

Inhibiting the Inevitable; Current Approaches to Slowing the Deterioration of Plastics

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Summary: Once plastics objects are registered in museum collections, the institution becomes responsible for their long term preservation, until the end of their useful lifetime. Plastics appear to deteriorate faster than other materials in museum collections and have a useful lifetime between 5 and 25 years. Preventive or inhibitive conservation involves controlling the environments in which objects are placed during storage and display, with the aim of slowing the major deterioration reactions. Once in progress, degradation of plastics cannot be stopped or reversed, so the aim of preventive conservation is to 'buy time' for the object. Inhibitive conservation of plastics involves the removal or reduction of factors causing or accelerating degradation including light, oxygen, acids, relative humidity and acidic breakdown products. Specific approaches to conservation have been developed for cellulose nitrate, cellulose acetate, PVC and polyurethanes by considering the most effective action to inhibit their major degradation pathways. The purpose of this article is to outline the main factors causing degradation of the least stable plastics in museum collections and present an overview of the conservation treatments established to date. Recent research has suggested that some of the conservation practices to slow the rate of deterioration in use today, particularly those for cellulose nitrate and acetate, are poorly effective and that alternatives should be evaluated. One alternative is low temperature storage.

Keywords: adsorbent; degradation; plastics; preventive conservation

Introduction

Today, most international museums and galleries possess collections which contain plastics. Plastics may be identified within building materials, defence equipment, ethnography, furniture, housewares, information technology, medical and sports equipment, modern art, photography and toys. Many incorporate metals, textiles and wood with plastics in their construction. While museums continue their policy to acquire objects which reflect both everyday life, technological and

historical events, the proportion of plastics in museums will increase.

In general, deterioration of plastics objects in museums is visible within 5–25 years of collection. Surveys of 3-dimensional objects containing plastics conducted in the United Kingdom and Scandinavia have shown that 1% of objects are actively deteriorating and are in immediate need of conservation, while 12% exhibit deterioration and require cleaning, stabilizing and repair.^[1,2] All the 'acute' objects contain cellulose nitrate, cellulose acetate, plasticized PVC or polyurethane foam. Most objects (60%) have been defined as low conservation priority; they are in stable condition but need some treatment such as cleaning. Only just over one quarter require no conservation treatment. Deterioration of plastics objects in museums has only been

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recognised as an important area worthy of research since 1991. [3] As a result, little is known about the conservation of plastics compared to other materials found in museums. To date, few conservation practices have been established, and the rate of development of new treatments cannot keep pace with degradation. Once deterioration has started, it cannot be stopped or reversed only slowed.

Conservators consider two approaches to conservation when planning treatment for degraded materials; active also known as interventive, and inhibitive also known as passive. Active conservation treatments are those involving practical treatments applied as necessary to individual objects to limit further deterioration. They include cleaning surfaces, adhering broken sections and filling missing areas to strengthen damaged objects. Established active conservation practices for plastics are few. The major cause is the sensitivity of many plastics to organic liquids, aqueous solutions and water itself, particularly if the polymer has deteriorated. Any coating or adhesive which adheres successfully to a plastic surface, must either soften, melt or otherwise damage the substrate. Such treatments change the appearance of the original, which does not comply with the ethical practice of reversibility, as summarized in the code of practice: [4]

'The conservation professional must strive to select methods and materials that, to the best of current knowledge, do not adversely affect cultural property or its future examination, scientific investigation, treatment or function.'

Since active conservation of plastics is poorly developed it will not be discussed further here.

Inhibitive conservation involves controlling the environments in which objects are placed during storage and display, with the aim of slowing deterioration reactions. Inhibitive conservation of plastics involves the removal or reduction of those factors either causing or accelerating degradation including light, oxygen, water and acidic

breakdown products. Specific inhibitive approaches to conservation have been used successfully to prolong the useful lifetimes of collections containing cellulose nitrate, cellulose acetate, plasticized PVC and polyether-based polyurethanes; these will be discussed in the article. Because museum collections are usually grouped according to historical periods and not by material type, one store is likely to contain objects comprising many different materials. A storage climate suitable for, say, metals is unlikely to be equally suitable for plastics. Microclimates specific to plastic type are currently achieved by introducing adsorbents or scavengers which adjust the composition of the surrounding air, into the relevant storage areas.

Cellulose Nitrate (CN) and Cellulose Acetate (CA)

Cellulose plastics, particularly cellulose nitrate (CN) and acetates were commercially developed at the start of the 20th century and were used to produce photographic films, textile fibres, fake ivory, tortoiseshell and amber. They were synthesized by esterification of paper or rags with acids thereby replacing some of cellulose's hydroxyl groups with other substituents, namely nitrate or acetyl groups. The resulting polymer underwent unacceptable shrinkage on moulding and plasticizers or softeners were necessary to minimise such effects. Due to their instability and short useful lifetime, semi-synthetic cellulose have been largely replaced by modern synthetics. Fresh cellulose nitrate is highly flammable and burns at a temperature up to 15 times higher than that achieved by burning paper; this was the major reason for its replacement.

Degradation of Cellulose Nitrate

Cellulose nitrate undergoes hydrolytic, thermal and photochemical reactions. In addition, breakdown of the polymer is autocatalytic; if not removed from the undegraded material, the products of breakdown catalyse a faster and more extensive reaction than the primary processes. The

major product of thermal deterioration is the highly reactive, oxidising agent nitrous oxide (NO_2), identified by its yellow vapour and distinctive odour. This is formed by cleavage of the N–O bonds joining the cellulose ring which are the weakest bonds in the molecule. Nitrous oxide reacts with moisture in air to form nitric acid, which in turn attacks organic materials and corrodes metals on contact. Chain scission along the backbone between the cellulose rings follows, resulting in a considerable reduction in molecular weight. CN is particularly susceptible to light of wavelengths between 360 nm–400 nm. Degradation is due to a nitrate ester cleavage in a similar manner to thermal decomposition. At shorter wavelengths, that is those with higher energy, disintegration of the cellulose ring occurs, causing a rapid decrease in molecular weight. Once started this process continues even in the absence of light.

An examination of cellulose nitrate adhesive taken from repairs in cuneiform (dried clay) writing tablets from the British Museum, where the date of the repair was known, suggests that the degradation of CN is retarded substantially by the plasticizer added during manufacture and that such adhesives are stable for at least 30 years.^[5] The relationship between loss of plasticizer and reduced stability of cellulose nitrate is also demonstrated by three-dimensional materials. Degradation can be divided into three stages. The first stage involves

the evaporation or migration of plasticizer manifested by shrinkage of the object. As degradation continues, internal cracks or crizzling develop as shown in Figure 1 and cellulose nitrate yellows. In the final stage, crizzling is so extensive that cellulose nitrate disintegrates. At this point, its flammability is much less than fresh cellulose nitrate. And is similar to that of paper.

Conservation of Cellulose Nitrate

Activated charcoal is widely used to reduce the rate of degradation of cellulose nitrate objects and has proven effective for ethnographic materials including mock tortoise-shell boxes, hair combs and shadow puppets.^[6] Wood, vegetables and coconut shells are destructively distilled to produce a fine, black powder which contains millions of microscopic pores, giving the resulting activated carbon a huge surface area density of 300–2000 m² per gram. Activated charcoal can also be obtained in the form of woven textiles, impregnated card or paper and pellets of various size. Pellets and powder are likely to adhere to tacky and uneven surfaces, so should not be allowed to come into contact with deteriorating CN. Although one of the most widely used adsorbents for industrial, domestic and medical applications, activated charcoal is more effective at adsorbing aromatic or benzenoid materials than aliphatic fatty acids and alcohols, trapping them in the pores primarily via weak London dispersion forces.

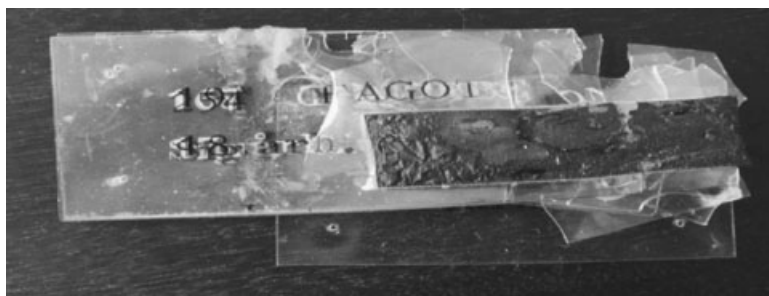


Figure 1.

Poster from Museum of Historical Music in Copenhagen, Denmark made from cellulose nitrate in the 1960s shows shrinkage and tackiness due to loss of plasticizer and crizzling of the polymer.

Activated charcoal cloth or charcoal-impregnated paper used as packing materials for cellulose nitrate objects readily adsorbs nitrogen oxide degradation products, rendering them unable to participate in autocatalytic breakdown of CN or to come into contact with metals in the vicinity. Because of the wide range of pollutants adsorbed by activated charcoal, water molecules from air may compete with nitrogen oxides for sites as shown in Figure 2. When all the pores of the active charcoal are filled, no further adsorption is possible; active charcoal packing materials should be renewed every three years. Activated charcoal can be regenerated by heating to 650 °C in an inert atmosphere, allowing adsorbed material to be desorbed.

However, activated charcoal may not be the most effective molecular trap for nitrogen oxides. Measurements using Draeger tube gas detectors to determine the amount of nitrogen oxides adsorbed by seven molecular traps, suggested that zeolites (hydrated silicates of calcium and aluminium) were just as effective as activated charcoal at adsorbing nitrogen oxides. Zeolites and activated charcoal adsorbed a concentration 250 times higher than calcium carbonate which may act as an alkaline buffer to neutralise the acid gases formed during deterioration of CN.^[7] In medical applications, doping zeolites

with positively charged ions pulls nitrogen oxides into their pores in preference to water or other gaseous pollutants.^[8] Such specificity in a molecular trap would prolong its lifetime so that replacement would be necessary less often than is the case with activated charcoal.

Deterioration of Cellulose Acetate

The major degradation reaction of cellulose triacetate is similar to that of cellulose nitrate, the primary reaction being deacetylation also known as hydrolysis, during which hydroxyl groups replace acetyl groups (COCH_3) on the cellulose ring. Deacetylation is accelerated by water (usually in the form of moisture in air), acid or base. Because the loss of acetyl groups from cellulose acetate results in the formation of acetic acid (CH_3COOH) which gives a distinct vinegary odour to degrading materials, the process is also known as the ‘vinegar syndrome’.

Cellulose acetate undergoes autocatalytic breakdown if acetic acid is allowed to remain in contact with the degrading polymer. This happens easily because the solubility of acetic acid in cellulose acetate is high, similar to the solubility of acetic acid in water in atmospheric moisture. The degradation product also attacks organic materials and metals in the vicinity as shown in Figure 3. Degradation does not

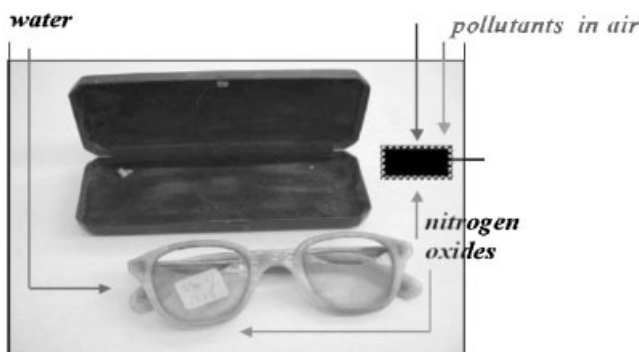


Figure 2.

Water molecules and pollutants from air compete with nitrous oxide to be adsorbed by activated charcoal (black rectangle to right of picture). Such competition reduces the effectiveness of activated charcoal in removing nitrous oxide from the vicinity of CN objects, including spectacle frames from the 1930s. If nitrous oxides are allowed to remain in contact with CN, autocatalysis leads to their rapid deterioration.



Figure 3.

Acetic acid produced by degrading knife handles from the 1950s, has 'burned' the paper in which they have been wrapped during storage. The knife blades have also undergone corrosion on contact with acetic acid.

follow a linear rate, but is slow during the initial, induction period and more rapid after the onset of autocatalysis. As deacetylation progresses, chain scission takes place with bonds breaking between the cellulose units, dramatically reducing the molecular weight, tensile strength and solubility of the polymer.

In addition to degradation of the cellulose acetate polymer, migration and subsequent evaporation of plasticizer from between the cellulose acetate chains give rise to shrinkage, tackiness and increased brittleness. The degradation of some plasticizers has been shown to increase acidity of cellulose acetate-containing materials. Triphenyl phosphate, used as a plasticizer for cellulose acetate since the 1940s, decomposes to form diphenyl phosphate and phenol. Diphenyl phosphate is a strong acid so is likely to accelerate the deacetylation of cellulose acetate.

Conservation of Cellulose Acetate

Zeolites were first shown in 1994 to inhibit the rate of deterioration of cellulose acetate photographic negative film.^[9] The technique has since been adapted to inhibit the deterioration of three-dimensional materials containing cellulose acetate including

handbags, jewellery and modern art.^[10] Zeolites comprise a family of hydrated silicates of calcium and aluminium with pores of pre-determined diameters which are introduced by removing water from the crystal lattices under intense heating. They are thought to inhibit the degradation of cellulose acetate by both trapping water vapour from the polymer, thereby minimising the rate of hydrolysis and by trapping acetic acid vapour which reduces the opportunity for more dominant, rapid autocatalysis to occur. However, when water and acetic acid are present together, they compete for sites in the zeolite lattice, reducing the effectiveness of adsorption of acetic acid by approximately one third.^[11]

Traditionally, movie films in archives have been stored in metal cans or plastic containers to protect the films both from mechanical damage during handling and from fire. Zeolites, usually molecular sieve Type 4A, are introduced to the container, themselves enclosed in polyethylene sachets. In contrast, three-dimensional objects containing cellulose acetate are rarely enclosed in air impermeable containers but are either stored in cardboard boxes or on open shelves, so the dilemma arises of whether to ventilate them to disperse acetic acid, perhaps inadvertently

in the direction of other objects, or to enclose them with zeolites. While enclosures prevent contact between water vapour in air and cellulose acetate, they reduce visibility of objects to curators, students and conservators and objects. Ventilation seems to be favoured for modern art containing cellulose acetate whereas ethnographic materials are more often enclosed with zeolites.^[12,13]

Plasticized Poly (vinyl chloride)

Plasticized poly (vinyl chloride) (PVC) has been one of the most economically and technically important plastics materials since the 1950s. Although its first application was as an effective replacement for rubber in electrical cable insulation during World War 2, world production today is higher than 20 million tonnes per year, making it the second most highly consumed plastics material. As a result, examples are present in many international museum collections in the form of clothing and footwear, furniture, electrical insulation, medical equipment, housewares, vinyl records, toys and packaging materials used to store photographs and other objects. Many plasticized PVC formulations are designed to function for less than 20 years; this is a short lifetime for a museum object.

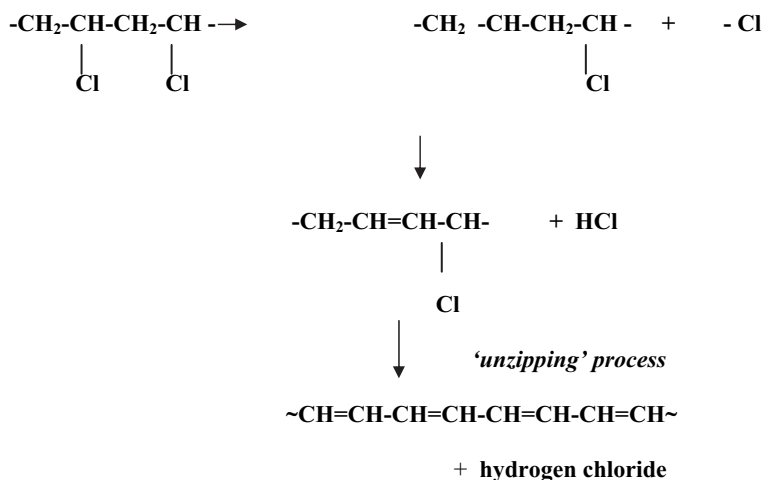
Compounding PVC involves adding sufficient quantities of modifiers to the raw polymer to produce a homogeneous mixture suitable for processing at the lowest price. Plasticizers are the major modifier for PVC formulations in terms of percentage weight (between 15% for vinyl flooring and 50%, for waterproof boots) and physical properties. A plasticizer is a material incorporated into a polymer or polymer mixture to increase its workability and its flexibility or elongation. Of the one million tonnes of plasticizers used annually in Europe, approximately 90% comprise phthalate esters. The largest single product used as a general purpose plasticizer worldwide since the 1950s is di (2-ethylhexyl) phthalate (DEHP).

Deterioration of PVC

Deterioration of plasticized PVC objects in museum collections is most frequently

manifested by discolouration, tackiness at surfaces and, in some cases, the presence of crystalline material. First, plasticizer migrates from bulk to surfaces which results in increased tackiness.^[14] At surfaces, DEHP either evaporates slowly or is hydrolysed to form crystalline phthalic acid. As esters, phthalate plasticizers are susceptible to hydrolysis when exposed to highly acidic or alkaline conditions; acidic conditions are provided by the gaseous product from thermal or photochemical degradation of the PVC polymer, namely hydrogen chloride. In addition, oxidation of DEHP results in the formation of phthalic acid. Such oxidative reactions are expected to occur above 200 °C, temperatures not usually experienced by materials in museum collections, but acidic conditions lower the necessary temperature.^[15]

It is usually assumed that dehydrochlorination starts at imperfections in the PVC structure and starts with the breaking of a C–Cl bond as shown in Figure 4. Loss of a chlorine atom is followed almost immediately by abstraction of a hydrogen atom and a shift of electrons in the polymer to form a double bond. The next chlorine becomes allylic, highly reactive and is readily removed. This leads to the progressive ‘unzipping’ of neighbouring chlorine and hydrogen atoms to form a conjugated polyene system (alternate single and double carbon bonds), accompanied by the formation of hydrogen chloride. As the conjugated polyene system develops, the polymer begins to absorb radiation in the ultraviolet part of the spectrum. After between 7 and 11 repeat polyene units have formed, absorption shifts to longer wavelengths until it is absorbing in the violet, blue and green parts of the spectrum. Each absorption maximum has been found to correspond to a specific polyene length. The rate of degradation can be followed using colour changes from white to yellow to orange to red, brown and, ultimately black. Dehydrochlorination is an autocatalytic reaction, that is, if the hydrogen chloride produced is not removed from the environment surrounding PVC, dehydrochlorination continues at an accelerated rate.

**Figure 4.**

Dehydrochlorination reaction of PVC results in the formation of polyenes and hydrogen chloride.

Conservation of Plasticized PVC

The rate and extent of deterioration of plasticized PVC and the migration of DEHP are related. In addition to functioning as a plasticizer, DEHP has a second role as anti-ageing additive for PVC. When DEHP either migrates to surfaces and evaporates or is adsorbed by another material, PVC materials discolour, become tacky to the touch and brittle. Materials with lower levels of plasticizer degrade more rapidly than those containing more.

The goal of conservation techniques for plasticized PVC is to prevent loss of

plasticizer, thereby protecting the PVC polymer from dehydrochlorination. Enclosing objects in an impermeable material such as a glass tank or jar or a heat-sealed polyester bag is effective. In contrast, low density polyethylene readily absorbs oily materials, including plasticizers as illustrated by the polyethylene fishing box used to store highly plasticized PVC lures for 20 years shown in Figure 5. With time, DEHP has diffused from the lures into the polyethylene, softening the box so that it has deformed to the shape of the lures and today resembles plastic fossils. Traditionally, polyethylene

**Figure 5.**

A polyethylene fishing box has absorbed plasticizer from plasticized PVC lures and formed polyethylene 'fossils' over 20 years.

bags have been used to store many types of objects; they are clearly unsuitable for the long term storage of PVC.

Calculations based on the weight lost by model sheets during accelerated thermal ageing, and the rule of thumb concerning the rate of reactions with temperature, indicate that the useful lifetime of plasticized PVC objects may be prolonged more than 10 fold at ambient conditions, by changing the storage environment from a polyethylene bag to a closed glass container. Enclosing plasticized PVC objects, whatever their level of deterioration, is inexpensive to implement, of low practical complexity and still allows public accessibility. Conservators and designers are usually advised either to improve ventilation or to include adsorbent materials to remove volatile degradation products from the air space surrounding plastics objects during storage. In the case of plasticized PVC, such action would accelerate the loss of plasticizer and thereby reduce the longevity of both new and deteriorated PVC objects.

Polyurethane Foam

Polyurethane polymers are products of a polyol, based either on a polyester or polyether, with several alcohol groups ($-\text{O}-\text{H}$), a di- or poly-isocyanate with several cyanate groups ($-\text{N}=\text{C}=\text{O}$) and a chain extender. The chain extender reacts with the polyol's alcohol groups, initiating an imbalance in negative and positive charges throughout the molecule which, after reaction with the isocyanate, results

in the formation of a urethane group ($-\text{NHCOO}-$) as shown in Figure 6.

To produce polyurethane (PU) foam, water is added to the polyol and isocyanate starting materials. The water molecules react with the cyanate groups to form amine groups ($-\text{NH}_2$) and carbon dioxide gas. The amine continues to react with isocyanate groups to form urea linkages ($-\text{HNCONH}-$) between the chains, instead of the urethane groups created in the absence of water. As polymerization progresses and molecular weight increases, carbon dioxide gas becomes trapped in the increasingly viscous liquid polymer. The trapped bubbles form cells in the polyurethane foam.

The physical properties of the final polyurethane are determined by those of the raw materials. The physical form in which polyurethanes are produced, whether as fibres or expanded foams, depend on the chemical formulae of both the isocyanate and the alcohol or components; these control the molecular weights and extent of cross-linking in the resultant polymer. Polyglycols, such as a polyethylene glycol with a molecular weight of around 2000, result in a higher molecular weight polyurethane than if a diol was used. Polyurethanes are noted for their resistance to most organic solvents and high tensile strength. As a result, they have found use as foams in upholstery where tensile strength is important and as modern art.

Deterioration of PUR

Polyurethanes ether (PURether) foams are thought to degrade primarily by oxidation,

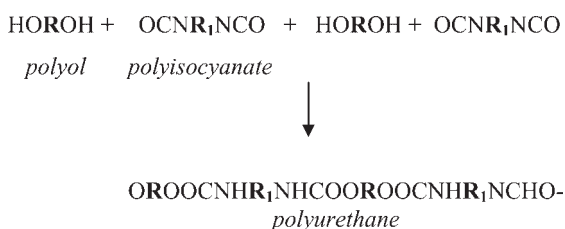


Figure 6.

Preparation of polyurethane polymers.

resulting in discolouration and a loss of mechanical properties. Since oxygen comprises 21% of air, it is difficult to prevent its contact with objects. Polyurethane foams degrade more rapidly than films or fibres since their many cells offer a greater surface area to volume ratio over which oxygen can have contact with the polymer. In addition, the processing of foams may involve blowing air through polyurethanes in liquid form, providing conditions favourable to oxidation processes. Exposure to moisture, heat and light leads to polyurethane ester's (PURester) degradation by hydrolysis. Degradation results in chain scission, in which energy breaks polymer chain bonds to create a polymer with two or more shorter chains, manifested by crumbling of foams. Such crumbling often starts at surface skins of foams and, when the surfaces crumble and fall away from the object, fresh, undegraded foam is exposed to light and moisture, perpetuating degradation to the point of complete failure.

Conservation of PURether

Since the degradation of PURether foams involves reaction with oxygen, removing oxygen limits the extent of the reaction. Packing objects in a nitrogen atmosphere is the traditional method to achieve oxygen-free storage, but its long-term effectiveness is dependent on using a perfect barrier to prevent ingress of oxygen from the surrounding air. A more convenient option has been used since the 1990s. Ageless[®] oxygen absorber is one of several similar commercial products designed to inhibit the oxidation of foods during transport, and was the first to be evaluated for its suitability for use with museum plastics.^[16] It comprises gas-permeable plastic sachets containing finely-divided iron which oxidizes to form iron oxides in the presence of oxygen and water, binding oxygen from the surrounding environment. Moisture is provided by the presence of potassium chloride in the sachet and is also a by-product of the oxidation reaction. Different grades of Ageless[®] are available; Ageless[®] Z is recommended for the preservation of

materials with a water content of between 0 and 85%, including plastics. Ageless[®] Z can be used as a low-cost, convenient alternative to flushing with nitrogen for long-term oxygen-free storage of polyurethane foams. It is claimed that Ageless[®] oxygen absorber reduces the oxygen concentration of an air-tight container down to 0.01% (100 ppm) or less.

Objects are placed in an oxygen-impermeable envelope, such as those prepared from Cryovac[®] BDF-200 film (a transparent laminate of nylon and polyolefins) or Escal[®], a ceramic-coated film into which Ageless[®] sachets have been introduced. Enclosures are flushed with dry nitrogen to remove any oxygen before being heat sealed as shown in Figure 7 with a natural rubber gas mask; rubber is the material which has most been studied in connection with this technique. When Ageless[®] reacts with oxygen, it undergoes an exothermic reaction producing a small amount of heat.^[17] In addition, as a by-product of this reaction, a small quantity of water is formed which causes the relative humidity to increase inside the enclosure. The presence of water has little effect on the rate of degradation of polyurethanes.

Ageless[®] Eye is the oxygen indicator supplied with Ageless[®]; it is in the form of a pressed tablet which changes colour from pale pink (less than 0.1% oxygen) to dark blue (greater than 0.5% oxygen). However, Ageless[®] Eye tends to lose its sensitivity to oxygen after approximately six months, manifested by unreliable colour changes, so an oxygen monitoring device is more reliable. An alternative method to using sachets of oxygen absorber is to enclose polyurethanes in a multilayer polymer film which incorporates the oxygen scavenger agents as one of the layers. Such films require exposure to ultraviolet radiation to initiate the scavenging reaction.^[18]

Conclusion

Considerable progress has been made since the 1990s by applying adsorbents and sto-



Figure 7.

Rubber gas mask being enclosed with oxygen absorber (indicated by white arrow to left of picture). The oxygen impermeable bag is flushed with nitrogen just prior to heat sealing closed (tube to nitrogen cylinder is clear to left of heat sealer).

rage techniques used in other disciplines to slow the degradation of plastics in museum collections. However, as experience in the field of plastics conservation grows and as technology of molecular traps develops, it is clear that the adsorbents widely in use today to adsorb acidic degradation products produced by cellulose nitrate and acetates are probably not the most effective available. Activated charcoal, used to adsorb nitrogen oxides from storage areas housing cellulose nitrate, is a poorly selective molecular trap which also adsorbs many other types of pollutants and water vapour. As a result, active charcoal becomes rapidly exhausted and frequently requires replacing. A possible alternative is a zeolite doped with positively charged ions which pulls nitrogen oxides into its pores in preference to water or other gaseous pollutants. The performance of zeolite, molecular sieve 4A which is currently used to remove acetic acid from cellulose acetate, is reduced by one third if water is present since water and acetic acid molecules compete with each other to occupy sites. Again, a more effective zeolite could be found.

Traditional storage of plasticized PVC objects in Low Density polyethylene (LDPE) bags to prevent contact between

their degraded, tacky surfaces and dust, finger grease or other objects, has recently been found to have a negative side-effect. Polyethylene adsorbs phthalate plasticizers readily when it is in contact with PVC. Because phthalate plasticizers have a dual role as anti-ageing additive, removal reduces the stability of the PVC polymer. Closed glass or polyester containers should replace polyethylene for storing plasticized PVC.

Oxygen-free microclimates for PUREMENT foams are currently achieved by introducing oxygen absorbent in sachets into an enclosure containing the object and made of an oxygen impermeable material. This is effective at slowing the rate of deterioration, but cosmetically unsatisfactory, particularly for modern artworks. One possibility for the future is to enclose foams in a multilayer polymer film which incorporates the oxygen scavenger as one layer.

A low technology alternative to using adsorbents and barrier films to store plastics, is long term low temperature storage which has been recommended to prolong the useful lifetime of many museum materials and in short periods to control insect infestations (-20 to -30 °C).^[19] Reducing the temperature by between 5 and 10 °C halves the rate of the most

common chemical degradation reactions of plastics, such as hydrolysis and oxidation. The importance of controlling both temperature and relative humidity (RH) has been recognised for the long term storage of composite materials which contain plastics in thin layers, such as magnetic carriers, optical media and photographic materials (recommendations include -5°C , 30–40%RH) for moving image colour film and $+20^{\circ}\text{C}$, 40%RH for optical media).^[20] At present, low temperature storage is only routinely applied to photographic archives and not to three dimensional objects, so we have limited practical experience of its effects. However the author has conducted a pilot study on the effect of cold storage on physical properties of selected plastics.^[21] Initial findings suggest that storage of plastics in a domestic freezer should be considered as an alternative to the present preventive conservation techniques for long term storage.

- [1] E. Then, V. Oakley, V & A *Conservation Journal*, **1993**, 6, 11–14.
- [2] K.B. Pedersen, National Museum of Denmark, Personal communication, **1999**.
- [3] U. Hummelen, D. Sillé, Postprints of Modern Art: Who Cares? (eds. U. Hummelen and D. Sillé), The Foundation for the Conservation of Modern Art and The Netherlands Institute for Cultural Heritage, August 1999, 14.
- [4] American Institute for Conservation, Code of ethics and guidelines for practice, Washington DC, 1994.
- [5] Y. Shashoua, S.M. Bradley, V.D. Daniels, *Studies in Conservation*, **1992**, 37, pp. 113–119.
- [6] C. Ward, Y. Shashoua, Preprints of 12th Triennial Meeting of International Council of Museums-Conservation Committee, 29th August–3rd September 1999, Lyon, II, 888–893.
- [7] S. Rempel, Western Association for Art Conservation Newsletter, **1996**, 1.
- [8] K. Davis, 'Pollution fighter turns clot buster', *New Scientist*, 5 February **2005**.
- [9] A.T. Ram et al, Preprints of Actes des deuxiemes journées internationales d'études de l'ARSAG, Association pour la Recherche Scientifique sur les Artes Graphiques, Paris, 1994, 121–127.
- [10] M. Derrick, E. Ornendez, Postprints of Saving the Twentieth Century: The Conservation of Modern Materials, Canadian Conservation Institute, Ottawa, 1993, 169–182.
- [11] F.J. Ligterink, in 'Contributions to conservation, Research in Conservation at The Netherlands Institute for Cultural Heritage', James and James, London, 2002, pp64–73.
- [12] M. Derrick, V. Daniel, A. Parker A., Preprints of the contributions to the Ottawa Congress, International Institute for Conservation of Historical and Artistic Works, 12–16 September 1994, London 207–211.
- [13] T. Van Oosten, Australian Institute for Conservation of Cultural Material Objects SIG Symposium and Workshop, 23–24th August 2005, 4–19.
- [14] Y. Shashoua, Inhibiting the deterioration of plasticized poly (vinyl chloride)-a museum perspective, PhD thesis, Technical University of Denmark, ISBN 87-89384-82-2, September 2001.
- [15] A.S. Wilson, 'Plasticisers: Principles and Practice', The Institute of Materials, London, 1995.
- [16] D.W. Grattan, M. Gilberg, 'Ageless[®] oxygen absorber: chemical and physical properties', *Studies in Conservation*, **1994**, 37, p. 267–274.
- [17] Y. Shashoua, Preprints of 12th Triennial Meeting of International Council of Museums-Conservation Committee, 29th August–3rd September 1999, Lyon, II, 881–887.
- [18] B.L. Butler, <http://www.sealedair.com/library/articles/article-os2000.html>, February **2006**.
- [19] S. Michalski, Preprints of 13th Triennial Meeting of International Council of Museums-Conservation Committee, 22nd–27th September 2002, Rio de Janeiro, 66–72.
- [20] United Nations Educational, Scientific and Cultural Organisation, Safeguarding of magnetic media, http://webworld.unesco.org/safeguarding/EN/txt_magn.htm (accessed February 2006).
- [21] Y. Shashoua, Preprints of 14th Triennial Meeting of International Council of Museums-Conservation Committee, The Hague, 12th–16th September 2005, 358–364.