCHES REICH

AUSGEGEBEN AM
13. JUNI 1940

REICHSPATENTAMT
PATENTSCHRIFT
№ 692 029
KLASSE 8i GRUPPE 5
I 54725 IVd/8 i

I. G. Farbenindustrie Akt.-Ges. in Frankfurt, Main*)
Waschmittel

Patentiert im Deutschen Reiche vom 5. April 1936 ab
Patenterteilung bekanntgemacht am 16. Mai 1940

Man hat schon vorgeschlagen, wasserlösliche Derivate der Cellulose, z. B. lösliche Salze der Celluloseschwefelsäureester, zum Schlichten und als Dispergierungsmittel zu verwenden. Eine praktische Anwendung als Waschmittel haben die wasserlöslichen Cellulosederivate bisher nicht gefunden, weil sie den Anforderungen, denen bei diesem Verwendungszweck genügt werden muß, nicht entsprochen haben.

Es wurde nun gefunden, daß man gut wirksame Waschmittel erhält, wenn man härtebeständige, synthetische organische Waschmittel mit löslichen Salzen von solchen Sulfonierungsprodukten der Cellulose oder von Celluloseäthern vermischt, in denen die Cellulose infolge besonders schonender Durchführung der Sulfonierung praktisch nicht abgebaut ist. Diese Sulfonierungsprodukte, beispielsweise von Cellulose, Methylcellulose, Oxäthylcellulose oder Methyloxäthylcellulose, geben verhältnismäßig viscose Lösungen.

Die Cellulosesulfonierungsprodukte, die für die erfindungsgemäßen Waschmittelmischungen verwendet werden, sind z. B. durch Einwirkung von Pyridinsulfonsäure bzw. Gemischen aus Pyridin und Chlorsulfonsäure auf Cellulose oder Celluloseäther bei verhältnismäßig niedrigen Temperaturen erhältlich. Ein anderer Weg ist der, daß man die Cellulose in flüssiger schwefliger Säure verteilt und Oleum oder Chlorsulfonsäure oder gasförmiges Schwefeltrioxyd zuführt. Im Schrifttum finden sich Angaben über die Herstellung dieser Stoffe, z. B. in Berichte der Deutschen Chemischen Gesellschaft, Jahrgang 61 (1928), S. 754 ff., und in der amerikanischen Patentschrift 2 025 073.

Waschmittel, denen die erfindungsgemäß anzuwendenden Cellulosesulfonierungsprodukte zuzusetzen sind, sind alle organischen Waschmittel, die gegen die Härtebildner des Wassers beständig sind, z. B. die Salze der sauren Schwefelsäureester von Fettalkoholen, Kondensationsprodukte aus Fettsäuren und Oxy- oder Aminoalkylsulfonsäuren oder Sulfonierungsprodukte von Verbindungen, die durch Einwirkung von Äthylenoxyd auf Hydroxyl-, Carboxyl- oder Aminogruppen enthaltende Stoffe entstehen.

Durch die Zugabe der Cellulosesulfonierungsprodukte zu den härtebeständigen Waschmitteln werden Produkte erhalten, die ein besseres Waschvermögen als die härtebeständigen Waschmittel allein besitzen.

*) *Von dem Patentsucher sind als die Erfinder angegeben worden:*
Dr. Ludwig Orthner in Frankfurt, Main, Dr. Karl Daimler in Frankfurt, Main-Höchst und Dr. Heinz Sönke in Bad Soden, Taunus.

AUSGEGEBEN AM
15. JANUAR 1945

DEUTSCHES REICH

REICHSPATENTAMT
PATENTSCHRIFT
№ 747 468
KLASSE 8o
I 60253 IVd/8 o

Dr. Ludwig Orthner, Dr. Carl Platz in Frankfurt, Main,
Dr. Hans Keller in Frankfurt, Main-Höchst
und Dr. Heinz Sönke, Bad Soden, Taunus,
sind als Erfinder genannt worden

I. G. Farbenindustrie AG. in Frankfurt, Main
Netzmittel

Patentiert im Deutschen Reich vom 18. Januar 1938 an
Patenterteilung bekanntgemacht am 3. Februar 1944
Gemäß § 2 Abs. 2 der Verordnung vom 28. April 1938 ist die Erklärung abgegeben worden, daß sich der Schutz auf das Land Österreich erstrecken soll

Es wurde gefunden, daß man Verbindungen, die durch direkte oder indirekte Einführung von hydrophilen Gruppen in Amine der allgemeinen Formel

$$\begin{array}{c} H \\ | \\ R - C - R_1 \\ | \\ N \\ \diagup \ \diagdown \\ R_2 \quad R_3 \end{array}$$

wobei R und R_1 aliphatische Kohlenwasserstoffreste mit mindestens 3 Kohlenstoffatomen bedeuten, und R und R_1 zusammen mindestens 11 Kohlenstoffatome besitzen und R_2 und R_3 Wasserstoff oder einen niedrigmolekularen Alkyl- oder Aralkylrest, der gegebnenenfalls durch Hydroxylgruppen substituiert ist, bedeuten, hergestellt werden, mit Vorteil als Netzmittel verwenden kann, gegebenenfalls in Verbindung mit anderen Textilhilfsmitteln. Das Netzvermögen der Verbindungen, auch in Mercerisierbädern, ist besonders ausgeprägt bei Stoffen, bei welchen die Reste R und R_1 verzweigte Ketten besitzen. Die Produkte, die gemäß der Erfindung als Netzmittel zur Verwendung kommen, besitzen gegenüber anderen Verbindungen von vergleichbarer Konstitution bei niedriger oder bei höherer Temperatur in neutralem oder alkalischem Me-

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den ist die Hydrierung beendet. Man filtriert vom Katalysator ab, destilliert Methanol ab, trocknet das zurückbleibende Amin und erhält 1200 Gewichtsteile eines Gemisches an tertiären Aminen. Bei der Destillation im Vakuum gehen zwischen 115 bis 165° bei 3 mm Druck 1150 Gewichtsteile eines farblosen Öles über, welches 5,03% titrierbaren Stickstoff und 4,98 % tertiären Stickstoff enthält.

28 Gewichtsteile des so erhaltenen Amingemisches versetzt man mit 18 Gewichtsteilen Bromessigsäureäthylester und rührt bei 90 bis 100° etwa 4 Stunden lang. Das Reaktionsprodukt ist in kaltem Wasser klar löslich und stellt einen Betainester dar, der durch Natronlauge leicht verseifbar ist. Das Reaktionsprodukt kann entweder als solches oder nach der Verseifung gebraucht werden. Das Produkt kann aber auch dadurch hergestellt werden, daß man an Stelle von Bromessigsäureäthylester Chloressigsäureäthylester verwendet, dem man einige Prozent Bromessigsäureäthylester zusetzt.

Beispiel 13

Ein Netzmittel mit guten Beständigkeitseigenschaften erhält man nach folgender Vorschrift:

28 Gewichtsteile 10-Aminononadecan versetzt man mit 0,5 g Natriummethylat und leitet bei 150 bis 160° 13 Gewichtsteile Äthylenoxyd ein. Dann versetzt man das Reaktionsprodukt mit 14 Gewichtsteilen Dimethylsulfat und rührt bei erhöhter Temperatur, bis sich das Reaktionsprodukt klar in Wasser löst und auch beim Versetzen mit wenig verdünnter Natronlauge in Lösung bleibt. Das Reaktionsprodukt besitzt folgende Konstitution:

$$\begin{array}{c} C_9H_{18}\cdot CH\cdot C_9H_{18} \\ | \\ CH_3\cdot N\cdot (CH_2 - CH_2O)_3H \\ \diagup \ \diagdown \\ CH_3 \quad OSO_3CH_3 \end{array}$$

Beispiel 14

Als gutes Netzmittel kann man ein Produkt, das man auf folgende Weise erhält, verwenden:

34 Gewichtsteile 8-Aminotricosan versetzt man bei 60 bis 70° unter Rühren mit 14 Gewichtsteilen Dimethylsulfat und rührt, bis sich eine Probe klar in Wasser löst und auch beim Versetzen mit wenig verdünnter Natronlauge klar bleibt.

Beispiel 15

Ein Netzmittel von großer Elektrolytunempfindlichkeit erhält man nach folgender Arbeitsweise:

6-Aminotricosan wird auf die gleiche Weise, wie im Beispiel 12 beschrieben, in 6-Dimethylaminotricosan übergeführt. 36 Gewichtsteile dieses Amins werden mit 2 Gewichtsteilen Bromessigsäureäthylester und 12 Gewichtsteilen Chloressigsäuremethylester versetzt und 5 Stunden unter Rühren auf 85 bis 90° am Rückflußkühler erhitzt. Nun wird mit der Lösung von 5,6 Gewichtsteilen Kaliumhydroxyd in 45 Gewichtsteilen Wasser verrührt und kurze Zeit bei 50 bis 60° gerührt. Das Reaktionsprodukt besitzt folgende Konstitution:

$$\begin{array}{c} C_5H_{11}\cdot CH\cdot C_{17}H_{35} \\ |+ \\ CH_3\cdot N\cdot CH_2\cdot COO - \\ | \\ CH_3 \end{array}$$

Beispiel 16

Als Heißnetzmittel eignet sich ein Produkt, das man wie folgt erhält:

Man führt 4-Aminoheptadecan in analoger Weise, wie es im Beispiel 4 beschrieben ist, in das Isocyanat über. Nun läßt man zu einer Lösung von 22 Gewichtsteilen Metanilsäure in 40 Gewichtsteilen Wasser, dem man die Lösung von 4 Gewichtsteilen Ätznatron in 10 Gewichtsteilen Wasser zugesetzt hat, unter gutem Rühren bei etwa 75° 28 Gewichtsteile des obigen Isocyanates tropfen und rührt etwa 10 Stunden bei der angegebenen Temperatur. Das Reaktionsprodukt ist klar in Wasser löslich. Es besitzt folgende Konstitution:

$$\begin{array}{c} C_3H_7\cdot CH\cdot C_{13}H_{27} \\ | \\ NH \\ | \\ C = O \\ | \\ NHC_6H_4SO_3Na \end{array}$$

Beispiel 17

Ein Netzmittel mit großer Beständigkeit gegen Alkalien wird auf folgende Weise erhalten:

28 Gewichtsteile 4-Aminoheptadecan versetzt man mit 19 Gewichtsteilen sulfoessigsaurem Natrium ($HO_2C\cdot CH_2\cdot SO_3Na$) und erhitzt auf 150 bis 160°, wobei man das auftretende Reaktionswasser azeotropisch mittels Xylol abdestilliert. Nach Beendigung der Wasserabspaltung und Entfernung des Xylols erhält man ein in heißem Wasser klar lösliches Produkt, das folgende Konstitution besitzt:

$$\begin{array}{c} C_3H_7\cdot CH\cdot C_{13}H_{27} \\ | \\ NH \\ | \\ O = C\cdot CH_2SO_3Na \end{array}$$

Figure 3.202: Hermann Ludwig Orthner developed synthetic organic detergents from the 1930s to 1945.

3.9.5 Chemical Fabric Treatments

Scientists at I.G. Farben developed a wide variety of chemical treatments to make clothing and other fabrics resistant to fire, water, stains, wrinkling, etc. By the early 1940s, those chemical fabric treatments were in widespread production and use in the German-speaking world. Especially important in this area were Gustav Schwen's (German, 18??–19??) group of chemists at I.G. Farben Ludwigshafen and August Gutmann's (German, 18??–19??) group at I.G. Farben Höchst.

After the war, those chemical fabric treatments were closely inspected and eagerly adopted by Allied countries. Figures 3.203–3.205 show examples from one postwar Allied report, BIOS 518, *Textile Auxiliary Products of I.G. Farbenindustrie: Application, Testing and Miscellaneous Information.*

Another report, BIOS 698, *Survey of the German Heavy Textile Proofing Industry*, explained the great importance and innovation of the chemical treatments, for example for making fabrics simultaneously fire-retardant and water-resistant (especially useful for protective clothing for firefighters):

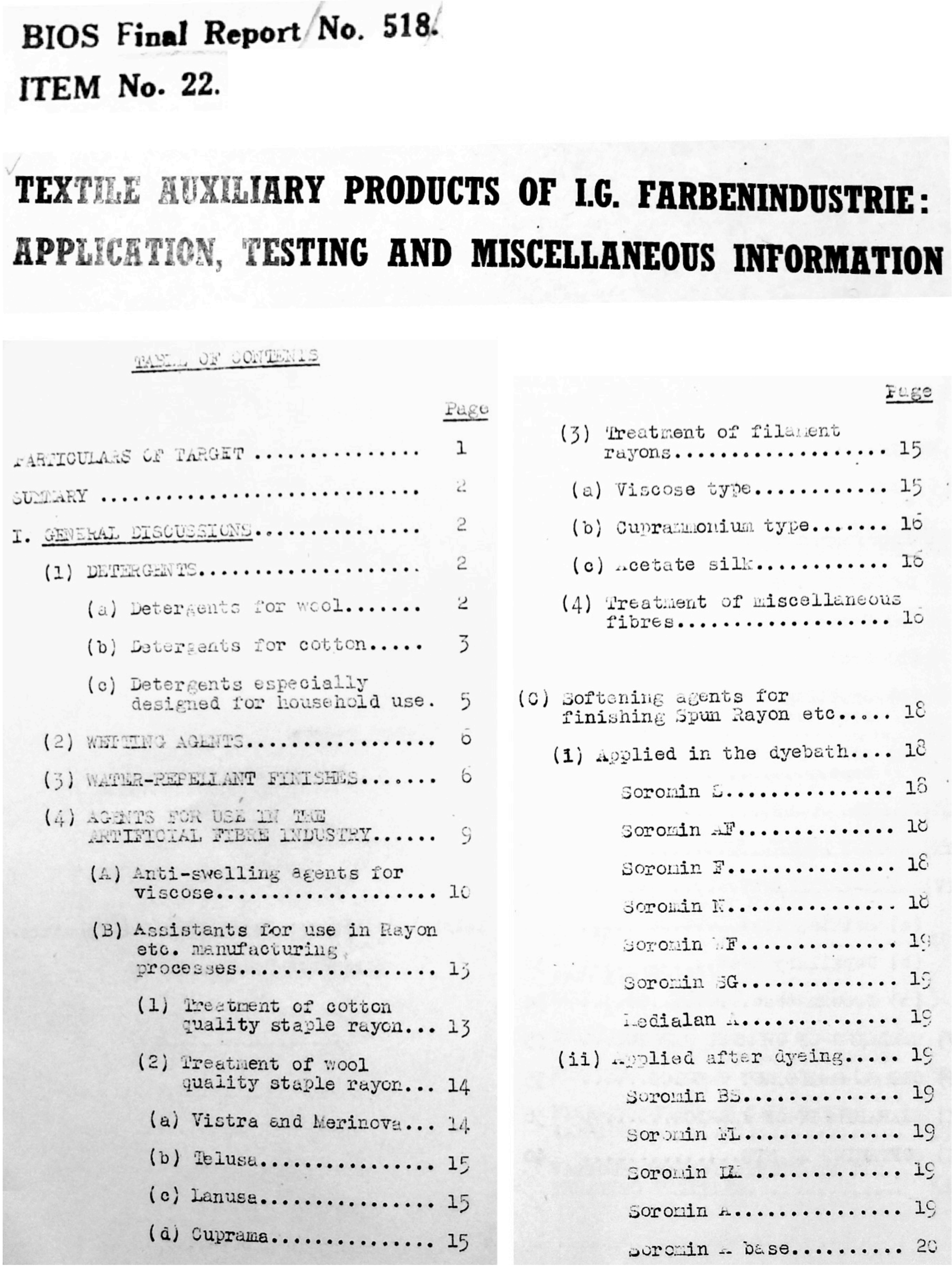
> FIREPROOFING
>
> Several of the firms visited had experience of this type of proofing mainly using the I.G. Akaustan products. The latter are mainly water soluble ammonium salts but Akaustan S is of particular interest in that it gives a water-insoluble fireproofing effect. It can be applied simultaneously with Persistol to give combined fireproofness and water repellency and there is reason to believe that this is probably the only known method of obtaining the combined proofing effects which does not interfere with the ventility of the cloth.

[See also FIAT 170.]

3.9.6 Firefighting Chemicals

In addition to creating fire-retardant fabrics, German-speaking scientists also made major improvements to chemical methods of fighting and extinguishing fires, and those were later adopted by Allied countries. For example, BIOS 704, *Mechanical Foam Liquid and Equipment*, reported:

> 6. <u>Conclusions and Recommendations.</u>
>
> (a) Substantial war time improvements were made in German foam fire fighting equipment.
>
> (b) Some German foam liquids are reported to be a blend of protein and synthetic materials. Protein foams were recognized as possessing the best fire extinguishing properties. Blending was necessary because of a shortage of protein materials.
>
> (c) The new standard German foam nozzle should be studied and tested.
>
> (d) The foam proportioner shown in Figure 2, has a very practical use in fire fighting. Development of a similar device for shipboard use is recommended.
>
> (e) Where adequate fire main pressure is not available to operate standard Navy foam fire fighting equipment, compressed air or carbon dioxide gas can be used to boost the pressure of water obtained from bilge pumps. Study and investigation of this principle for use on small Naval Craft is recommended.



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ITEM No. 22.

TEXTILE AUXILIARY PRODUCTS OF I.G. FARBENINDUSTRIE: APPLICATION, TESTING AND MISCELLANEOUS INFORMATION

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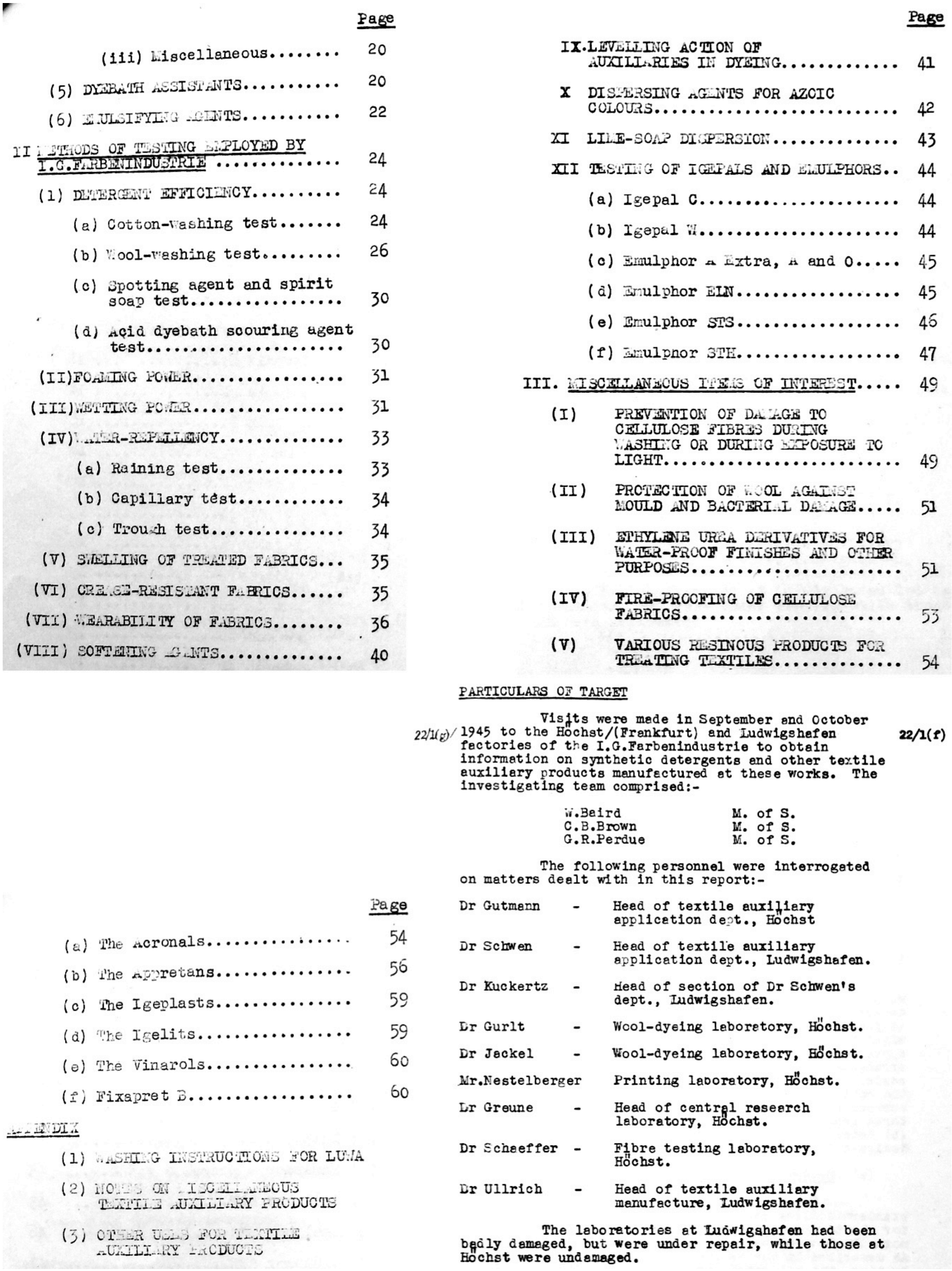
Figure 3.203: Scientists at I.G. Farben developed a wide variety of chemical treatments to make fabrics resistant to fire, water, stains, wrinkles, etc. Those chemical fabric treatments were adopted by Allied countries [BIOS 518].



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APPENDIX

(1) WASHING INSTRUCTIONS FOR LUWA

(2) NOTES ON MISCELLANEOUS TEXTILE AUXILIARY PRODUCTS

(3) OTHER USES FOR TEXTILE AUXILIARY PRODUCTS

PARTICULARS OF TARGET

22/1(g)/ Visits were made in September and October 1945 to the Höchst/(Frankfurt) and Ludwigshafen factories of the I.G.Farbenindustrie to obtain information on synthetic detergents and other textile auxiliary products manufactured at these works. The investigating team comprised:- 22/1(f)

W.Baird	M. of S.
C.B.Brown	M. of S.
G.R.Perdue	M. of S.

The following personnel were interrogated on matters dealt with in this report:-

Dr Gutmann - Head of textile auxiliary application dept., Höchst

Dr Schwen - Head of textile auxiliary application dept., Ludwigshafen.

Dr Kuckertz - Head of section of Dr Schwen's dept., Ludwigshafen.

Dr Gurlt - Wool-dyeing laboratory, Höchst.

Dr Jackel - Wool-dyeing laboratory, Höchst.

Mr.Nestelberger Printing laboratory, Höchst.

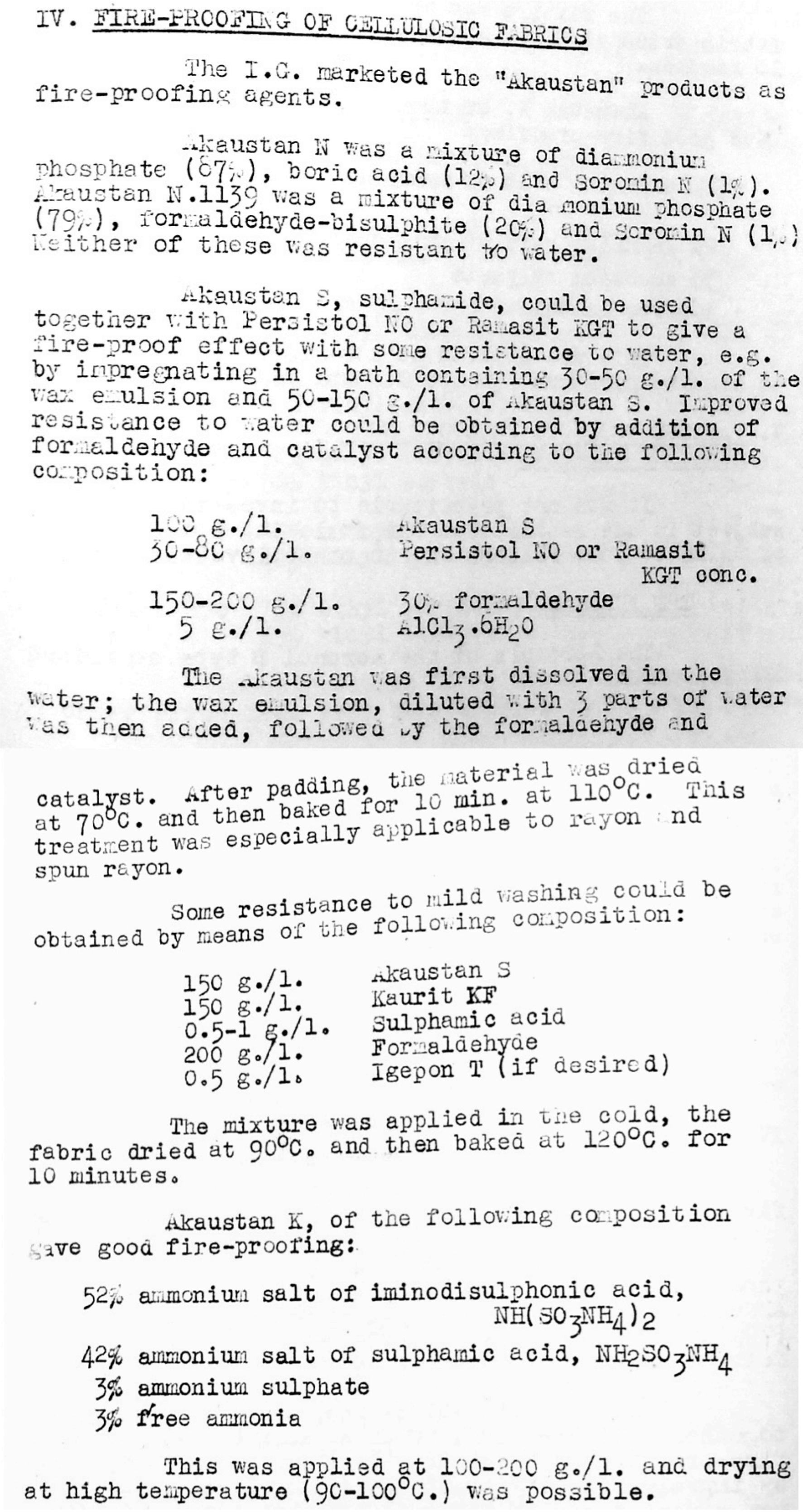
Dr Greune - Head of central research laboratory, Höchst.

Dr Scheeffer - Fibre testing laboratory, Höchst.

Dr Ullrich - Head of textile auxiliary manufacture, Ludwigshafen.

The laboratories at Ludwigshafen had been badly damaged, but were under repair, while those at Höchst were undamaged.

Figure 3.204: Scientists at I.G. Farben developed a wide variety of chemical treatments to make fabrics resistant to fire, water, stains, wrinkles, etc. Those chemical fabric treatments were adopted by Allied countries [BIOS 518].



IV. FIRE-PROOFING OF CELLULOSIC FABRICS

The I.G. marketed the "Akaustan" products as fire-proofing agents.

Akaustan N was a mixture of diammonium phosphate (67%), boric acid (12%) and Soromin N (1%). Akaustan N.1139 was a mixture of diammonium phosphate (79%), formaldehyde-bisulphite (20%) and Soromin N (1%). Neither of these was resistant to water.

Akaustan S, sulphamide, could be used together with Persistol NO or Ramasit KGT to give a fire-proof effect with some resistance to water, e.g. by impregnating in a bath containing 30-50 g./l. of the wax emulsion and 50-150 g./l. of Akaustan S. Improved resistance to water could be obtained by addition of formaldehyde and catalyst according to the following composition:

100 g./l.	Akaustan S
30-80 g./l.	Persistol NO or Ramasit KGT conc.
150-200 g./l.	30% formaldehyde
5 g./l.	$AlCl_3.6H_2O$

The Akaustan was first dissolved in the water; the wax emulsion, diluted with 3 parts of water was then added, followed by the formaldehyde and catalyst. After padding, the material was dried at 70°C. and then baked for 10 min. at 110°C. This treatment was especially applicable to rayon and spun rayon.

Some resistance to mild washing could be obtained by means of the following composition:

150 g./l.	Akaustan S
150 g./l.	Kaurit KF
0.5-1 g./l.	Sulphamic acid
200 g./l.	Formaldehyde
0.5 g./l.	Igepon T (if desired)

The mixture was applied in the cold, the fabric dried at 90°C. and then baked at 120°C. for 10 minutes.

Akaustan K, of the following composition gave good fire-proofing:

52%	ammonium salt of iminodisulphonic acid, $NH(SO_3NH_4)_2$
42%	ammonium salt of sulphamic acid, $NH_2SO_3NH_4$
3%	ammonium sulphate
3%	free ammonia

This was applied at 100-200 g./l. and drying at high temperature (90-100°C.) was possible.

Figure 3.205: Scientists at I.G. Farben developed a wide variety of chemical treatments to make fabrics resistant to fire, water, stains, wrinkles, etc. Those chemical fabric treatments were adopted by Allied countries [BIOS 518].

3.9.7 “Superglue”

The family of isocyanate “superglue” products was developed in the 1930s by a large research group led by Otto Bayer (German, 1902–1982) at I.G. Farben Leverkusen. (The same group also developed polyurethane and other related products—see Fig. 3.160.)

BIOS 719, *Interview with Professor Otto Bayer, Formerly Member of the Directorate and Head of the Scientific Laboratories of the I.G. Farbenindustrie, Leverkusen*, provided information on that program:

> This interview was to obtain information on the chemistry of isocyanates and particularly the new polyisocyanates and their derivatives which have been intensively studied in Germany for some years.
>
> Professor Bayer confirmed that he had pioneered and developed this new isocyanate chemistry and stated that at Leverkusen he had had about 50–60 chemists and 200 other workers engaged on these problems.
>
> Professor Bayer was obviously an expert in his subject and had considerable knowledge of the synthesis, analysis, chemical properties, and industrial uses of the polyisocyanates and their derivatives. [...]
>
> Professor Bayer said that about 50 polyisocyanates have been prepared and examined in the laboratory. The more important of these are the following: [...]
>
> (c) Desmodur R. Triphenylmethane triisocyanate.
>
> This material was of importance for bonding rubber and Buna to various other surfaces, e.g. metals and textiles. [...]
>
> It is suggested by Professor Bayer that the adhesion obtained by the use of polyisocyanates in bonding rubber to metal is due to a film of oxide and moisture on the metal surface, the water producing ureide bridges between two isocyanate groups and such bridges then forming complexes with metal oxide films.
>
> On the rubber interface, adhesion is thought to be due to solubility of isocyanates in the rubber and to secondary valence forces. With cellulose, bonding results from the unavoidable water present in the cellulose reacting preferentially with the isocyanate.
>
> Leather can be bonded by means of isocyanates by reaction between the amino groups of the leather and the isocyanate.

These German-developed adhesives were intensively studied by Allied countries [e.g., BIOS 629; BIOS 719; BIOS 1691; BIOS 1699] and came to be used around the world after the war.