Reassessment of anoxic storage of ethnographic rubber objects

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REASSESSMENT OF ANOXIC STORAGE OF ETHNOGRAPHIC RUBBER OBJECTS

Keywords: rubber, preventive conservation, SPME, GC-MS, anoxic storage, Ageless, Cryovac

ABSTRACT

This paper revisits the 1991–1995 British Museum field trial on anoxic storage, where 23 registered ethnographic rubber objects were enclosed in oxygen barrier film Cryovac BDF-200 with sachets of the oxygen absorbent Ageless Z. A unique opportunity for study was presented since most of the enclosures have remained sealed since 1995. Techniques such as solid phase micro-extraction (SPME) combined with gas chromatography-mass spectrometry (GC-MS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and variable pressure scanning electron microscopy (VP-SEM) together with visual assessments were employed in assessing both condition of the objects and effectiveness of anoxic storage methodology. Anoxic storage is of increasing interest to those caring for modern/ethnographic collections. This study has helped to establish that, despite concerns for the long-term effectiveness and impact of prolonged storage under oxygen-depleted conditions, it is an effective and convenient means of slowing the deterioration of rubber artefacts in museum collections.

RÉSUMÉ

Cet article réexamine les essais sur le terrain menés de 1991 à 1995 par le British Museum sur l'entreposage anoxique, au cours duquel 23 objets ethnographiques en caoutchouc répertoriés ont été emballés dans du film Cryovac BDF-200 constituant une barrière contre l'oxygène, en présence d'un absorbeur d'oxygène Ageless Z. Dans la mesure où la plupart des emballages sont demeurés scellés depuis 1995, ils représentent une opportunité d'étude unique. Des techniques comme la micro-extraction en phase solide

INTRODUCTION

In 1999 at the ICOM-CC meeting (Lyon), Yvonne Shashoua presented *Ageless oxygen absorber: from theory to practice,* detailing the findings of a 1991–1995 field trial held at the British Museum (BM) investigating the long-term storage of ethnographic rubber-containing artefacts in anoxic conditions. The trial followed recommendations by Clavir (1982) and work by Shashoua and Thomsen (1993), suggesting that anoxic storage of rubber objects slowed their degradation measurably. In this field trial oxygen-depleted microclimates were achieved by enclosing rubber objects in Cryovac BDF-200, a thin, transparent, multi-layered, co-extruded polyalkene oxygen barrier film designed to package foods for transport manufactured by Sealed Air Incorporated (http://www.sealedair.com) together with sachets of the oxygen absorbent Ageless Z, commercially developed for the food industry by Mitsubishi Gas Chemical Company Inc.

Thus, in October 1991, 23 registered objects from the Ethnography collection were selected for anoxic storage trials. They included toys, footwear and tools, and most incorporated additional organic materials or metals in their construction. Their conservation conditions ranged from good to partially degraded, manifested by stickiness, cracking and opaque bloom on surfaces. The field trial aimed to compare the rates of degradation of rubber in real time in the absence and presence of oxygen. In practice, eleven of the objects were sealed in Cryovac enclosures with Ageless and the remaining twelve were enclosed without oxygen absorber.

In 1995, after 42 months during which the condition of all the artefacts had been assessed at six-month intervals, the anoxic storage method was deemed effective and the ability of an oxygen-depleted microclimate created using Ageless to inhibit the deterioration of rubber was established. The trial objects including controls were therefore repackaged with Ageless for long-term storage.

15 years on, the use of anoxic storage conditions is now firmly established in preventive conservation. There is also growing concern for the fate of modern materials that are less stable than expected. Anoxic storage may provide practical, inexpensive solutions for some plastics and is thus of great interest to those caring for modern collections. However, the long-term effectiveness and impact of prolonged storage under oxygen-depleted

associée à la chromatographie en phase gazeuse-spectrométrie de masse, la spectroscopie infrarouge à transformée de Fourier par réflectance totale atténuée et la microscopie électronique à balayage à pression variable ainsi que des évaluations visuelles ont été utilisées afin d'évaluer à la fois l'état de conservation des objets et l'efficacité du procédé de stockage anoxique. Le stockage anoxique présente un intérêt croissant pour les personnels en charge de collections modernes ou ethnographiques. Cette étude contribue à montrer que, en dépit des préoccupations à propos de l'efficacité à long terme et des conséquences des conditions de stockage dans un environnement privé d'oxygène, ce procédé est un moyen efficace et pratique de ralentir la détérioration des artefacts en caoutchouc présents dans les collections de musées.

RESUMEN

Este artículo revisa las pruebas de almacenamiento anóxico realizadas en el British Museum entre 1991 y 1995, para las que 23 objetos etnográficos de goma registrados se envolvieron en una película de barrera de oxígeno Cryovac BDF-200, con bolsas absorbentes de oxígeno Ageless Z. Esto presentó una oportunidad única de estudio ya que en la mayoría de los contenedores han permanecido sellados desde 1995. Se emplearon técnicas como la microextracción en fase sólida (MEFS) combinada con cromatografía de gases acoplada a espectrometría de masas (CG-EM), espectroscopía infrarroja de transformada de Fourier acoplada con reflectancia total atenuada (IRTF-RTA) y microscopía electrónica de barrido de presión variable (MEB-PV), además de análisis visuales para estudiar tanto el estado de los objetos como la eficacia de la metodología del almacenamiento anóxico. El interés por el almacenamiento anóxico ha ido en incremento entre los responsables de colecciones modernas y etnográficas. Este estudio ha ayudado a establecer que, a pesar de las preocupaciones por la eficacia y los impactos a largo plazo del almacenamiento prolongado en condiciones de privación de oxígeno, éste es un medio eficaz y fácil para reducir el deterioro de objetos de goma en las colecciones de los museos.

conditions has not been established mostly due to insufficient samples that have remained undisturbed in anoxic conditions for long periods.

The subjects of the 1991–1995 BM field trial represent such a set of samples. Since being packed, few of the objects have been removed from their enclosures for study. A unique opportunity was thus presented to revisit the enduring effects of anoxic storage and reassess the efficacy of the methodology employed. Techniques such as solid phase micro-extraction (SPME) in combination with gas chromatography-mass spectrometry (GC-MS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and variable pressure scanning electron microscopy (VP-SEM), which were not available at the time of the initial trials, were invaluable in the current assessment of the suitability of anoxic conditions for long-term storage of rubber artefacts in museum collections.

EXAMINATION PROCEDURE & TECHNIQUES

Procedures for the enclosure and examination of the rubber artefacts included in the 1991–1995 field trial, as well as calculations of Ageless Z quantities used have been detailed by Shashoua (1999). The artefacts were heat-sealed in double enclosures to reduce risk of admitting oxygen.

Objects were examined using optical microscopy and were photographed at the start of the trial and at the end of each period of evaluation. Line drawings were also made to record degradation. The integrities of the Cryovac enclosures were documented and a set of criteria developed for the assessment of the active lifetime of Ageless. For the current study, the wide variety of analytical techniques available permitted analysis and examination both prior to and after the opening of the Cryovac enclosures. The analytical techniques and methodologies are summarized in Table 1.

Table 1.
Examination procedure established for the assessment of rubber objects

Information	Technique/Procedure
Stage 1: Before removal from Cryovac enclosure	
Examination of gaseous atmosphere in unopened enclosures	SPME/GC-MS
Examination of the integrity of the enclosures	– Visual examination – Percentage Oxygen Content – Relative humidity – pH of enclosed air
Stage 2: After removal from Cryovac enclosure	
Condition assessment	– Visual examination of objects – Optical microscopy
Investigation of any chemical changes on the surface	FTIR
Determination of physical transformations to the material surface	VP-SEM

Examination of gaseous atmosphere in unopened enclosures

Formation of volatiles during breakdown of natural rubber has been well-documented (Hoven and Rattanakaran 2003). However, characterization of such gaseous degradation products from museum artefacts has not been reported to date.

SPME is a technique which allows the sampling of volatiles using a fibre coated with an extracting phase. After extraction, the analytes are desorbed from the fibre and analysed by GC-MS, which allows their detection at extremely low concentrations. The methodology used in this study for the identification of gaseous products emitted by sealed rubber, using SPME in combination with GC-MS was optimized using a pilot study. To simulate degraded rubber, samples of bicycle inner tube rubber (0.9 g) were artificially aged in Mininert vials in the presence and absence of oxygen achieved using Ageless. Mininert vials employ leak-tight closures with a septum and valve which allow a syringe to sample the headspace gases generated. A set of samples labelled OA and comprising two repeats were aged in an oven at 60±2°C for 300 hours (Hoven and Rattanakaran 2003). Control samples comprising either empty vials or vials containing only Ageless were also heat-aged. An analogous set of samples was kept in the dark at room temperature (20–22 °C) to simulate real time storage in the dark.

Sampling proceeded by inserting the needle of a SPME portable field sampler (Supelco) into the vial and exposing the 75 µm Carboxen/PDMS coated SPME fibre (optimized for the analysis of low molecular weight, polar species) to the vial headspace. After exposing for 60 minutes the fibre was retracted and the gases desorbed and analysed by GC-MS.

GC-MS analysis was carried out using an Agilent 6890N gas chromatograph coupled to an Agilent 5973N mass spectrometer. System control and data collection/manipulation were achieved using G1701DA Chemstation (G1701DA) software. The capillary column used was a DB-FFAP poly(ethylene glycol) (30 m x 0.25 mm, 0.25 µm film thickness). SPME fibres were injected in split mode (split ratio of 25:1) at 16 psi and 36 °C rising to 280 °C at a rate of 81ºC/min. The carrier gas was helium in total flow mode at 1.7 mL/min. After a 5 minute isothermal hold at 35 °C the temperature was increased to 230 °C at 15 °C/min with the final temperature held for 3 min. Data was collected and analysed using the MS in scan mode (50-600 amu/sec) to identify all species of interest. Mass spectra acquired using the scan method were interpreted manually with the aid of the NIST/EPA/NIH Mass Spectral Library version 2.0.

Measurement of the gaseous atmosphere in the unopened object enclosures proceeded as described for the pilot study samples. Sampling pockets were created by isolating areas of the enclosure with a heat-sealer in order to preserve the environment around the objects while maintaining intact areas for further analysis. Since each object was enclosed in double bags of Cryovac, both the atmosphere in the inner bag containing the object and the surrounding outer bag were probed. The SPME fibres were exposed to the atmosphere of the enclosures for 2 hours.

Among the initial group of objects studied in the 1990s, six which had been kept intact were chosen for investigation using SPME. Since the objects studied contain materials other than rubber which could also contribute to the volatiles in the enclosures, the predominant gaseous products detected were compared to the data obtained from the pilot study samples. Only volatiles likely to have arisen from rubber degradation are included in the Results and Discussion section. Contributions from the enclosure materials themselves were eliminated by studying empty or Ageless-containing Cryovac bags sealed in 1995.

Integrity of the enclosures and oxygen content

Assessment of the integrity of the Cryovac enclosures was determined by visual examination, measuring percentage oxygen content to gauge retention of anoxic conditions, pH to determine whether the enclosed objects had off-gassed acidic oxidation products during enclosure and relative humidity to indicate diffusion of water vapour through the double bags with time. The percentage oxygen content was measured using a Mapcheck oxygen monitor. Relative humidity within the bags was measured by inserting a Rotronic hygrometer probe through a small opening. Because pH meters can only measure a wet surface or solution, a Danchek strip containing acid-sensitive dyes, was inserted into the opening.

Visual and optical microscopic examination of the rubber objects

Enclosures were opened to assess the condition of rubber objects using visual and optical microscopic examination following the procedure set out by Shashoua (1993). The results were compared with documentation from 1991–1995.

Investigating surface chemical changes by ATR-FTIR spectroscopy

The use of FTIR as a destructive technique for the condition assessment of rubber-containing museum artefacts was discussed by Shashoua (1995). Since 1995, there have been considerable advances in non-destructive FTIR. These require good contact between rubber and an internal reflection element often made of diamond. Chemical transformations on the surface of the rubber can thus be characterised without sampling. The ATR-FTIR spectra were measured using the Smart iTR diamond accessory on the Nicolet 6700 between 4000 and 550 cm^{-1} using 16 scans at a resolution of 4 cm^{-1} and automatic gain.

Investigating changes in surface morphology by VP-SEM

The use of SEM in the investigation of sample and object surfaces is now commonplace in museum environments. Recently, the use of elevated gas pressures in the sample chamber of a scanning electron microscope (i.e., VP-SEM) has afforded imaging and examination of samples without preparation. In addition whole objects subject to their stabilities and dimensions, can be placed in the sample chamber providing a unique insight into the morphology of their degraded surfaces in situ and in real time. A Hitachi S3700N Variable Pressure SEM was used. Analysis proceeded in variable pressure mode at a working distance of 10 mm. The electron beam was operated at 20 keV.

RESULTS AND DISCUSSION

Pilot study samples

Table 2 summarizes the volatiles detected and the percentage oxygen content in the headspace of the pilot study samples. Only qualitative information should be taken from the percentage oxygen content readings, as the Mininert vials were not purged with nitrogen to produce perfectly anoxic initial conditions but it is evident that in the sample vials containing Ageless, the oxygen content was lower than ambient readings, whereas in vials not containing Ageless and in the empty control vials, oxygen concentration approaches ambient. Ageless was thus effective at more than halving the oxygen content and maintaining that low level even when rubber samples were present.

Table 2.
Summary of the volatiles and percentage oxygen content in the headspace of the pilot study samples

Peak Number	Retention time (mins)	Chemical component	Molecular weight	Empty control	Empty control (OA)	Ageless only (OA)	Rubber + Ageless (OA)	Rubber only (OA)	Rubber only	Rubber + Ageless
1	2.073	Carbon disulphide	76				√	√		
2	9.676	N,N'-dimethylformamide	73					√	√	
3	10.414	3,4,4-Trimethyl-1-pentyn-3-ol	126						√	√
4	10.570	N,N'-dimethylacetamide	87					√		
5	11.000	Acetic acid	60	√	√	√	√	√	√	
6	11.078	Tetramethyl urea	116					√	√	
7	11.729	Benzaldehyde	106	√				√	√	
8	13.191	2,5-dimethyl-1-pyrroline	97					√		
9	13.508	Benzylacetate	150					√	√	
10	14.363	N,N'-dimethylmethanethioamide	89					√	√	
11	15.031	N,N'-dimethylurea	88					√		
12	15.357	Benzothiazole	135					√		
13	15.627	Phenol	94	√				√		
		% Oxygen content		20.6	20.9	3.67	6.86	20.0	20.0	10.3

OA-Oven aged at 60 °C for 300 hrs.

As expected, the highest proportion of volatiles was produced in the sample oven-aged in the absence of Ageless. The chromatogram for this sample is shown in Figure 1(a). The range of gaseous products observed, which included carbon disulphide, acetic acid, N,N'-dimethylformamide and N,N'-dimethylacetamide, was in keeping with other publications (Hoven and Rattanakaran 2003). By contrast, rubber which was heat-aged in the presence of Ageless produced only carbon disulphide and minimal amounts of acetic acid (trace amounts of which were also observed in the empty control samples) (Figure 1(b)).

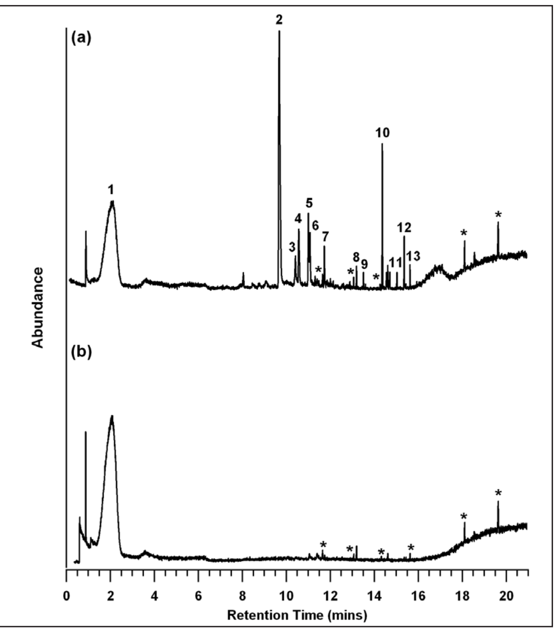


Figure 1
Chromatograms showing the volatiles from samples of inner tube rubber oven-aged (a) without and (b) with Ageless. Numbering refers to compounds in Table 2. * denote peaks associated with the SPME fibre material

Examination of unopened enclosures

Table 3 identifies the gases detected inside the enclosures expected to originate only from the degrading rubber. All the object enclosures contained a proportion of volatiles attributed to rubber degradation from the pilot samples and literature studies (Hoven and Rattanakaran 2003). Acetic acid was present in all the enclosures, with carbon disulphide and benzothiazole present in many.

Table 3.
Summary of the volatiles associated with rubber degradation observed in the object enclosures

Retention time (mins)	Chemical component	MW	Ball	Toy catapult	Toy catapult	Toy catapult	Guatemalan sandals	Yemen bucket
			1908Ty.274	Af1981,02.36	Af1984,4.443	Am1969,16.90	Am1973,03.72	As1979,01.189b
1.933	Carbon disulphide	76		√	√			√
9.693	N,N′-dimethylformamide	73						√
10.574	N,N′-dimethylacetamide	87						√
10.996	Acetic acid	60	√	√	√	√	√	√
11.077	Tetramethyl urea	116						√
11.719	Benzaldehyde	106						√
15.355	Benzothiazole	135		√	√		√	√
15.617	Phenol	94	√		√			

MW-Molecular weight

Of the object enclosures tested, that containing a bucket from Yemen (As1979,01.189b) had the highest proportion of volatiles in common with the pilot study samples. These species are marked on the chromatogram for this sample (Figure 2) using the numbering system detailed in Table 2.

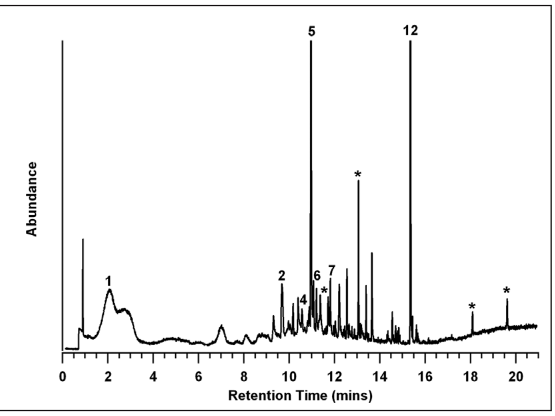


Figure 2
Chromatograms showing the volatiles from the inner Cryovac enclosure containing the bucket from Yemen (As1979,01.189b). Numbering refers to compounds in Table 2. * denote peaks associated with the SPME fibre material

In general, the composition and relative abundance of gaseous species in the object enclosures differed from that observed in the pilot study where new rubber was used. Objects are likely to have degraded and off-gassed significantly prior to enclosure and also contained materials other than rubber. Nonetheless, sufficient recognized markers of oxidative rubber degradation such as acetic acid were detected to establish that some ingress of oxygen had occurred, either via pinholes in the Cryovac plastic itself or in the sealed seams, allowing oxidative degradation within the enclosures.

Findings from the visual assessment and pH measurements to assess integrity of all the object enclosures are summarized in Table 4. In general, the seals and Cryovac film of the unopened enclosures appeared in good condition. The oxygen content was similar to ambient (~20.6 percent) in all the enclosures, thus indicating that the initial anoxic conditions had not persisted. Similarly, relative humidity within the bags was similar to ambient. In all instances, the pH measured inside the enclosures was between 5–6, and was attributed to the acidic volatile species within the enclosures.

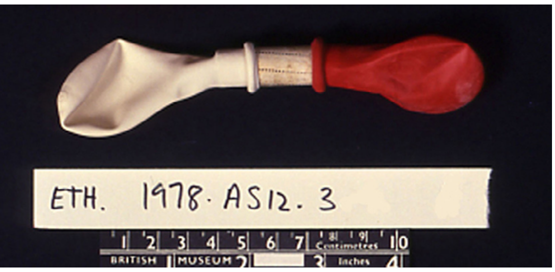
The oxygen concentration inside enclosures and the detection of oxidation products indicate that although the Cryovac plastic has retained its

Table 4.
Assessment of rubber objects enclosed in Cryovac with Ageless oxygen absorber and flushed with nitrogen

Registration number	Object description	Materials (ID 2010)	Object Condition 1995	Object Condition 2010	Cryovac (2 bags) 2010	Ageless 2010	Danchek strip pH after 2hrs
As1905.6.19	Gong beater	Wood Gutta percha*	'Rubber': Cracks: sticky, flaking	Hard, flaking, not sticky. Strong, sweet smell	Sealed Flakes/ powder in bag	0)Soft I)Very soft	—
As1978,12.4	Musical instrument with orange and green balloons	Paper cylinder Rubber balloons	Balloons intact	Balloons slightly sticky. Rubber smell	Only one bag, seal broken 2007?	Soft	—
As1978,12.3	Musical instrument with red and white balloons	Paper cylinder Rubber balloons	Balloons intact	Red balloon very sticky. White balloon very hard, broken. Rubber smell	Only one bag, seal broken 2007?	Soft	—
As1974.15.9	Bird trap	Wood, string, wire, black rubber	Severe cracking on rubber binding	No change. Rubber smell	Sealed	O) Hard I) Soft	5.5
As1979.1.189b	Bucket	Black rubber	Rubber base severely cracked	Possible slight increase in cracking. Rubber smell	Sealed	Hard	5
As1981,13.78	Toy rat on card	Ceramic rat, black rubber (inner tube) tail, paper card	Tail: cracks in tail	Tail: brittle and broken off at end. Large crack came apart as removed from bag.	Sealed	O) Hard I)Soft	5.5
Af1980.14.145	Chin rest	Mainly wood Black rubber strap	Bloom on knots and strap	Wood white bloom. Possibly very slightly more bloom on strap	Sealed	No ageless present	4.8-5
Af1984.N14.443	Toy catapult	Black rubber (inner tube). PVC, metal wire, wood	Slight cracking visible on rubber. Yellowish deposits	No change. Woody smell	Sealed	O) Soft with hard lumps I) Very soft	5
Af1989,05.27b	Xylophone beater	Wooden handle Bitumen*head. PVAc identified on bitumen.	Surface of 'rubber' very sticky	No change	Sealed . Sticky area wrapped in silcone release paper.	O) Soft I)Very soft	5.0
Af1989,05.27c	Xylophone beater	Wooden handle Wooden handle Bitumen* head. PVAc and animal glue identified on bitumen.	'Rubber' slightly sticky	No change	Sealed	O) Soft I)Very soft	5.0
Af1984,14.454	Toy ox cart	Clay, nylon twine, wood, flip flop 'rubber' wheels	No cracks	No change.. Rubber smell	In clear polystyrene box. 3 bags, sealed	Hard	—
Af1984,14.441	Model truck	*Ethylene vinyl acetate foam (flip-flop 'rubber') wheels, wood, galvanized steel.	Foam –variable hard and soft areas.	No change	Card box. Sealed	O) Soft I)Very soft	5.5
Af1908,Ty.274	Ball	Rubber: *non-vulcanized	Areas both hard and soft	No change. Slight sulphur smell	Sealed	O)Very soft I)Very soft	5.5
Af1984,14.440	Model car	Wood, metal, sharp unprotected edges, flip-flop 'rubber' wheels	Wheels brittle	No change	Sealed Scratches to outer bag.	All ageless very hard	5.5
Af1981,2.36	Catapult	Black rubber tyre, hide, wood	Cracks on rubber tie	No change. Smells as fresh rubber	Sealed	O) Soft I)Very soft	6

Registration number	Object description	Materials (ID 2010)	Object Condition 1995	Object Condition 2010	Cryovac (2 bags) 2010	Ageless 2010	Danchek strip pH after 2hrs
Am1969,16.90	Toy catapult	Wood, leather, black rubber	Rubber: Crack on one arm open to 4mm	No change. Rubber smell	Sealed	O) Soft I) Soft	5.5
Am1981,28.2.53a&b	Sicuri dance sandal	Black tyre rubber, metal staples	Cracks on outside edge of soles. Pitting on inside edges	No change	No Cryovac, in polythene bag	No ageless	—
Am1973,3.72a&b	Sandals	Black tyre rubber, metal staples	Pitting associated with metal staples	No change	Sealed	O) Soft I)Very soft	5.5
Am1981,28.19a&b	Sandals	Black tyre rubber, metal staples	a) Cracks evident along outer edge b) Good	No change	In polythene bag PE(sealed). Cryovac bags recently removed	Soft	—
Am1981,28.101a&b	sandals	Black tyre rubber, metal staples	a) Yellowish areas b) No data	a) No change b)Slight bloom on tie	In polythene bag PE(sealed). Cryovac bags recently removed	—	—
Am1981,28.102a&b	sandals	Black tyre rubber	Cracks along outer edge of soles. White bloom (paraffin wax)	No change	Sealed PE Cryovac bags recently removed	Soft	—

*identified by FTIR (originally thought to be rubber)
O – outer bag. I – inner bag



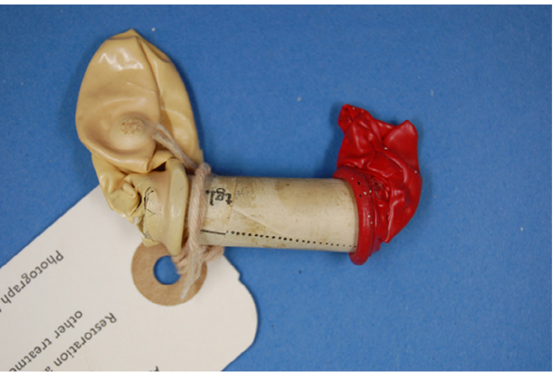


Figure 3
Balloons from a toy musical instrument (As1978,12.3) at the start of the trials

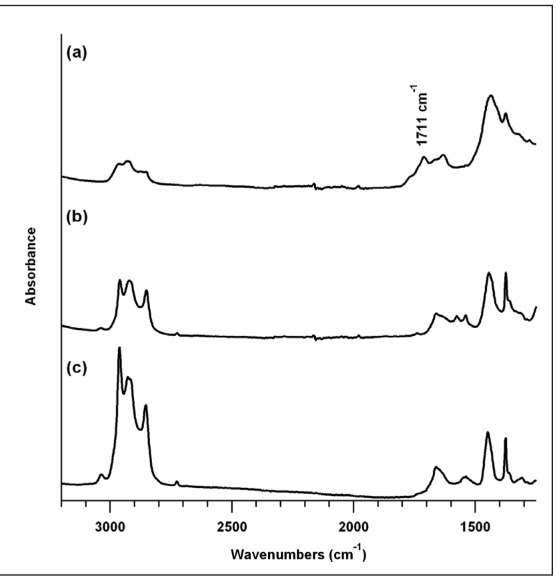
Figure 4
Balloons from a toy musical instrument (As1978,12.3) as in this study

transparency and flexibility and the seams are not visually breached, anoxic conditions are likely to have been compromised over time. Previous studies on the assessment of the active lifetime of Ageless (Shashoua 1999) recommended that the sachets be replaced every five years. As no such replacement took place during a fifteen-year period, such findings are not surprising. It should also be considered that Cryovac packaging films are intended for use by the food industry and are designed to protect food for a maximum of three months.

Examination of the rubber objects

A summary of the condition of the objects studied after opening of the enclosures is given in Table 4. In general, very few of the objects that had remained enclosed for fifteen years exhibited additional degradation compared to their condition in 1995. By contrast, certain objects in enclosures that had been opened in the intervening period between 1995 and the present study showed additional crazing, discolouration and softening.

Of particular note were the balloons forming part of toy musical instruments (As1978,12.3&4). New at the start of the 1991–1995 trials (see Figure 3), they were subsequently exposed to air when the enclosures were opened in 2007 and appeared visibly deteriorated when assessed for this study (Figure 4). The red balloon was sticky and had adhered to itself and the white balloon was hard, brittle and cracked in several areas. The objects were investigated further by VP-SEM.



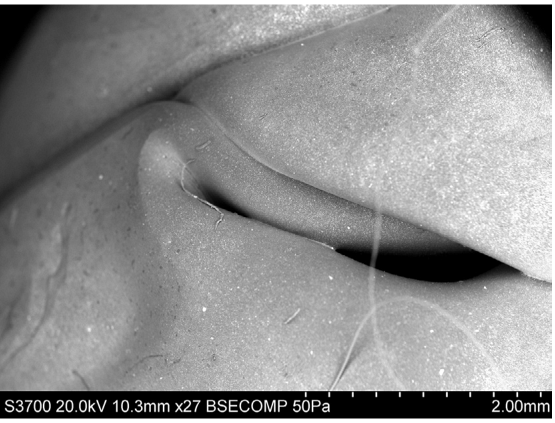


Figure 5
FTIR spectrum (a) of a white balloon from a toy musical instrument (As1978,12.3) and reference spectra of (b) a new white balloon and (c) native rubber

Figure 6
Backscattered electron image of a red balloon from a toy musical instrument (As1978,12.3)

Figure 7
Backscattered electron image of a white balloon from a toy musical instrument (As1978,12.3)

Chemical transformations in the objects were investigated by ATR-FTIR spectroscopy. Although all the available objects were analysed in this manner, good quality spectra were obtained only from those objects made of natural rubber, such as the toy instrument with balloons (As1978,12.3) shown in Figure 5 where the spectrum acquired from the visibly degraded white balloon is compared with reference spectra of a new balloon and natural rubber. A band at 1711 cm^{-1}, the marker for degraded natural rubber, is evident in this spectrum.

An important additional outcome of the FTIR analysis of the objects was that it yielded identification of the materials under study. In many cases, this was as expected. However there were occasions when materials had been mislabelled. Material identification and compatibility of materials is very important when deciding how to store objects and whether anoxic storage is a viable option. Some plastics, particularly the semi-synthetics, undergo accelerated deterioration when enclosed.

The toy musical instrument (As1978,12.3) discussed earlier, and a toy catapult (Af1981,02.36) were studied further by VP-SEM. Figures 6 and 7 show the backscattered electron images produced by the degraded rubber components. The flowing behaviour leading to the stickiness observed in the red balloon (Figure 4, right) can be seen from the smooth curved folds formed by the rubber in Figure 6. Cracking occurred over the flowing material in the white balloon (Figure 4, left) shown in Figure 7, offering an insight into the progressive nature of the deterioration.

Figure 8 shows the contrast in condition between areas of rubber in the toy catapult under various levels of tension. The rubber in relaxed areas is in good condition, whereas damage in the form of crazing patterns and distortion is observed in highly stretched regions including windings around the handle. This observation highlights the importance of monitoring a range of areas within the same object.

CONCLUSIONS

This study presented the rare opportunity to return to a group of ethnographic rubber objects stored under oxygen-depleted conditions and naturally-aged over 15 years. Reassessment focussed on the condition of the objects and the effectiveness of anoxic storage methodology, and employed a variety of techniques for appraisal.

Visual examination suggested that with the exception of objects enclosed in bags subjected to deliberate/inadvertent opening, the condition of the objects had remained almost unchanged in fifteen years. However, percentage oxygen content measurements indicated that ambient conditions were present in the enclosures, even when apparently not breached. This was supported by studies using SPME/GC-MS, which showed that the gaseous microenvironment within the object enclosures contained products consistent with oxidative degradation from the rubber objects. ATR-FTIR spectroscopy provided further evidence for the presence of rubber oxidation on the surfaces of the objects but this was much more prevalent in objects whose enclosures had been opened during the 15 period and where visible surface degradation was observed. In these cases, VP-SEM gave some insight into the changes in surface morphology upon degradation.

The ambient conditions present in the enclosures are not surprising considering previous work that recommended Ageless sachets be replaced every five years. Because an excess of Ageless was already present in the trials, it seems unlikely that additional adsorbent would extend the lifetime of the oxygen-free environment. However, from comparisons with objects whose enclosures had been opened, it is clear that anoxic storage has been beneficial and will continue to be recommended for the storage of these objects. Investigations into how best to repackage these artefacts and other candidates for anoxic storage, using the more effective oxygen barrier materials now available and guidelines to ensure the longevity of these enclosures for long-term storage, are currently underway.

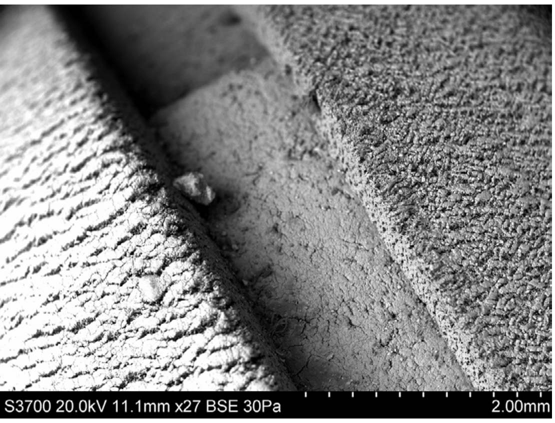


Figure 8
Backscattered electron image of rubber windings on a toy catapult (Af1981,02.36)

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