Abstract

Plasticized poly (vinyl chloride) (PVC) in museum collections deteriorates by migration, loss and chemical break-down of the plasticizer, accompanied by dehydrochlorination of the polymer. The extent, rate and mechanisms of deterioration of new and deteriorated plasticized PVC were compared during and after accelerated thermal ageing in various environments. Weight loss was used to quantify total loss of plasticizer. Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to quantify the concentration of di (2-ethylhexyl) phthalate plasticizer (DEHP) at the surfaces of samples. Optical densitom-etry was used to quantify darkening of the PVC component of samples. Degradation of new and deteriorated PVC was inhibited by enclosing it in a non-adsorbent material, such as glass containing non-agitated air. Such storage inhibited migration and loss of DEHP.

Keywords

PVC, DEHP, phthalate, plasticizer, plastic, adsorbents, ATR-FTIR, degradation

Figure 1. Cockled and distorted PVC photograph pocket (Top), and crystalline phthalic acid deposited on photographic positive from PVC photograph pocket (Bottom)

Deterioration and conservation of plasticized poly (vinyl chloride) objects

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Introduction

Plasticized poly vinyl chloride (PVC) has been one of the most economically and technically important plastics materials since the 1950s. As a result, examples are present in many international museum collections, as clothing and footwear, furniture, electrical insulation, toys and packaging materials. Many plasticized 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°C. Compounding PVC involves adding sufficient modifying components to the polymer to produce a homogene-ous mixture suitable for processing at the lowest price. Plasticizers are the major modifier for PVC formulations in terms of percentage weight (between 15 and 50%) and physical properties (see Table 1). They have two main functions: to assist in the processing stage by reducing the viscosity and melting temperature, and to soften the final PVC product (Wilson 1995).

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 is di (2-ethylhexyl) phthalate plasticizer (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 plasticized PVC

Examination of deteriorated PVC objects and storage materials plasticized with DEHP and in the care of the National Museum of Denmark suggested that plasticizer first migrated from bulk to surfaces (Shashoua 2001). This was manifested by increased tackiness. From the surface, DEHP either evaporated slowly or hydrolyzed to crystalline phthalic acid (see Figure 1). Later, the PVC polymer component degraded to form conjugated polyene systems of increasing length that discoloured the objects. Degradation of objects was first detected within 10 to 35 years of acquisition. Although discoloration was aesthetically damaging,

Table 1. Typical applications for plasticized PVC formulations

DEHP (per hundred parts PVC, phr)	DEHP (% by weight based on PVC and DEHP)	application
20	16.7	vinyl flooring[1]
30	23.1	upholstery cover[2]
40	28.6	document folder[1]
50	33.3	garden water hose[3]
60	37.5	electrical cable sheath[3]
80	44.4	shoe sole[2]
100	50.0	rubber (wellington) boots[2]

[1]Wickson 1993   [2]Wilson 1995   [3]Brydson 1999

Figure 2. Microscope cover had a developed a cloudy appearance and was tacky to touch after 15 years

tackiness due to the presence of plasticizer 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. Particulates and fibres suspended in surrounding air adhered to tacky surfaces. There was also concern that handling and contact with DEHP at surfaces might pose a risk to health, mainly because of its behaviour as an œstrogen 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 plasticized PVC in various storage environments.

Preparation and accelerated ageing of plasticized PVC

Model samples were prepared to represent the full range of PVC/DEHP formulations present in museum collections. In addition, two objects, also plasticized 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 represent the environment in a museum store.

Preparation of model sheets

Sheets were prepared from PVC plastisol by Hydro Polymers in Norway. The sheets comprised a liquid dispersion of PVC polymer, DEHP and barium/zinc laurate as the thermal inhibitor. Pigments were omitted, since they were likely to confuse perception of discoloration by the PVC component. To produce model sheets containing the range of plasticizer concentrations found in museum collections, the plastisol was diluted using DEHP, resulting in plasticizer concentrations of 33.3%, 37.5%, 44.4% and 50.0%.

The plastisols were heat pressed at 180°C 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). 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 plasticized with DEHP, were included 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 (see Figure 2). Dust particles and fibres adhered to the outer surface. Samples (1 g) were cut from a side panel.

A transparent flexible PVC tube (1 cm outside diameter, 0.2 cm wall thickness) had been used to transport water for five years. Since its 'retirement' 10 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 with a 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

Model sheets and naturally aged objects were exposed to various environments, all of which are frequently used to store materials in museums (see Table 2). 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). The materials were selected for their very low absorption of phthalates and high chemical stability. Samples of model sheets and objects were suspended in the

Table 2. 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 oxidation pest 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 (20mL) 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°C)	freezer for storage or pest control	inhibit deterioration	sheets suspended in closed flask in domestic chest freezer

* all environments were maintained at 70 ±1°C except for freezer

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 plasticizers from PVC compounds is evaluated commercially at temperatures of 70°C (DIN53-405-1981, ASTM D1203 1994), 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 the freezer (-20±1°C), for a period of 65 days.

Examination of plasticized 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 from weight loss, concentration of DEHP at surfaces and colour measurements are presented here.

Weight lost by model sheets

Weight loss was one of the earliest techniques used to evaluate the performance of plasticized PVC. In the 1950s, permanence of plasticizers was defined as weight loss when plasticized 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 a flask, glass plate or 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 plasticizer during ageing. Table 3 shows environments rated in increasing order of plasticizer loss after ageing. Although the results presented are those for model sheet containing 33.3% DEHP by weight, the rating applied to all sheets. After 65 days, samples aged with silica gel in an open oven and on an open glass plate and enclosed in a LDPE bag continued to lose weight. Samples in other ageing environments had stopped losing weight.

Table 3. DEHP lost by model sheets containing 33.3% plasticizer after accelerated thermal ageing for 65 days

accelerated ageing environment[1]		% DEHP lost after 65 days (%)	mass DEHP lost after 65 days (g)
high relative humidity	(lowest DEHP loss)	0.0	0.000
freezer		0.4	0.002
closed		0.7	0.004
Ageless® oxygen absorber		3.0	0.015
silica gel		3.6	0.019
activated carbon		3.7	0.021
open oven		5.7	0.031
open glass plate		5.9	0.032
LDPE bags	(highest DEHP loss)	10.1	0.044

[1] all environments were maintained at 70°C with the exception of freezer (-20°C)

Model sheets aged in high relative humidity (RH), freezer and closed environments lost less than 1% of their original plasticizer content, while those aged in an open oven on a glass plate and in LDPE bags 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 plasticizer 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 the glass was not readily accessible by moving air to promote evaporation. However, 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 to 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).

Mass of DEHP lost from model sheets during ageing in a closed environment (lowest loss) and an open oven (higher loss) are presented in Figure 3 for comparison. Loss of DEHP in closed environments was between 0.002 g and 0.004 g, and in environments containing activated carbon was between 0.011 and 0.015 g from a 1 g sample when evaporation ceased. These results suggest that the activated carbon adsorbed very little DEHP vapour from the model sheets prior to the concentration of plasticizer vapour in the air and on the surface of the model sheets equilibrating.

The model sheets in high RH did not lose weight, but in some cases gained it, probably by adsorbing water vapour or liquid water from condensed vapour. This was explained by the fact that water vapour is an efficient plasticizer 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% plasticizer (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. The percentage of weight lost increased in the order shown in Table 4.

Samples of the microscope cover lost more weight than did the tube samples in all environments during the same period of ageing. Percentage weight losses from both objects were lower than those from model sheets, so that the rate of loss during the experimental period was slower for objects. This was attributed to the fact that during their 15-to-20-year period of natural ageing, some plasticizer and other volatile materials had already been lost. Samples aged in an open oven on an open glass plate and in LDPE bags lost weight rapidly in the first 10 days of ageing before
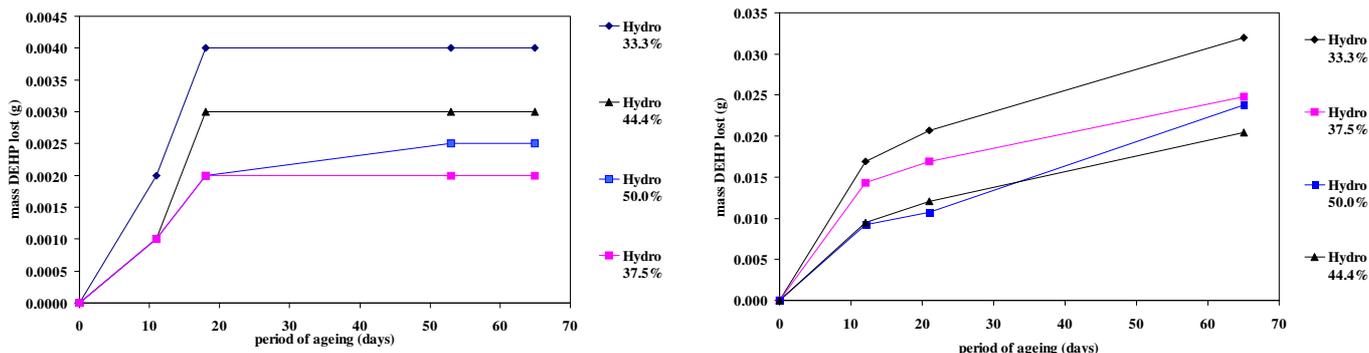
Figure 3. Comparison of mass DEHP lost from model sheets during accelerated thermal ageing in closed environments (left) and in open oven (right)

Table 4. Weight loss from objects

environment		% weight lost by tube after 65 days (%)	% weight lost by microscope cover after 65 days (%)
high relative humidity	(lowest % weight loss)	0.0	0.0
closed		0.0	0.2
freezer		0.2	0.1
Ageless oxygen absorber		0.4	0.8
silica gel		0.4	1.4
activated carbon		0.6	1.6
open oven		1.6	1.6
open glass plate		1.7	2.6
LDPE bags	(highest % weight loss)	1.9	2.8

Table 5. Influence of storage environment on loss of plasticizer from PVC

storage environment category	examples
enclosed with still, unstirred air (lowest loss of plasticizer)	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 plasticizer)	LDPE bags

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 the model plasticized PVC samples and percentage weight loss from objects increased in the order of environment types presented in Table 5.

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 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 plasticized 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 two microns (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 the model sheet and object surfaces were calculated by setting the ratio for 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).
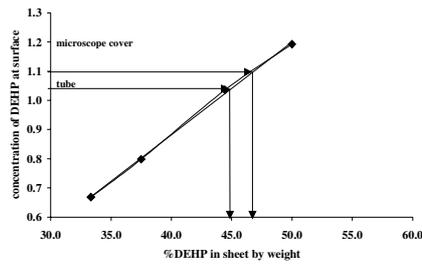
Figure 4. Fitting concentration of DEHP at surfaces of objects to that of the best straight line for concentrations at surfaces of model sheets

Since 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 (10 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 LDPE bags 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 and a freezer, and with adsorbents, allowed plasticizer at the surfaces of the 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 the unaged microscope cover had a mean DEHP concentration of 1.1 concentration units at the surface. 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% (Figure 4).

Ageing in an open oven on an open plate and in LDPE bags 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 on an open glass plate and in an 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 plasticizer. 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.

An 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 Figure 4).

Ageing in an open oven on an open plate and in LDPE bags 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 were 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% plasticizer by weight after ageing. In the same period, the extent and rate of loss of plasticizer 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 a 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

Figure 5. Model sheets before (bottom row) and after 65 days accelerated ageing with activated carbon. From right to left: sheets contained 33.3%, 37.5% 44.4%, 50.0% DEHP. Edges of sheets appeared darker than the bodies. IS THIS CAPTION CORRECT
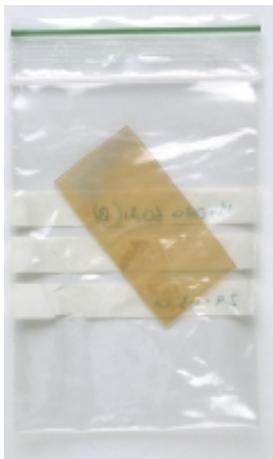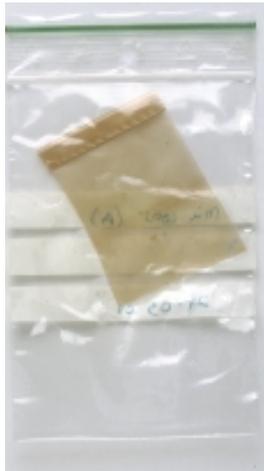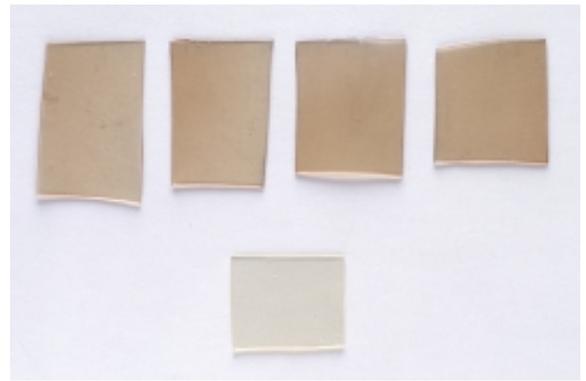
density filter was used. The mean reading at three positions of each sample was calculated.

In general, where discoloration occurred, model sheets containing lower concentrations of DEHP exhibited greater darkening than more highly plasticized 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 5).

Ageing model sheets in LDPE bags caused the bags to soften and deform and the samples to yellow (see Figure 6). 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 plasticizers (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-stabilizers 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, which had been parallel to the base of the flask and thus closest to the adsorbent materials, became darker than the upper side closest to the cap (see Figure 7). This suggested that adsorbents did not distinguish between pollutants and plasticizer vapour, and removed both from the enclosed air.

Exposure to high RH caused the model sheets and objects to become opaque (see Figure 8). However, after dehydrating under ambient conditions, little change in the original optical density was visible.

Figure 6. LDPE bags softened and crinkled after adsorbing plasticizer during use as accelerated thermal ageing environments for model sheets and objects

Figure 7. Tube before (left) and after accelerated thermal ageing with activated carbon. Note the uneven discoloration of the aged sample. The darker half was closest to the carbon during ageing. Sample dimensions: 1.5 mm diameter x30 mm
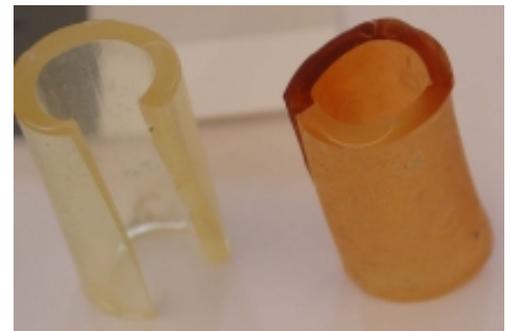

Figure 8. Tube before (left) and after thermal ageing at high RH for 65 days. The achieved opacity was reversed on dehydrating under ambient conditions. Sample dimensions: 1.5 mm diameter ´ 30 mm

Conclusions

The rate and extent of deterioration of plasticized PVC and the migration of DEHP plasticizer were related. DEHP inhibited the degradation of the PVC polymer; therefore, when it evaporated the PVC became discoloured and tacky. Materials with lower levels of plasticizer were more susceptible to discoloration than more highly plasticized ones. Degradation was inhibited from both model formulations and objects by enclosing them in a non–adsorbent material, such as glass containing non–agitated air. Storage in a freezer also successfully minimized loss of plasticizer. Storage in environments where air circulated around PVC objects, including an open glass shelf, or wrapping objects in an adsorbent packaging material such as polyethylene, or with adsorbents to control air quality, resulted in high losses of DEHP.

Enclosing plasticized PVC objects, whatever their level of deterioration, is inexpensive to implement, of low practical complexity and allows public accessibility to plastics objects.

Acknowledgements

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Standard test procedures

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 plasticizers, determination of migration of plasticizers.

Suppliers of chemicals used in the research project

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