Care of plastics: malignant plastics

Introduction

This article is an attempt to give readers a place to start when confronted with the problems particular to plastics. Only a few aspects of the care of plastics can be presented in a newsletter format. However, I have listed the following sources and the references at the end of the article for those who need more in-depth coverage of the subject. The resources noted below should be surveyed regularly to keep abreast of rapidly accumulating new developments.

The most current and complete compilation of information on the care of plastics in museums and in private collections is the book *Plastics—Collecting and Conserving* (Quye and Williamson 1999). This contains much information from recent conferences (Saving the twentieth century—the conservation of modern materials (Grattan 1993), From marble to chocolate—the conservation of modern sculpture (Heuman 1995), Resins—ancient and modern (Wright and Townsend 1995), etc.) and updates and expands on information in the book Conservation of Plastics (Morgan 1999). As well, a short Museums and Galleries Commission Fact Sheet entitled Conservation of Plastic Collections (Winsor 1999) is available on-line at http://www.museums.gov.uk/pdf/conserv/Conservation_of_Plastics.pdf.

There is much ongoing research in the field of conservation and treatment of plastics. Most often it is reported in special conferences like those mentioned, in the proceedings of international conservation conferences, especially the Modern Materials Working Groups of the ICOM-CC, IIC, in the Newsletter and the Plastiquarian from the Plastics Historical Society, and in the reports of the Historical Plastics Research Scientists Group.

200 Years of Plastics History: A Concise History of Plastics (Fahey 2001) gives a very nice history of plastics with good hyperlinks to make navigation easy. It nicely states when and how each plastic was introduced into commerce. It lacks a nice really big comprehensive chronology, but does have a nice little one. It is available on-line at http://www.nswpmitb.com.au/historyofplastics.html.

Plastics in Collections—How Serious Is the Problem of Degradation

Several surveys of the occurrence and condition of plastics, carried out in European museums, help put the issue in perspective. The results of two of these are shown in Table 1. The surveys showed that a wide variety of plastics are present in museum collections, but that only a few percent of the objects were in dire need of treatment, and those comprised a small group of plastic types. At the British Museum, all objects in need of immediate treatment and many of those requiring essential work were PVC.

<table>
<thead>
<tr>
<th>Conservation priority</th>
<th>Victoria and Albert Museum</th>
<th>British Museum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 None: object in perfect condition</td>
<td>&gt;50%</td>
<td>27.5%</td>
</tr>
<tr>
<td>2 Low priority: slightly damaged but stable, need cleaning, await resources, no immediate danger</td>
<td>24%</td>
<td>60%</td>
</tr>
<tr>
<td>3 Essential work needed: damaged and unstable, no immediate danger</td>
<td>13%</td>
<td>12%</td>
</tr>
<tr>
<td>4 High priority: extremely unstable and requiring urgent treatment, active deterioration, destruction imminent, mostly PVC</td>
<td>1%</td>
<td>0.6%</td>
</tr>
</tbody>
</table>

At the V&A most damage is surface dirt/grease, abrasion, and scratches, with much of this from poor handling and storage prior to museum accession, plus yellowing and staining mostly from self-adhesive tape and adhesives. Of the total damage observed 23% was physical damage such as cracks, fractures, and chips, and only 13% was chemical damage, typically to rubber parts such as tires and...
tracks of model tanks and tractors. This pattern has also been observed during IR spectroscopic analytical surveys by the author.

The most serious condition problems, one finds, are related to a small number of plastics. Kenegan and Quye (1999) list the four plastics most vulnerable to ageing as poly(vinyl chloride), cellulose nitrate, cellulose acetate, and polyurethane especially polyurethane foam. Because of its potential for causing damage to other objects, notably metals, rubber, especially fully vulcanized hard rubber (ebonite and vulcanite), should be added to this list. As they degrade, all these plastics produce harmful degradation products that cause damage to other plastic and nonplastic objects in the vicinity. I call these plastics that damage their neighbors malignant plastics. Because of their malignancy, conservation strategies must deal with these plastics as a first priority.

Although all plastics degrade over time—as indeed do all organic materials—for most other plastics, the damage is mainly to the plastic itself, and not to its neighbors. These benign plastics are not so dangerous to the collection as are the malignant plastics.

Environmental agents of deterioration

As with all organic materials, all plastics, benign and malignant alike, are degraded by exposure to light, heat, moisture, and pollutants, depending on the object composition, fabrication, and environmental history. Decreasing exposure to agents of deterioration will decrease the degradation of plastics. General guidelines on control of agents of deterioration are given in the on-line version of the Framework for Preservation of Museum Collections at http://www.cci-icc.gc.ca/framework/index_e.shtml.

Light levels should be reduced to the minimum required for display and access and storage should be dark. UV radiation should be eliminated.

Variations in temperature and humidity should be avoided. Thermal expansion and contraction or swelling and shrinking as water content increases and decreases with raised and lowered RH creates mechanical stresses which lead to warping and fracture, especially in constrained pieces.

Some plastics are more susceptible to specific agents so it is therefore beneficial to concentrate on controlling that specific agent for that specific plastic (see Table 2 on following page).

<table>
<thead>
<tr>
<th>Plastic</th>
<th>UV radiation and excess light</th>
<th>Moisture (high relative humidity) and moisture fluctuations</th>
<th>Pollutants</th>
<th>Danger to neighbors</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylics</td>
<td>resistant</td>
<td>resistant</td>
<td>dissolved, swelled, stress cracking</td>
<td>none</td>
</tr>
<tr>
<td>casein formaldehyde, protein derivatives</td>
<td></td>
<td>formaldehyde gas, cracking due to swelling/shrinking, moldy, brittle when dry</td>
<td></td>
<td>formaldehyde, hydrogen sulfide, other sulfur containing gases</td>
</tr>
<tr>
<td>cellulose acetate</td>
<td>yellowed brittle</td>
<td>hydrolysis produces acetic acid, oily plasticizer liquids</td>
<td>dissolved, swelled</td>
<td>acetic acid gas, oily plasticizer and degradation products on surface</td>
</tr>
<tr>
<td>cellulose nitrate</td>
<td>yellowed, brittle</td>
<td>hydrolysis produces acidic and oxidizing nitrogen oxide gasses</td>
<td>dissolved, swelled</td>
<td>acidic and oxidizing nitrogen oxide gasses, plasticizer and degradation products on surface</td>
</tr>
<tr>
<td>nylon (polyamide)</td>
<td>yellowed, brittle</td>
<td>potential hydrolysis at extreme conditions</td>
<td>softened, swelled</td>
<td>none</td>
</tr>
<tr>
<td>phenolics (phenol formaldehyde)</td>
<td>discolored and more matte</td>
<td>discolored and more matte</td>
<td>fillers swell and surface mottles with solvents</td>
<td>phenol and formaldehyde with severe degradation</td>
</tr>
<tr>
<td>polyolefin (polyethylene, polypropylene)</td>
<td>yellowed, brittle</td>
<td>resistant</td>
<td>swollen by some organics</td>
<td>none</td>
</tr>
<tr>
<td>polystyrene</td>
<td>yellowed, brittle</td>
<td>resistant</td>
<td>dissolved, swelled, stress cracked</td>
<td>none</td>
</tr>
</tbody>
</table>
polyurethane | yellowed, brittle, sticky, crumbles | yellowed, brittle, sticky, crumbles | swelled, stress cracked | nitrogenous organic gases and liquids
---|---|---|---|---
**poly(vinyl chloride)** | yellowed, brittle | resistant | dissolved, swelled, embrittled by plasticizer extraction | oily plasticizer liquids, maybe hydrochloric acid gas under extreme conditions of moisture and light exposure
rubber, ebonite, vulcanite | brittle, discolored, increase in matteness | hydrogen sulfide and other gases, sulfuric acid on surfaces | surface mottled by solvents | hydrogen sulfide and other sulfur containing gases, sulfuric acid on surfaces
all plastics (and organics) | should be considered as prone to damage by UV radiation usually resulting in yellowing and embrittlement | condensation plastics like esters, amides, and urethanes are subject to hydrolysis with subsequent weakening | thermoplastics may dissolve, thermosets may swell, stress cracking | harmful gases from plastics with chlorine, sulfur, and pendant (not main chain) ester groups

Special Considerations for Malignant Plastics

Environmental conditions that reduce the degradation of the malignant plastics will invariably be beneficial to benign plastics, so concentrating on the malignant plastics, does not neglect the rest of the collection.

Cellulose esters (cellulose nitrate, cellulose acetate)

Cellulose esters produce acidic gaseous degradation products. Cellulose nitrate produces acid smelling nitrous oxides which converts to nitric acid by reaction with moisture in the atmosphere or in other objects. This is a strong oxidizing acid which causes tendering and decomposition of cellulose and protein, and corrosion of metals, etc. Cellulose acetate produces acetic acid (vinegar odor, hence the term "vinegar syndrome" to describe cellulose acetate degradation) and cellulose butyrate and cellulose acetate butyrate produce butyric acid which has a distinctive and characteristic vomit odor. These organic gases are not so strong as nitric acid, but they also cause tendering, decomposition, and corrosion. Because they produce acidic degradation products, the cellulose ester plastics become acidic themselves.

Cellulose nitrate

Cellulose nitrate is found in many forms, including sheets or films (e.g., photographic film base), varnishes and lacquers, and solid objects, especially those which imitate natural materials like ivory (often called "French ivory"), tortoiseshell, and horn.

Cellulose nitrate degrades to produce acidic and oxidizing nitrogen oxide gases which can seriously damage objects that are nearby or in contact. This deterioration is accelerated by increased temperatures, elevated relative humidity, and acidic conditions. Enclosures (drawers, cabinets, display cases, etc.) that contain cellulose nitrate should be well ventilated to prevent buildup of acid vapors. Special storage conditions and locations should be considered for cellulose nitrate, including cold storage.

Cellulose nitrate was commonly plasticized with camphor (e.g., Celluloid). This material sublimes from the plastic, causing the object to become more brittle and to shrink. The shrinkage tension set up in the brittle plastic often leads to severe cracking or crizzling. This problem may not be so severe in cellulose nitrate plasticized by materials other than camphor which are less volatile. Advice on the conservation of cellulose nitrate has been given by Reilly (1991) and Williams (1994). A simple spot test for identifying cellulose nitrate in minute chips or scrapings from museum objects is described by Williams (1994). The use of papers and threads containing the sulfone-phthalein indicators Cresol Red and Cresol Purple to detect degradation in cellulose nitrate objects on display and in storage has been described by Fenn (1995).

Cellulose Acetate

Cellulose acetate is commonly encountered in two grades characterized by different degrees of substitution, namely, cellulose triacetate (CTA) most commonly found in sheets like photographic film base and fibers, and cellulose diacetate (CDA) in thicker sheets and 3-dimensional shapes and objects often simulating tortoiseshell, ivory, wood, and mother-of-pearl. The CTA and CDA are easily confused with cellulose nitrate when compared by visual appearance alone. Cellulose acetate objects usually contain plasticizers.

Cellulose acetate degrades primarily by acid hydrolysis, which causes deacetylation. Deacetylation cleaves pendant acetate groups from the cellulose polymer backbone and depolymerizes the backbone. Deacetylation causes the emission of acetic acid gas from the plastic creating acidic surfaces on the plastic and acidic atmospheres in enclosures. This process is analogous to that which happens with cellulose nitrate. Depolymerization leads to decrease in mechanical strength and fracture plus deformations and warpage. Acetic acid is a volatile gas that diffuses through the display or storage space, and can cause corrosion of metals, or acidic catalyzed degradation of other paper and textiles.
Additives, especially plasticizers, migrate and may be lost, or are hydrolyzed or oxidized to acidic compounds. This leads to warpage, embrittlement, and fracture, and to the development of acidic and sticky surfaces, sometimes with surface deposits of plasticizer or acidic degradation products.

Cellulose acetate should be displayed and stored under ventilated conditions or with acetic acid scavengers if stored in unventilated enclosures. Cellulose acetate objects should not be stored in enclosures with, or in proximity to, acid sensitive (particularly acetic acid sensitive) materials such as metal, textiles, and paper. Problems caused by cellulose acetate in collections and conservation treatments for cellulose acetate objects are described by Aubier et al. (1996) and Pullen and Heuman (1988).

The main conservation strategy for cellulose esters is to reduce exposure to moisture, primarily by reducing relative humidity (RH). Reducing temperature is also effective, since, in common with all chemical reactions, decreasing the temperature decreases the rate of degradation reactions. Decrease temperature also reduces the rate of plasticizer loss and retains plastic flexibility (although the plastic may be less flexible at the reduced temperature). It is also essential to ensure that there is adequate ventilation to remove harmful gaseous degradation products to prevent damage to objects in the vicinity. Objects that are badly degraded or in the process of degrading rapidly should be removed and segregated from the rest of the collection.

**Poly(Vinyl Chloride)**

Pure poly(vinyl chloride), PVC, degrades to produce hydrochloric acid at temperatures needed to form it into usable products by molding or extrusion. As a consequence, heat stabilizers are always added to overcome this problem. Also, pure PVC is a rigid plastic, so, to create a flexible plastic, compounds called plasticizers are added. Plasticizers are typically oily polar organic liquids, which are very good solvents for many materials. Many other additives are used in PVC formulations to enable a wide variety of products to be fabricated.

The greatest problems with PVC are related to the additives. Migration of plasticizer and other additives creates accretions on the PVC surface. These deposits of additives on the surface of the plastic, called bloom, can seriously stain or corrode the surface of other materials they contact. Shashoua (2001) has found that plasticizer bloom will form if the plasticizer content is more than 30% of the PVC weight and that phthalate ester plasticizers can hydrolyze to form crystals of phthalic acid and phthalic anhydride.

The bloom can be removed by wiping or mild solvent treatment (not recommended), but usually returns. Formation of bloom is driven by an inherent incompatibility between the plastic and the additive. Additives and their consequences for museum objects have been discussed by Williams (1993). The presence of bloom on the PVC is not damaging to the PVC, although it does indicate that the PVC is degrading. It need not be removed if contact with other objects is prevented by shields, interleaves, and packaging.

Although PVC is susceptible to degradation by light and heat, this is not usually the most serious problem in museums. Exposure of PVC to light (especially ultraviolet radiation) and heat will cause a degradation reaction, called dehydrochlorination, which produces hydrochloric acid and causes the PVC to change color from yellow to brown to black. Manufacturers control this by adding light and heat stabilizers. Unfortunately these stabilizers are consumed as they do their job, until at some time the stabilizers are exhausted, and additional exposure suddenly results in deterioration. Thus a PVC object that has been surviving nicely under lights for several years may suddenly begin rapid deterioration. This was a common scenario for the vinyl roofs on cars. They would be in good shape for several years then suddenly rot away. In experiments on PVC degradation Shashoua (Shashoua 1996, Shashoua and Ward 1995) did not detect dehydrochlorination at room temperature in the dark after 6 months. However in accelerated aging experiments dehydrochlorination did occur but incorporation of zeolites or epoxidized soya bean oil (ESBO) inhibited the discoloration of PVC caused by dehydrochlorination. Shashoua suggests including zeolite pellets in storage boxes containing PVC objects to inhibit discoloration.

**Polyurethane**

Polyurethane occurs in collections as polyurethane foams, coatings, and fibers. There are two types of polyurethane foams—one based on polyether polyols and the other based on polyester polyols. The polyether polyurethanes are particularly susceptible to oxidation, especially in the presence of light (photooxidation). Foam degradation is particularly devastating usually leading to complete crumbling of the foam object starting at its surface. Polyester polyurethanes are much less susceptible to oxidative degradation, but are subject to hydrolytic degradation at high RH.

Oxidation is initiated and accelerated by exposure to light, especially UV radiation. Kenegan and Quye (1999) note that coated and painted foams tend to be more resilient because they have a protective barrier against oxygen. This could also be due to protection against light in the coated areas. Since oxygen is present in the atmosphere, oxidative degradation can be stopped only by placing the polyurethane into an oxygen free enclosure (anoxic storage). Anoxic storage requires that the object be sealed into a package where there is no ventilation. This exacerbates degradation if the degradation products catalyze degradation, so sealing degrading plastics into packages must be very carefully tested and monitored.

Although avoiding exposure to light may slow oxidative degradation, degradation will not stop in the absence of light. There are many examples of polyurethane foam used for supporting objects in dark storage drawers that have completely degraded to powder. Kerr and Batcheller (1993) describe properties and degradation of polyurethane in detail, particularly in the context of textiles (foam pads, elastic fibers, artificial suedes, and fabric coatings). Recommended environmental conditions are typical for textiles, with good ventilation to remove volatile degradation products. Also, there should be no contact between polyurethane objects and other objects, including other parts of the object itself, to prevent sticking. Silicone and teflon coated fabrics have been used as nonstick interleaves.
Vulcanized Rubber, Especially Hard Rubber (Vulcanite and Ebonite)

When mixed and heated with a few percent of sulfur or sulfur compounds, natural rubber latex can be crosslinked, a process initially called vulcanizing, to make the familiar elastic rubber. Hard rubber (ebonite or vulcanite), an inelastic thermoplastic, is produced if as much as 30% sulfur is used. Both the elastic rubber and the hard rubber are malignant materials because they emit sulfurous gaseous degradation products. Hard rubber also develops extremely acidic surfaces covered in droplets or a film of sulfuric acid.

It was recognized early on that rubber rapidly oxidized in air and stabilizers were developed to prevent degradation. Unfortunately many of the early stabilizers were volatile colored materials. It is very common to find bright yellow stains on tissues and plastics used for wrapping and storing early rubber objects, especially dark colored ones where the yellowness of the stabilizer was not so apparent. Rubber objects that have these volatile yellow antioxidants must not be stored too close to, or sealed up with, other objects that could absorb these additives and be stained.

Hard rubber with its high sulfur content poses two major conservation problems. It can emit reducible sulfur compounds that will tarnish silver, and, the sulfur compounds can be oxidized by atmospheric oxygen to produce sulfur oxides gases which react with atmospheric water vapor to produce acids which can remain on the surface, thereby creating very acidic surfaces. This creates damage whenever the sulfuric acid coated surface of the hard rubber contacts acid sensitive materials. A common use of hard rubber was as an electrical insulator in early telegraphy equipment and much corrosion occurs where the hard rubber is in contact with copper alloys used as conductors.

A spot test to detect materials, including hard rubber, that release reducible sulfur compounds was described by Daniels and Ward (1982). The conservation concerns and how to deal with acidic surfaces was discussed by Bacon (1988) and Stevenson (1993).

Identification of Plastics

Having dwelt on all the problems of specific plastics, perhaps it is time to help you determine what plastics you may have in your collection. There are two options for plastics identification—wet chemical spot tests and instrumental analysis, particularly infrared (IR) spectroscopy. Spot tests are notoriously ambiguous and spectroscopy is preferred (Coxon 1993). Until recently spectroscopy had the disadvantage of requiring samples to be taken from objects and sent to remote laboratories for analysis. Now portable IR spectrometers are available so IR spectroscopy can be carried out nondestructively on-site in the museum without taking samples. The author has been conducting on-site IR spectroscopic analytical surveys of museum collections for several years (Williams 1997, 1999).

Although spot tests are generally ambiguous, fortunately, there are good spot tests that yield relatively unambiguous results for the detection of the five most malignant plastics. A summary in given in Table 3 below and complete information can be found in the references.

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Spot test</th>
<th>Test result</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose nitrate</td>
<td>Diphenylamine/sulfuric acid reagent</td>
<td>colorless to blue solution</td>
<td>CCI Note 17/2 SPNHC Leaflet No. 3</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Alkaline hydroxylamine plus ferric chloride acidified</td>
<td>burgundy red color develops</td>
<td>Coxon 1993</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>Beilstein test—copper wire heated in torch flame</td>
<td>colorless flame turns green</td>
<td>CCI Note 17/1 SPNHC Leaflet No. 3</td>
</tr>
<tr>
<td>Sulfur vulcanized rubber (ebonite, vulcanite)</td>
<td>Iodine/sodium azide reagent for reducible sulfur compounds</td>
<td>bubbles develop in reagent</td>
<td>Daniels and Ward 1982</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Dimethyl amino benzaldehyde in glacial acetic acid</td>
<td>canary yellow color develops</td>
<td>Roff, et al 1971</td>
</tr>
</tbody>
</table>

References


Williams, R. S. 1997. On-site non-destructive mid-IR spectroscopy of plastics in museum objects using a portable FTIR spectrometer


