10　Inhibiting the deterioration of plasticised poly (vinyl chloride) in museum collections

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Abstract　Plasticised poly (vinyl chloride) (PVC) is found in museum collections both as three- dimensional objects and packaging materials. Many PVC materials deteriorate within 25 years of acquisition. Migration and chemical breakdown of plasticiser, accompanied by dehydrochlorination of the polymer, are the major mechanisms of deterioration.

The extent, rate and mechanisms of deterioration of new and naturally aged PVC containing di-(2-ethylhexyl)-phthalate (DEHP), the most commonly used plasticiser, were examined during accelerated thermal ageing in various environments. Weight loss was used to quantify loss of plasticiser. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to quantify concentration of DEHP at surfaces. Optical densitometry was used to quantify darkening of samples.

Degradation of new and deteriorated PVC was inhibited by enclosure in a non-adsorbent material such as glass, containing un-stirred air. Such storage minimised migration and loss of DEHP, thereby prolonging the useful lifetime of PVC objects tenfold.

Keywords: preventive conservation, PVC, plasticiser, phthalate, ATR-FTIR, plastic, DEHP

Introduction

Plasticised 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 and cassette tapes, toys and packaging materials used to store objects. Many plasticised PVC formulations are designed to function for less than 20 years; this is a short lifetime for a museum object (European Union Commission 2000).

Attempts to process pure PVC using heat and pressure, result in severe degradation of the polymer (Nass 1977). Hydrogen chloride is produced and rapid discoloration of the starting material from white to yellow to brown to black is observed at processing temperatures, around 150 ºC. Compounding PVC involves adding sufficient quantities of modifiers to the raw polymer to produce a homogeneous mixture suitable for processing at the lowest price.

Plasticisers 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 plasticiser is a material incorporated into a polymer or polymer mixture to increase its workability and its flexibility or elongation (Wilson 1995). Plasticisers are essentially semi-volatile solvents with solubility parameters close to that of the polymer. Non-polymeric plasticisers are typically high boiling, oily, organic liquids – usually esters. Addition of plasticiser to a PVC polymer has two main functions: to assist in the processing stage by reducing the viscosity and melting temperature, and to modify the final product by softening it.

The plasticisation process involves mechanically milling the solid polymer with liquid plasticiser to reduce the particle size. During this process, plasticiser molecules are evenly dispersed throughout the PVC and attach themselves weakly to the surfaces of polymer particles. Van der Waals interactions take place between the plasticiser and polymer particles. Such physical interactions have enthalpy values in the order of $20\,kJ\,mol^{-1}$; this value is approximately ten times lower than equivalent values for the covalent, chemical bonds.

Of the one million tonnes of plasticisers used annually in Europe, approximately 90% comprise phthalate esters. The largest single product used as a general-purpose plasticiser world-wide is di-(2-ethylhexyl)-phthalate (DEHP). It has set the standard for performance to price relationships since the 1950s, partly due to its documented high compatibility with PVC (Titow 1984).

Deterioration of plasticised PVC in the museum environment

Examination of both new and deteriorated PVC objects and storage materials plasticised with DEHP and in the care of the National Museum of Denmark suggested that degradation was first detected within 10–35 years of acquisition. It was manifested by discoloration, tackiness at the surface and, in some cases, the presence of crystalline material.

During deterioration, plasticiser first migrated from bulk to surfaces (Shashoua 2001); this was accompanied by increased tackiness. At the surfaces, DEHP either evaporated slowly or hydrolysed to form crystalline phthalic acid. As esters, phthalate plasticisers are susceptible to hydrolysis when exposed to strongly acidic or alkaline conditions. Phthalic acid and alcohol are two of the products of such reactions. In addition, oxygen attack on the two identical tertiary carbons in the alkyl groups of the DEHP molecule also results in the formation of phthalic acid. Such oxidative reactions are expected to occur above 200 ºC, temperatures not usually experienced by materials in museum collections, but acidic conditions lower the necessary temperature (Wilson 1995). It is likely that highly acidic conditions are provided by the breakdown of the PVC polymer in the presence of heat or light.

The degradation mechanism by which degradation of PVC takes place is complex. In general, it comprises one major reaction: the evolution of hydrogen chloride (dehydrochlorination process). In addition, cross-linking and chain scission reactions affect the physical properties of the degraded PVC. Cross-linking results in high molecular weight, stiff polymers, while chain scission reduces the molecular weight, thereby increasing solubility. Dehydrochlorination of the PVC polymer component in the museum objects examined was manifested as progressive discoloration attributed to the formation of conjugated polyene systems of increasing length.

A colour positive from the National Museum's Ethnographic Collection mounted in an acid-free card frame, depicting a painting by Albert Eckhout, exhibited typical damage due to storage in a PVC photograph pocket for about 15 years. The pocket exhibited cockling and distortion in the rectangular area corresponding to the window in the card frame (125 × 110 mm), directly above the positive image (see Fig. 10.1).

The image present on the positive was largely obscured by a layer of white crystals, unevenly distributed to form a pattern across the surface. The arrangement of crystals correlated well with the points at which the cockled PVC sheet made contact with the surface of the colour positive. A sample of the crystals was taken from the surface of the colour positive and analysed using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The spectrum was an excellent match with that of phthalic acid.

Since the object itself contained neither PVC nor DEHP, it is likely that DEHP diffused out of the photograph pocket and evaporated into the small airspace (approximately $13 \, cm^3$) between itself and the positive. When the airspace became saturated with DEHP vapour, it condensed onto the surface of the positive forming a thin film. With time, and favourable conditions, the condensed film degraded to form crystalline phthalic acid.

Although discoloration was aesthetically damaging, tackiness due to the presence of plasticiser at PVC surfaces was of greater concern from a conservation perspective. Packaging materials adhered to tacky surfaces making storage and transport of deteriorated objects difficult. Particulate matter and fibres, suspended in surrounding air, adhered to tacky surfaces. There was also concern that handling and contact with DEHP at surfaces may pose a risk to health, mainly due to its behaviour as an oestrogen mimic (European Union Commission 2000).

For these reasons it was decided to investigate the factors associated with migration of DEHP, and the possibilities for inhibiting its loss from new and deteriorated plasticised PVC in various storage environments.

Preparation and accelerated ageing of plasticised PVC

Model samples in the form of thin sheets were prepared to represent the full range of PVC/DEHP formulations present in museum collections. In addition, two 'objects', also plasticised with DEHP and exhibiting deterioration, were included in the experimental work to examine the effect of the environments on non-ideal materials. Due to lack of time, accelerated thermal ageing was used instead of natural ageing. Accelerated thermal ageing in the absence of light was used because it was thought to best represent the environment in a museum store.

Figure 10.1 Cockled and distorted PVC photograph pocket after 30 years in use (left). Crystalline phthalic acid formed on the surface of the positive image from degradation of DEHP plasticiser deposited by the photograph pocket (right).

Preparation of model sheets

Sheets were prepared from a PVC plastisol, commercially prepared by Hydro Polymers in Norway, comprising a liquid dispersion of PVC polymer, DEHP and barium/zinc laurate as thermal inhibitor. Chemical composition of the plastisol was characterised by thin-layer chromatography (TLC) of an ethereal extract. To produce model sheets containing the range of plasticiser concentrations found in museum collections, the plastisol supplied was diluted using DEHP, result-

ing in plasticiser concentrations of 33.3%, 37.5%, 44.4% and 50.0% by weight. Pigments were omitted since they were likely to confuse perception of discoloration by the PVC component.

Plastisols were heat pressed at 180 ºC for 90 seconds, achieving complete fusion between PVC and DEHP with minimal yellowing. Sheets 0.5 mm thick without solvent residues were produced and conditioned for 14 days under ambient conditions (ASTM D 2115-67 1980). Rectangular-shaped samples weighing 1 g (approximately 50 mm × 30 mm) were cut from the sheets for inclusion in accelerated ageing experiments.

Preparation of 'objects'

Two naturally aged PVC materials, both plasticised with DEHP, were included in the experimental work to evaluate the effect of various storage environments on deteriorated objects. A microscope cover in use for 15 years had developed slight opacity and a tacky outer surface. Dust particles and fibres adhered to the outer surface. Samples of 1 g were cut from a side panel.

A transparent, flexible PVC tube (1 cm outside diameter, wall thickness 0.2 cm) had been used to transport water for five years. Since its 'retirement' ten years ago, it had been suspended vertically and was open at the lower end. The tube appeared yellow and was tacky to touch. Samples (1 cm long and 1 cm outside diameter) were taken from at least 15 cm away from the nylon connector to avoid the area with very high DEHP content.

Preparation of storage environments used in thermal ageing

Model sheets and naturally aged 'objects' were exposed to various environments, all of which are frequently used to

store materials in museums (see Table 10.1). Adsorbent materials were used either to modify the properties of the air inside flasks prior to ageing or to remove degradation products formed during the ageing process.

Environments were created in wide-neck Pyrex glass flasks (100 ml) fitted with heavy-duty melamine resin screw caps lined with Teflon (polytetrafluoroethylene); materials were selected for their very low absorption of phthalates and high chemical stability. Samples of model sheets and 'objects' were suspended in the centres of flasks in order to provide equal opportunity for movement of gaseous materials around all surfaces of the sample.

Accelerated thermal ageing

Since volatile loss of plasticisers from PVC compounds is evaluated commercially at temperatures of 70 ºC (DIN53-405-1981, ASTM D1203-94), this temperature was used to accelerate the thermal ageing process in this study. It was also higher than the glass transition temperature of all model formulations used. Thermal ageing was conducted using a convection oven, with the exception of samples exposed to a low temperature, which was achieved using a domestic freezer (–20±1 ºC) for a period of 65 days. An initial trial suggested that this period was sufficient to initiate visible deterioration in all model sheets. The maximum period used to evaluate the performance of plasticised PVC in commercial tests is 30 days; 24 hours is more usual. Museum objects are intended to be kept for at least 50 years; the relatively long accelerated ageing period was intended to reflect this.

Examination of plasticised PVC

Non-destructive examination techniques were used to identify and quantify changes in visual, chemical and structural properties of the samples during thermal ageing. Findings

Table 10.1 Experimental storage environments used to thermally age model sheets and objects

Environment *	Equivalent museum storage	Function	How achieved
Closed	box or other container	exclude dust, buffer climate variations	Sheets suspended in closed screw-cap flask
Open oven	naturally ventilated storage area or display case	avoid build-up of pollutants	Sheets suspended in convection oven
Open glass plate	open shelf or cupboard	display	Sheets on Pyrex glass plate in convection oven
Activated carbon (AC)	activated carbon or activated charcoal cloth	adsorb and remove volatiles	AC placed in base of closed flask
Ageless® oxygen absorber	oxygen-free environment	inhibit oxidationpest control	One Ageless® Z sachet placed in base of each flask, before flushing with N_2
Silica gel	low relative humidity (RH)	dry air	silica gel placed in base of closed flask
High relative humidity	high RH	moisten air	water (20 mL) in base of closed flask
Low density polyethylene (LDPE) bag	self-seal polyethylene bags	exclude dust and facilitate handling	sheet placed in LDPE bag before sealing
Freezer (–20 ºC)	freezer for storage or pest control	inhibit deterioration	sheets suspended in closed flask in domestic chest freezer

* All environments were maintained at 70 ± 1 ºC except for freezer

from weight loss, concentration of DEHP at surfaces and colour measurements are discussed here.

Weight lost by model sheets and 'objects'

Weight loss was one of the earliest techniques used to evaluate the performance of plasticised PVC. In the 1950s, permanence of plasticisers was defined as weight loss when plasticised PVC samples were exposed to various conditions during use (Quackenbos 1954). Model sheets and 'objects' were weighed to four decimal place accuracy before and during ageing. Samples were removed from their ageing environment, whether it was flask, glass plate or low-density polyethylene (LDPE) bag and conditioned for five hours to ambient temperature (20–23 °C) without drying their surfaces prior to weighing.

The environment in which model sheets were aged clearly influenced the extent and rate of loss of plasticiser during ageing. After 65 days, samples aged with silica gel in an open oven, on an open glass plate and enclosed in a LDPE bag continued to lose weight. Samples in other ageing environments had stopped losing weight.

Model sheets aged in high relative humidity (RH) and freezer environments lost less than 1% of the original plasticiser content, while those aged in an open oven, on a glass plate and in a LDPE bag lost more than 5%, resulting in increased stiffness. There was very little difference between weight lost during ageing in a freezer and that lost in a closed microclimate at 70 °C for the same period of time, indicating that the storage temperature was a less important factor than the opportunity for the plasticiser to migrate or evaporate.

Loss from sheets hanging in an open oven, with all surfaces available for evaporation, was almost the same as that from sheets aged on open glass plates, despite the fact that the surface in contact with glass was not readily accessible by moving air to promote evaporation. In fact, DEHP was lost from the surface in contact with glass, observed by the presence of droplets between the underside of sheets and the glass. These droplets remained on the glass when sheets were removed for weighing.

DEHP was lost rapidly within the first 7–10 days of the ageing period, after which it was lost more gradually at a rate proportional to time. In closed environments and those containing activated carbon, loss of DEHP ceased after 14 days, suggesting that the concentration of DEHP vapour in the air surrounding the model sheets and the concentration at their surfaces had equilibrated. This was a good indication that the rate of loss was evaporation-controlled (Quackenbos 1954).

Loss of DEHP in closed environments was between 0.002 g and 0.004 g; in environments containing activated carbon it was between 0.011 g and 0.015 g from a 1 g sample when evaporation ceased. These results suggested that activated carbon adsorbed very little DEHP vapour from the model sheets before the concentration of plasticiser vapour in the air matched that at the surface of model sheets.

Model sheets in high RH did not lose weight – in some cases, weight was gained, probably by adsorbing water vapour or liquid water from condensed vapour. This was explained by the fact that water vapour is an efficient plasticiser for PVC polymer (Martin and Johnson 1974). After 65 days, model sheets containing 33.3% DEHP had gained more weight (0.005 g) than those containing 50.0% plasticiser (0.0025 g).

Weight lost by 'objects'

As for model sheets, the environment in which 'objects' were aged influenced the extent and rate of loss of volatiles during the 65-day period of ageing. Loss was greatest when 'objects' were stored in LDPE bags and lowest when aged in high RH environments.

Samples of the microscope cover lost more weight than tube samples in all environments during the same period of ageing. Percentage weight losses from both 'objects' were lower than those from model sheets (between 0% and 2.8%), so that the rate of loss during the experimental period was slower for 'objects'. This was attributed to the fact that during their 15–20 year period of natural ageing, some plasticiser and other volatile materials had already been lost. Samples aged in an open oven, on an open glass plate and in a LDPE bag lost weight rapidly in the first 10 days of ageing before the rate of loss slowed. After the initial rapid loss, percentage weight lost was directly proportional to ageing time, a good indication of loss by evaporation.

It was concluded that percentage DEHP loss from model plasticised PVC samples and percentage weight loss from 'objects' increased in the order of environment types presented in Table 10.2.

Table 10.2 Influence of storage environment on loss of plasticiser from PVC

Storage environment category	Examples
Enclosed with still, unstirred air (lowest loss of plasticiser)	Freezer, closed, high relative humidity
Enclosed with adsorbent materials in the same air space	Ageless oxygen absorber, silica gel, activated carbon
Lightly stirred air	Open oven, open glass plate
Enclosed in contact with highly adsorbent material (highest loss of plasticiser)	LDPE bags

Concentration of DEHP at surfaces of model sheets

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to quantify levels of DEHP present at surfaces of all samples (Fieldson and Barbari 1993). Spectra were collected over 30 scans at a resolution of 4 cm^{-1} between 4000 cm^{-1} and 600 cm^{-1}, using the ASI DurasamplIR single reflection accessory in a Perkin-Elmer Spectrum 1000 FTIR spectrometer. The high refractive index of the diamond internal reflection element compared with that of plasticised PVC (2.4 and 1.5 respectively) allowed absorbance data to be collected from a depth approximately equal to that of the wavelength of the infrared radiation, a maximum depth of approximately 2 μm

(Coombs 1999). Intimate contact between the diamond internal reflection element and the samples was achieved using a pre-set pressure device.

Beer's Law, which specifies that spectral absorbance is proportional to the concentrations of two components in a mixture, was applied to the spectra. Concentrations of DEHP at model sheet and 'object' surfaces were calculated by ratioing the absorbance intensities of peaks at 2860 cm^{-1} (C-H stretch, due only to DEHP) against those at 1426 cm^{-1} (C-H stretch, due only to PVC) on raw absorbance spectra (Tabb and Koenig 1975).

The surface concentration values represented the mean of five measurements, each of which comprised 30 scans taken at random positions on both upper and lower surfaces of aged model sheets and 'objects' (ten measurements in total). The level of significance was determined using a t-distribution statistical test (Miller and Miller 1993). Mean concentrations of DEHP at the surfaces of aged model sheets and 'objects' were compared with those measured for unaged samples to establish whether a minimum 95% confidence interval between the mean values existed. If not, it was concluded that there was no significant difference in the surface concentration of DEHP before and after ageing.

Ageing in an open oven, on an open plate and in a LDPE bag significantly reduced the surface concentration of all model sheets. This indicated that loss of DEHP in such environments occurred too rapidly for it to be replaced immediately by diffusion, indicating that diffusion had become the rate-determining step of the loss process.

Ageing in closed environments, freezers and with adsorbents, allowed plasticiser at the surfaces of aged model sheets to be replaced at the same rate as it was lost, by diffusion from the bulk of the sheet. As a result, no change in surface concentration was detected; evaporation was the rate-determining step by which DEHP was lost.

Concentration of DEHP at surfaces of 'objects'

Samples of an unaged microscope cover had a mean DEHP concentration of 1.1 concentration units at its surfaces. Fitting this value to the calibration curve obtained for unaged model sheets suggested that the surface concentration of DEHP corresponded to a bulk concentration of 46.5% (see Fig. 10.2).

Ageing in an open oven, on an open plate and in a LDPE bag significantly reduced the surface concentration of DEHP for the microscope cover. All other environments enabled the microscope cover to retain its original surface concentration. These results indicated the presence of two mechanisms by which DEHP was lost. The rate-determining step by which DEHP was lost during ageing in a freezer and with adsorbents was evaporation. However, loss of DEHP from the surface of the microscope cover during ageing in an open oven, open glass plate and in a LDPE bag occurred too rapidly for it to be replaced immediately by diffusion from the bulk.

Loss of DEHP from the surface of the microscope cover was compared with that lost by model sheets containing 44.4% and 50.0% DEHP by weight, since all three materials contained similar levels of plasticiser. After ageing, the extent and rate of loss of DEHP from the surface of the microscope cover were similar to that of the equivalent model sheets.

The unaged tube had a mean concentration of 1.04 concentration units at its surfaces. This value was fitted to the calibration curve obtained for unaged model sheets; it corresponded to a bulk concentration of 44.8% DEHP (see Fig. 10.2).

Ageing in an open oven, on an open plate and in a LDPE bag significantly reduced the surface concentration of DEHP for the tube. After ageing in all other environments the 'object' retained its original surface concentration. The mechanisms by which DEHP was lost were as described previously for the microscope cover.

Loss of DEHP from the surface of the tube was compared with that lost by the model sheet containing 44.4% plasticiser by weight after ageing. In the same period, extent and rate of loss of plasticiser from the surface of the tube was similar to that of the equivalent model sheet. For example, ageing in a LDPE bag for 65 days resulted in a reduction of 0.1 concentration units for the model sheet with 44.4% DEHP by weight; the same conditions produced a reduction of 0.3 units for the degraded tube.

Discoloration of model sheets and 'objects'

An electronic densitometer model Densy 301 from Barbieri was used in transmission mode to measure the optical density of model films and 'objects' before and after ageing (Hendriks 1991). Since all colour changes were due to yellowing, a blue density filter was used. The mean reading at three positions of each sample was calculated.

In general, where discoloration occurred, model sheets containing lower concentrations of DEHP exhibited greater darkening than more highly plasticised samples. Ageing in a closed environment produced no change in optical density, while ageing with activated carbon and silica gel produced unacceptable darkening. Discoloration was always visible at the edges of the sheets before it was observed at the surfaces.
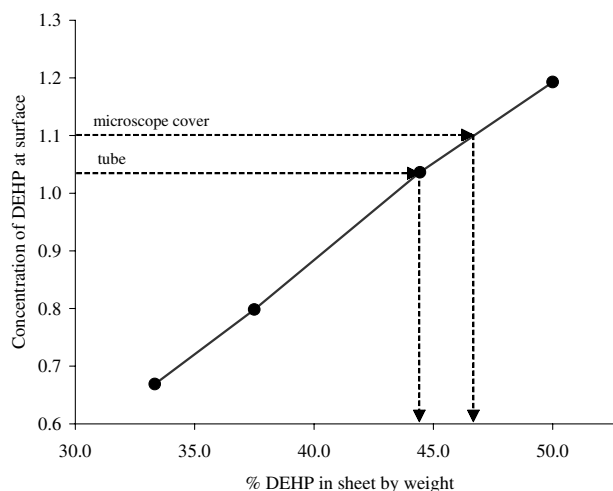

Figure 10.2 *Fitting concentration of DEHP at surfaces of microscope cover and tube 'objects' to that of the best straight line for concentrations at surfaces of model sheets.*
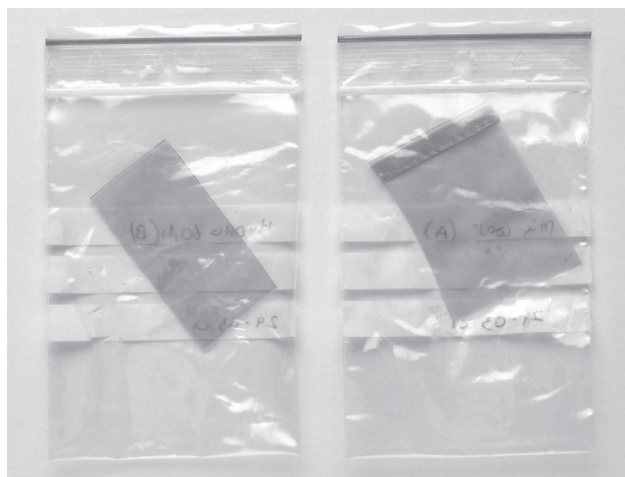
Figure 10.3 LPDE bags softened and crinkled after adsorbing plasticiser during accelerated thermal ageing of model sheets and 'objects'.

Ageing model sheets in LDPE bags caused the bags to soften and deform and samples to yellow (see Fig. 10.3). Droplets of DEHP were identified on an area corresponding to that of the model sheet on the inside surface. Polyethylene is known to be a good adsorbent for phthalate plasticisers when in contact (Sears and Darby 1982).

The microscope cover and tube were already slightly discoloured due to natural ageing. It was likely that most of the thermal and photo-stabilisers included at the formulation stage were now exhausted; this was the most likely cause of the increased discoloration compared with model sheets during ageing.

Ageing in a freezer caused no change in optical density and ageing with activated carbon caused the greatest increase in optical density for both 'objects'. One side that had been parallel to the base of the flask – and thereby closest to the adsorbent materials – became darker than the upper side closest to the cap. This suggested that adsorbents did not distinguish between pollutants and plasticiser vapour, and removed both from the enclosed air.

Figure 10.4 Tube before (left) and after thermal ageing at high relative humidity for 65 days. The achieved opacity was reversed on dehydrating under ambient conditions. Sample dimensions: 1.5 mm × 30 mm.

Exposure to high RH caused model sheets and 'objects' to become opaque (see Fig. 10.4). However, after dehydrating under ambient conditions, little change in the original optical density was visible.

Conclusions

The rate and extent of deterioration of plasticised PVC and the migration of DEHP plasticiser were related. DEHP inhibited the degradation of the PVC polymer, therefore when it either migrated to surfaces or was adsorbed by contact with polyethylene, PVC materials discoloured, became tacky to the touch and embrittled. Materials with lower levels of plasticiser degraded more rapidly than those more highly plasticised. Degradation was inhibited in both model formulations and 'objects' by enclosing them in a non-adsorbent material such as glass containing non-agitated air.

This is rather contra-intuitive. Museum 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 plastic objects during storage. The results obtained from this research suggest that such actions would accelerate the loss of plasticiser and thereby reduce the longevity of both new and deteriorated PVC objects.

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, clearly indicated that the useful lifetime of plasticised PVC objects may be prolonged more than tenfold at ambient conditions by changing the storage environment from a polyethylene bag to a closed glass container, or by placing the object in a freezer. Enclosing plasticised PVC objects – whatever their level of deterioration – is inexpensive to implement, of low practical complexity and allows public accessibility.

Acknowledgements

Suppliers

Hydro plastisol and DEHP: Technical Centre PVC, Hydro Polymers Nordic, 3907 Porsgruun, Norway

Silica gel-self indicating: Merck KGaA, 64271 Darmstadt, Germany

Ageless oxygen absorber: Mitsubishi Gas Chemical Company Inc., Mitsubishi Building, 5-2 Marunochi 2-chome, Chiyoda-ku, Tokyo 110, Japan

Activated carbon: Prolabo, Merck Eurolab, Z.I. de Vaugereau, 45250 Briare le Canal, France

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Standard test procedures

These may be viewed at the British Library or purchased through the appropriate website:

- http://www.astm.org for ASTM standards
- http://www.din.de for DIN standards

ASTM D2115-67 (1980), Recommended practice for oven heat stability of poly (vinyl chloride) compositions.

ASTM D1203-94, Standard test methods for volatile loss from plastics using activated carbon methods.

DIN 53-405-1981, Testing plasticisers; determination of migration of plasticisers.

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