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Safe storage? An assessment of polyethylene for the storage of heritage objects

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Abstract

Sealable polyethylene bags are widely used to protect and store heritage items. While polyethylene is regarded as a stable material, consideration should be given to potential chemical interactions between the polymer and stored objects. The presence of additives used in manufactured polyethylene storage materials should also be considered when they are used in contact with objects. For this study, infrared spectroscopy has been successfully used to identify storage materials and associated additives, as well as to characterise the chemical changes that they undergo. Three case studies are presented that demonstrate that polyethylene bags can undergo chemical changes when exposed to the typical storage conditions used for heritage objects. The storage of degrading cellulose nitrate items shows that polyethylene undergoes oxidation when exposed to the cellulose nitrate degradation products and is identified as detrimental to long term storage viability of the polyethylene. An investigation of the yellow discolouration of polyethylene bags suggests that the oxidation of antioxidant additives, rather than the polyethylene, is responsible for the colour change. It is also demonstrated that polyethylene bags used in a procedure for the consolidation of archaeological ceramics shows an interaction between the adhesive solvent employed and the bag additives.

Keywords: polyethylene; attenuated total reflectance infrared spectroscopy; additives; degradation; cellulose nitrate; Paraloid B-72.

Introduction

Resealable polyethylene (PE) bags are widely employed for the storage of museum and archaeological objects as they provide an easy means of protecting and separating items. The selection of PE bags for storage is associated with the ready availability, low cost and the comparative chemical stability of the polymer [Bergmair et al. 2010; Schmitz & Janocha 2012]. Although PE is perceived as an inert substance, consideration should be given to the possible presence of additives used in this manufactured storage material when they are employed in contact with stored objects. A range of chemical additives are used during the commercial production of polymers to improve the properties and longevity of these materials. Additives fulfill a range of purposes, including protection against degradation processes that can occur during processing or due to environmental exposure, assisting with processing or providing superior physical properties [Pelzi *et al.* 2018; Vasile 2000]. The principal classes of additives used in the production of PE films that should be considered are stabilisers and processing agents that are used to aid the stability and flow during the processing of PE [Tolinski 2015].

During the polymerisation process used to synthesise PE some molecular defects, such as unsaturated C=C bonds, hydroperoxide or carbonyl groups, may be retained by or introduced into the synthesised polymer. PE films are produced using an extrusion processing method, which involves feeding the polymerised PE beads into a heated barrel of an extruder with a rotating screw [Schmitz & Janocha 2012]. As such, the polymer is subjected to heat and mechanical shear in order to form the resulting film and these factors can also be responsible for defects, making the polymer more susceptible to degradation.

PE can undergo a free radical photooxidation process due to the actions of ultraviolet light and oxygen and the process can ultimately result in polymer chain scission or crosslinking reactions, which has a detrimental effect on the physical properties [Fay & King 2018; Edge 2006]. Exposure to heat, shear stresses and residual catalysts in the presence of oxygen during processing can lead to autooxidation. Hydrogen is abstracted from the polymer chain during autooxidation to form alkyl free radicals (R•). Oxygen can combine with free radical species to form peroxy radicals (ROO•) and hydroperoxides (ROOH):

$R\bullet + O_2 \rightarrow ROO\bullet$

$ROO\bullet + RH \rightarrow R\bullet + ROOH$

The hydroperoxides formed are also reactive and create new free radical species such as alkoxy (RO•) and hydroxy (•OH) radicals:

$ROOH \rightarrow RO\bullet + \bullet OH$

The autooxidation process is a continuous process as the subsequent reaction of the polymer with the radicals formed by the hydroperoxides produces non-radical by-products, including oxygenated carbonyl compounds. In the process, two more polymer radicals are formed. As the process continues, more radicals and transformation products are produced, with polymer chains degrading. The formation ketones, aldehydes, alcohols, carboxylic acids, keto acids, esters, lactones and alkenes are all potential products resulting from the various mechanisms and these compound types can produce further chain scission or crosslinking in the polymer [Gardette *et al.* 2013, Therias *et al.* 2021, Salvalaggio *et al.* 2006].

Certain classes of additives are widely employed in PE film formation to stabilise the polymer and to improve processability: antioxidants, acid scavengers and processing agents. Antioxidants are added to polymers to provide protection against the oxidative degradation caused during processing and/or environmental exposure. A traditional stabilisation system involves a combination of hindered phenolic and phosphite antioxidants [Allen & Edge 2021; de la Rie 1988; Fay & King 2018; Vasile 2000]. Hindered phenolic compounds act as primary antioxidants, intercepting radicals as they form ('scavenging') and, thus, can minimise the free radical species attacking the polymer. This type of phenolic compound contains an OH functional group that can act as a hydrogen donor to peroxy radicals, stabilising the polymer against oxidation by forming less damaging products. Phosphites act as secondary antioxidants by reacting with hydroperoxides and generating inactive products, so play a role in stabilising the polymer.

A class of stabilisers used for PEs is the acid scavengers, incorporated into the polymer formulation prior to processing to neutralise acidity [Sherman & Kern 2018; Allen & Edge 2021]. Acidic catalyst residues can remain after the polymerisation process and, if not counteracted, can cause damage to processing equipment as well as to the polymer itself. The most commonly used acid scavengers include metal carboxylates or zinc oxide, and the mechanism involves standard acid-base chemistry. For example, in the case of calcium stearate:

$$Ca(C_{17}H_{35}O_2)_2 + 2HCl \rightarrow CaCl_2 + 2(C_{17}H_{35})OOH$$

Acid scavengers are usually added at a concentration level of 0.05-0.1 w%.

The production of polymer film also requires the use of processing aids, such as slip and antiblocking agents. Slip agents modify the polymer surface and enable better handling by

reducing the friction between film layers and between the film and processing equipment [Gray & Breuer 2018; Tolinski 2015]. Such additives are intentionally incompatible with the polymer and are designed to migrate to the polymer surface during processing. The most used slip agents for PE films are fatty acid primary amides such as erucamide [$CH_3(CH_2)_7CH=CH(CH_2)_{11}CONH_2$], oleamide [$CH_3(CH_2)_7CH=CH(CH_2)_7CONH_2$], stearamide [$CH_3(CH_2)_{16}CONH_2$] and behenamide [$CH_3(CH_2)_{20}CONH_2$], but metal stearates are also used due to their ability to act as acid scavengers [Tolinski 2015; Bart 2005; Gray & Breuer 2018]. The normal quantity of slip agent is of the order of 0.05-0.1 w% of the formulation. Antiblocking agents prevent adhesion between stacked film layers and are mostly comprised of inorganic minerals.

Although usually present only in small quantities, additives have the potential to react with compounds produced by degrading artefacts or objects that have been treated with conservation grade materials that are subsequently housed inside storage bags. There is also potential for PE to degrade during the long-term storage of items. As such, an investigation has been undertaken into the composition and behaviour of PE storage bags containing additives, within a heritage context. This paper presents the results of three case studies where chemical changes have been observed for PE storage bags: bags used for the storage of cellulose nitrate (CN) objects; unused bags showing yellow discolouration; and bags used in an adhesive consolidation process for archaeological ceramics involving exposure to a solvent.

Fourier transform infrared (FTIR) spectroscopy has been utilised to examine the chemical changes to PE bags, their additives and stored items. The technique is a widely adopted technique for the examination of polymers due to an ability to identify both the organic and

inorganic components of this class of materials. A non-destructive attenuated total reflectance (ATR) sampling technique has been employed and is instrumentation that is commonly available in conservation laboratories.

Materials and methods

Cellulose nitrate artefacts stored in PE bags

Plastic artefacts excavated from the Commonwealth Block: Black Eagle and Oddfellows Hotels archaeological site in Melbourne during 1990 were stored in PE resealable bags at Museums Victoria [Willis 2010]. The bags were stored in Coreflute polypropylene archival boxes (Figure 1). An inspection of the stored items revealed signs of storage material deterioration, with changes observed to the barcoded label and the adhesives attaching the label to the PE bag. A bag containing combs and associated fragments (Museums Victoria accession number LL77385) was examined for the current study.

ATR-FTIR spectra were collected for the LL77385 items and the storage bag using a Bruker Alpha FTIR spectrometer equipped with a diamond ATR accessory. Thirty two scans were collected at a resolution of 4 cm^{-1} over the 4000-400 cm^{-1} range. Stored plastic items were also analysed using a Bruker Tracer III-V+ portable x-ray fluorescence (XRF) spectrometer containing a rhodium target. The spectrometer was operated at 20 μA and 40 kV and a measurement time of 120 s.

Discolouration of PE storage bags

Resealable PE bags stored in original packaging at the South Australian Museum for approximately 8 years exhibited yellow discolouration (Figure 2). Although bags from the same period were used to house collections, none of those used exhibited the same yellow discolouration observed for the batch of unused bags under study. ATR-FTIR spectra were collected for the bags using a Nicolet iS10 FTIR spectrometer equipped with a diamond ATR accessory. Sixty four scans were collected over the 4000-500 cm^{-1} range at a resolution of 4 cm^{-1}.

Archaeological ceramic consolidation method using PE bags

Paraloid B-72 resin (Rohm and Haas) was dissolved in acetone (ChemSupply) to prepare a 10 w% solution. Two PE resealable bags (7.5 × 12.5 cm), one placed inside the other, were used to carry out a ceramic consolidation process according to the method described by Koob [2009]. The bags were labelled with the excavation code, the number of fragments, and then the sherds were placed within. The Paraloid B-72 solution was pipetted along the inside of the inner bag until approximately one-third of the ceramic was immersed. After 24 h, excess consolidant was poured away. For this method, the PE bags act as a vapour chamber and are permeable to acetone, which migrates out through the plastic. The ceramic was left in the bag until the solvent within the bag had evaporated. The evaporation time varied between one-week to one-month and depended on the porosity and thickness of the sherd. After the ceramic was removed the adhesive film deposited on the interior of the PE bag was removed using tweezers. A separate Paraloid B-72 film was prepared by pipetting the solution on a microscope slide to form a thin film on evaporation of the

solvent. ATR-FTIR spectra were acquired for each sample at a resolution of 4 cm^{-1} using a Nicolet iS10 FTIR spectrometer equipped with a diamond ATR accessory. Sixty four scans were collected over the range 4000-500 cm^{-1}.

Results and discussion

Cellulose nitrate artefacts stored in PE bags

Excavated combs stored in PE bags by Museums Victoria (Figure 1) were examined using ATR-FTIR spectroscopy and a representative spectrum is shown in Figure 3. These comb fragments exhibit the spectral characteristics of cellulose nitrate and zinc oxalate (Table 1) [Quye *et al.* 2011, Bussiere *et al.* 2014, Simonsen *et al.* 2020]. Moulded CN was introduced in the 1870s and found wide application for imitating natural materials in household objects, such as hair combs. Its usage began to decline in the 1930s when other plastics were developed with more attractive properties [Shashoua 2008; Quye *et al.* 2011]. The presence of an oxalate on the comb surface is a sign of oxidative degradation in CN [Quye *et al.* 2011]. An initial scission process in cellulose produces a keto derivative, which in acidic conditions will decompose into oxalic acid. Zinc oxalate ($ZnC_2O_4.2H_2O$) can form by interaction with zinc ions and the likely source is zinc oxide, commonly used as a filler and acid scavenger for CN objects [Reilly 1991]. Zinc oxide has been shown to transform into zinc oxalate on ageing in artworks [Simonsen *et al.* 2020, Poli *et al.* 2014]. The presence of zinc oxide in the comb is also supported by XRF analysis. An XRF spectrum of the comb is shown in Figure 4, with the dominant peaks due to zinc (Zn Kα1 at 9.6 eV; Zn Kα2 at 8.7 eV; peaks near 20 eV attributed to the instrument source) [Quye *et al.* 2011].

The broadening of the CN bands in the spectrum shown in Figure 3 and the relatively low intensity of NO_2 bands indicates degradation of the CN component [Nunes *et al.* 2020, Berthumeyrie *et al.* 2014]. The visible signs of CN deterioration observed for the comb include yellow discolouration, internal and external cracking and crazing, as well as a strong odour released when the PE bag was opened. These observations are aligned with the symptoms exhibited by degrading CN objects in collections [Shashoua 2008]. The comb was brittle and had fragmented into multiple pieces with some in powder form. An initial denitration step is followed by the formation of oxidation products, which subsequently react to produce chain scissions in the CN structure, leading to embrittlement and yellowing [Berthumeyrie *et al.* 2014, Bussiere *et al.* 2014]. Embrittlement may also be due to the loss of camphor, a commercial plasticiser that was commonly added in the manufacture of CN products before the 1930s, the loss of which leads to the plastic shrinking and becoming brittle [Shashoua 2008].

The plastic resealable bag used to store the CN combs was also analysed, internally and externally, using ATR-FTIR spectroscopy. There was no evidence of discolouration of the storage bag at the time of removal of the items and analysis. Representative ATR spectra of both the exterior and interior of the storage bag after removal of the CN items are shown in Figure 5 and the assignment of the infrared bands appearing in these spectra are listed in Table 2.

The spectra for both the interior and exterior regions of the bag show characteristic spectral features of PE, with the major characteristic bands observed at 3000-2800 cm^{-1} (C-H stretching), 1475-1375 cm^{-1} (C-H bending) and 730-715 cm^{-1} (C-H rocking) [Stuart 2004; Coates 2006; Chercoles Asensio *et al.* 2009]. The polymer is identified as low-density

polyethylene (LDPE) due to the relative absorbance ratios of the 1379 and 1368 cm^{-1} bands observed in the spectrum: the 1379 cm^{-1} is more intense relative to the 1368 cm^{-1} contribution. The ratio for these bands is recognised as a measure of chain branching and is, therefore, able to be used to discriminate LDPE and high-density polyethylene (HDPE) [Gulmine *et al.* 2002].

The spectra illustrated in Figure 5 also show a series of weak bands at 1750-1700, 1660-1600, 1575-1540 and 1075-1025 cm^{-1}. These are attributed to the presence of a stearate additive, a widely employed acid scavenger for the processing of PE that also acts as a slip agent [Sherman & Kern 2018]. The band positions provide evidence that a combination of zinc stearate and calcium stearate has been employed during the production of this PE [MacKenzie *et al.* 1983].

The spectrum for the interior region of the bag used to store the CN combs, illustrates a number of bands in addition to those components observed for the exterior of the bag. A broad band in the 1800-1600 cm^{-1} region comprised of multiple components provides evidence of the presence of oxidation products. The carbonyl region of the infrared spectrum provides a well-established means of monitoring the oxidation process for PE [Gardette *et al.* 2013; Therias *et al.* 2021; Salvalaggio *et al.* 2006, Yagoubi *et al.* 2015]. Contributions in the 1800-1700 cm^{-1} region can be separated based on the nature of the carbonyl-containing class of compound present. The intensity of the 1713 cm^{-1} band is used as a means of quantifying the extent of oxidation (the carbonyl index) as this wavenumber is mainly a measure of carboxylic acids, the final oxidation products. In Figure 5 the band maximum (as a shoulder) is observed at 1710 cm^{-1}, indicating that the late oxidation products, such as carboxylic acids, are likely to be a main contributor. A very broad O-H

stretching band centred at 3400 cm^{-1} is also characteristic of carboxylic acids. The broadness of the carbonyl band region indicates that other carbonyl containing products are also present. Additional carbonyl contributions are observed below 1700 cm^{-1} and known oxidation products of PE, including α,β-unsaturated ketones, show a contribution at 1684 cm^{-1} [Salvalaggio *et al.* 2006; Yagoubi *et al.* 2015]. Also in the 1700-1600 cm^{-1} region are C=C stretching contributions, providing evidence of the presence of unsaturated groups [Coates 2006, Stuart 2004].

The oxidation products identified on the interior surface of the storage bag are most likely to be a consequence of the degradation of the CN stored in the bag and the interaction of the degradation products with the PE. The CN degradation process is well-established and involves side and main chain scission processes [Edge *et al.* 1990; Nunes *et al.* 2020; Bertumeyrie *et al.* 2014]. Cleavage of the RO-NO_2 bond forms an alkoxy radical species (RO•) and NO_2• is released. The NO_2• can transform to nitrous acid (HNO_2) and nitric acid (HNO_3) through a reaction with water. The introduction of an acid can initiate oxidative degradation processes in the PE. Previous studies on the effect of nitric acid on PE have shown that carboxyl groups can be introduced on exposure to the acid and that carboxylic acids form as a major product [Rueda *et al.* 1981; Garaeva *et al.* 2010].

Another potential source of carboxylic groups is the presence of degradation products formed by camphor, a widely adopted plasticiser used for CN objects [Reilly 1991; Elsasser *et al.* 2020]. Camphor undergoes an oxidation reaction with nitric acid to form a dicarboxylic acid, camphoric acid, and this compound could be a contributor to the carboxylic spectrum [Rajitha *et al.* 2017]. Camphor can comprise up to approximately one third of the mass of the composition of a CN object. However, as CN objects age, the camphor is lost via

sublimation at room temperature, explaining the lack of characteristic bands for camphor in the spectrum shown in Figure 3. The main band observed for camphor is the C=O stretching bands in the 1750-1700 cm^{-1} range, but weaker contributions associated with sublimation loss may be hidden by the very broad C=O stretching band by CN.

Discolouration of PE storage bags

The discolouration of unused storage bags at the South Australian Museum was examined with the aim of establishing whether the source of the yellow colour was likely to cause damage to stored objects or represented disintegration of the bags themselves, rendering them unsuitable for storage purposes. The yellow colour was observed to be more prominent at the edges of the white label printed on the exterior of the bag, as well as internally in the region behind the label.

Figure 6 shows a representative ATR spectrum collected for a yellowed bag. The strongest bands in the spectra are characteristic of LDPE, as reported in Table 2, confirming the composition of the bag material. The spectrum also shows a series of bands that may be attributed to the presence of a metal stearate slip agent, as was observed for the bag used for CN storage [MacKenzie *et al.* 1983]. Contributions in addition to stearate in the 1800-1600 cm^{-1} region of the spectrum are observed in the spectrum shown in Figure 6. Components due to C=O and C=C stretching in this region can be associated with the presence of oxidation products with quinones, a class of highly coloured compounds, being a likely source [Fuson *et al.* 1954; Socrates 2004]. Closer inspection of the fingerprint region of the spectrum shows a series of overlapping bands in the 1325-1070 cm^{-1} region of the spectrum. Bands in this region are complex and can contain contributions from C-C

stretching, C-O stretching, CH_2 rocking and CH_2 wagging, and support the observation of contributions due to oxidation products. A weak band at 890 cm^{-1} is attributed to the presence of calcium carbonate, which is used as an antiblocking agent for PE films [Xanthos 2005].

The bright yellow colour observed in the bags studied is a regularly encountered phenomenon for PE films and is widely attributed to oxidation products of phenolic antioxidant additives. If processing conditions are too severe, over-oxidation of phenolic antioxidants contribute to the gradual discolouration of PE [Allen & Edge 2021]. The phenolic antioxidant butylated hydroxytoluene (BHT) (2,6-di-*tert*-butyl-6-methylphenol) is used to stabilise PE during processing and its mechanism as a phenolic stabiliser has been well studied [Allen & Edge 2021, Pospišil *et al.* 2002, Pospišil 1973]. Transformation products that result from BHT include quinone methides, benzoquinones and stilbene quinones [Pospisil 1973; Kovarova *et al.* 1995; Daun *et al.* 1974]. One of these products, 3,3',5,5'-tetra-*tert*-butyl-stilbene-4,4'-quinone, the structure of which is illustrated in Figure 7, has been identified as responsible for yellow discolouration observed in polymers [Allen & Edge 2021; Pospišil *et al.* 2002; Pospišil 1973, Daun *et al.* 1974]. Although it is accepted that the presence of such quinones does not contribute to PE degradation, awareness of their presence is important as they may have influence on stored items in bags in direct contact, especially as quinones readily undergo sublimation.

The infrared spectrum of the white label of the bag indicates that it is principally comprised of ethylene bis(stearamide) (EBS), a waxy white material commonly used as a coating, and a titanium dioxide pigment [Nakhaei *et al.* 2018]. The appearance of the more intense yellow

colour in the locations adjacent to the printed label is likely to be a result of thermal printing of the label during processing. The additional thermal exposure during the printing process may cause more extensive phenolic antioxidant transformation to occur and this would result in an increased yellow quinone product in those sections of the bag.

Archaeological ceramic consolidation method using PE bags

Paraloid B-72 is an acrylic resin comprised of an ethyl methacrylate – methyl acrylate copolymer and is regularly used by conservators for the consolidation and conservation of objects. A method adopted for the consolidation of archaeological ceramics involves the use of Paraloid B-72 in acetone solution as an adhesive [Koob 1986]. Acetone is favoured as a solvent due to its solubility and volatility. In order to control the rate of evaporation of acetone when using the Paraloid adhesive, a modified method of application has been developed for the consolidation of pottery sherds [Koob 2009, Jones-Amin 2014]. By carrying out the procedure within PE sealed bags, the acetone evaporates through the bags and excess Paraloid dries as a thin film on the inside surface of the bag. As acetone is a solvent for additives that may be present in PE, an examination of potential changes to the bag during the consolidation procedure has been performed.

An ATR spectrum of a PE bag from the supply used for a pottery consolidation procedure was collected (Figure 8). In addition to known LDPE bands, the spectrum shows small N-H stretching bands at 3390 and 3196 and a 1645 cm^{-1} band associated with C=O stretching and NH_2 bending [Stuart 2004; Coates 2006]. These bands are characteristic of a saturated fatty acid amide and can be matched to the presence of behenamide, a common slip agent used

for PE films [Dulal *et al.* 2017]. An ATR spectrum was also collected for a bag that had undergone the Paraloid in acetone adhesive formation procedure. The spectrum shows that behenamide has been lost from the internal bag surface, based on the absence of bands in the N-H and C=O stretching regions of the spectrum (Figure 8).

A spectrum for a Paraloid film cast from a 10 w% acetone solution on a glass slide is illustrated in Figure 9. A Paraloid film formed after acetone evaporation and deposited internally was collected and the ATR spectrum for that film was also collected. A comparison of the N-H stretching region of the two Paraloid films demonstrates that a low concentration of behenamide has been retained in the film formed during a consolidation process (Figure 10). Weak N-H stretching bands are observed in the Paraloid film, indicating that the slip agent has dissolved in acetone and has been cast with the Paraloid film. The uptake and retention of slip agent within the dried adhesive raises the question of how the presence of the additive can impact the consolidated object. Consideration should be given to the long-term effects that the presence of such additives has on the properties of consolidated objects. Significantly, the presence of the amide slip agent has the potential to interfere with future interpretation of ceramic residue analysis, where lipids are identified [Reber 2008].

Conclusions

This study has demonstrated that despite a reputation for inertness, PE can undergo chemical change when used for the storage of certain materials. Degrading CN was shown to cause oxidation of the polymer storage material, which can be detrimental to the long-term stability of PE bags. The yellow discolouration of bags yet to be used for item storage

was proposed to be associated with the formation of coloured oxidation products, most likely quinone compounds. Such compounds are a result of the oxidation of phenolic antioxidant additives, and while they are perceived as harmless for general use of PE bags, there is potential for stored heritage items to interact with these organic compounds if in direct contact. The use of a solvent, acetone, in a consolidation process involving PE bags has also demonstrated that polymer additives can be dissolved and removed from storage bags. In the case study presented here, the transfer of a fatty acid amide processing agent to a ceramic item has the potential to interfere with future lipid analysis.

Thus, the interaction of stored items with PE and the associated additives should be considered when using such storage materials because of their potential to interact and undergo potentially damaging changes. Although the most readily available PE bags contain the additives described, there are so-called ‘cleanroom’ PE bags that have become commercially available in recent years and these may provide a suitable alternative for the storage of heritage items. Such bags are intentionally manufactured for cleanroom conditions without the use of traditional additives in order to meet requirements in medical and aerospace industries, for instance. Cleanroom PE bags can be manufactured without the use of slip or antiblocking agents, that as identified in the current study can be present in conventional grades of PE. Different polymer classes undergo a variety of degradation mechanisms and utilise a variety of additives depending on their fundamental chemistry and physical properties, so it will be beneficial to investigate other polymer storage materials, such as polyester and polypropylene, to add to the knowledge base about storage options and their potential implications.

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Declaration of interest statement

There are no conflicts of interest reported by the authors.

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Table 1. Infrared band assignments for stored cellulose nitrate comb.

wavenumber / cm^{-1}	band assignment	source
3600-2800	O-H stretching, C-H stretching	CN, zinc oxalate
1800-1500	C=O stretching	zinc oxalate
	NO_2 stretching	CN
1460	C-H bending	CN
1364,1315	C-O stretching	zinc oxalate
1265	NO_2 stretching	CN
1054	C-O-C stretching	CN
820	O-C-O stretching	zinc oxalate
750-550	O-NO_2 deformation	CN
	O-C-O bending	zinc oxalate

Table 2. Infrared band assignments for cellulose nitrate storage bag.

wavenumber / cm^{-1}	band assignment	source
3400	O-H stretching	oxidation products
3000-2800	C-H stretching	PE
1800-1600	C=O stretching, C=C stretching	oxidation products, stearate
1575-1540	COO^- stretching	stearate
1475-1375	C-H bending	PE
1370-1300	CH_2 wagging	PE
1320	C-O stretching	oxidation products
1075-1025	C-O-C stretching, C-C stretching	oxidation products, stearate, PE
840	C=C bending	oxidation products
730-715	CH_2 rocking	PE

Figure captions

Figure 1. Stored cellulose nitrate artefacts from the Commonwealth Block: Black Eagle and Oddfellows Hotels archaeological site, Melbourne. Photographs by Sharon Wong.

Figure 2. Discoloured unused PE bags at the South Australian Museum. Photographs by Sharon Wong.

Figure 3. ATR spectrum of stored cellulose nitrate comb. C – cellulose nitrate; Z – zinc oxalate.

Figure 4. XRF spectrum of stored cellulose nitrate comb.

Figure 5. ATR spectra obtained for interior and exterior locations of cellulose nitrate storage bag. P – polyethylene; S – stearate; O – oxidation products.

Figure 6. ATR spectrum of external yellow region of discoloured storage bag (a) full spectrum; (b) expanded 1800-800 cm^{-1} region. P - polyethylene; S - stearate; O – oxidation products; C – calcium carbonate.

Figure 7. Chemical structure of 3,3’,5,5’-tetra-*tert*-butyl-stilbene-4,4’-quinone.

Figure 8. ATR spectra of interior of PE bags before and after Paraloid / acetone treatment: (a) N-H stretching region; (b) C=O stretching region.

Figure 9. ATR spectrum of Paraloid B-72 film.

Figure 10. N-H stretching regions of the ATR spectra of pure Paraloid B-72 film and film removed from bag interior.