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Yellowing and Appearance of Conservation Adhesives for Poly(methyl methacrylate): A Reappraisal of 20-Year-Old Samples and Test Methods

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Abstract

This study establishes a framework for investigations of conservation adhesives for poly (methyl methacrylate) (PMMA).

Six adhesives that had been assessed nearly 20 years ago for suitability as conservation repair materials for PMMA furniture, objects, and sculpture were reassessed:

- HXTAL NYL-1
- Neocryl BT20
- Norland OA65
- 1:1 Paraloid B-67:Paraloid F-10
- Plextol D514
- Tensol 70

These samples had been aged naturally and artificially in five environments of intense light, heat, or a combination of both, and stored in the dark for 19 years. The current investigation focused on measuring the yellowing of the adhesives with a portable spectrophotometer. Fourier transform infrared spectroscopy (FTIR) and Pyrolysis gas chromatography mass spectrometry (Py GCMS) were used to characterize the polymers in the adhesives. The detection of molecular differences resulting from the aging environments was explored with FTIR. The adhesives were also assessed for visual acceptability for repairs and aging characteristics.

The results showed that:

- 1:1 Paraloid B-67:Paraloid F-10 did not become yellow in natural or artificial aging environments
- the HXTAL NYL-1 samples have maintained a good appearance with minimal yellowing after accelerated aging
- thermal aging caused the most yellowing (which means that the experimental protocol for the aging environments should be modified in future studies)

This investigation demonstrates that sample design and yellowness measurement provide useful information to evaluate adhesives for treatment, and presents test methods to improve future studies.

Titre et Résumé

Jaunissement et aspect général d'adhésifs utilisés pour la restauration du poly(méthacrylate de méthyle) : réévaluation d'échantillons vieillis pendant 20 ans et méthodes d'essai connexes

Les travaux de recherche faisant l'objet du présent article ont permis d'établir un cadre de travail pour les études sur les adhésifs utilisés pour la restauration du poly(méthacrylate de méthyle) [PMMA].

Six adhésifs, qui avaient déjà été évalués il y a près de 20 ans afin de déterminer s'ils constituaient des matériaux de restauration adéquats pour le mobilier, les objets et les sculptures en PMMA, ont été réévalués; voici la liste des adhésifs :

- HXTAL NYL-1;
- Neocryl BT20;
- Norland OA65;
- Mélange 1/1 de Paraloid B-67 et de Paraloid F-10;
- Plextol D514;
- Tensol 70.

Les échantillons avaient été vieillis naturellement et artificiellement, dans cinq milieux distincts présentant des conditions intenses d'éclairage ou de chaleur, ou une combinaison des deux; ils ont ensuite été entreposés dans le noir pendant 19 ans. L'étude actuelle visait à mesurer le jaunissement des adhésifs au moyen d'un spectrophotomètre portatif. La caractérisation des polymères présents dans les adhésifs a été réalisée par spectroscopie infrarouge à transformée de Fourier (IRTF) et par chromatographie gazeuse à pyrolyse couplée à la spectrométrie de masse (PyCG-SM). La détection des différences de nature moléculaire, attribuables aux conditions des milieux de vieillissement, a été étudiée par IRTF. L'aspect général des adhésifs a aussi été évalué afin de déterminer leurs propriétés esthétiques, en fonction des réparations antérieures et des effets du vieillissement.

Voici une liste des constatations découlant des résultats des analyses :

- Le mélange 1/1 de Paraloid B-67 et de Paraloid F-10 ne jaunit pas, que ce soit dans des conditions de vieillissement naturel ou artificiel;
- Les échantillons de HXTAL NYL-1 ayant subi un vieillissement accéléré conservent un aspect adéquat et ne présentent qu'un jaunissement minime;
- Le vieillissement thermal provoque le jaunissement le plus important (ce qui implique que le protocole expérimental relatif aux milieux de vieillissement doit être modifié pour toute future étude).

Les résultats de la présente étude démontrent que la conception des modèles d'échantillons et les mesures du jaunissement fournissent des renseignements utiles qui facilitent l'évaluation d'adhésifs utilisés en restauration, et fournissent des méthodes d'essai pouvant améliorer la pertinence de futures études.

Introduction

Known by manufacturers' names such as Perspex or Plexiglas, poly(methyl methacrylate) or PMMA is found in collections ranging from fine art and design to social history. Since the first significant use of PMMA as aircraft glazing during the Second World War, its desirable qualities have been exploited in exquisite architecture, sculpture, furniture, jewellery and other items of artistic, historic and cultural significance.

Conservators face complex challenges when selecting adhesives appropriate for the safe repair of damaged PMMA due to its susceptibility to stress-crazing when exposed to degreasing solvents or adhesives. The selection of adhesives is complicated further because of the transparency, water-white appearance and high level of internal reflection at interfaces, which makes it difficult to produce seamless joints and amplifies the perception of yellowing.

The aim of this study is to re-assess the adhesive samples and testing methodology of two previous investigations in order to inform a programme for studying additional adhesives (Sale 1993; 1995). In the 1993 study, a series of tests were performed on eleven adhesives of five types to identify those that would not induce stress-crazing or cracking in PMMA following American Society for Testing and Materials (ASTM) test methods (ASTM F484-83; F791-82); the tensile strengths of the adhesives also were measured (ASTM D3262-73). In the second investigation, the tensile strengths and yellowing of six adhesives of five types were measured and compared after exposure to seven different conditions of accelerated and natural aging (Sale 1995).

This investigation focuses on measuring yellowing and assessing the visual acceptability for treatment of the adhesive samples prepared and aged in 1992. Further aims of this study are to identify refinements of the sample designs, simplify the test methods and develop procedures that will improve investigations of adhesives for conservation repairs of PMMA.

Experimental

Materials

The properties and polymers in the adhesives are summarised in Table 1.

Table 1 PMMA and Adhesives: Refractive Index (n), Glass Transition Temperature (T_g) and Composition.

<i>Name</i>	<i>n</i>	<i>T_g</i>	<i>Adhesive type</i>	<i>Polymer composition</i>
Perspex	1.49	105°C	test material	PMMA
HXTAL NYL-1	1.52	Not known	two- part epoxy resin	4,4- isopropylidenedicyclo-hexanol epichlorohydrin
Neocryl BT20	Not known	35°C	polymer dispersion	pEA/MMA - poly (ethyl acrylate co methyl methacrylate) (Horton-James et al 1991)

Norland NOA65	1.52	Not known	UV curing	Trade Secret - unidentified mercapto ester (www.Norland.com) & acrylate monomer (Pinto-Iguanero et al 2002)
Paraloid B-67	1.49	50°C	polymer in solvent	piBMA (in petroleum spirit) poly (<i>iso</i> -butyl methacrylate)
Paraloid F-10	1.48	20°C	polymer in solvent	pnBMA (as supplied 9:1 aliphatic: aromatic) poly (<i>n</i> -butyl methacrylate)
1:1 Paraloid B-67 & F-10	1.48	Estimate 30°C - 40°C	Polymers in solvent mixture	1:1 pnBMA & piBMA
Plextol D514	Not known	30°C	polymer dispersion	pnBMA/MA poly (<i>n</i> -butyl methacrylate co methyl acrylate) (Horton-James et al 1991; www. MFA Boston) or pnBA/MMA (<i>n</i> -butyl acrylate co methyl methacrylate) (Hodgkins et al 2011) or pnBMA/pnBA/MMA (Ormsby 2011)
Tensol 70 (ICI 1992)	Not known	Not known	two-part polymer in monomer & solvent & catalyst	PMMA

In the previous studies, six adhesives were evaluated and five were found to be safe to apply to stressed PMMA without causing crazing or cracking (Sale 1993; 1995). Tensol 70 cracked stressed PMMA and is *not* appropriate for conservation repairs (Sale 1993).

HXTAL NYL-1 has been evaluated further (Johnson 2008; Laganá 2011) and used for conservation repairs of PMMA (Johnson 2008). 1:1 Paraloid B-67: Paraloid F-10 has been used for conservation repairs since presentation in 1991 when assessed and presented as a potential conservation adhesive (Sale 1993; Lorne 1999; Johnson 2009). This resin mixture has been assessed further and found safe to apply to stressed PMMA (Comiotto 2009) and to produce stress-free repairs (Laganá 2011).

Sample preparation

Twenty-one samples of two types were prepared for each adhesive. All adhesives were applied to 3 mm clear cell-cast ICI Perspex supports to monitor long-term aging.

Open samples comprise a rectangular island of adhesive on a sheet of PMMA.

Laminate samples contain a layer of adhesive between two layers of PMMA. Two samples had been made for each adhesive and aging method to compare degreaser impact. 'AnalaR' petroleum spirit and Synperonic 'N' non-ionic detergent were compared for impact on joint integrity of laminate samples of PMMA.

Table 2: Aging Conditions 1992-93. Further details in Sale (1995).

<p><i>Dark aged ambient conditions (DA)</i> Samples were aged naturally in dark ambient museum conditions.</p>
<p><i>Room aged ambient conditions (RA)</i> Samples were aged with low levels of ultraviolet (UV) filtered light for 16 weeks.</p>
<p><i>Indoor daylight aging (WA)</i> Samples were aged in a museum window with filtered sunlight for 14 weeks until British Standards Institute blue wool standards BWS 1-6 fading was equivalent to that in the light-aging unit.</p>
<p><i>Light-aging with fluorescent lamps (LA)</i> Samples were exposed for 16 weeks at approximately 14,000 lux with no UV below 380nm and at temperatures near 30° C (Sale 1995); following the reciprocity principle, in a museum with 3,000 hours of light per year, this is equivalent to 85 years at 150 lux which is the level of illumination recommended for the display of colourless PMMA (Waentig 2008).</p> <p>To ensure that light-aged samples would be exposed to equivalent levels of illumination BWS 1-6 were exposed with the rotating samples during aging and monitored for fading with a Minolta CR221 chromameter over a select white tile that was used throughout the study in 1992-95.</p> <p>The unit and test procedures were designed to create intense continuous museum lighting at low temperatures; ventilation fans were used to lower the temperature and the accumulation of volatile organic compounds (VOCs) (Sale 1995). The prototype light-aging unit has been rebuilt to be more robust and continues to be used at Tate.</p>
<p><i>Thermal-aging (TA)</i> Samples were aged for eight weeks at 70°C and 55% relative humidity.</p>
<p><i>Thermal-aging followed by light-aging (TL)</i> Samples were thermal-aged for four weeks followed by light-aging for four weeks.</p>
<p><i>Light-aging followed by thermal-aging (LT)</i> Samples were light-aged for four weeks followed by thermal-aging for four weeks.</p>
<p><i>Sample storage 1992 – 2003</i> Samples were divided into groups by adhesive and stored in covered trays with activated charcoal in dark cabinets in an air-conditioned museum in a rural environment.</p>
<p><i>Sample storage 2003-2010</i> Samples were packed into loose polyethylene bags and stored together in a dark card box that had been sealed from dust in temperatures ranging from 10°C - 35°C. The samples were exposed to VOCs from the other samples until the end of 2010.</p>

Sample characterisation

Fourier transform infrared spectroscopy (FTIR) was used to characterise the polymers and to investigate its use in detecting molecular differences resulting from the aging environments. Transmission spectra were collected (64 scans at 4 cm⁻¹ resolution) on a 2000 series FTIR with a Thermo scientific Nicolet iN10 MX microscope using a diamond cell (Hodgkins et al 2011).

FTIR spectra of DA, LA and TA open samples of the adhesives were compared as well as new casts of the original 1:1 Paraloid B-67: Paraloid F-10 in solution (Hodgkins et al 2011).

Pyrolysis gas chromatography mass spectrometry (Py GCMS) was used to identify the polymers in three adhesives, Neocryl BT20, Norland OA65 and Plextol D514, using a GSG Pyromat Curie point pyrolyzer interfaced to a Varian Saturn 2000 GC-MS. Pyrolysis conditions: 625° C for 10

seconds. GC conditions: held at 40°C for 2 minutes then ramped to 320°C at 10°C/min then held for further 2 minutes at 320°C. Column: Phenomenex Zebron ZB-5 column (30m length; 0.25mm i.d.; 0.25µm film thickness). MS conditions: EI mode (70eV); scanned 40 - 399 amu every 0.49 seconds (Ormsby 2011).

Video Spectral Comparator (VSC)

Laminate samples were examined and images recorded with a Foster & Freeman Video Spectral Comparator model VSC[®]6000 / LF (www.foster&freeman.com).

Digital micrometer

A selection of samples was measured with a hand held digital micrometer (Axminster), to determine the depth of the adhesives, investigate the impact of sample thickness on the colour measurement data and assess the sample preparation techniques.

Colour measurement

A Konica Minolta 2600d spectrophotometer was used to measure yellowness of the samples with the CIELAB 1976 system using illuminant C in reflectance with the specular component and UV included, and a measuring aperture of 3 mm.

L*a*b* coordinates of CIELAB 1976 were recorded and b* values (yellow-blue scale) are presented because this coordinate is appropriate for measuring yellowing and was used in the previous study.

In this study the transparent samples were measured over the white calibration tile supplied for a chromameter. A measurement on the original PMMA sample material over the tile, the mean of 5 readings, was subtracted from the mean of 5 sample readings over the tile to ensure that the b* referred to the adhesive and not the PMMA or the tile. Samples were not compared to the original b* background tile which was different, since the one used in 1992 had been broken.

Results

The yellowness measurements of the adhesives, 19 years after aging in the dark following artificial and natural aging, are found in Figure 1. Visual assessments of the adhesives are located in Tables 3 and 4.

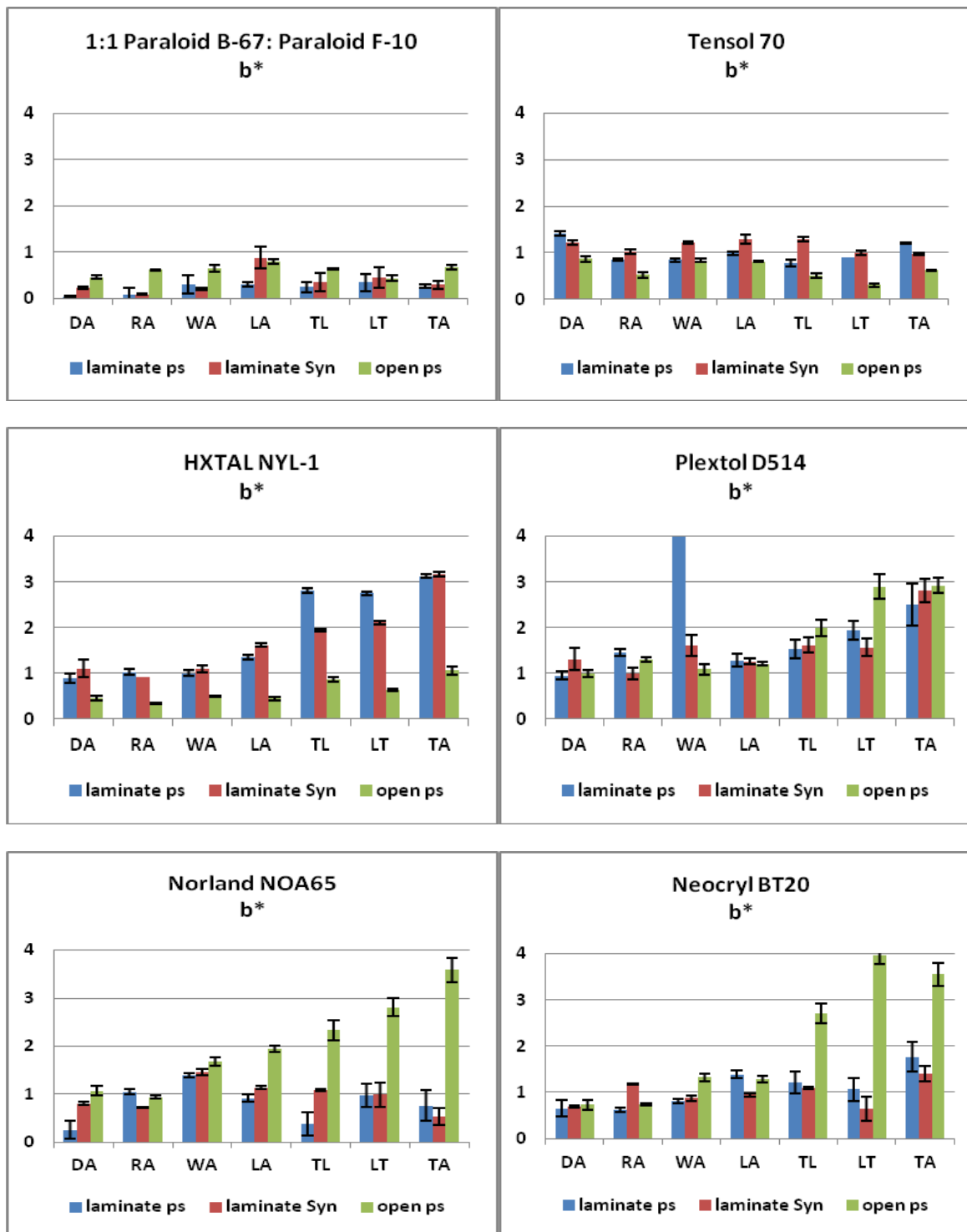


Figure 1 Yellowness in CIELAB 1976 coordinate b^* of adhesives. Measurements were taken after 19 years of aging in the dark following artificial and natural aging. The aging conditions in the graphs are listed in Table 2.

Table 3 Open Samples: Visual Assessment

	HXTAL NYL-1	Neocryl BT20	Norland NOA65	1:1 Paraloid B-67 & Paraloid F-10	Plextol D514	Tensol 70
Open samples						
Overall assessment	Good	Poor	Poor	Good	Poor	Dissolved PMMA
Damage to PMMA	None	None	None	None	None	Dissolved – but no crazing
Transparency	Excellent	Cloudy	Good	Excellent	Cloudy	Excellent
Surface texture & appearance	smooth; glossy small bubbles & inclusions due to long curing time	granular textured inclusions & bubbles smooth when heat-aged due to melting	matt inclusions bumpy edge	smooth glossy slight ridges fibres in heat-aged samples due to melting fine scratches from dusting	granular ridged inclusions & bubbles smooth when heat-aged due to melting	smooth glossy watery surface no inclusions more bubbles than epoxy
Visible aging impact & colour change on heat aging	Slight yellowing	Cloudy yellow	Cloudy yellow & developed inclusions	None	Yellow	None
Physical properties currently	Very hard but scratched	Slightly rubbery & tacky	Tacky to touch; acrylic smell	Hard but scratched	Slightly rubbery & tacky	Hard
Working properties	Excellent long to set / cure but hard	Easy to use; slightly granular & viscous after evaporation	Easy to use; easy to set using a UV light	Excellent – could apply in thinner layers.	Easy to use; slightly granular & viscous after evaporation	Difficult to control; rapid setting & hard
Further investigations, comments & tests	Investigate free radical scavengers to reduce yellowing - anticipate impact on curing (de le Rie 2011)	No – but possibly investigate main polymer alone? Dispersions are easy to use	No – but investigate other UV curing adhesives after identification	Long-term solubility; bulking agents; different % mix & aliphatic hydrocarbons; other MW piBMA & piBMA & dyes Investigate polarity impact on adhesion	No – but possibly investigate main polymer alone? Dispersions are easy to use	No – but possibly investigate PMMA trade adhesives further
Conclusion: Test further	Yes	No	No	Yes	No	No

Table 4 Laminate Samples: Visual Assessment

	HXTAL NYL-1	Neocryl BT20	Norland NOA65	1:1 Paraloid B-67 & Paraloid F-10	Plextol D514	Tensol 70
Laminate samples						
Overall assessment	Good	Poor	OK Good appearance but voids later	Good qualities but poor gap filling due to voids	Poor	<i>Not</i> a conservation material
Damage to PMMA	None	None	None	None	None	Dissolved but no crazing
Transparency	Excellent	Partly cloudy	Excellent	Excellent	Partly cloudy	Excellent
PMMA joint interface	Excellent	Good where joined	Excellent where joined	Excellent where joined	Good where joined - white area?	Excellent Slight blanching at PET spacer
Gap filling and appearance	Excellent	Poor, voids, bubbles, discoloured components separated white ring from edge	Started good; later developed linear voids from edges & spacers	Poor large voids Can be improved	Poor, voids, bubbles, discoloured components separated white from spacer	Excellent
Voids, gaps, bubbles, size	Few bubbles & some larger from edge	Small star shaped & striated medium sized	Tiny bubbles & wavy line voids	Large striated voids where solvent evaporated	Large voids at edge small - medium sized bubbles central area	Few small bubbles
% area with voids	2 %	30-60%	10-15 %	50-60%	30%	3 %
Visible aging impact & colour change	Yellowed slightly when heat-aged	When heat-aged melted; larger voids no longer star-shaped	Voids iridescent	None	Yellow edges when heat-aged	None
Physical properties currently	Low viscosity; slow cure risks later voids from edge	Voids from solvent evaporation	Acrylic smell; voids in lines from edge; pin-sized voids appeared much later (did it shrink, is solvent present?)	Voids from solvent evaporation	Voids from solvent evaporation	Hard & dissolved PMMA (tbc)

Working properties	Excellent long to set / cure	Easy to use	Good; easy to manage UV light	Good; could apply in layers, cast sheets or use bulking agents	Easy to use	Sets hard fast
Further investigations & tests	Investigate radical scavengers such as HALS to reduce yellowing (anticipate impact on curing)	No – but possibly investigate main polymer alone?	No – but interested in other types of UV curing after identification	Resolve voids; test other joints; separately; differ % mix; range aliphatic hydrocarbons; bulking agents; other MW piBMA & p <i>n</i> BMA. Investigate polarity impact on adhesion	No – but possibly investigate main polymer alone?	No
Conclusion: Test further	Yes	No	No	Yes	No	No

Discussion

Adhesives

Yellowing represented by b^* in Figure 1 is discussed in relation to the following: individual adhesives, trends related to the aging environments and differences related to the sample type. Experimental design evaluation and recommendations for improvements are discussed also.

CIELAB 1976 b^* values for 1:1 Paraloid B-67: Paraloid F-10 showed no significant yellowing after artificial or natural aging, and the laminate and open samples behaved in a similar manner.

Tensol 70 followed the same trend as the Paraloid mixture with no significant differences in sample yellowing after exposure to the various aging environments even though the b^* values indicate some yellowing. However, the undesirable physical properties noted previously and summarised in Tables 3 and 4 have indicated already that Tensol 70 is unsuitable as a conservation adhesive for PMMA.

Of the four remaining adhesives, a pattern of yellowing emerged that is related to the aging regimes; refer to Figure 1. The most pronounced yellowing was caused by thermal-aging. Light-aging followed by thermal-aging (LT) caused less yellowing while aging in the reverse order (TL), caused even less. However, an important consideration with the thermal-aging in this study is that the adhesive samples were aged at the same time in the unvented oven and VOCs released from the adhesives may have increased the yellowing of the samples.

The yellowing behaviour differed also between the open and laminate samples irrespective of the thickness of the adhesive layer; refer to Figure 1 and Tables 3 and 4. It was anticipated that open samples would have yellowed the most when aged artificially because a greater surface area of adhesive (albeit thinner) would have been exposed to the intense environments, as well as to VOCs, hydrolysis and oxidation, while the adhesive in the laminate samples would have

been protected by two layers of PMMA; however, not all of the results were consistent with this assumption.

HXTAL NYL-1 open samples have yellowed to a similar minimal level with the thermal-aged samples having slightly higher b^* values. Yet the b^* values of the open samples are significantly lower than those of the laminate samples, particularly those that had been aged thermally or with light. The laminate samples have an excellent appearance and visibly the colour change is nearly undetectable, but the yellowed internal layer can be seen when viewed from the sample side, along the visual plane where the depth of the adhesive layer is greatest. The proportionately greater yellowness measured with the laminate samples may relate to the adhesive thickness, which is greater than with the open samples. The yellowing of the laminate samples requires investigation because most joints comprise layers of adhesive between layers of PMMA, even though the adhesive thickness was intentionally greater than in a typical repair.

Two issues to investigate with HXTAL NYL-1 are reactions that produce yellow chromophores related to conjugated double bond formation when the adhesive is sealed between two layers of PMMA. Chemical reactions may also explain the reduced yellowness of the aged open samples, where a greater surface area of adhesive is exposed to reactions such as hydrolysis and oxidation, that could break the conjugated double bond systems that produce the yellow chromophores, thereby eliminating them, while the adhesive in the laminate samples is protected from these reactions by two layers of PMMA.

A further difference noted with HXTAL NYL-1 is that the two light-aged laminate samples were the only light-aged samples where yellowing was slightly greater than samples that were not aged artificially. The higher b^* value was measured in both laminate samples, but was not found in the open sample; see Figure 1. Yellowing had not been detected immediately after light-aging in 1992 or in 1995 but is evident after 19 years of storage in the dark. This apparently unique pattern of yellowing may result from the intense light or the slightly elevated temperatures in the light-aging unit, since thermal-aging caused yellowing of the laminate samples of this adhesive, but this requires confirmation and further investigation.

Plextol D514 laminate samples illustrate the importance of visual analysis when comparing the yellowness measurements of the samples; refer to Figure 1 and Table 4. The Plextol D514 laminate samples appear visibly to have yellowed considerably more than any of the adhesives evaluated, but this is not reflected in the b^* values measured. The lower than anticipated b^* values reflect measurements taken from the centre of the samples while the yellowing is concentrated on the outer edges. Measurements taken from the sample centre will not identify yellowing at the edge of the laminate samples.

The yellowing of Plextol D514 may result from VOCs or the harsh environments entering the adhesive layer at the edge where it is not protected between two layers of PMMA. The yellowing at the exposed sample edge may be an indication that the exposed upper-most surface of open samples yellow most and not throughout the adhesive; this issue has been raised in the conservation literature (Tennent and Townsend 1987).

Whether open or laminate, the Plextol D514 samples have nearly identical yellowing patterns according to the b^* values in Figure 1. There are many differences in the aging behaviour of the sample types including yellowed edges and voids of the laminate samples, but the b^* values are very similar to the open samples even though the adhesive layer is thinner and they do not appear yellow unless thermal-aged.

One sample of Plextol D514 showed a clear impact of VOCs on yellowing with b^* exceeding a value of five; this sample was stored accidentally with samples of a different adhesive and VOC's from the other adhesive may explain the yellowness.

As anticipated, the open samples of Neocryl BT20 and Norland NOA65 that were thermal-aged showed more yellowing than the corresponding laminate samples, although they are thinner. VOCs from the other adhesives within the thermal-aging oven may have contributed to the increased yellowing of these open samples.

Finally, the open samples of Norland NOA65 also have higher b^* values and visibly are more yellow and cloudy, and the surface is also tacky, marked and soiled when compared to the laminate samples of this adhesive. The adhesive layer of the open samples yellowed more and became cloudy after aging even though it is not as thick as the laminate samples. Many factors could have contributed to the cloudiness and tacky surface of the open samples as a result of aging including oxidation, VOCs, lowering of the glass transition temperature (T_g) and migration of low molecular weight components to the surface of the adhesive. These factors affect the aging of the adhesive samples and works of art already conserved with them.

Comparison to results from 1995 study

The yellowing trend of the Tensol 70 samples in this investigation differs from the trend of the same samples in 1995 when Δb^* values, comparing the measurements taken before and after thermal-aging, had been higher than those of samples aged by other methods. The reversion of yellowing after thermal-aging has been noted previously and warrants investigation (Sale 1995; Down 1995; 1996).

The 1995 study demonstrated also that light-aging had bleached samples that had yellowed as a result of thermal-aging; the relationship between yellowing and aging conditions is similar in this study.

Degreasers

The study data and visual examination indicates that the degreasers appeared to have had no impact on adhesive aging or with the joint interface between the adhesives and PMMA. Detergents are useful degreasers when coatings are sensitive to aliphatic hydrocarbons.

FTIR

No significant differences were noted between the differently aged open samples of adhesives even though some samples were visibly yellow, cloudy or tacky to touch. These changes may relate to the aging of additives or small amounts of alteration products that are not detectable by FTIR (Hodgkins et al 2011).

Py GCMS

This technique was useful for characterising adhesives when the FTIR results differed from the published composition or when there were no reference spectra for comparison (Ormsby 2011).

Micrometer

The hand-held digital micrometer (Axminster) produced some meaningful data. Nevertheless, its use was discontinued due to the damage caused by the sharp hard-edged polished steel measuring surfaces when in contact with the relatively soft adhesives and PMMA. Also, it is not straightforward to use with these samples because of difficulty in ensuring consistent pressure and the variance in the thickness of the adhesive layers and PMMA supports.

VSC

This equipment was extremely useful for visual examination due to the sophisticated user-friendly software for multi-spectral examination and imaging with standard lighting settings. The images are excellent for examination, reports and presentations and the instrument proved most useful for the laminate samples.

Conclusion

This investigation found that 1:1 Paraloid B-67: Paraloid F-10 and HXTAL NYL-1 may be suitable as conservation adhesives for PMMA.

1:1 Paraloid B-67: Paraloid F-10 has not yellowed and has maintained a silvery water-white colour after 19 years following exposure to the accelerated and natural aging environments. It does not appear to be sensitive to relative humidity, temperature or VOCs from other samples and it has adequate tensile strength, or load at break, for repairs (Sale 1995). It can be applied using a variety of techniques that offer flexibility in making repairs; and it is the only adhesive tested that has the potential to maintain solubility with safe aliphatic hydrocarbons. It merits further investigation that includes additional joint types, fillers and dyes.

HXTAL NYL-1 also warrants further investigation because it is an established structural adhesive in conservation and it maintained a good appearance of both sample types with only slight yellowing in laminate samples that were thermal-aged, light-aged or in combination. The delayed yellowing following intense light-exposure that was found in a few samples requires close investigation. This adhesive may prove useful for repairs; even though it is not reversible in solvents, it is assumed that it will be possible to re-treat PMMA should joints fail.

Evaluation of Study of 1992-95 and Future Research

Samples

The samples are useful for measuring yellowness and accessing appearance since the flat surfaces are large enough to measure changes in colour, and the transparent edges and joints replicate repair needs. Nevertheless, it would be easier to measure changes in colour with larger samples.

The study highlighted the importance of ensuring that some laminate and open samples are of equal thickness for comparison after aging. It also highlighted the need for duplicate samples for natural and accelerated-aging. Purpose designed holders for aging, storage and transit would improve sample condition during aging.

Aging environments

The relationship between adhesive yellowing and the aging environments provided useful data but future investigations should consider the following: long-term aging at 30°C would be more similar to natural aging and below the T_g of the adhesives. Long-term natural-aging and light-aging nearer to room temperature will replicate display and storage conditions. Different light sources may provide useful comparisons due to conditions where modern materials are displayed, including out of doors. Artificial and natural aging environments that are anoxic, or without VOC's, and the impact of specific VOC's on the adhesives, warrant investigation.

Yellowness Measurements

In future studies the methodology for measuring the yellowing of transparent materials will be investigated further. CIELAB colour difference equations adopted since CIELAB 1976 (Luo et al 2001) and different spectrophotometer illuminants such as D65, will be investigated, as well as calculations of chroma and hue (CIE 1978) and the ASTM Yellowness Index. ΔE^* will be investigated due to adhesives becoming cloudy white (L*) and brown (a*) (green-red coordinate).

An important consideration when designing future investigations is that measurements taken from the sample centre will not identify yellowing at the edge of the laminate samples. The small aperture size of a microfading spectrophotometer may be useful in measuring colour changes at the outer edge of these adhesive samples.

Methodology

Guidelines to improve methodology of long-term aging studies when measuring yellowness include the following: the development of a long-term monitoring programme to ensure instrument maintenance including the light source, servicing, calibration, reference data and preparation for differences in replacement spectrophotometers.

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Neocryl BT20 (web general)

Norland NOA65 - www.norlandprod.com

Paraloid B-67 and Paraloid F-10 – www.Dow.com

Perspex – www.perspex.co.uk and www.lucitesolutions.com

Petroleum spirit, AnalaR' (web)

Tensol 70 – (web and Bostik)

Video Spectral Comparator model VSC[®]6000 / LF, (www.foster&freeman.com)

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Donald Sale a obtenu un baccalauréat en histoire de l'art à la Virginia Commonwealth University (1984) et une maîtrise ès sciences en conservation-restauration des objets et des sculptures à l'issue du programme d'études supérieures en restauration d'œuvres d'art de l'Université du Delaware et du Winterthur Museum (1988). Il a effectué un stage de perfectionnement à la Tate, à Londres (Royaume-Uni), a travaillé en conservation-restauration des sculptures au Victoria and Albert Museum, et mis en chantier une recherche en conservation-restauration des objets en plastique en collaboration avec la Tate. En 1992, il a été nommé conservateur adjoint (Conservation) et par la suite, chef de la conservation et de la gestion des collections au Sainsbury Centre for Visual Arts, de l'Université East Anglia, à Norwich (Royaume-Uni). Il s'est joint au Royal Pavilion and Museums de Brighton (Royaume-Uni) en 2003 à titre de spécialiste en conservation préventive et est devenu gestionnaire de la conservation préventive en 2006. En 2009, il a entrepris un détachement de 14 mois en tant que gestionnaire de la conservation préventive aux Historic Royal Palaces de Londres, et est revenu au Royal Pavilion en 2010. Donald Sale est un conservateur-restaurateur accrédité par l'Institute of Conservation (Royaume-Uni).

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