

PRESERVING MODERN MARVELS: THE PLASTICS COLLECTION AT THE NATIONAL MUSEUM OF AMERICAN HISTORY

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Introduction

The Division of Medicine & Science at the Smithsonian Institution's National Museum of American History (NMAH) has a collection of historical plastics that provides research opportunities for curators and conservators alike. Representing over 3,000 objects, NMAH's collection provides a sweeping overview of the rise to dominance of synthetic materials in the United States. The diversity of its holdings, especially those made from Celluloid, Bakelite, Nylon, and PVC, serves as a valuable resource to curators and historians studying the material foundations of modern American culture. Materials in the collection, containing everything from raw materials to finished prod-

ucts with accompanying laboratory notes and trade patent papers, form an authentic and reliable material resource for conservators and conservation scientists. Conservators from the Smithsonian's Museum Conservation Institute (MCI) have utilized the collection in identifying plastics with an analytical technique called Attenuated Total Reflectance (ATR) FTIR [1], which has enabled the creation of a comprehensive reference database for polymers. This paper documents the collaborative efforts among Smithsonian curators and conservators, highlighting the study of Bakelite and related thermosetting plastics.

Bakelite, A Historical First

NMAH has a wealth of artifacts, many demonstrating unique stories of American inventiveness. It is for this reason that the artifacts in the Bakelite collection were first assembled, as Bakelite was the world's first synthetic plastic, invented in the United States by Dr. Leo H. Baekeland in 1907. Along with such common items as telephone handsets, radio cases and helmets, NMAH's Bakelite collection holds a diversity of objects including raw resin materials;

Fig 1. Portrait of Dr. Leo H. Baekeland, Bakelite photo-engraving plate, date unknown. Gift of Celine B. Karraker. Dimensions: 7 1/4" (W) 9 1/2" (H) and 3/16" (D) Smithsonian Institution.





Fig. 2. Bakelizer, cast iron, ca. 1907. Gift of Union Carbide Corporation Thru: Dr. Nathan L. Zutty, President Specialty Chemicals Division and Warren M. Anderson, Chairman. Dimensions: 35" (W) 40" (D) 72" (H). Smithsonian Institution.

unique experimental objects, such as a Bakelite music recording disc; Bakelite printing plates; salesman's materials; archival documents; and artifacts used by Baekeland (fig. 1) himself, including the first makeshift "bakelizer" (fig. 2).

Dr. Leo H. Baekeland (1863-1944), a Belgian chemist, studied chemistry at the University of Ghent under Theodore Swartz before immigrating to the United States in 1889. Soon after his arrival, Baekeland developed Velox printing paper for the nascent photo industry. After selling the rights to Velox to George Eastman, of Kodak fame, Baekeland became independently wealthy and retired to his home in Yonkers, New York to conduct chemical research on various projects.

Dr. Leo H Baekeland and His Invention

Like many of his contemporaries, Baekeland was intrigued with finding artificial replacements for natural materials that were viewed as diminishing commodities in the decades prior to the turn of the twentieth century. While others

sought substitutes for animal products such as ivory and tortoiseshell, Baekeland focused on shellac, a varnish made from insect secretions found in the trees of South Asia.

What Baekeland found proved to make a profound impact upon modern society. In 1907, he created the first successful phenolic resin by combining phenol and formaldehyde, heating the mixture as a liquid, and drying it into a solid within the "bakelizer," a large iron vessel resembling a diving bell attached to a car engine in his barn. In so doing, Baekeland introduced a new substance to the world, the first fully synthetic plastic, Bakelite.

In 1909, Baekeland was granted a patent for Bakelite from the United States Patent Office. After finding success with various applications, many done with the cooperation of the Boonton Rubber Company of New Jersey, he presented the first scientific paper concerning his invention, "The Synthesis, Constitution, and Uses of Bakelite," that September to the New York section of the American Chemical Society.

In 1910 Baekeland established the General Bakelite Company to manufacture and license Bakelite. Competitors such as Redmanol and Thomas Edison's Condensite emerged, but after some legal wrangling the rivals merged, becoming the Bakelite Corporation in 1923.

The Material

Bakelite is based on a phenol formaldehyde resin with the chemical name of polyoxybenzyl methylene glycol anhydride and is the product of the condensation of phenol with formaldehyde [2]. The pre-polymers are short polymeric chains with low molecular weight, and the final products are highly crosslinked thermoset plastics. An advantage to working with Bakelite is that by adjusting the ratio of phenol to formaldehyde, one could obtain non-linear polymers with different degree of cross-linking. Early Bakelite resin came in many grades with various composites such as paper, canvas, and linen. Later, it could be laminated or reinforced with nylon. The resin could be molded into almost any shape and was cast into rods, tubes, sheets, and blocks.

Bakelite provided some advantages over other commonly used materials. Unlike metals, Bakelite did not conduct electricity. It was not as affected by temperature as rubber or wood. With these qualities, Baekeland quickly realized that his invention would prove important

to the advancement of new technologies. He soon got to work testing the capabilities of the material.

The Bakelite Corporation called its product the "Material of a Thousand Uses," incorporating the infinity symbol within its logo to emphasize this claim. Bakelite was used in the manufacture of everything from buttons, distributor caps, and ash trays to airplane propellers, radio casings and costume jewelry. Bakelite's insulating properties made it a useful component in the burgeoning electrical field. Its aesthetic and physical properties made it an indispensable component of many automobiles, telephones, and home radios. The production of Bakelite influenced modern, streamlined design and was vital to the development of the art deco movement into streamline modern [3]. (fig.. 3)

Recognizing its historical importance, NMAH curators have amassed hundreds of artifacts illustrating Bakelite's diverse uses. This has raised questions (questions shared by most collectors of modern materials, from large museums to individual enthusiasts), about how to best store and treat synthetics for their preservation. In an effort to better understand these issues, museum curators have collaborated



with conservators to study the collection. In so doing, they have discovered that research techniques used by conservation scientists, such as ATR-FTIR could assist them in the correct identification of various synthetics, overturning mistaken understandings influenced primarily by inaccurate visual readings or erroneous information provided by donors. Meanwhile, the breadth and depth of the collection has provided a valuable resource for conservators and conservation scientists interested in identifying Bakelite (fig.. 4) and other plastics, work that has enabled the building of a reliable reference database of polymers.

Identification

The analyses conducted by the Smithsonian's Museum Conservation Institute had three main targets: to verify the material information in the curatorial files, to complement the curatorial records on dates and provenance, and to build IR references for researchers in the greater museum community.

Infrared spectroscopy is the most direct means of identifying polymers. References facilitate the quick identification of unknown polymers. However, there are limited records of historical plastics available in the current commercial IR reference spectra. Systematically building the IR reference from this premier plastics collection is one of the goals of the project. This effort will allow researchers to identify peaks caused by chemical groups associated with a specific class of plastic in correlation with known man-

Fig 4. Bakelite color samples, 35 disks, each disk is 50 mm diameter and 8 mm deep. Late 1920's. Gift of Plastics Institute of America Thru: J. Harry Dubois. Smithsonian Institution.

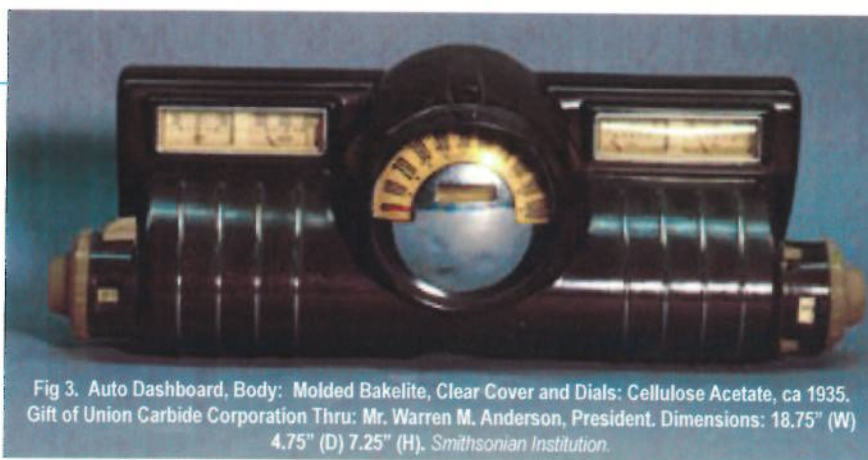


Fig 3. Auto Dashboard, Body: Molded Bakelite, Clear Cover and Dials: Cellulose Acetate, ca 1935. Gift of Union Carbide Corporation Thru: Mr. Warren M. Anderson, President. Dimensions: 18.75" (W) 4.75" (D) 7.25" (H). Smithsonian Institution.

ufacturers or dates, and strengthen research by verifying documentation of collections.

Proper identification of plastics allows curators and conservators to track down the early warning signs of degradation, such as acids released from the degraded cellulose nitrate and cellulose acetate, and to isolate problematic plastics. The analysis for this study was completed on a Thermo/Nicolet 6700 Fourier Transform Infrared Spectroscopy (FTIR) with Smart Golden Gate Diamond ATR accessory. ATR requires minimal or no sample preparation. A spectrum can be obtained 64 seconds after placing the sample in the instrument.

Malignant plastics such as cellulose nitrate, cellulose acetate, and PVC along with much less known early plastics were analyzed. An earlier survey [4] conducted in 2005--2006 by Mary Coughlin, objects conservator at NMAH, focused on those plastics that posed the greatest risk. The more stable plastics like Bakelite were not fully represented. The current project includes the survey and IR analysis of Bakelite. The comparison of Bakelite with other early thermoset plastics such as Catalin, urea formaldehyde, and thiourea formaldehyde was carried out using IR spectra to differentiate and identify each class of those plastics. Visual identification of these plastics was possible but inaccurate at times. Instrumental analysis of these early thermosets by ATR-FTIR is investigated in this study.

ATR-FTIR Analysis

The ATR-FTIR analysis of group of phenol formaldehydes such as Bakelite resin, Bakelite with a filler, and Catalin (cast phenolic with colors), and a group of urea plastics, such thiourea formaldehyde and urea formaldehyde, was carried out (Fig 5). Using IR, it is possible to distinguish between

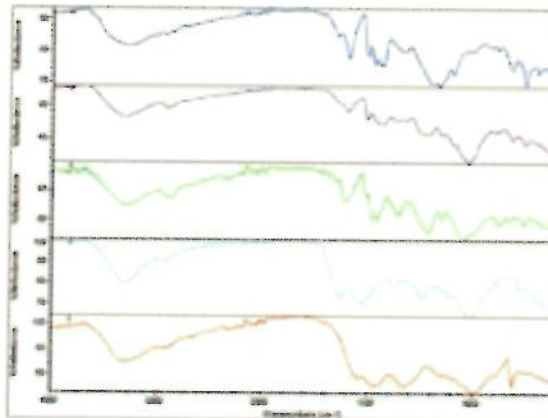
phenol formaldehyde plastics and urea or thiourea formaldehyde plastics.

The spectra of Bakelite, Bakelite resin, and Catalin (table 1) contain very similar patterns of peaks between 1330 and 1600 cm^{-1} caused by the stretching of carbon-carbon bonds within an aromatic ring. A small, nearly hidden peak near 3050 cm^{-1} is caused by the stretching of carbon-hydrogen bonds where the carbon is sp^2 hybridized, further suggesting the presence of an aromatic ring. A very broad peak centered near 3300 cm^{-1} suggests the presence of an oxygen-hydrogen bond, and peaks near 1050 cm^{-1} and 1220 cm^{-1} are caused by the bending and stretching motions of a phenolic carbon-oxygen bond. A peak near 1475 cm^{-1} is caused by the bending motion of the methylene group connecting the aromatic rings.

The infrared spectra of urea formaldehyde and thiourea formaldehyde (Table 2) show a different pattern of peaks from those of the phenol-formaldehyde plastics. In urea formaldehyde, the peaks at 1538 cm^{-1} and 1625 cm^{-1} are a distinctive indicator of the nitrogen-hydrogen bend and the carbonyl stretch of an amide. The broad peak centered at 3307 cm^{-1} is caused by the stretching of the same nitrogen-hydrogen bond and the peak at 1237 cm^{-1} is caused by the stretching of the carbon-nitrogen bond in the amide.

The most significant difference between the spectra of urea formaldehyde and thiourea formaldehyde is the absence of a peak near 1625 cm^{-1} in the spectrum of thiourea form-

Fig. 5. (From top to bottom) FT-IR spectra of A) Bakelite Resin, B) Bakelite, C) Catalin, D) Urea Formaldehyde, and E) Thiourea Formaldehyde



Wavenumber (cm ⁻¹)	Assignment
3300 (broad)	N-H stretch
2900-2950	C-H stretch (sp ³)
1625	Amide C=O stretch
1538	Amide/Thioamide N-H bend
1455	CH ₂ bend
1237-1330	Amide/Thioamide C-N stretch
993	Thioamide C=S stretch

Table 1. Characteristic peaks for urea formaldehyde and thiourea formaldehyde.

Wavenumber (cm ⁻¹)	Assignment
3300 (broad)	O-H stretch
3050	C-H stretch (sp ²)
2850-2950	C-H stretch (sp ³)
1330-1600	Aromatic C=C-C stretch
1475	CH ₂ bend
1050, 1220	Phenolic C-O stretch, bend

Table 2. Characteristic peaks for Bakelite and other phenol formaldehydes plastics.

aldehyde. Because the amide has been replaced by a thioamide, the peak caused by the carbonyl stretch is replaced by a peak at 993 cm⁻¹ caused by the stretching of the thiocarbonyl. The other peaks indicative of the thioamide are very similar to the peaks indicative of an amide.

Conservation

In general, Bakelite is not considered a high-risk plastic. Surface disfiguration such as white blooms and discoloration (dull or faded) are the two known defects. White blooms have been associated only with phenol formaldehyde with fillers, not cast phenol formaldehydes. In general, the white bloom is initiated by high humidity and fluctuation of humidity. Bakelite can be bleached by ultraviolet light. While there are no universally accepted environmental guidelines for Bakelite, the environmental guidelines for paper are often applicable.

Conclusion

Working together with the National Museum of American History's collection of historical plastics has allowed museum curators and conservators to expand their knowledge of their re-

spective fields. Using ATR-FTIR, it is possible to distinguish between phenol formaldehyde plastics and urea or thiourea formaldehyde plastics. It is possible to subdivide the phenol formaldehyde plastics into smaller classes of Bakelite, Bakelite resin, and Catalin based on smaller chemical differences in these plastics resulting from differences in manufacturing process and fillers. Visual examination, curatorial and historical information, and research in the commercial trade literature, in conjunction with ATR-FTIR instrumental analysis, provide aid in identifying Bakelite with greater certainty. Close collaboration between curators and conservators is the first step in what will be a long-term systematic study.

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