CHEMICAL & ENGINEERING NEWS
WASHINGTON, DC
WEEKLY 135,000
SEP 7 1992
BURRELLE'S

SCIENCE/TECHNOLOGY

Deterioration of Polymer Materials In Museums Challenges Chemists

9475

■ ***Current research focuses on methods to preserve plastic and synthetic fiber artifacts, from lace to space suits***

Stephen Stinson,
C&EN Northeast News Bureau

WASHINGTON, D.C.

People have spent the past 150 years making things from synthetic polymers. Now the samples piling up in museums are posing problems for curators trying to preserve them.

For examples, conservators trying to preserve plastic and synthetic fiber artifacts do not completely understand the processes of deterioration. Synthetic resins used to restore or protect objects in the past actually may be causing more damage than they prevent. And knowledge about changes in resins and paint pigments leaves doubt about whether modern artists' works will be as brilliantly colored in the 25th century as those of 15th-century masters are today.

To focus on these issues, a symposium by the Division of Polymer Chemistry explored problems encountered and progress made in the polymer chemistry of conservation science.

There are many opportunities for polymer chemists in museum conservation and restoration, according to Mary T. Baker, who organized the symposium. She is a conservator at the Conservation Analytical Laboratory of the Smithsonian Institution, Suitland, Md. In the past, emphasis was on "inorganic" analysis (as of metals in pigments). Techniques for "organic" analysis (as of polymers) that do not need unacceptably large samples from artworks or historical objects have become available only recently.

The fate of early 20th century cellulose nitrate sculptures was the subject of study by conservators Michele Derrick and Dusan Stulik of the Getty Conservation Institute in Marina del Rey, Calif., and Eugenia Ordonez of the Museum of Modern Art (MoMA) in New York City. The study focused on works of the Russian-born brothers Antoine Pevsner (1886–1962) and Naum Gabo (1890–1977). (Gabo changed his name from Pevsner to distinguish himself from his brother.)

Sculptures illustrate cellulose nitrate deterioration (above, clockwise): Detail of "Head of a Woman" by Naum Gabo (ca. 1917–20, after a work of 1916), construction in celluloid and metal, 62.2 × 48.9 × 35.4 cm, collection of the Museum of Modern Art, New York City (purchase 397.38); "Bust" and detail by Antoine Pevsner (1923–24), construction in metal and celluloid, 53 × 59.4 cm, collection of the Museum of Modern Art, New York City (purchase 396.38)

The two artists were leading exponents of a school called constructivism. As a modern art form, constructivism was supposed to incorporate such materials of modern industry as glass, metals, and plastics. Rather than rely on the mere mass of materials, the resulting constructions were to use transparent, opaque, and metallic planes and surfaces to shape the volumes of space between them and express motion.

Derrick points out that concern about deterioration of such sculptures arose from a catastrophe at the Philadelphia Museum of Art in 1960. Staff members noted drops of liquid appearing on surfaces of a sculpture titled "Construction in Space—Two Cones," done by Pevsner in 1927. They opened the sealed display case and were met with an outpouring of "noxious gas."

The next morning, the base of the construction had disintegrated and the components fallen apart.

The Getty-MoMA conservators examined six sculptures by Pevsner and Gabo created between 1917 and 1926. These years the brothers worked with transparent and opacified cellulose nitrate, sometimes using sheet-metal backgrounds and metal bolts. Today, conditions of the works range from minor fine cracks and yellowed spots to profound deterioration.

As Derrick explains, resin producers in the past rendered cellulose nitrate pliable and resilient by compounding it with 20 to 40% camphor as plasticizer and stabilizer. Phosphates, phthalates, oils, resins, and gums were also used as plasticizers.

However, camphor can sublime from such mixtures over time, leading to crazing (minute surface cracks) in camphor-depleted areas. The fine cracks expose more inner surface of the cellulose nitrate, leading to loss of more camphor, producing, in turn, more crazing. In addition, Derrick says, impurities in camphor could cause yellowing.

Cellulose nitrate also undergoes slow photochemical and thermal degradation with production of nitrogen oxides. These oxides can react with atmospheric moisture and oxygen to produce nitrous and nitric acids that can hydrolyze ester bonds, liberating more acid. Derrick calls this an autocatalytic cycle.

This mechanism may explain the incident at the Philadelphia museum. Nitrogen oxides could have built up in the sealed case. When the case was opened, air and moisture would have entered, leading to formation of large amounts of acid. Throughout her presentation, Derrick stressed the importance of the design of display cases for cellulose nitrate objects.

Gabo's "Head of a Woman," done about 1917–20 in Moscow, is in fair condition, Derrick says. Acquired by MoMA in 1938, it is constructed of pieces of cellulose nitrate, opacified to creamy white with zinc oxide. There are long cracks in some pieces, others are broken or missing, and a few are yellowed. Fourier-transform infrared (FTIR) spectroscopy identified the resin, and x-ray diffraction distinguished the zinc oxide. The investigators could not discover the cause of yellowing.

By contrast, a sculpture also called "Head of a Woman" made by Pevsner in Berlin in 1923 is in such bad shape that the Hirshhorn Museum in Washington, D.C., no longer shows it. It is made from joined pieces of transparent cellulose nitrate on a base of zinc-oxide-opacified cellulose nitrate. The base is severely yellowed and cracked. The joints between the pieces have separated.

The Hirshhorn acquired the Pevsner "Head of a Woman" in the early 1970s and displayed it in a sealed glass case. In 1982, curators noted "beads of clear, oily liquid" on the surfaces. They sent the piece to the Smithsonian's Conservation Analytical Laboratory where chemists identified the beads as aqueous basic zinc nitrate solution and cleaned the work.

Back in its sealed case at the Hirshhorn, Pevsner's "Head of a Woman" had again become densely covered with the oily beads by 1988 and had deteriorated severely. It is now stored out of sight in an open plywood box.

"Bust," created by Pevsner in Berlin in 1923–24, is in good condition at MoMA, Derrick says. It is made of translucent and zinc-oxide-opacified cellulose nitrate pieces, mounted in a copper background with iron bolts. However, there is some discoloration of translucent pieces, cracking of all pieces, corrosion of copper and iron where they contact the cellulose nitrate, and brown drops on several pieces.

Analyses of drops by FTIR and x-ray fluorescence and diffraction spectroscopy indicate that zinc and calcium nitrates and sulfates are leaching out of the resin. Affected surfaces are depleted of zinc oxide to a depth of 20 μm, resulting in a change of color to what Derrick calls "soft white" from "creamy white."

Degradation already suffered by these pieces cannot be reversed. For the future, the task is to halt the deterioration processes. One thought is to freeze

Closeup of Chardonnet artificial silk card (above, right), 1896, showing that undyed sample is in good condition, dyed sample has degraded; various colored skeins of viscose (right) made by Cross & Bevan, ca. 1914, in varying states of preservation (some faded, perhaps owing to strong light when displayed or dyes used); and woven Stearn artificial silk samples (above), 1900s, that are fragile and discolored in places. Photos courtesy of Trustees of the Science Museum, London

the pieces in the way that cellulose nitrate movie film is preserved, though Derrick says this is impractical for these sculptures. Perhaps the only solution is to design display cases based on each piece's composition and present condition so as to minimize exposure to temperature changes, humidity, and ultraviolet light.

Decomposition of cellulosic materials is also a problem in the synthetic fibers collections of the Science Museum in London, according to conservator Susan Mossman. For example, Sir Joseph Swann invented an artificial silk in 1883 by extruding acetic acid solutions of cellulose nitrate solution through pinholes into ethanol to coagulate filaments. He then denitrated the filaments by soaking them in aqueous ammonium sulfide.

Mossman showed a slide of a handkerchief made in 1883 of natural silk with a border of Swann's artificial silk lace. The lace border has darkened, become brittle, and in some places disappeared.

Hilaire de Chardonnet invented a similar artificial silk in France in 1884. His first process was to extrude ether-ethanol solutions of cellulose nitrate into water. He later turned to filament formation by evaporation of the solvent. At first de Chardonnet did not denitrate the fibers. Thus fabrics made from them were explosively flammable, and the French government banned the product. When de Chardonnet denitrated fibers, they became brittle.

Mossman showed a sample of de Chardonnet silk from 1896. Undyed fibers are in good condition, but dyed fibers are yellowed and degrading. Mossman suggests that research is needed into dyes as accelerants of decomposition of early cellulosics.

Another early synthetic fiber discussed by Mossman is viscose rayon. This fiber was invented in England in 1892 by Charles F. Cross and Edward J. Bevan. They dissolved cotton in aqueous sodium hydroxide and carbon disulfide to make a xanthate intermediate. Expression of this solution into dilute acid coagulated silky filaments of desulfurized cellulose.

Cross and Bevan founded the Viscose Spinning Syndicate with Charles Stearn, and the company began producing so-called Stearn silk in 1903. Mossman showed that sample skeins of Stern silk fiber from 1903 are in good condition, but woven goods are fragile and discolored at the edges. She suggests that a glue once used to mount samples may have caused discoloration.

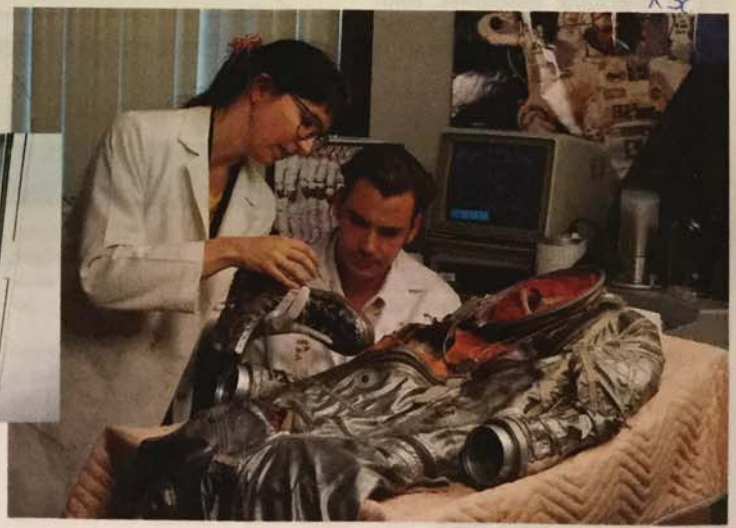
Some viscose samples made by Cross and Bevan in 1900 are in good condition; others have lost luster and have faded. Mossman notes that these samples had long been displayed under strong light, and that dyes may have accelerated degradation processes.

Modern chemists can understand the susceptibility of Gabo's and Pevsner's sculptures or of Swann's and de Chardonnet's materials to deterioration, but few people could have thought that America's historic space suits would deteriorate as rapidly as they have. These suits and the passenger capsules of their wearers are the only "documents" from former U.S. space programs, having been into space and back. Conservators Eric B. Lange at the Smithsonian's Conservation Analytical Laboratory and Ed McManus at the National Air & Space Museum, Washington, D.C., are seeking ways to halt the disintegration.

Lange says the space suits in the National Air & Space Museum were designed to function in hostile environments at temperatures from −250 to 120 °C and to be puncture-proof by micrometeorites, with zero tolerance for failure. They were made of advanced materials such as poly-*m*-phenyleneisophthalamide aramid textiles, aluminized polyimide films, and silicon fibers coated with polytetrafluoroethylene.

One obvious effect of the aging process is photolytic yellowing of once-white aramid cloth. But the most profound decomposition is in the elastomers used. For example, aluminized cloth is flaking owing to failure of a nitrile rubber adhesive. And elastomer layers intended to hold pressurized air have oxidized and disintegrated.

As Lange describes, in the first phase of degradation, polymer chains in these elastomer layers break, and the rubber becomes tacky and flows. Some suits then contort into unnatural postures with glove fingers gnarled and boots bent at right angles. Then the rubber hardens and becomes brittle, making it difficult to straighten out the suits.



Smithsonian Institution stores historic space suits at 5 °C (above); conservators Baker and Lange assess deterioration of space suit boot at the Smithsonian

Carpet illustrating how quick, cheap repairs with latex hasten deterioration. Photos show a 19th-century copy woven in India of a 15th-century Spanish carpet. Left photo shows carpet face with pattern, the other shows the back with a slathering of latex

One measure to halt such processes has been refrigerating the suits to 5 °C to stop oxidation. But low temperatures accelerate crystallization of elastomers into brittle phases. And the museum would like to have some suits out of storage for show or loan.

Lange suggests that suits removed from cold storage could be kept at 40 °C for 72 hours to reverse crystallization. But such treatment could accelerate oxidation and increase rates of flowing of degrading elastomers. And there is the question of how many chilling and warming cycles the suits can tolerate.

Current research at the Smithsonian laboratory focuses on rates of oxidation and crystallization, reversal of crystallization, and relative properties of oxidized-crystalized and oxidized-but-not-crystalized elastomers. Indeed, one unexpected finding there was that oxidized rubbers could still crystalize.

Elastomers are also the problem in conserving old carpets, says Mary Ballard of the Smithsonian laboratory. In the 1950s and 1960s, dealers routinely slathered coats of rubber latex onto carpet backs to hold repairs that had been made or just to keep carpets from sliding on floors.

The trouble is that latex coatings harden and fragment into thin, stiff shards with razor-sharp edges. Tensions in carpets rolled in storage can cause these shards to slice whole pieces out of them. And because the damage starts on the back, owners might not notice until damage is extensive.

Working with Paul Czubay, a textile conservator in Rochester, N.Y., Ballard investigated ways to remove latex backings. She notes that some of the latexes used have carboxyl groups at the ends of styrene-butadiene chains. Zinc salts are added to cross-link elastomer chains through these carboxyl groups. Conservators can use x-ray fluorescence to detect the zinc and identify this kind of latex.

Ammonia normally functions to sequester the zinc and break the cross-link, rendering the resin easier to soak off with chlorinated solvents. But because aqueous ammonia itself would be too hard on carpets containing wool or silk fibers, Ballard and Czubay experimented with 10% aqueous ammonium acetate.

Now the concern was to avoid bleeding or color changes of natural dyes used in past centuries. Ballard and Czubay dyed modern wool with traditional dyes, with and without mordants, using old recipes. Then they gauged degree of extraction of dyes into ammonium acetate solution with UV-visible spectrophotometry.

They found that the dyes catechu, cochineal, dyer's buckthorn, lac, old fustic, safflower, safflower carmine, saffron, and walnut shell were susceptible to extraction by ammonium acetate solution. These dyes as well as red sanderswood also changed color on the fiber. Dyes unaffected by ammonium acetate soaking included alkanna red, henna, indigo, kamala, logwood, orleans, turmeric, and weld.

Ballard's and Czubay's work shows that this once intractable problem of textile conservation can be solved. But conservators must test dyes in advance and think about the whole logistics of the cleaning system to be used. □

Water's effect on petroleum formation studied

WASHINGTON, D.C.

Only in the past decade has the importance of water as a source of hydrogen and oxygen in the geochemical formation of hydrocarbons, particularly petroleum, become appreciated.

Details of those geochemical processes are still being worked out. But a group of investigators at the U.S. Geological Survey in Denver has been focusing on the role of water, and has reached some preliminary conclusions.

Michael D. Lewan, one of the investigators, told the Division of Fuel Chemistry that to understand this role better a series of experiments was carried out subjecting aliquot parts of a shale sample to both hydrous and anhydrous pyrolysis in a vessel under helium pressure of 241 kilopascals (nearly 2.5 atm). Three different temperatures, 300, 330, and 350 °C, were employed with experimental runs of 72 hours. The experiments show that two major overall reactions occur under these conditions. These reactions appear to be responsible for the formation of petroleum, Lewan says.

The first reaction occurs below 330 °C and involves the cleavage of weak noncovalent bonds in the kerogen of the shale to form a soluble, high molecular weight, tarry bitumen. This bitumen im-