

100 Years of Bakelite, the Material of a 1000 Uses**

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Baekeland, Leo Hendrik · bakelite · history of science · phenol formaldehyde

Introduction

“In the meantime, the natural resins... are now being gradually displaced by a variety of chemically produced resins or resinoids with decidedly superior qualities of those of the products of nature.”

From a speech given by Leo H. Baekeland in 1932.

On July 13 1907, just over one hundred years ago, Leo H. Baekeland^[1] applied for a patent for the processing of a product that had an enormous influence on the development of our technology and which changed our habits forever.^[2] Bakelite was the first synthetic plastic and was, as such, a great contributor to the entrance of mankind into the “plastics age”. It was the aim of its inventor, Leo Hendrik Baekeland (1863–1944, Figure 1), to make a material that could be used in a large variety of applications in daily life. Bakelite was revolutionary not only because it was the first fully synthetic plastic, but also because it was possible

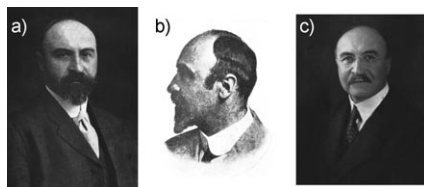


Figure 1. Leo Hendrik Baekeland a) 1904, b) 1916 on receiving the Perkin Medal in New York, and c) 1935.^[1]

to combine the production and shape processing of items made from it. Bakelite was also used as matrix for composites from a very early stage.

Herein, we describe the steps that led Baekeland to synthesize the first curable synthetic resin, or thermoset. We consider his early work and that of other chemists as well as the development of new technologies that made the invention possible. We explain why the production and use of Bakelite generated such fantastic enthusiasm and why, starting in the mid 1940s, the material experienced a slow but continuous decline. But even if the production of phenol formaldehyde is now relatively small in comparison to the other plastics, the Bakelite material had a huge impact on the sciences, on our economy, and on society as a whole. The legacy of Bakelite is strongly rooted in our civilization, in which the plastics age now prevails.

The Route to the Discovery of Bakelite

“Be it known that I, Leo H. Baekeland, a citizen of the United States, residing at Yonkers, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Condensation Products and Method of

Making Same, of which the following is a specification.”

Leo H. Baekeland, 1907.^[3]

Leo Hendrik Baekeland was born in 1863 in Ghent, Belgium. He studied chemistry and completed a doctoral thesis in Ghent under the supervision of Professor Théodore Swarts, the successor to the famous August Kekulé who established the first Belgian research laboratory in chemistry. Baekeland graduated at the age of 21 and taught as a research assistant at the same university. In 1889, he applied for and was awarded a scholarship to travel to the United States, while being promoted to “agrégé special de chimie”^[4] at the University of Ghent and keeping this position honoris causa during his travels.^[5] In the same year, he married Celine Swarts, the daughter of his doctoral advisor, whom he called “my most important discovery at the university”. In the United States, Baekeland wanted to continue the development of a photographic process that he had invented. Before traveling to the United States, Baekeland registered a patent in Belgium describing the development of photographs in water and started his own company to exploit the patent. Unfortunately, this business experience turned sour, plunging his parents, who had invested heavily in the company, into misery. In addition to the great appeal that the United States held for Europeans at the time, this private motive might also have played a role in Baekeland’s decision. He was certainly also impressed by the economic vigor of the United States, where, according to Maurois, the country was being covered by factories, and successful inventors such as Morse, Bell, and Edison found a flourishing market for their inventions.^[6] In 1891, Professor C. F. Chandler of the

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Columbia University successfully convinced him to stay and work as a chemical expert at the A. & H. Anthony Company, which developed photographic material.

Ernest Solvay, a fellow countryman of Baekeland's, obtained his first patent on the technical production of soda in 1861. This patent was the beginning of a successful worldwide business for the production of sodium carbonate by the Solvay group. Gillis notes that the destiny of Ernest Solvay was certainly also an example for Baekeland.^[1]

Baekeland then worked independently as a consultant and continued his work on photographic material. In 1892, he invented a fast-copying photographic paper called Velox and created the Nepera Chemical Company to exploit the invention. In this period, Baekeland had serious financial difficulties owing to the depression of 1893, and he worked without rest to improve the process he had invented.^[7] He sold the process and the fabrication seven years later to Eastman Kodak for the quite substantial sum of \$750 000. This sizeable amount gave him financial independence, and he could spend his time on private research. For this purpose, he converted stables in Yonkers near New York into a private laboratory (Figures 2 and 3). He started his private research there and sometimes employed assistants to help him. This was the very happiest period of his life; he could commit himself to his passion without constraint. This episode of his life recalls one of his famous contemporary scientist. Arthur Eichengrün also possessed a successful pharmaceutical patent, which allowed him to conduct independent research on cellulose acetate. However,



Figure 2. Leo H. Baekeland's laboratory in Yonkers.^[1]

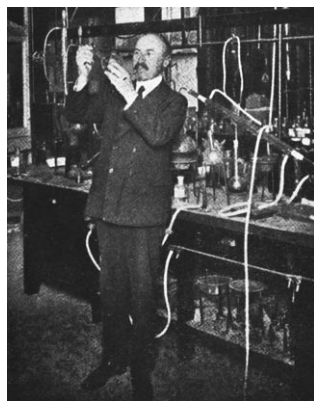


Figure 3. Leo Hendrik Baekeland in his laboratory (1930).^[1]

as a Jew in the Third Reich of the Nazis, he was confronted with much more significant difficulties.^[8]

After improving his knowledge of electrochemistry during a stay at the electrochemical laboratory of the Technological Institute of Charlottenburg (Berlin, Germany), in 1904 Baekeland collaborated with C. P. Townsend to build a plant to exploit Townsend's electrolytic cell.^[9]

The combination of intensive laboratory work on phenolic resins started in Yonkers in 1905 and a very good understanding of the investigations of his fellow chemists led him to the discovery of a material that he called Bakelite.^[2] If Baekeland alone cannot be credited with the discovery of the phenol formaldehyde resin, he was the first to develop a sufficiently inexpensive process to produce these resins on a large scale and in a controlled manner. Baekeland's motivation, as he confessed to one of his friends, was primarily to make a lot of money. He sought to replace the shellac materials that were used as insulators by the emerging electrical industry with a synthetic substitute. Shellac was a resin produced by the East Asian lac bugs *Kerria lacca* and hence was quite expensive. The demand for efficient insulating materials quickly exceeded the production of shellac, and the development of a new insulating material was of great interest. Baekeland had found a niche, and Bakelite found promising markets and applications.

Like many other breakthroughs, Bakelite could not have been invented without the intense efforts of other

chemists. Baekeland was very well-informed about the work of his colleagues on the reaction between aldehydes and phenols. He performed a comprehensive literature study of the topic and repeated experiments reported in various journals and patents.

As early as 1859 Butlerov synthesized a material derived from formaldehyde^[10] that was identified as polyformaldehyde by Staudinger in the 1920s.^[11] In 1872, Adolf von Baeyer showed that phenol reacts with aldehydes to form colorless, resinous substances.^[12,13] He noticed the presence of a reddish-brown mass produced during the reaction of pyrogallol and bitter almond oil. However, the material was not considered further because of the high cost of the synthesis and difficulties with the characterization. Similarly, Claus and Trainer synthesized a resinous material from formaldehyde and a two-fold molar excess of phenol in the presence of hydrochloric acid.^[14] The resulting resin was soluble and had a melting point of 100°C, but again no supplementary investigations were performed, because the researchers found that the material could not be crystallized. In 1891 Kleeberg employed an excess of formaldehyde and hydrochloric acid and obtained an insoluble cross-linked resin.^[15] Ammonia was used as a catalyst by Speier in the reaction of resorcinol and formaldehyde, which gave also an insoluble material.^[16] Finally, Smith was granted a patent for phenolic resins.^[17] He proposed the material to be used as a substitute for wood and ebonite (hard vulcanized rubber with a very high sulfur content) but also stressed the insulating properties of the material. At this point, research into phenolic resins accelerated significantly as their potential applications became clearer. In 1902, the Louis Blumer Company was granted a patent for the production of phenolic resins,^[18] whereas Luft introduced the use of plasticizers in the formulation of the resins.^[19] The most important pre-Baekeland experiment may be the reaction between phenol and formaldehyde in the presence of sodium hydroxide performed by Henschke, who also obtained an insoluble resin.^[20]

Thus, according to Thinius, the published knowledge before the major in-

vestigations of Baekeland on the reaction between phenol and formaldehyde can be summarized as follows:^[21] in the presence of a base or an acid, phenol and formaldehyde react to yield a resin. Depending on the experimental conditions, the resin can be soluble and fusible, or it can be a thermoset. Before Baekeland's breakthrough, the reaction between phenol and formaldehyde took place at temperatures lower than 100 °C. Thus, porous materials were obtained after long reactions, owing to the liberation of formaldehyde gas during heating. These materials were not suitable for commercial use.

Baekeland was the first to have a broad overview of the different reactions and hence fully realized the potential and the value of the phenolic resins. According to Knop and Scheib,^[22] Baekeland was the first to describe the three steps for the production of phenol formaldehyde resins.^[3] Baekeland used a large variety of organic and inorganic acids and bases to catalyze the reaction between formaldehyde and phenol. He did not observe major differences while varying the nature of the base, and he stated that the use of larger amounts of base yielded materials with poorer properties. Baekeland divided the formation of the phenol formaldehyde thermoset into three distinct phases, which are related to three different products he called A, B, and C.^[23] Product A is soluble in various solvents and can be melted. Product B is obtained by heating A; it can swell in different solvents, such as acetone, and is a solid that cannot be melted. Product B is hard at room temperature but softens if heated and can be molded under pressure. Finally, product C is obtained by heating B under pressure with or without a mould. Product C cannot be melted nor dissolved and degrades at temperatures above 300 °C.

Baekeland called the apparatus to produce product C (Figure 4) a "Bakelizer". He pointed out early on that the material was an excellent insulator compared to all other plastics known at the time. He also reported the formation of composite materials by compounding Bakelite with sawdust, colorants, and asbestos.

Baekeland stressed the difficulty in characterizing the Bakelite material,



Figure 4. The autoclave that served to produce Bakelite in Yonkers (1907–1909).

since the product was insoluble, infusible, and could be neither evaporated nor crystallized. However, he tried to understand the composition of the materials and hence proposed a chemical structure for product B (Figure 5).

Today, the reaction between phenol and formaldehyde is also understood to be divided into three steps: 1) addition of formaldehyde to phenol, 2) synthesis

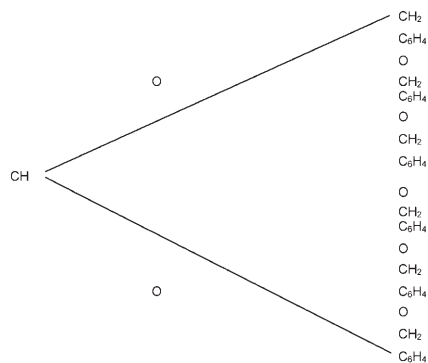


Figure 5. Baekeland's proposed structure of product B. Re-drawn according to reference [23]

of a prepolymer, and 3) cross-linking of the prepolymer. The prepolymer structure depends on the pH value of the reaction. For the polycondensation reaction, the functionality of the phenol monomer ranges from one to three, whereas the formaldehyde monomer has a functionality of two. Thus, complete cross-linking of the phenol formaldehyde polymer shown in Figure 6 is ideally performed by the addition of 1.5 mol formaldehyde to 1 mol phenol. Other monomers can also be used in the reaction (Figure 7).

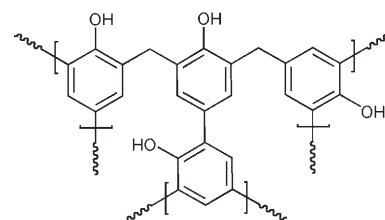


Figure 6. Chemical structure of a phenol formaldehyde Bakelite thermoset with complete three-dimensional cross-linking.

Under acidic conditions, a molar ratio of formaldehyde to phenol of less than one is used (Figure 8). The resulting product is a low-molecular-weight linear oligomer (ca. 2000 g mol⁻¹) called novolak. Novolaks are thermoplastic materials that can be subsequently cross-linked by the addition of hardeners such as hexamethylenetetramine. They are used as powders for injection and compression molding.

Under basic conditions and with a molar ratio of formaldehyde to phenol greater than 1.5, the reaction yields hydroxymethyl phenols called resols. The hydroxymethyl phenols can be subsequently cross-linked by further heat-

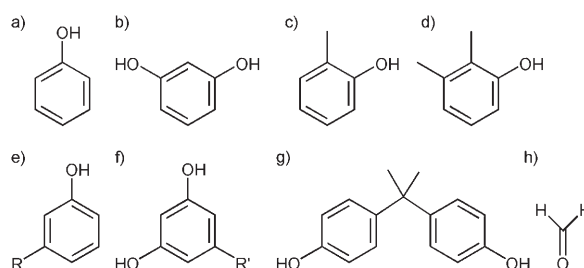


Figure 7. Chemical structures of the main components in phenolic resins: a) phenol, b) resorcinol, c) *m*-cresol, d) 2,3-xyleneol, e) cardanol, f) cardol, g) bisphenol A, h) formaldehyde. R and R' are C₁₅ hydrocarbon chains containing one or two double bonds. Not all of the cresol and xyleneol isomers are depicted.

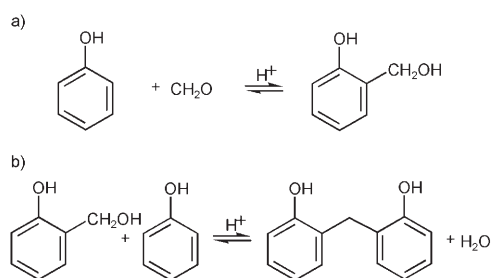


Figure 8. a) Reaction of formaldehyde and phenol under acidic conditions. b) Subsequent reaction of the unstable methylol group with phenol. The resulting di(hydroxyphenyl)methane can react further with formaldehyde or methylol groups to yield the novolak oligomers.

ing (120 °C). The degree of polycondensation is controlled by the temperature. Resols are used to make paints, lacquers, and glosses.

The Rise and Fall of Bakelite

“From the time that a man brushes his teeth in the morning with a Bakelite needled brush, until the moment he falls back upon his Bakelite bed (in the evening), all that he touches, sees, uses, will be made of this material of a thousand uses...”

The Time, September 22, 1924

Once Baekeland found a suitable process to produce small and large articles from Bakelite, he immediately patented the new invention and sought to start industrial production of the resin. The first plants were established in 1910 in the USA under the name General Bakelite Company, followed by the construction of plants in Germany, France, Canada, Britain, Sweden, Italy, and in Japan, where it was the first Western industry to be established. Especially the factory in Letmathe (Figures 9 and 10) was important in Europe until the 1970s. The resins were often composite materials in which Bakelite was mixed with fillers such as wood flour or asbestos. Originally, Baekeland was not interested in the marketing of his products; he would have preferred to license his invention. However, he found that potential industrial partners were quite reluctant to use the new, albeit simple methods, that he had developed. Moreover, Baekeland was willing to collaborate with the competi-

tion rather than fight them. Thus, he entered into an industrial collaboration with the Damard Lackquer Company, founded in 1910 in Britain, and other companies to create the Bakelite Ltd. Company.

The early production of Bakelite is closely connected to the development of electricity in industrialized countries. At the time, there was a huge need for an inexpensive insulating material for cables and electrical systems. As a result, Bakelite was first used

ucts such as rubber and ivory began to be exhausted, which increased the need for a substitute material. Indeed, Bakelite displayed properties superior to those of many natural materials: it was resistant to chemicals, heat, scratching, and dry rot.

An issue of the “*The Time*” in 1924 had a cover photograph with Baekeland, indicating that he was recognized as a known personality. The fantastic enthusiasm generated by the material is stressed by the quote from “*The Time*” cited above. The Ford Model A, for instance, was equipped with some Bakelite items. The invention coincided perfectly with the development of the automotive and electric industries. Cars, telephones, jewelry, cameras, radios, and televisions began to permeate households in industrialized countries. Thomas Edison originally chose Bakelite to construct gramophone records. Bakelite was also employed as an insulating material in electrical devices. The enthusiasm was even supported by poetry, and Mumford invented the term Bakelise to mean semantics derived from Bakelite.^[25] For Kras, Bakelite was the next logical step following cast iron in the Industrial Revolution.^[26] Cast iron was used for the creation of infrastructure and populated our landscapes, while Bakelite was used for consumer goods and populated our homes. The myriad of applications for Bakelite justifies the infinity symbol displayed in the Bakelite Corporation logo (Figure 11). The large number of lawsuits pursued by Baekeland to protect his some 400 patents also attests to the success of the material. According to Knop et al., even in 1979 more than 2/3 of phenolic resins were used as molding compounds, for insulation, and for the woodworking industry.^[22]



Figure 9. Production of phenolic resins in the Bakelite GmbH factory in Letmathe (Germany) around 1960.^[24]



Figure 10. Scientific laboratory of the Bakelite GmbH in Letmathe (Germany) around 1960.^[24]

as an insulation material, for example in radios. Later, the novelty of the material and the development of colored Bakelite resin made it an attractive material for the casings of radios and other electrical systems. By 1928, it was possible to produce transparent cast phenolic resins by a novel process, whereas the old process had produced only dark resins that were difficult to dye. At the same time, the supply of natural prod-

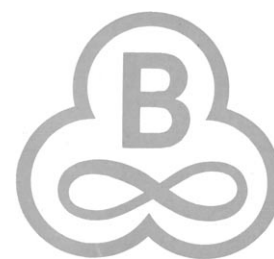


Figure 11. Logo of the Bakelite Corporation.

Baekeland also received a series of awards and honors for his numerous achievements. For example, he was honorary professor at Columbia University in New York between 1917 and 1944 (Figure 12), president of the Elec-



Figure 12. Baekeland as an Honorary Professor at Columbia University, New York (1930).^[5]

trochemical Society (1909), president of the American Institute of Chemical Engineers, and president of the American Chemical Society (1924). In 1936, he was elected as a member of the National Academy of Sciences. The many awards he received include the Nichols Medal and the Willard Gibbs Medal of the American Chemical Society (1909 and 1913), the John Scott Medal of the Franklin Institute (1910), and the Perkin Medal for industrial chemical research (1916).

Some articles produced from Bakelite are historically significant, and others became popular collectibles. Many of these articles are presented in Clark's book "Bakelite Style".^[27]

The German Volksempfänger (people's set, Figure 13a) is one of the most notorious Bakelite items, even if it is not considered a rare item by collectors. These radios were single-waveband sets used to disseminate Nazi propaganda speeches. They were also popularly known as "Goebbelsschnauze" (Goebbels's snout) after Joseph Goebbels, the minister of "public enlightenment and propaganda". Bakelite was also appreciated as a construction material for cameras (Figure 13b).

In 1939, Baekeland finally sold his company to the giant American chem-

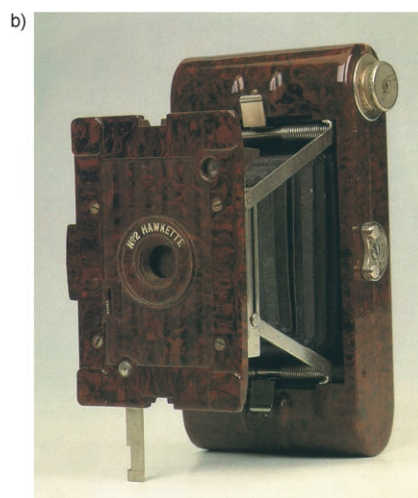


Figure 13. a) The Volksempfänger VE301GW (1935). b) Hawkette camera by Kodak (1927).^[27]

ical manufacturer Union Carbide and Carbon Corporation, now a subsidiary of The Dow Chemical Company called Union Carbide Corporation. He died in Beacon N.Y. in 1944. At the time of his death, the world production of Bakelite had reached 175 000 tons.

Despite the qualities of the Bakelite, the material experienced a decline after World War II. The strong residual odor of Bakelite became associated with this time of despair and with the poor quality of the resins synthesized during this period. Bakelite was even used to make pennies during the war, owing to a copper shortage. Bakelite's major market disadvantage was the fact that the production of the resins was more expensive than that of the new generation of plastics, that is, polyvinylchloride, polystyrene, the nylons, and the polyolefins. These new plastics could be

synthesized in large quantities by cheap processes and also displayed excellent performance. The new thermoplastic polymers could also be processed easily, and the monomers were often simple derivatives from petroleum products. Even if the production of phenol formaldehyde still continues, the golden age of Bakelite is definitively a thing of the past.

The Legacy of Bakelite: Scientific and Socioeconomic Impact

"
We can truly say that the scope of chemistry and its applications are endless.
"

From a speech by Leo H. Baekeland given in 1932.

After the invention and commercial distribution of Bakelite, there were many reports on the material. These fall into three categories: 1) The publications of Baekeland himself, explaining the chemistry and engineering of Bakelite materials.^[28–36] 2) Publications dealing with the properties of Bakelite. We find, for instance, studies of the influence of radium rays,^[37] light,^[38] and water^[39] on the material. There are also studies on the electrical^[40] and mechanical^[41] properties of Bakelite. 3) Publications describing objects made of Bakelite and used in analytical^[42–43] or biomedical applications.^[44–47]

However, as noted above, the production of Bakelite today is not very important in comparison to current commodity plastics. Therefore, Baekeland's most important legacy is not Bakelite itself, but rather the fact that he can be considered the true father of modern synthetic plastics. The early plastics were quite often a cheap substitute for luxury goods like amber or ivory. Krätz, for instance, related the story of galalith, a semisynthetic plastic made from casein.^[48] With the introduction of Bakelite, plastics emerged as materials with novel applications, such as electrical insulation and later structural materials. Thus, Bakelite is considered the starting point of the overwhelming position of plastics in daily life. Later, plastics that were cheaper and with better properties than Bakelite were more practical for industrial pro-

duction and became the leading commodity plastics. In 1979, the production by volume of plastics outstripped that of steel.

The invention of Bakelite is also related to the development of Art Déco. Examples of items produced with cast phenolic resins in the Art Déco style are shown in Figure 14. The development of this style is closely related to the burgeoning of Bakelite items in households. Interestingly, the label “Art Déco” was first used in Paris in 1966 at an exhibition referring to the “Exposition des Arts Décoratifs et Industriels Modernes” from 1925. In 1907, the “Deutsche Werkbund” (German crafts federation) was founded in Munich by German and Austrian artists who expressed the objective of bringing together art and industry. This artistic school thus had a strong affinity for industrial pro-

duction.^[49,50] In the 1930s, Coco Chanel introduced Bakelite items in jewelry accessories, and the material came into fashion. The fame of Bakelite was revived thanks to the artist Andy Warhol. In 1988, one year after his death, his collection of Bakelite items was sold at Sotheby’s New York.

Bakelite is now greatly appreciated by collectors, who still have to differentiate between real phenol formaldehyde Bakelite items and items made with parent polymers or fake items sold as Bakelite and amusingly called “Fake-lite”. It is said, for instance, that the distinguishing nose can differentiate phenol formaldehyde and urea formaldehyde when a hot needle is introduced into the item in question. If it gives a fishy smell, then it is urea formaldehyde, whereas a medical smell from formaldehyde is typical for phenol formaldehyde material. A famous hint known by the collectors is the “clunk” produced when two pieces of Bakelite are bumped together.

Conclusions

“It was 20th century alchemy. From something as vile as coal tar came a remarkably versatile substance.”

The Time, Ivan Amato, March 29, 1999

The production of phenolic resins in proportion to other plastics has decreased considerably over the years. During the oil crisis in the 1970s, there was speculation that Bakelite production could be resuscitated, since the phenol monomer can be produced from coal tar.^[21] However, the current quest for more environmentally responsible materials does not favor this option.

In a letter written to a friend in 1934, Baekeland deplored not having devoted his work “for the betterment of the human race”.^[51] However, looking back at the accomplishments stemming from Bakelite, Baekeland appears to have been unfair to himself. Baekeland’s inventions were used extensively for radio and telecommunications, in the electrical industry, and for photography. Moreover, as the “Father of Plastics”, he would have been astonished to see to what extent plastics are used and to observe that artificial muscles, prosthe-

ses, and baby bottles can all be made of plastics. The invention of Bakelite was certainly a decisive step for mankind and can reasonably be compared with the discovery of the production of ammonia. Baekeland succeeded in finding a product that could answer the huge need for a cheap, easily formed material with good mechanical properties. The use of Bakelite was the consecration of the entrance of plastic items into our households and our daily lives.

Finally, Baekeland is also an example for researchers, especially those who work in applied science, of someone who succeeded in bringing his invention “from the laboratory to the factory and from the factory to the public”.^[52]

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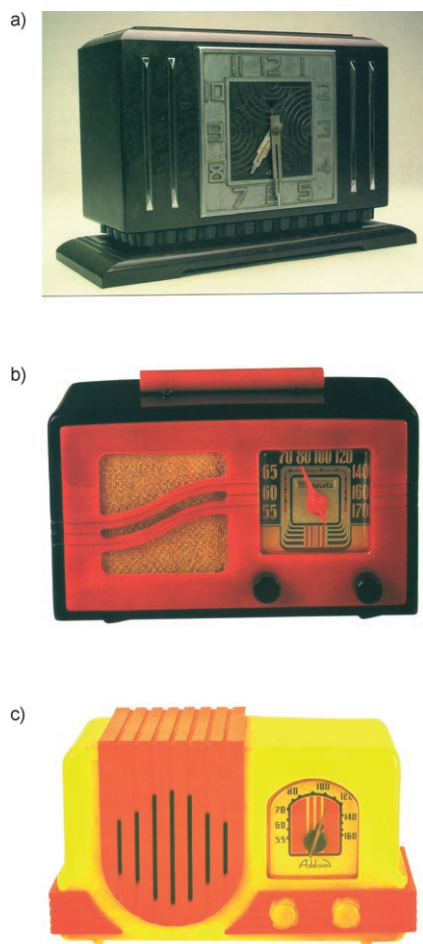


Figure 14. a) Clock by JAZ (1934). This item is typical of French Art Déco style. Cast phenolic resin and chromium; b) Motorola radio; c) Addison radio (1940).^[27]

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