Canadian Conservation Institute
Institut canadien de conservation

CCI Notes 15/1

Care of Objects Made from Rubber and Plastic

Deterioration of Rubber and Plastic Objects

Natural and synthetic rubber, and plastic deteriorate continuously. It is, therefore, important for custodians of collections to be aware that by properly controlling the agents of deterioration, the lifetime of these materials can be extended.

Like all organic materials, rubber and plastic deteriorate in different ways at rates that vary widely and that are unpredictable. Deterioration may be chemical, caused by oxidation or hydrolysis, or may be physical, or biological. These processes may cause changes in the chemical composition, physical properties, and appearance of these materials. Vapours harmful to other objects may be released, and exudations or accretions may appear on the surfaces of plastic and rubber objects.

For example, the strength and flexibility of rubber may change. It may become brittle, hard, or cracked, or it may soften and become spongy, or sticky. Plastics may lose strength, and, at the same time, become brittle, crack and shrink with age. Rubber and plastic surfaces may be altered by cracking, developing chalky or dusty surfaces, or becoming sticky. Colour changes may be caused by reactions that change the molecules of the polymers that constitute plastics and rubbers, or by changes in dyes or pigments that accompany general deterioration. Plasticiser, an additive that gives flexibility, may be lost if it is volatile (that is, evaporates readily), or may be rejected as the polymer molecules link to each other (crosslink), or as its solubility parameters (a measure of its capacity to dissolve materials) alter during aging. Poly(vinyl chloride) and the cellulose esters (cellulose nitrate and cellulose acetates) are particularly prone to this behaviour. Stabilizing additives may evaporate, creating less stable plastics and rubbers.

Determining the precise composition and designing the proper care for rubber and plastics in museum collections is difficult because rates of decay are variable, and because there are practical difficulties in performing chemical analyses and in identifying the composition of plastics or rubber. However, some generalizations can be stated:

- Cellulose esters deteriorate by hydrolysis — that is, they react with atmospheric moisture and become increasingly acidic as deterioration proceeds. Dry, cold conditions effectively decrease this reaction. Because these plastics release acidic vapours as they age, they should be separated from other objects in the collection. As well, these objects should be well ventilated or enclosed with materials that absorb acidic vapours (acid scavengers).

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For example, Kodak has recommended putting absorbent molecular sieves in film cans in order to absorb acetic acid given off by deteriorating film (Manas, 1994). Enclosing objects made of cellulose esters without including scavengers will trap the volatile acids and hasten degradation. Lead objects and any objects containing carbonates are very sensitive to volatile acids and therefore should be kept away from cellulose esters. As well, ferrous metals are at risk of corroding when near cellulose esters.

- Natural rubber, especially if not blended or filled with carbon black, is particularly prone to oxidative deterioration due to reaction with oxygen in the air. Oxidation, however, can be retarded by storing the object in an oxygen-free environment (Shashoua and Thomsen, 1993; see below under "Oxygen").
- Ebonite is often mistaken for Bakelite in museum collections, because both are often hard, black plastics. Bakelite is relatively stable. Ebonite is a hard, highly vulcanized rubber that contains sulfur compounds, which react first with oxygen and then with water as the product ages, and eventually produce sulphuric acid. Ebonite therefore can have very acidic surfaces that are dangerous to other objects. Ebonite items must be separated, ventilated or placed in enclosures along with scavengers to trap acidic gases. Decreasing the relative humidity will also decrease the amount of acid produced.
- Old plastics are more at risk than new ones because plastics produced more recently benefit from the increased use of stabilizing additives, and the increased understanding of the chemistry of plastics degradation.

At present, we advise custodians of collections to:

- try to identify the composition of objects accurately. (CCI has a portable infrared spectrometer with a non-contact probe that can be taken to museums in order to analyse and identify plastics in situ, nondestructively, whether on display or in storage. See, Nilsen and Williams, 1997);
- segregate objects likely to release volatile products — particularly if metals or other sensitive materials are present. As a rule of thumb, if something smells, then it is releasing volatile compounds and probably should be segregated from other objects and the enclosure ventilated;
- examine plastic and rubber objects on a regular schedule for signs of decay;
- pay special attention to older plastics and to all rubber objects; and
- mechanically clean objects regularly by brushing, wiping, or vacuuming unless the object has become too fragile to sustain even careful cleaning. Avoid using aqueous and organic solvents.

Be aware that when deterioration is visibly obvious, it may be occurring at such a rapid rate that drastic action is necessary.

Agents of Deterioration and Recommendations for Their Control

The primary agents that cause rubber and plastics to deteriorate are radiation, high humidity, high temperature, oxygen and pollutant gases, and stress and other direct physical forces. However, not all rubber and plastics are attacked to the same extent by each agent.

Radiation

Exposure to ultraviolet (UV) radiation is damaging. For some plastics and rubbers, visible light also causes deterioration. The higher the intensity of light, the faster the deterioration. High levels of UV radiation, for example from unfiltered daylight and some fluorescent lamps, and any high-intensity light, should be avoided.

The intensity of illumination should be kept as low as possible, and should never exceed 150 lux. Ultraviolet light levels should be maintained below 75 micro watts/lumen. UV radiation can be controlled by selecting lamps with low UV emission (CCI Technical Bulletin 7, *Fluorescent Lamps*), or by installing UV filters (CCI Note 2/1, *Ultraviolet Filters*).

Humidity and Temperature

High humidity accelerates the degradation of cellulose esters and Ebonite, although it does not affect other plastics and rubbers as much. However, it does promote the damaging action of acidic atmospheric pollutants and acidic by-products of deterioration. Moreover, it creates conditions favourable to the growth of fungi, which, though not as likely to develop on rubber and plastic as on cellulosic materials, does occur, and does cause damage. For these reasons, RH values over 65% should be avoided for plastics and rubbers.

Certain plastics, such as the cellulose esters, casein, nylon, and polyester, as well as plastics filled with wood powder (e.g., early forms of Bakelite), absorb moisture and respond dimensionally. That is, they may swell in damp conditions and shrink when drying out. Depending on how fast or how extreme the RH fluctuation is, this may cause cracking. Plastics and rubbers should therefore be kept at constant, moderate to low levels of RH.

The higher the temperature, the faster the rate of deterioration. Cooler conditions, therefore, promote longevity. Avoid hot lights, proximity to any heat source, or any storage or display practice that heats objects.

Ideally, rubber and plastic objects should be stored in cold, dark, dry, and oxygen-free conditions. Cold, dark, dry conditions can be found in the refrigerator section of a frost-free refrigerator or in a low relative humidity cold storage room. The freezer compartment of frost-free refrigerators and frost-free deep freezers have high relative humidity and should not be used to store objects, unless they are protected by waterproof containers (Wilhelm and Brower, 1993). To reduce humidity around objects, they should be placed in sealed glass or vapour-proof plastic containers along with dry indicating silica gel that occupies about one-third of the air space in the container. The indicating silica gel will remain blue as long as the air in the container is dry. When it turns to a pink colour, it should be replaced with a fresh quantity (CCI Technical Bulletin 10, *Silica Gel*). Monitoring should be done at least once a year. Please note, however, that plastics are more brittle when they are cold. Well-padded boxes and trays, as well as careful handling, will be required.

Oxygen

For many plastics and all rubbers, excluding oxygen from the air surrounding the objects is beneficial. Using an oxygen-absorbing material, such as Ageless, in envelopes or packages made from flexible, heat-sealed oxygen-barrier film is a simple and economic way of achieving oxygen-free conditions. Museums are beginning to adopt this technique to stop oxidation of many types of objects, or to eradicate insects (Burke, 1996). Ask a qualified conservator or conservation scientist how to use this technique. More elaborate systems were used before the advent of the simpler Ageless technique. These older systems used rigid containers flushed and then filled with inert gases (Frydryn and Grattan, 1984; Maltby, 1988; Maekawa, et al., 1989).

Materials that release acidic gases as they degrade, such as cellulose esters and Ebonite, should not be stored in this way because their rapid emission of acidic gases into the gas-tight, enclosed space creates an acidic environment that speeds up degradation.

Pollutants

Certain atmospheric pollutants, such as sulphur dioxide and nitrogen dioxide, may accelerate decay. These gases are acidic, and, therefore, may cause harmful effects, especially in humid conditions. Ozone, which might be produced by ultraviolet radiation or by an electrostatic high-voltage source, such as an electrostatic air cleaner, can cause very rapid deterioration, especially of rubber. Some photocopier machines produce ozone, though this tends to dissipate within a few metres of the copier. Most ozone emanates from exterior air pollution entering buildings.

Other pollutants come from objects and materials in the museum as they degrade, such as nitrogen oxides from cellulose nitrate, acetic acid from cellulose acetate, many woods and fresh paints, formaldehyde from particleboard, and sulfur from many vulcanized rubbers. Good ventilation is essential to prevent a build-up of harmful vapours, particularly if it is not feasible to place objects in cold storage.

Use of scavengers is recommended where ventilation is not possible. Ask a qualified conservator or conservation scientist how to use these materials effectively and safely. Combining the use of scavengers with the use of indicators, such as cresol red and cresol purple that detect nitrogen oxides produced by degrading cellulose nitrate (Fenn, 1995), is an effective method to both slow the rate of deterioration, and detect the presence of noxious vapours if degradation does occur. If the indicator has detected the presence of noxious vapours, it is time to replace the scavengers.

Stress and Other Physical Forces

Degraded plastics and rubbers can be surprisingly brittle. Well-padded supports, boxes, trays and mounts are therefore necessary for storage, display and handling. Do not assume that, because rubber is flexible, it is not necessary to support rubber objects during travel, storage and display. Stress, such as that created by stretching rubber, can increase the rate of its chemical (oxidative) deterioration. Cracks will tend to appear at right angles to the direction of the applied stress. For example, cracks may develop along a fold. Objects stored in a stressed state may harden into that form. Crosslinking "freezes" the polymer in the stressed (or, deformed) shape. Displaying and storing objects with proper supports, and in their proper shapes, will avoid stress and will avoid them hardening into incorrect shapes. For instance, rubber shoes should be supported by a stiff interior form, for example a form made from polyethylene foam. However, if the rubber is sticky, line the support materials with a non-stick material, such as sheets of Teflon, Gore-Tex, polyethylene, polypropylene or silicone release fabric.

Because degraded rubber objects may become sticky and adhere firmly to materials they are in contact with, they should not be allowed to touch one another or other objects. If necessary, use the non-stick materials listed above as barriers. If folds are necessary, smooth, non-stick sheets should be interleaved between layers. Contact with materials that are fibrous (e.g., paper) or porous (e.g., foams) should be avoided to prevent fibres from sticking to the rubber, or the rubber flowing into the pores of the storage material.

Cleaning

Do not use solvents or even water-based cleaning solutions on rubber and plastics. Although recommendations have been made in the literature to use water with soap, this is now regarded as a dangerous practice. In fact, under certain circumstances using water can lead to the destruction of an object (Sale, 1993). The best approach is to clean objects under dry conditions by careful brushing or vacuum cleaning. If simple techniques do not work, custodians are strongly advised to seek expert help.

Replicas

Consider displaying replicas of particularly valuable objects where normal environmental conditions in the display may accelerate the deterioration of the object. The original object can then be stored in more ideal conditions.

Conclusions

Plastic and rubber objects degrade continuously through the action of complex mechanisms. However, by following relatively simple precautions and procedures for display and storage, custodians of collections can significantly increase the life expectancy of these objects. Broken plastic and rubber objects should be repaired by qualified conservators.

Glossary of Terms

Additive
A substance added to another substance usually to improve properties. Additives include plasticizers, initiators, heat and light stabilizers, antioxidants, and flame retardants.

Chalking
A dry, chalklike, powdery residue on the surface of a material resulting from degradation or migration of an ingredient, or both. Chalking may be a designed-in characteristic.

Crosslinking
The setting up of chemical links or chemical bonds between different molecules in a polymer. This usually leads to the formation of a three-dimensional polymer (a network polymer) by means of interchain reactions resulting in changes in physical properties.

Filler
A relatively inert material added to a plastic to modify its strength, permanence, working properties, or other qualities, or to lower costs.

Hydrolysis (hydrolytic deterioration)
The chemical decomposition of a substance due to reaction with water. Of primary concern for plastic objects is the decomposition of the polymer by reacting with water vapour in the air, which occurs more quickly as the relative humidity increases.

Molecular sieves (Molecular traps, zeolites)
Inorganic crystalline substances with molecular or crystal structures that have pores and cavities where gaseous pollutants can be absorbed and trapped. Zeolites, microporous crystalline aluminosilicates, are one type of molecular sieves. Molecular sieves can be designed and manufactured to target a specific size of pollutant molecule.

Oxidation (oxidative deterioration)
The chemical reaction of a substance with oxygen in the air. For plastic and rubber objects, this invariably leads to deterioration.

Plastic
A material that contains, as an essential and predominant ingredient, one or more organic polymeric substances of large molecular weight; that is solid in its finished state; and that, at some stage in its manufacture or when it is being processed into finished articles, can be shaped by flow. Although materials such as rubber, textiles, adhesives, and paint may in some cases meet this definition, they are not considered plastics. The terms plastic and polymer often are used interchangeably, but the term polymer should be reserved to denote the basic material as polymerized, while the term plastic encompasses compounds containing polymers plus plasticizers, stabilizers, fillers, and other additives (i.e., the base polymer plus additives).

Plasticizer
A substance incorporated into a material to increase its workability, flexibility, or stretchability. Sometimes called flexibilizer or softener.

Polymer
A substance formed by the reaction of simple molecules (monomers) having functional groups that permit their combination to proceed to high molecular weights under suitable conditions. A polymer consists of molecules characterized by the repetition of one or more types of monomeric units.

Rubber
A material that is capable of recovering from large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent, such as benzene, methylethylketone, and ethanol-toluene azeotrope. A rubber in its modified state, free of diluents, retracts within one minute to less than 1.5 times its original length after being stretched at room temperature (18 to 29°C) to twice its length and held for one minute before release.

Scavenger
A substance capable of absorbing and holding other substances. Scavengers are used in closed environments to absorb gaseous pollutants from the atmosphere of that environment. Molecular sieves (molecular traps) such as zeolites, and activated charcoal are examples of scavengers.

Solubility parameter
A characteristic of a compound used in predicting solubility of that compound in a given liquid or the solubility of other substances in the compound.

Stabilizers
A substance used in plastics formulation to help maintain physical and chemical properties during processing and service life. These include antioxidants, and heat and UV stabilizers.

Vulcanization (vulcanized rubbers)
An irreversible chemical reaction (for example, crosslinking) during which the physical and chemical properties of a rubber compound are changed resulting in decreased plastic flow, decreased surface stickiness, increased tensile strength, increased resistance to swelling by organic liquids, and increased or improved elastic properties that extend over a greater range of temperatures.

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