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Fill Materials and Methods for Scratch Repair on Poly(methyl methacrylate) Used in Face-Mounted Photographs

Abstract

A primary conservation issue for the sustained use of face-mounted photographs is the inherent susceptibility of the acrylic sheet surface to abrasions. Scratches disfigure the entire surface of the poly(methyl methacrylate) (PMMA) sheet by changing the surface topography and distracting the viewer from the photograph. Scratches on acrylic sheet surfaces can be the result of improper handling, storage, and routine cleaning, and can range from micrometers to centimeters in size. The care, storage, and conservation of these acrylic face-mounted photographs have become growing subjects of debate and preservation experiments among the conservation community.

The primary goal of this study was to determine the quality of scratch repairs for acrylic sheeting and their suitability for the conservation and preservation of face-mounted photographs. Scratches were made on acrylic samples and repair was attempted through the use of scratch reduction techniques and fillers. The fill materials (Paraloid B-72, Dymax 4-20638, and Hxtal NYL-1) are products with refractive indices similar to PMMA, low viscosities, a resistance to yellowing, and favourable working times. Scratch reduction techniques, attempting to decrease the amount of light refraction by the scratch ridges, included flattening and scraping. Coupons were subjected to accelerated thermal and light ageing to detect any negative effects on the poly(methyl methacrylate) caused by the application of these scratch fillers. Repairs underwent analytical tests with a spectrophotometer and glossmeter for color and surface change, as well as visual comparisons of ensuing scratch reduction without negatively impacting the finishing surface. With accelerated ageing the Paraloid-B72 coupons displayed the potential for the largest negative change in b* (yellowing) values and decreased surface gloss while the Hxtal NYL-1, in both color and gloss, was able to surpass and replicate the closest values to an unmodified acrylic surface. A comparative observational study revealed that both the scratch-scraped Hxtal NYL-1 coupon and the scratch-unmodified Paraloid-B72 coupon were the most visually effective in reducing the prominence of surface scratches.

1. INTRODUCTION TO FACE-MOUNTED PHOTOGRAPHS

In a museum or gallery environment, the condition of artifacts and works of art falls under the jurisdiction of the chosen institution. Their care and stability are closely regulated in order to maintain the historical, emotional, physical, and financial value associated with each object. More often than not, the value of a piece has the potential to decrease over time. While this will mainly be dependent on deterioration related to the type of material(s) involved in its production, the stability and longevity of the object will also depend on the care and condition in which it is stored. Face-mounted photographs (hereafter referred to as FMP), for example, maintain their value based on the photograph they protect and consequently on the surface security that the finish provides.

Initially developed by Switzerland's Heinz Sovilla-Bruhlhart in the late 1960's and early 1970's, the face-mounting process is used as a finish for dye-coupler or inkjet-printed photographs (Pénichon and Jürgens 2001). The easily accomplished process eliminates the need for heavy and hazardous glass frames by adhering the photograph directly to a poly(methyl methacrylate) (PMMA) sheet. This method allows the photograph to be adequately protected from harmful deteriorating agents such as ultra-violet radiation (UV), air-borne pollutants, fingerprints, and mold (Pénichon and Jürgens 2005). The original patent from 1972 describes the use of a moisture-curing silicone sealant as an adhesive to set the photograph in the anoxic environment between the photographic emulsion and the acrylic sheet (Jürgens 2001). The mechanical application of the photograph to the acrylic and the long curing time of the adhesive allows technicians to carefully manipulate and scrutinize the image, as well as easily remove any impurities that could compromise the quality of these 'perfect' prints.[1] The rigidity of the PMMA allows the print to be displayed without a distinct frame, thus opening the image to the viewer with no subconscious barrier. Slowly becoming a preferred method for many contemporary artists to showcase their work, face-mounting allows the colors from the photograph to seemingly permeate fully throughout the acrylic sheet, giving the

[1] Erik Stoffers (Wilcovak, Hoogeveen, Netherlands) and Keith Reid (KayMounting Service, London, United Kingdom) personal communication, July 10, 2014

completed work an absorbing and 'wet' look[2] (fig. 1). The patented method was given the name Diasec and is presently maintained by licensed members and approved manufacturers since the process and its guidelines continue to be highly secretive.

Unlicensed manufacturers have been known to use commercial silicone rubber adhesives of varying thicknesses or transparent double-sided adhesive films to secure the photograph to the acrylic finish (Jürgens 2001). These companies use the basic term 'face-mounting' to describe their work; however since only the licensed methodology is strictly regulated, the overall quality of these unrestricted photographic prints can be unpredictable in regards to their long-term preservation.

Fig. 1. Diasec - Face-mounted photograph with 5mm clear cast acrylic. Kaymounting.co.uk 03/16/15

Fig. 2. Diasec - Face-mounted photographs in gallery setting. Artproof.fi 04/29/15

[2] Artist Sabine Hornig uses face-mounting for her work because the flat, pristine, and glossy surface of the acrylic perfectly defines the 'reflective' window-like quality of the work she presents (Karnes and Jennings 2005, 355).

The preservation, conservation, and safe storage of these photographs have become subjects of exploration and discovery among conservators. Yet due to their relatively recent increase in popularity, the exact nature of the longevity and specific preservation requirements for different types of FMP is still relatively unknown. Since these pieces are composite works, the requirements for the individual materials still needs to be evaluated with reference to each other.

When considering the long-term preservation of the materials in general, the finished work consists of a PMMA sheet, an adhesive, and a photograph. While long-term designations for photographs involve cold storage, we have yet to fully examine how the photograph would react to cold storage while adhered to the PMMA. Furthermore how would the PMMA react to its adhesion to the photograph, how the adhesive would behave and would the adhesive fracture from either of the two materials in the intense cold. If cold storage was found to not be an acceptable environment for the FMP then perhaps a standard museum dark storage would be sufficient for the preservation of the work. As with most works of art, the environment where an object is stored plays an exceedingly important role in its long-term 'health'.

Since the finishing process irreversibly adheres the photograph to the PMMA, the acrylic sheet becomes a significant feature in the viewing and interpretation of the object. If the acrylic is ever sufficiently scuffed or cracked, the FMP would need to be fully replaced. This can be an expensive process as prices for printing a FMP can range from hundreds to thousands of dollars depending on the size of the photograph, the type of acrylic sheeting and protection required, as well as the method by which the photograph is re-printed. A print using high quality ink may last longer than those printing processes using inferior materials and methods; but if the chosen acrylic sheet doesn't offer adequate UV protection and is bombarded with too much light, the type of ink comprising the photograph would be irrelevant because after a certain amount of time the colors will surely fade. Even while the acrylic can sufficiently protect the photograph from physical harm, the susceptibility of the PMMA to abrasions will cause just as many obstacles for the preservation and presentation of face-mounted photographs.

A scratch on a smooth acrylic surface is composed of a trough (the depressed centre) and ridges (created by the displaced acrylic material) (fig. 3). When light is reflected by the raised ridges on either side of the trough, there is a visual disturbance that is seen as a scratch. As proposed by Kim and Breitung (2007), the visibility of the scratch could be reduced if the raised edges are smoothed in some type of ridge modification techniques.

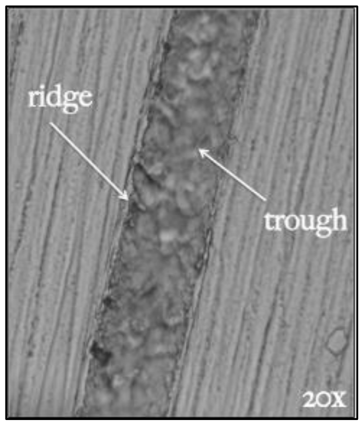

Fig. 3. 20x scratch on PMMA illustrating depressed trough and raised ridges

Attempts to conserve the surface finish of the PMMA after abrasions occur, in order to prolong the shelf-life of these prints and reduce replacement costs, can only be accomplished through the application of irreversible treatments. Because of the ethical conservation concerns of invasive and irreversible treatment on an object, any attempt to modify surface scratches on PMMA to reduce their visibility will remain a risk and subject of debate for conservators (Horie 1982).

While the study of degradation and conservation of plastics only gained formal recognition in the early 1990s (Grattan, 1993), the durability and life expectancy of FMP is a concept not yet fully examined by conservators. In a museum collection under optimal storage conditions, PMMA-based art works have good long-term potential, however unforeseen changes to their storage environment could result in advanced degradation. Added research on proper care and preservation conditions for FMP can only enhance the current understanding of their composite behaviors and optimize their time in museum and educational collections.

The research presented in this paper examined different methods by which three specific adhesives, as scratch fill materials, could be used with surface modification methods, to repair damaged FMP by reducing the visibility of abrasions on the PMMA surface. The adhesives were tested in terms of their color and surface morphology changes throughout an ageing process that simulated museum storage and exhibit conditions.

Conservation Research to Date

Current literature on FMP covers long-term stability and durability. Pénichon et al. (in 2001, 2002, and 2005) discussed the suitability of different finishing methods for photographs in regards to longevity and visual distinction, and analyzed the stability of these photographs in light and dark ageing environments. In 2011, Zorn and Dobrusskin examined light ageing results once more. Van Oosten (2002) and Granowsky et al. (2007) discussed some factors in the catalyzation and degradation of acrylic glazing while Breitung (2007) surveyed abrasion-resistant acrylics. Experiments on the suitability of adhesives for PMMA scratch filling by Sale (1993, 1995, and 2011) and Kim and Breitung (2007) influenced much of the background research for this paper.

Allen (1984) expanded this author's basic understanding of fundamental adhesive qualities, while Haddon and Smith (1991) focused on UV-curing adhesives. Koob's (1986) enthusiastic approach to Paraloid B-72 produced an in-depth understanding. Horie (1982), Swanson (1965), Shashoua (2008), and Fuchs (1989) all surveyed solvent use and restrictions for poly(methyl methacrylate), as well as discussing plastic-production techniques and influencing environmental factors. Finally Tennent and Townsend (1984) provided a fundamental overview of refractive indices as well as their significance during conservation treatment.

1.1 MATERIALS

Acrylic Sheeting for Face-Mounted Photographs

Internationally produced commercial acrylic sheets are incredibly versatile and chemically stable plastics comprised of poly(methyl methacrylate) monomers. Large-scale production of this compound began in 1936 by Röhm and Haas in Germany under the trade name Plexiglas® and has since evolved to many companies selling similar base-compound products with variations of fillers, colorants, and UV-inhibitors among other additives (Swanson 1965). PMMA is rigid, clear, dimensionally stable, lightweight, weather and heat resistant, allows 92% light transmittance, and will not shatter like glass (Cyro 2001). While acrylic sheets do not specifically block radiation below 400nm (Evonik Industries), PMMA is often used as a replacement for glass in frames or for protecting works of art on display. These factors make it incredibly valuable for museum environments wanting to give extra security to priceless artifacts. Acrylic sheets can be manufactured in many ways. When it is cell-cast it has the ability to withstand more internal stresses than acrylic sheets that have been extruded. The added stability of cast acrylic sheets makes them excellent candidates for use with FMP. Their flexibility allows the completed FMP to be easily handled while their strength and resistance to shattering implies prolonged protection for the print.

An important property of PMMA for face-mounting is its refractive index. The refractive index (n) is a dimensionless number describing how light is transmitted through a medium. The relationship is defined as the speed of light in a vacuum (c) relative to the speed of light passing through the polymer (υ) and can be explained by the following equation (1):

$$n = \frac{c}{\upsilon}$$

The refractive index of PMMA is 1.4893 at 23°C (Seferis 1989). This means that materials used to fill scratches on PMMA need to have similar refractive indices (thus the potential to transmit light in a similar way) thereby reducing the visibility of scratches. In face-mounting, the acrylic sheet acts like a varnish on a painting to the surface of the photograph. Light is transmitted through the PMMA and the silicone adhesive, and then reflects uniformly from the surface of the photograph. From this viewpoint, the acrylic and the photograph seem to meld into one single surface, enhancing the perceived color of the photograph.

When the surface PMMA of a FMP is damaged (i.e. by scratches or abrasions), any and all imperfections are noticeably distracting to the work. Therefore if conservation treatments to fill the scratches and reduce their visibility were to be performed, it would stand to reason that the refractive index of the chosen material would be critical since light would need to be refracted through the PMMA at similar angles in order to go unnoticed (Tennent and Townsend 1984).

As the nature of this research deals with the modification and attempted improvement of the surface topography of scratched PMMA coupons, the necessity of experimenting with actual FMP samples is not necessarily required. Whereas other research experiment may deal with the physical properties of this finishing technique, this research studied the visual characteristics and possible changes of the surface itself in terms of its interaction with the fill material, meaning that simple acrylic sheets are sufficient for our testing purposes.

Commercial Fill Materials for Scratch Reduction

While many acrylic sheet manufacturers will often suggest high strength polymerization adhesives (such as ACRIFIX), for working with PMMA, for the purpose of this study these were thought to exceed the bonding requirements of surface scratch fillers. Furthermore, reaction adhesives such as these can become quite costly as they must be ordered from the manufacturer and can only be used for bonding or large gap-filling purposes. The adhesives materials chosen for this experimental research can be used in many different laboratory situations therefore, not only would they be multifunctional, but the reduction in overall cost would be substantial.

A second feature for the selection of fill materials for this study is their practicality. For this reason, abrasive polishing materials, such as NOVUS Plastic Polish, which require a tremendous amount of time and effort for reducing the visibility of even the lightest of scuffs, were not tested here. While the polishing techniques would be advantageous in that they do not add further material to the FMP surface, the circular motion required to remove these scuffs with the abrasive compounds, if not carefully monitored, can cause serious surface deformations (such as divots) well beyond the scratch area and be potentially more obvious to viewers than the scratch itself.

The following three commercial adhesive fill materials were selected in terms of availability, quality, and variety. While the Dymax UV-curing adhesive is not as well-known, the Paraloid B72 and Hxtal NYL-1 can be found in many conservation labs. All three fill materials advertise optimal working abilities with a long cure time, low viscosities, and refractive indices in similar ranges to that of poly(methyl methacrylate). These fill materials have previously been tested by Sale (1993, 1995, and 2011) and Kim and Breitung (2007) and demonstrated promising results for resistance to yellowing and reducing scratch visibility.

Acrylic Co-Polymer in Solvent

Paraloid B-72 has quickly become a favorite in conservation labs. Since its inception in the 1970s, it has been considered stable and all-purpose by most. This versatile thermoplastic resin has properties that tend to resist yellowing, hydrolysis, and oxidation. Koob (1986) is one of its most eager supporters and recommends it as a consolidant, a barrier, a coating, an adhesive, and even a finish on certain materials. Paraloid B-72 is a copolymer of ethyl methacrylate (70%) and methyl acrylate (30%) manufactured by Röhm and Haas, used commercially as a surface coating vehicle for certain inks (Chapman and Mason 2003). Some of B-72's indispensable qualities for this experiment are its refractive index (n=1.49) and that it is soluble in some solvents (hexane and toluene) that are safe for use with PMMA without causing internal environmental stress cracking (ESC).

Previous analysis with this adhesive for scratch-repair posed some challenges for application due to its high viscosity state (>500 cP). As Paraloid resins cure by solvent evaporation, a reliable repair for micro-scratches must use solvents with a slow rate of volatilization and be able to completely penetrate into the exposed polymer areas of the scratches prior to curing. Based on the work of Kim and Breitung (2007), this paper examines application techniques and scratch visibility of a 20% Paraloid B-72 solution in a 1:4 mixture of hexane and toluene.

Two-Part Epoxy Resin

Often the first choice in terms of conservation glass repair, Hxtal NYL-1 has been tested extensively for its ability to resist yellowing when exposed to light (Tennent and Townsend 1984). The removal of color-inducing metal ions during the manufacture of the adhesive give it "ultra-purity"[3] compared to other products used in similar situations. In order to be fully effective, the two components of the epoxy, 3:1 Part A to Part B, must be weighed out accurately. Freshly made Hxtal is very thin with a low surface tension and sets very slowly, often taking up to several hours to thicken. For this experiment the moderate viscosity (335-362 cP; ASTM D-445) of the adhesive is actually a desired quality. The thinner the epoxy, the better it should be able to wick into the minuscule scratches on the PMMA surface. Optical properties of the adhesive for this purpose also include its refractive index of 1.52 (Sale, 1995). The Hxtal should still be able to match the refractive index of PMMA in order to fill, cover, and visibly reduce the appearance of the scratches. While Hxtal contains no solvents, Blank (1990) suggests that some epoxy resins have been known to act as solvents for certain polymers, therefore the careful application and continued use of Hxtal on PMMA compound surfaces should be monitored in case of any adverse effects.

UV-Curing Adhesive

With a long working time and extremely low viscosity (65 cP ; ASTM D-1084), Dymax Ultra Light-Weld® 4-20638, is a urethane and acrylate based decorative adhesive coating (fig. 4) that claims to cure to a clear, transparent, and abrasion-resistant surface

[3] Hxtal NYL-1 product information from Talas Suppliers (www.talasonline.com)

(Dymax 2002). Since the adhesive will not harden until exposed to a UV source, the ease of application as well the ability to flow into surface scratches far exceeds that of the other two chosen adhesives. To cure, Dymax lists a 20-second exposure time using the company's 5000-EC flood lamp with an output of 150 mW/cm^2 that delivers filtered UVA light between 320 and 400nm. Direct curing, or polymerization, of the adhesive allows for less oxygen interference, controlled bonding and therefore less shrinkage and better adhesion to the PMMA surface (Haddon and Smith 1991; Daly 2002). Though the adhesive does not perceptibly yellow when cured, the use of UV radiation directly on the image side of a FMP is a potentially serious hazard for fading the emulsion layer of the photograph itself; however the exposure time, being quite brief, should ideally not have any negative effects on the print, even if the artist did not choose a special UV-absorbing acrylic sheet for their FMP finish.

The Dymax Corporation had no listing of the material's refractive index therefore Cargille liquids were used to determine this value. Since visual inspection showed that the cured Dymax compound was similar in light transmission to PMMA, Cargille liquids were chosen based on their starting similarity to the refractive index of PMMA. The exploration of several refractive index matching liquids over shards of hardened Dymax adhesive found that the refractive index of the fill material is very close to n~1.504. Fourier transform infrared (FT-IR) spectroscopy of the cured Dymax 4-20638 with a comparative acrylic paint showed that the adhesive material is indeed an acrylic based compound (fig. 4).

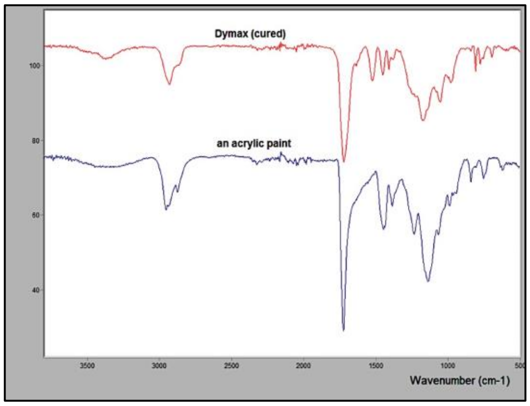

Fig. 4. FT-IR spectrum of Dymax 4-20638 (cured urethane acrylate) with a spectrum of acrylic paint

Table 1. Summary of Fill material properties

Fill Material		Refractive Index	Viscosity
Acrylic Co-polymer in solvent	20% Paraloid B72 in 1:4 hexane toluene	1.49	>500 cP
Two-part Epoxy	Hxtal NYL-1	1.52	335-362 cP
UV-Curing Adhesive	Dymax 4-20638	~1.504	65 cP

1.2 METHODS

Minolta CM-700D Spectrophotometer

The hand-held Minolta Spectrophotometer was used to measure color co-ordinates of fill materials on the surface of the PMMA. This instrument used the 1976 CIE L*a*b* color space; an opponent color system based on the earlier L a b Hunter 1942 space. The idea of color opposition is linked with innovations in the mid-1960s that somewhere between the optical nerve and the brain, retinal color stimuli are translated into individual signals between light and dark, red and green, and blue and yellow (Adobe 2000). These values are indicated by the three axes: L*, a*, and b* (fig. 5). The central vertical axis represents the lightness (L*) whose value runs from 0 (black) to 100 (white). The horizontal axes run from positive to negative and are based on the fact that a color can't be blue and yellow or both red and green, because they are respectively complementary. On the a* axis, positive values indicate redness while negative values indicate a change to green. A positive b* values indicates yellowness while negative values for b* indicate blueness. The spectrophotometer uses the transition between these color values to measure the chroma, hue, and luminosity of each samples' cumulative color change.

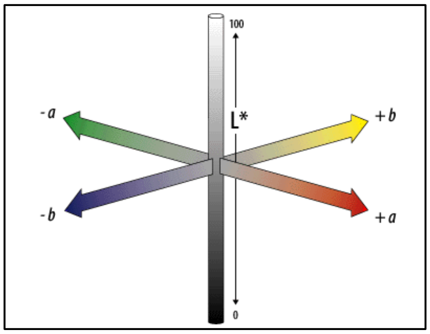

Fig. 5 (right). CIE L*a*b* color change where L* denotes the change from light to dark, a* the change from red to green, and b* yellow to blue.

The value of a total color change (that incorporates all three axes) is ΔE* and is calculated from the following equation (2):

$$\Delta E* = \sqrt{((\Delta L^{*\,2} + \Delta a^{*2} +)\ \Delta b^{*2})}$$

Under optimal conditions a change in color is considered perceptible to the human eye if it is greater than one otherwise it can only be visually detected at a very minimal level. A successful fill material treatment would have an initial color change less than one, indicating that the introduction of the new material does not change the appearance of the object.

As PMMA is clear, transparent, glossy, and tending to –b* (blueness) values, therefore the specific degree of change in the b* axis will be of particular interest to this experiment. Any positive change in this region will demonstrate a yellowing of the adhesive material in relation to the original PMMA surface and therefore a potential increase in scratch visibility. In order to mitigate any surplus reflections of light into the spectrophotometer from outside sources during data collection, all readings were taken in the dark over a glazed white tile.

BYK Gardner Micro-Tri-Gloss 20/60/85° Glossmeter

The BYK Gardner Glossmeter was used to determine the ability of the fill material to fill the scratch and reduce visual damage, as well as replicate the undamaged smooth surface of the PMMA on a microscopic scale. Gloss is an optical property of a surface, measuring its ability to reflect light in a specular direction. Some principle factors affecting gloss are the refractive index of a material, the angle of incident light, and the surface topography. The gloss degree of the surface ultimately determines the selection of available illumination and reflection angles for measurement. Matte surfaces should be measured using the 85° geometry, while semi-gloss surfaces and glossy surfaces should use 60° and 20° geometries respectively (fig. 6). The PMMA samples in this experiment were measured using the 60° geometry for data collection.

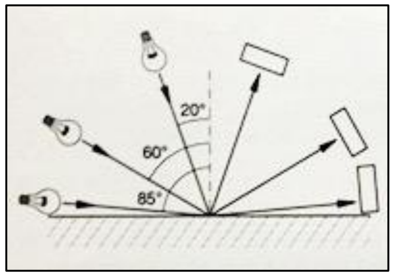

Fig. 6. The “gloss” of the surface determines optimal geometry for measurement. 20° for high gloss surfaces, 60° for semi-gloss, and 85° for low gloss.

In this experiment, the reduction of the scratch ridges by surface modification techniques and the fill material’s ability to cover the scratches, will play a key factor in determining the gloss outcome of the final PMMA surface. Changes in gloss values over the course of the experiment indicate an increase or decrease in the surface roughness of the fill material samples compared to the PMMA; this will affect how the viewer perceives the finished surface. Multiple measurements were taken for a reasonable standard deviation.

2. EXPERIMENTAL

PMMA coupons were abraded in a consistent way to create scratches. Three different fill materials (Paraloid B-72, Hxtal NYL-1, and Dymax 4-20638) were used to treat the scratches. With these materials, methods were used to remove the scratch ridges and reduce their visibility; by flattening and scraping the ridges away in order to properly introduce the adhesive materials. Thermal and light accelerated aging techniques each simulated one hundred years in storage and gallery exhibition environments. Colorimetry and Glossmeter measurements measure color and surface texture deviations from the original acrylic sheeting. A successful fill material minimizes the presence of scratches on the PMMA surface and remains transparent, glossy, and colorless after ageing.

2.1 COUPON PREPARATION

Coupons were cut from large commercially available cast PMMA sheets, Acrylite® by Cyro Industries, into nine 20cm x 8cm coupons that were degreased with mineral spirits. Each sample was analyzed in 15 spots; 10 for the fill material/modification area while five remained as scratch controls (fig. 7).

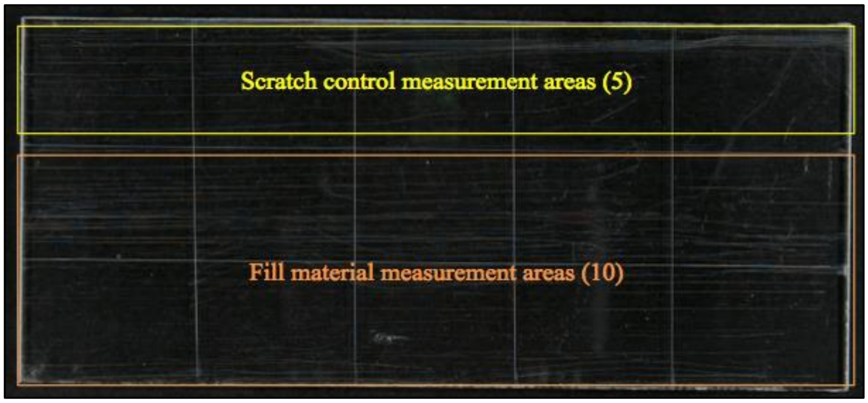

Fig. 7. Each coupon (scratched, scratch-flattened, and scratch-scraped) uses this division of scratch control and fill material/modification areas.

Three coupons were given to each fill material [B72 (B), Dymax (D), Hxtal (H)] and categorized as (i) scratches with fill material [B, D, H], (ii) scratch-flattened with fill material [FB, FD, FH], and (iii) scratch-scraped with fill material [SB, SD, SH] respectively (table 2). Comparisons were made regarding the efficiency of the modification and fill material application techniques and the ease of manipulation as well as the overall reduction of scratch visibility. Cellophane tape was cut down to a 0.5mm width and used as a barrier at the edge of the samples to prevent the fill material from dripping off the samples.

Table 2. Coupon distribution by technique and fill material with the number of measurements

Coupon Sets	Paraloid B-72	HXTAL NYL-1	DYMAX 4-20638
Scratched PMMA control	5 for each sample below		
Fill material over unmodified scratches **(scratched)**	10 **[B]**	10 **[H]**	10 **[D]**
Fill material over flattened scratches **(scratch-flattened)**	10 **[FB]**	10 **[FH]**	10 **[FD]**
Fill material over scraped scratches **(scratch-scraped)**	10 **[SB]**	10 **[SH]**	10 **[SD]**

Scratching the Acrylic Sheets

In order to recreate statistically relevant scratches on all of the coupons, a ‘rub test’ machine was used to standardize the horizontal force by inducing similarly sized scratches on the surface of the PMMA (Beauchamp 2014). A small weight of 760g with 80 garnet sandpaper at the PMMA interface was attached to a rotating arm on a small motor to glide back and forth over the coupons on a plastic railing, with equal downward pressure (fig. 8, 9). The rotation speed of the motor allows for 50 passes of the weight over the surface in 60 seconds (Beauchamp 2014). Imaging of the scratches was done with a Nikon S-Kt Olympus system microscope.

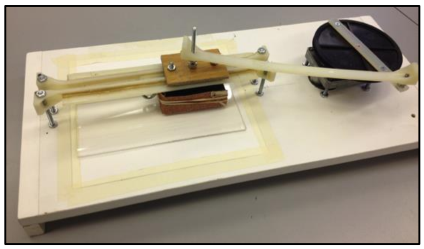

Fig. 8. Rub-test machine (Beauchamp 2014) uses a mechanized wheel to pull a weight covered in sandpaper over PMMA coupons.

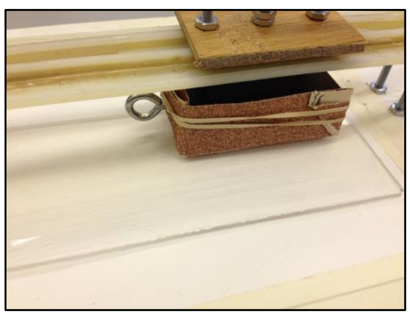

Fig. 9. Close up of scratching PMMA with rub-test machine

Manipulating the Scratch Ridges

The flattening treatment strategy in this research involved the use of localized heat by a heated MashIR flattening microscopy tool to soften the ridges of the PMMA scratches in an attempt to reduce their visibility. Cyro Industries (2001) states that PMMA can be safely heated to temperatures between 171 and 193°C in order to make the sheet malleable. Therefore the tool was pre-heated to 200°C in a furnace and applied directly to the scratch surface upon removal from the heat source. The tool was manually rolled across the sample surface with even pressure and full passes and was replaced in the furnace every 2 minutes in order to maintain the sufficient heat level. Flattening was considered adequate when the scratch ridges no longer perceptible by touch.

The flattening technique above attempted to equalize the topography on the scratch ridges, the scraping treatment however quickly and easily removed the scratch ridges in an effort to reduce any perceptible visual disturbance created by the disfigurement (fig. 10). The scraping treatment used a one-sided razor blade dragged manually at a moderate speed across the entire scratch surface with light and even pressure for ten seconds.

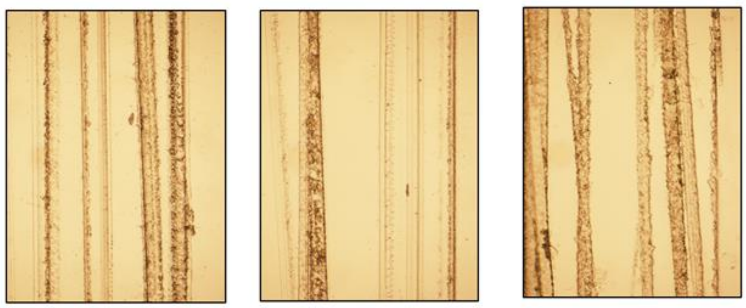

Fig. 10. 10x: scratches on PMMA (left), scratch-scraped PMMA (centre), and scratch-flattened PMMA (right)

Application of the Adhesives

Adhesives were prepared based on the specific preparation instructions of each material. The fill materials were applied in a fume-hood with good ventilation with either a brush or syringe over the entire testing area and leveled out naturally and with a silicon wedge for an even surface distribution. The Paraloid B-72 and Hxtal NYL-1 samples cured for four weeks respectively. While Dymax lists quick exposure of their product with a high voltage UV lamp, the curing time was modified in order to accommodate the lower voltage UV lamps available. The Dymax 4-20638 samples were exposed to ultra-violet radiation for over twenty minutes in order to achieve a full cure in the thinnest areas of adhesive. After the long curing time, the Dymax adhesive demonstrated a slight yellowing however this faded back to clear transparency after being set aside for the remainder of the curing period.

2.2 METHODS OF INVESTIGATION

Color and Glossmeter Measurements

The CIE 1976 L*a*b* color space on the spectrophotometer was used to measure color co-ordinates of fill materials on the surface of the PMMA. Measurements were taken at each stage of the experiment: before application of adhesives (BA), after application of adhesives (AA), after thermal ageing (AT) and after light ageing (AL). Ten measurements were taken over the fill material/modification areas on each of the nine coupons [B, FB,SB, D, FB, SB, H, FH, and SH]. The scratched PMMA control areas (five on each of the nine coupon) were measured for the overall effect of scratch reduction. The large number of measurement areas was devised in order to calculate a reasonable standard deviation since the scratching method was not accurately duplicated with each sample. The information was transferred to a spreadsheet where the changes in b* values in particular (denoting the change from yellow to blue) were analyzed further for significant color changes in the fill material and in the original PMMA surface. Readings were taken in the dark over a glazed white tile and the spectrophotometer was recalibrated every dozen samples.

The glossmeter was used to determine the ability of the fill material to replicate the surface of the acrylic. Ten measurements were taken at the 60° geometry on all of the coupons previously analyzed with the spectrophotometer. Data was collected at each stage of the experiment. The large number of measurements was taken in anticipation of a wide standard deviation.

Visual and Photographic Analysis

A visual examination of each sample set was used to supplement data collected from the spectrophotometer to determine if any samples had perceptibly yellowed after ageing. To accurately determine the suitability of these repairs for FMP, the scratches on the samples were photographed against all-black and all-white backgrounds before and after each ageing technique. These backgrounds were created from glossy white and black photographic paper to simulate a real FMP. Each color allowed different scratch properties to be evaluated: black grounds allowed the white appearance of scratches to be seen while white grounds detected any shadows transmitted by any remaining unfilled scratches. To compensate for any personal bias, the samples were also analyzed by fellow classmates for visual changes and apparent yellowing as well as overall scratch reduction.

METHODS EMPLOYED TO AGE COUPONS

Thermal Ageing

Due to the unknown base chemical content of two of the fill materials, thermogravimetric analysis (TGA) was done to determine the thermal degradation activation energy (E_a) of both Hxtal NYL-1 and Dymax 4-20638. The analysis was performed in the Queen's University Polymer Characterization Lab on a TA instrument G500 equipped with a 16-sample pan carousel auto sampler. Each material was run from 25-500°C at 10, 20, and 30° min^{-1} ramps. Paraloid B-72 was not tested with the TGA since the E_a of the constituent copolymers is already known.

Thermal ageing is based upon the idea that ageing represents kinetically driven chemical reactions within and between the molecules of a given material. From the Arrhenius equations as rearranged by Flynn and Wall (1966) (3):

$$E_a \propto \frac{d\ln(\beta)}{d\left(T^{-1}\right)}$$

The thermal degradation activation energy (E_a) was determined by plotting the natural logarithm of the heating rate (β) vs. three temperatures of equivalent weight loss for each material (T) and multiplying this value by the gas constant (R). For these calculations the reaction order was assumed to be one (See Appendix I). The activation energies of the materials (Dymax 140.46kJ mol^{-1}, Hxtal 123.5kJ mol^{-1}, and B-72 200kJ mol^{-1}) was then used to estimate an equivalent age of 100 years to mimic storage conditions by using the following Arrhenius equation (4):

$$k = A\, e^{\frac{-E_a}{RT}}$$

$$\text{acceleration} = e^{\left[\frac{E_a}{R}*\left(\frac{1}{T_{23^\circ C}}-\frac{1}{T_{Acc.\ Age}}\right)\right]}$$

$$\text{ageing time} = \frac{\text{equivalent age}}{\text{acceleration}}$$

Based on these calculations, the Dymax and Hxtal samples were thermally aged for 12.15 hours and 47 hours respectively in a Despatch LEA 1-69 oven at 95°C and 50% relative humidity for an equivalent ageing of 100 years. The B-72 samples were aged for 4.53 hours at approximately 85°C (instead of 75°C) and similar relative humidity conditions (table 3) for over 100 years. Samples were placed on the oven shelves lined with white blotting paper. All samples were aged separately.

Table 3. Thermal ageing of coupons - Each fill material was aged separately

	FILL MATERIAL		
	Paraloid B-72	**HXTAL NYL-1**	**DYMAX 4-20638**
Temperature	4.53 hours	47 hours	12.15 hours
Time	85°C	95°C	95°C

Light Ageing

Light ageing was accomplished simultaneously in two specially designed sealed LED accelerated light fading chambers with adjustable lux settings to simulate 100 years in a gallery setting (fig. 11). Samples were exposed to visible light intensities set at a constant 100,000 lux at 25-40% RH and 39-43°C for 438 hours based on the following calculation (5):

$$\text{ageing light intensity x ageing time} = \text{normal light intensity x equivalent age}$$

$$\frac{\text{equivalent age x normal light intensity}}{\text{ageing light intensity}} = \text{ageing time}$$

$$[\text{equivalent age} = 8 \text{ hours day}^{-1} x \text{ 365 day year}^{-1} x \text{ 100 years} = 292000 \text{ hours}]$$

$$\text{ageing time} = \frac{292\,000\text{hours } x \text{ 150lux (standard museum environment)}}{100\,000\text{lux}} = 438 \text{ hours}$$

To ensure that all samples were exposed to the same levels of illumination within the unit, the samples were rotated clockwise within each chamber every three days over the 18 day period. The samples were not placed on blotting paper since the base of the chamber is mirrored, meaning that some light was reflected back through the samples.

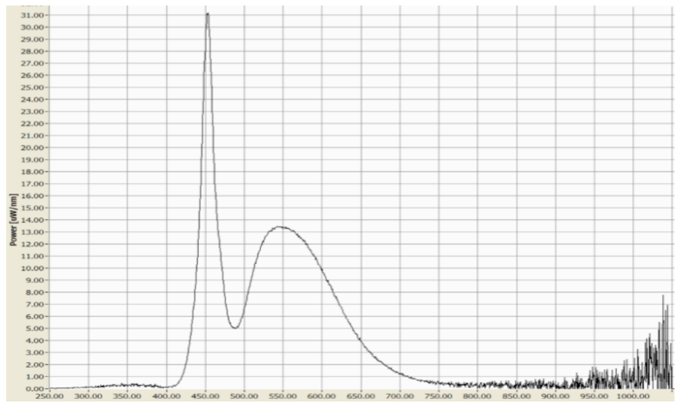

Fig. 11. Spectral power distribution curve for the sealed light boxes used for accelerated light ageing of the coupons. Note: As the curve represents an LED system it has a blue bias

3. RESULTS AND DISCUSSION

3.1 ASSESSMENT OF ADHESIVES

Dymax 4-20638

As a fill material, the Dymax UV-curing adhesive is extremely non-viscous with a very long working time. Since curing did not take place until exposed to a UV source, the material was allowed to flow well into the sample areas. Using the syringe supplied by the manufacturer, it was easily dispensed and manipulated into the scratch areas. After the fill material application, minor scratches were the least visible in the scratch-flattened coupon (FD). Larger scratches and some minor abrasions were still visible in the scratched sample (D), while the scratch-scraped coupon (SD) showed the most remaining scratches under the smooth matte material surface. While the surface of the coating was not abrasion-resistant, it did replicate the PMMA surface quite well. However within the unexpected and overly long curing time, dust and other particulates were adhered to the surface thus adding further distraction within the coating. Due to the unavailability of specific UV fluorescent lamps, the curing time for the coupons vastly exceeded the short time listed by the manufacturer. Instead of 20 seconds as expected, the difference in wattage with the available bulbs demanded a curing time of over 40 minutes. The Dymax actually did not cure completely until two months after application time, when the samples were removed from the light ageing boxes. During the original exposure time, it was noted that the material yellowed slightly from prolonged UV exposure, but reverted back to the clear coating it maintains four months later. The fill material did not perceptibly yellow after accelerated ageing.

Colorimetry results showed that none of the surface modification methods significantly affected the resulting range of color changes (see table 4 and Appendix III for spectrophotometer results.) With accelerated ageing the scratched D coupon had a shift in Δb* values of -0.35 +/- 0.05 [$p < 0.01$] from the untouched PMMA control samples while the SF sample had Δb* values -0.37 +/- 0.08 [$p < 0.01$] and the SD sample Δb* values of -0.37 +/- 0.07 [$p < 0.01$] from the PMMA control surface. The values indicating a negative b* (less yellow) change justify the dull appearance of the coupons after ageing, as opposed to the positive yellow shift that briefly appeared over the long curing time. Measurements with the glossmeter (see Appendix IV for glossmeter results) found that the only surface modification method able to replicate a surface similar to that of unscratched PMMA is the simple scratch method (Δ gloss from unscratched PMMA control -7.67 +/- 5.77 [p=8.06E-03]). The FD method generated the highest value change after the ageing of the adhesives (Δ gloss -22.55 +/- 6.79 [p=7.23E-03]). The modified SD coupon showed the mid-range surface reduction from the original unscratched PMMA surface, where the change in gloss was -17.68 +/- 5.81 [p=2.29E-04].

Table 4. Dymax colorimetry and surface change from the PMMA control, before and after ageing

DYMAX 4-20638	**Color Change**		**Gloss Change**	
	Δ b values	[p]	Δ gloss units	[p]
Scratched (D)	-0.35 +/- 0.05	<0.01	-7.67 +/- 5.77	8.06 E-03
Scratch-Flattened (FD)	-0.37 +/- 0.08	< 0.01	-22.55 +/- 6.79	7.23 E-03
Scratch-Scraped (SD)	-0.37 +/- 0.06	< 0.01	-17.68 +/- 5.81	2.29 E-04

20% Paraloid B72 in 1:4 Mixture Hexane:Toluene

The working properties of this material showcase many reasons for Paraloid B-72’s favour among conservators. In terms of a fill material, while it was the most viscous of the three, it cured to the smoothest surface. Scratches are still quite visible, more so than the Dymax coupons, however the surface has remained clean and free of a great deal of particulates during the volatilization of the solvents, making it a great deal more favorable to work with. This fill material cures to a clear, transparent, hard, and smooth abrasion-resistant surface on the PMMA. Minor scratches are heavily reduced while only some of the larger abrasions are still visible. It must be noted that application marks from the smoothing wedges are still visible on the adhesive surface as proof that curing began soon after application. The scratched (B) and scratch-flattened (FB) coupons display similar scratch covering power, with the flattening coupon only slightly surpassing the other.

Colorimetry results for B-72 were mostly similar to the Dymax coupons (table 5). All three methods again maintained b* values lower than an untouched PMMA surface signifying a material tending to a less yellow surface. After accelerated ageing the scratched B72 coupons had a shift in Δb^* values of -0.33 +/- 0.07 [$p < 0.01$] from the untouched PMMA control samples while the FB sample had Δb^* values -0.46 +/- 0.07 [$p < 0.01$] and the scratch-scraped (SB) sample Δb^* values of -0.33 +/- 0.08 [$p < 0.01$] from the PMMA control surface. These values demonstrate that the FB coupon produced the greatest color change to less yellow of the three methods, however the distinction between all three sets is still slim. Glossmeter results indicate that the only surface modification method able to replicate a variable similar to that of unscratched PMMA is the simple scratch method (B) (Δ gloss from unscratched PMMA control -7.33 +/- 7.64 [p=1.19E-03]). The flattening method generated the most matte surface result of all fill material sample sets with a gloss reduction of -44.18 +/- 6.97 [$p < 0.01$]. The SB coupon resulted in a similar loss of gloss in the sample data, where the surface was reduced -35.30 points +/- 8.64 [$p < 0.01$].

Table 5. B-72 colorimetry and surface change from the PMMA control, before and after ageing

20% Paraloid B-72 in 1:4 hexane: toluene	**Color Change**		**Gloss Change**	
	Δ b values	[p]	Δ gloss units	[p]
Scratched (B)	-0.33 +/- 0.07	<0.01	-7.33 +/- 7.64	1.19 E-03
Scratch-Flattened (FB)	-0.46 +/- 0.07	<0.01	-44.18 +/- 6.97	< 0.01
Scratch-Scraped (SB)	-0.33 +/- 0.08	< 0.01	-35.30 +/- 8.64	< 0.01

Hxtal NYL-1

Of all the fill materials tested, this conservation-grade glass repair adhesive has the best covering power. While upon very close inspection some minute scratches are still discernable, all other visual examinations provide a clear and unburdened look through the coupon. As some bubbles were formed during the mixing of the epoxy, throughout the long curing time the remaining bubbles re-emerged in the cured fills. While the scratches are satisfactorily covered, the surface is noticeably raised from the rest of the PMMA. Since the adhesive is extremely thin, the shallow surface scratches were easily filled while only some of the deepest abrasions are still visible. Of the modification methods, the scratch-scraping (SH) treatment did not cover as well as either of the simple scratched (H) and scratch-flattened (FH) coupons.

Colorimetry results for the Hxtal coupons cumulatively displayed the least amount of color change from the PMMA control surface. With accelerated ageing the scratched Hxtal coupon had a shift in Δb* values of -0.33 +/- 0.07 [$p < 0.01$] from the untouched PMMA control samples while FH sample displayed Δb* values -0.25 +/- 0.07 [$p < 0.01$] and SH sample had Δb* values -0.29 +/- 0.08 [$p < 0.01$] from the PMMA control surface. Not only did the FH coupon have the smallest effect on sample color change, it also had the highest gloss increase of all samples (Δ gloss +13.04 +/- 10.62 [p=2.42E-03]). By flattening the ridges, the surface became smoother and the ridges were no longer able to diffract light in the same way, thus reducing the visibility of the scratches. After the flattening method, the scraping method was the second highest gloss increase (Δ gloss +8.63 +/- 9.84 [p=8.05E-02]). With a change in gloss of +3.05 +/- 11.33 [p=0.66], the scratched Hxtal coupon is the closest to replicating the original PMMA surface gloss, while still displaying a larger gloss increase than the cumulative data of either the other two fill materials.

Table 6. Hxtal colorimetry and surface change from the PMMA control, before and after ageing

Hxtal NYL -1	**Color Change**		**Gloss Change**	
	Δ b values	[p]	Δ gloss units	[p]
Scratched (H)	-0.33 +/- 0.07	< 0.01	+3.05 +/- 11.33	0.66
Scratch-Flattened (FH)	-0.25 +/- 0.07	< 0.01	+13.04 +/- 10.62	2.42 E-03
Scratch-Scraped (SH)	-0.29 +/- 0.08	< 0.01	+ 8.63 +/- 9.84	8.05 E-02

Summary of Test Results

While the Hxtal coupons displayed the least amount of color change from the original unscratched PMMA control surfaces, both the Dymax and Paraloid B-72 coupons displayed similarly small color changes to 'less yellow' in the b* values. Contrary to the original impression from the Dymax during application, none of the fill materials yellowed greatly during, or after accelerated ageing.

The scratched Dymax coupon (D), the scraped (SB) and scratched B72 (B) coupon, and the flattened (FH) and scratched Hxtal (H) coupon all display the least amount of change in the fill materials from the original PMMA surface after accelerated ageing (table 7). The scratched Dymax sample had the best results with both the spectrophotometer and glossmeter however the long cure time allowed too much distracting dust to be ingrained in the fill surface. The SB and scratched B-72 had varying results between instruments yet reduced both minor and some larger scratches. Of all samples, the scratched Hxtal coupon represented the most comparable gloss values to untouched aged PMMA and the FH coupon in turn displayed the least amount of color change for b* values with the spectrophotometer. While the Hxtal coupons had an uneven surface, surface scratches were heavily reduced and mostly indiscernible (fig. 12).

Table 7. Displays the best (or least amount) to the worst (or greatest amount) of change in regards to the delta b* and glossmeter values from the original unscratched PMMA surface.

<table>
<tr><th></th><th></th><th>Smallest change</th><th></th><th>Largest change</th></tr>
<tr><td rowspan="2">Dymax</td><td>Color</td><td rowspan="2">Scratched</td><td>Flattened</td><td>Scraped</td></tr>
<tr><td>Gloss</td><td>Scraped</td><td>Flattened</td></tr>
<tr><td rowspan="2">B-72</td><td>Color</td><td>Scraped</td><td>Scratched</td><td rowspan="2">Flattened</td></tr>
<tr><td>Gloss</td><td>Scratched</td><td>Scraped</td></tr>
<tr><td rowspan="2">Hxtal</td><td>Color</td><td>Flattened</td><td rowspan="2">Scraped</td><td>Scratched</td></tr>
<tr><td>gloss</td><td>Scratched</td><td>Flattened</td></tr>
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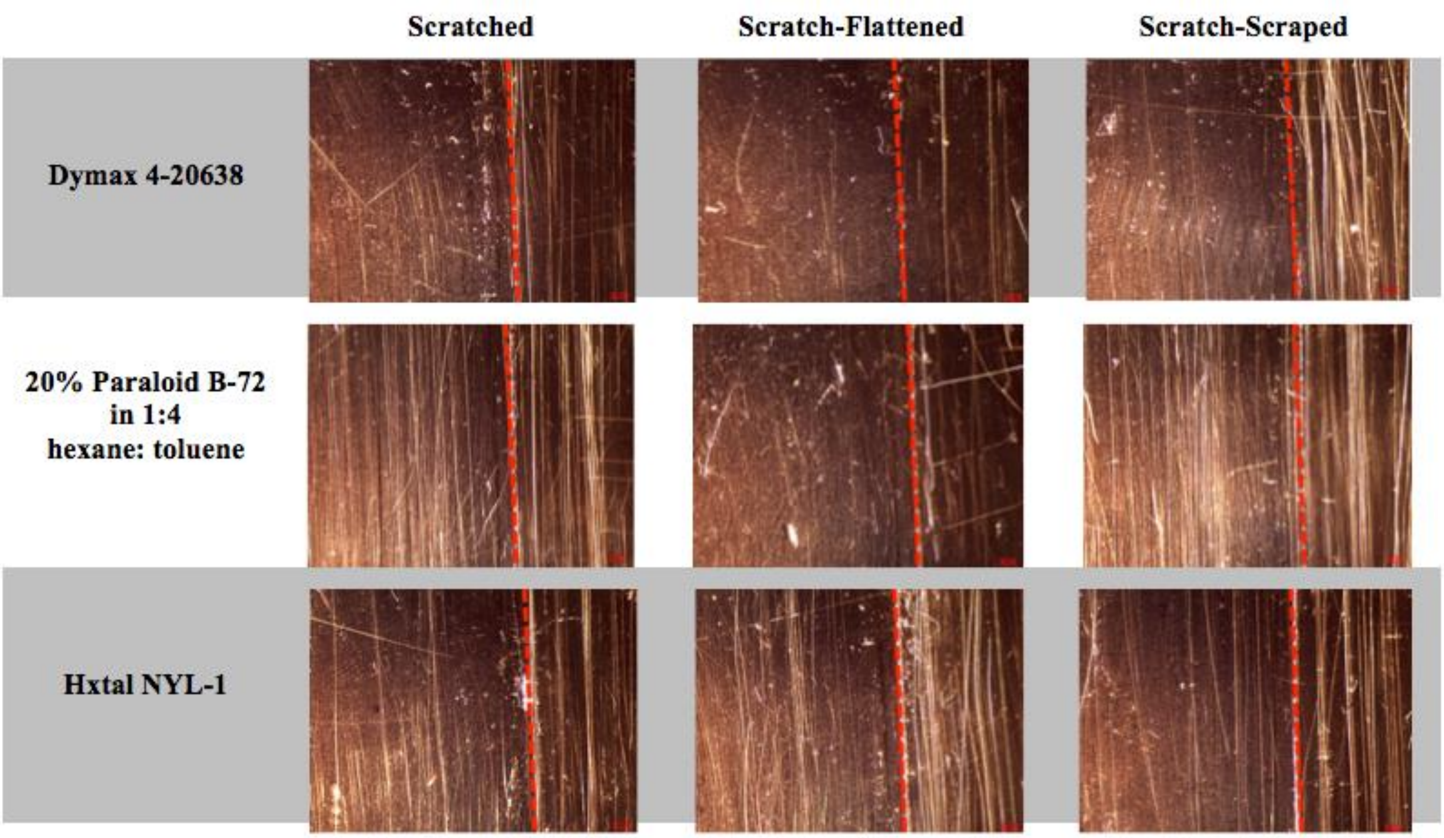
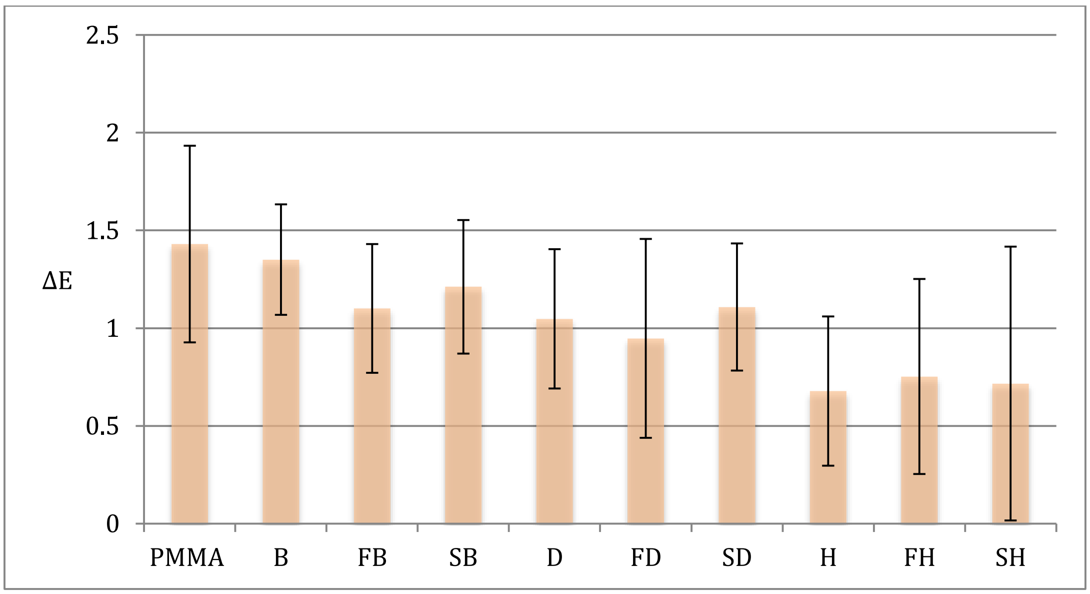


Figure 12. Sample images demonstrating the effect of scratch reduction for each fill material and surface modification method in raking light.

3.2 VISUAL EXAMINATION

In most cases with colorimetry data, values denoting a change of more than 0.5 from the original surface would comply with a noticeable color change. With fill material results, the scratch-flattened B-72 coupon recorded the highest b* change (-0.46 from unscratched control PMMA surface) with all others having less change, around the -0.3 range. Even so, no coupon samples perceptibly yellowed during accelerated ageing. The maximum possible Δ E* color change for the samples from the original PMMA surface, taking into account the standard deviation, was calculated in order to demonstrate the most extreme color change the coupons could suffer throughout ageing. The sample potentially suffering the largest and most visible color change was the scratched B-72 coupon (ΔE^*_{max}= 1.63) while the sample with the smallest possible color change was the scratched Hxtal coupon (ΔE^*_{max}=1.06). A list of the ΔE^*_{max} color changes can be found in table 8 below.

Table 8. The ΔE* for all fill materials and manipulation methods. Chart (top) shows data listed in table (bottom). Note that the B72 coupons produced the greatest color change, while Hxtal coupons produced the least amount of color change. [Scratched B72 (B), Flattened (F), Scraped (S), Dymax (D), Hxtal (H)]

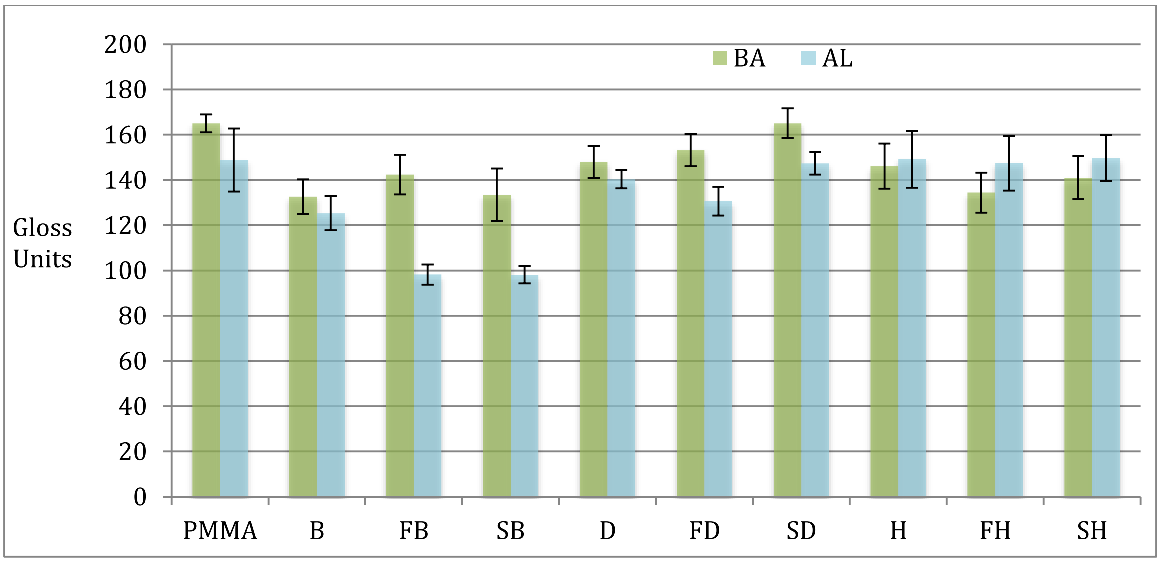


	PMMA control	Scratch B72	FB	SB	Scratch Dymax	FD	SD	Scratch Hxtal	FH	SH
ΔE*	1.43	1.35	1.10	1.21	1.05	0.95	1.11	0.68	0.75	0.72
ΔE^*_{max}	1.93	1.63	1.43	1.55	1.40	1.46	1.43	1.06	1.25	1.42

For surface gloss of the samples, deviations from the original unscratched PMMA control surface are easily detected (table 9). The scratch-flattened B-72 coupon showed the greatest gloss decrease from the values noted by PMMA. With a change of -44.18 points, these samples comprised the most matte surface created by the fill material. The other two B72 coupons, the scratched and scratch-scraped, had gloss reductions of -7.33 and

-35.30 respectively. As the Dymax materials accumulated dust and other debris particles during the long cure time, the surface gloss was distorted. With increases of +3.05 (H), +8.63 (SH), and +13.04 (FH) respectively, the Hxtal coupons represent the only samples that increased in surface gloss after accelerated ageing.

Table 9. The gloss transition for all fill materials and manipulation methods. Chart (top) depicts the data listed in table (bottom). Note that the B72 coupons produced the greatest gloss reduction, while Hxtal coupons produced the greatest gloss increase. [Scratched B72 (B), Flattened (F), Scraped (S), Dymax (D), Hxtal (H)]



	PMMA control	Scratch B72	FB	SB	Scratch Dymax	FD	SD	Scratch Hxtal	FH	SH
BA	165.06	132.65	142.37	133.46	147.98	153.18	165.06	146.11	134.4	141.01
AL	148.81	125.32	98.19	98.16	140.31	130.63	147.38	149.16	147.44	149.64

To compare the accuracy of the final results, the samples underwent a blind observational exercise to evaluate the effectiveness of the materials as scratch fillers. Twelve classmates were asked to view the samples over a black background, in a room with incandescent lights. Participants were asked to vote on the best scratch reducing material over two rounds of testing. Votes for the overall winners of the study, displaying the best scratch covering ability in reflected light, are as follows: scratch-flattened Hxtal (1), scratched Hxtal (1), scratch-flattened Dymax (1), scratched B-72 (4), and scratch-scraped Hxtal (5). While the two highest rated material differ by a large enough range, the participants considered the scratch-scraped Hxtal (SH) and scratched B-72 (B) the most effective scratch reducers.

3.3 EVALUATION OF PROCEDURES

While surface modification methods were not evident to the naked eye, the effects on the scratches can be seen microscopically (fig. 13). Flattening scratch ridges with the MashIR roller was difficult to engage precisely since the head is only 5mm wide compared to the 5cm scratch modification area. Furthermore since heat was dissipated quickly from the roller, the continuous need to return it to the furnace for reheating was an unwelcome addition to the already lengthy surface modification process.

While the flattening treatment with the MashIR roller did not seem to effectively reduce the scratch ridges, the scraping treatment instantly produced a smooth surface for the fill material to ‘wet-out’. While this method effectively smoothed the PMMA surface, it did not seem as successful in significantly reducing the visibility of the surface scratches. The use of a brush instead of a syringe for the application of non- viscous fill materials often created an irregular surface on the PMMA. Even when used in combination with the silicon wedge, the surface was not sufficiently leveled prior to the first stages of curing or volatilization of the fill materials. The wedge produced an unreliable surface application of the material and more often than not, an uneven adhesive surface. Unfortunately the wedge was also unable to fully force the fill material into large scratch areas. Further experimentation with wicking techniques may provide the potential to fill isolated scratches without creating an overflow of residue on the PMMA surface.

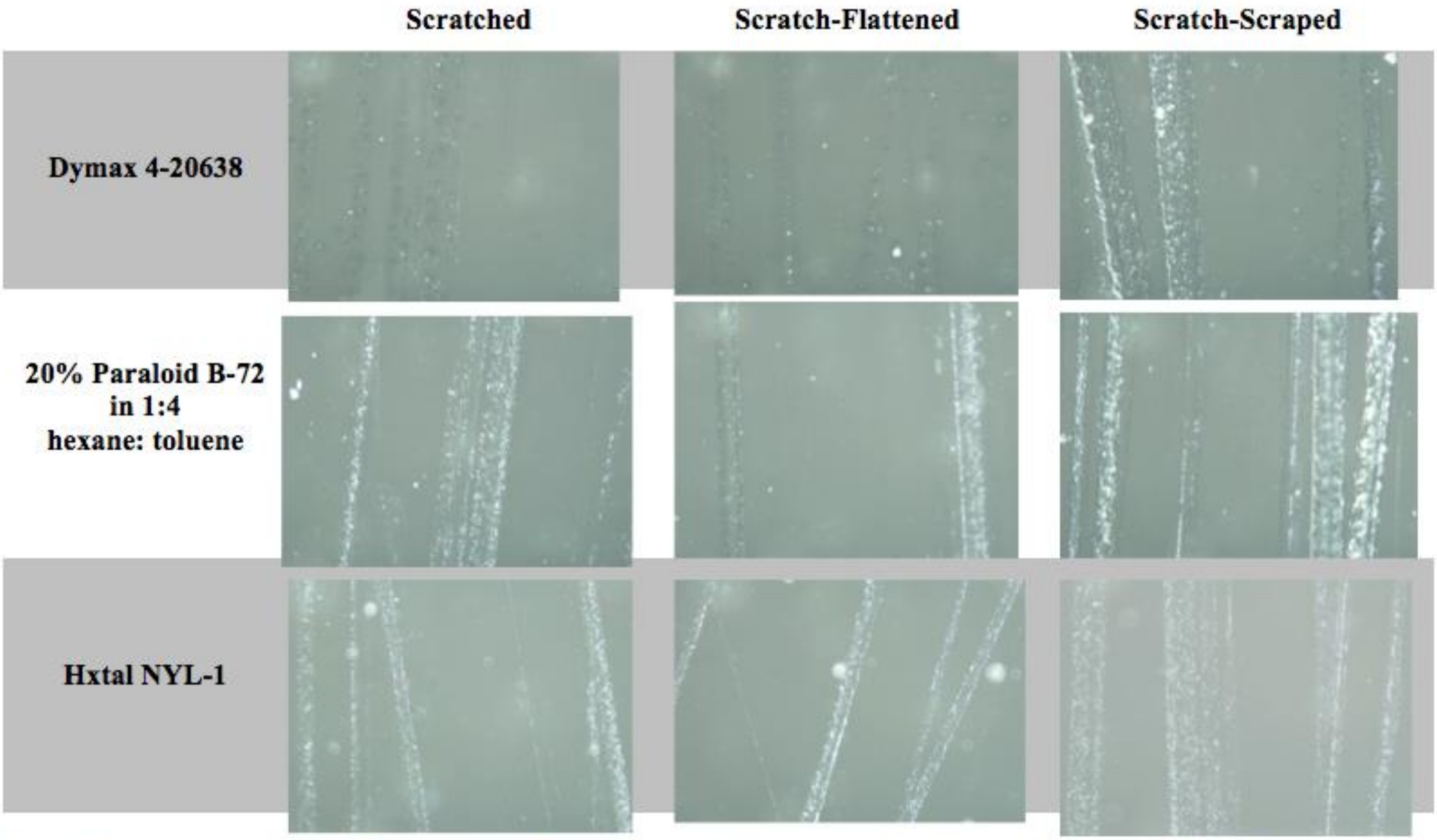


Figure 13. Sample photomicrographs demonstrating the effectiveness of the surface modification methods in transmitted light.

4. CONCLUSIONS

The conclusions reached in this study show the surface effectiveness of each fill material in visually reducing surface scratches on PMMA used for FMP when completely covering the scratch. Accelerated ageing studies performed here demonstrated the extent to which three fill materials could potentially be altered in color and surface gloss. The effectiveness of each material for filling individual scratches requires further experimentation; however the conclusions attained in this study are listed as follows:

1. None of the samples demonstrated any perceptible color change.
   a. Paraloid B-72 had the greatest color change (cumulative b* ~ -0.37), and the greatest color change potential (cumulative ΔE^*_{max} ~1.54).
   b. Hxtal NYL-1 had the smallest color change (cumulative b* ~ -0.29), and the least potential for color change (cumulative ΔE^*_{max} ~ 1.24).

2. Gloss variation between the three fill materials was very perceptible.
   a. Paraloid B-72 produced the most matte surface (Δ gloss ~ -28.94).
   b. Hxtal NYL-1 produced the glossiest surface (Δ gloss ~ +8.24).

3. The scratch-flattening technique was able to replicate a similar PMMA surface gloss better than scratched or scratch-scraped samples.

4. An observational study (in reflected light) suggests that scratched and scratch-scraped coupons covered with Paraloid B-72 (B) and Hxtal NYL-1 (SH) respectively, were the most effective in visually reducing surface scratches.

ADHESIVE APPLICATION AND SURFACE MODIFICATION

Application of the fill materials with brushes and syringes created a very uneven and spotty surface (table 10). The silicon wedge was too large to effectively force the adhesive to penetrating into deep surface scratches. While filling individual PMMA scratches can be problematic, additional study into adhesive application with glass capillary tubes or by 'wicking-in,' could provide applicable methodologies for adequately filling solitary deep surface scratches.

During surface modification, the flattening treatment did not noticeably flatten scratch ridges while the scraping treatment instantly produced a smooth surface. When compared to the raking light images in figure 12 however, the flattening produced more indiscernible scratches for Dymax and B-72. Potential reasons for this could be to the remaining presence of the flattened scratch ridges. While original theories anticipated that completely removing the ridges would allow the fill material to better penetrate the scratches, it seems that the lack of ridges allowed the material to pass over the scratch without any draw into the scratch trough. Flattened scratch ridges therefore could have provided enough of a draw for the fill material to be pulled in and fill the scratch. Although when comparing this theory to the voted 'best scratch reducers' (scratched B72 and scratch-scraped Hxtal), the conclusion demonstrates that there are many more factors in effect that the surface modification method alone.

Table 10. Overview of techniques and results

Method/Material	Reversible?	Visual Affect	Comments
Scratch-flattening (localized heat)	No	Flattened edges, decreased shadows	Difficult to be consistent over large areas
Scratch-scraping	No	Smoothed edges; decreased reflections from scratched areas	Efficient way to smooth surface quickly
Acrylic Co-polymer in solvent	Yes	Better clarity and shadowing, matte surface	Hard to control, cures quickly
UV-curing adhesive	No	Better clarity and shadowing, dusty surface	Correct UV-wattage necessary
Two-part Epoxy	No	Better clarity and shadowing, glossy surface	Avoid bubbles when stirring

FURTHER RESEARCH – PASSIVE SCRATCH-REDUCTION

Since various factors affect the visibility of surface scratches, maybe the solution to reducing their visibility is something other than active surface reduction. If the scratch cannot feasibly be removed, remove the ability of the viewer to see the scratch (Jürgens**,** pers. comm. 2015). Since the viability of these experimental results was different based on the illumination, by altering lighting conditions, changing the direction of the light source or implementing barriers to only allow direct viewings of the FMP, the reflection of light might be dissipated enough to achieve a passive-visible reduction in surface scratches. Furthermore, the image content of the FMP itself will affect how well the scratch is seen by the viewer. For example, a scratch over a FMP of a grey concrete floor will be much less noticeable than a scratch over a FMP depicting a pure black background. The level of distraction presented by any surface scratch will play a key role in terms of its long-term care and preservation.

Passive scratch reduction could also be investigated when combined with non-obstructing frame options. If a clear and transparent substance with a refractive index similar to PMMA could be held in contact with the FMP surface by another sheet of PMMA, the refraction of light may be enough to make any scratches vanish (Hess Norris, pers.

comm. 2015). This option, if successful, would present a reversible, inexpensive, and easily changed 'finish-frame' that would be able to protect the original FMP surface from further scratches while restoring a surface previously abraded for viewers to enjoy (fig. 14). Additionally, the presence of an 'invisible' frame would not interfere with the originally intended open quality of the work. The substance held between the new 'frame' (only mm in thickness) could even enhance the colors of the photograph further.

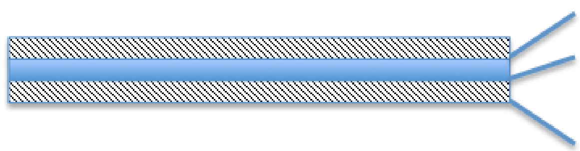


Fig. 14. Tentative framing research suggestion involving a second PMMA sheet and a liquid substance of similar refractive index to mitigate the appearance of scratches on the original FMP.

Essentially, a scratch is only a disruption when it is visible to the viewer. By reducing the visibility of the scratch enough, it no longer becomes a problem when viewed. In this sense, while commercial scratch polishers may be ineffective in completely reducing scratches, the creation of smaller and smaller micro-scratches around the original scratched area may be able to provide enough of a distraction to the original deep scratch to build an illusion of a smooth surface. If these new scratches can only be viewed under a microscope, then the scratch reduction task has been accomplished.

FILL MATERIAL AND REDUCTION OF SCRATCH VISIBILITY

While originally theorized that the Dymax UV-curing adhesive, due to its extremely low viscosity, would most actively penetrate and fill surface scratches to reduce their visibility, this was not the case. Though some minor scratches were reduced, the long cure time (due to the low wattage UV sources) allowed too many dust particles to be adhered onto the surface. Therefore even though the visibility was reduced for many scratches, the disturbance created on the surface by the dust was far too distracting to be considered effective. Further experimentation using appropriate radiation sources would certainly affect the outcome of these results.

Curiously enough, the B-72 (found to have the greatest color change and gloss reduction) and the Hxtal (with the least color change and greatest gloss increase) were both found to effectively reduce the visibility of surface scratches in the observational study. Comparatively the photomicrographs in figure 13 show that the Dymax samples were the most effective in scratch reduction. Since imaging was conducted with reflected, raking and, transmitted incandescent light sources, it can be inferred that as the light source changes, so will the visibility of surface scratches on PMMA. Other than the light source, the viewing angle and image in the photograph itself of a FMP will also affect the prominence, and inherent visibility, of surface scratches. Further research and understanding in all of these areas will greatly increase the conservator's understanding of FMP and methods by which, if possible, disfiguring scratches can effectively be reduced.

ACKNOWLEDGEMENTS
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Appendix 1. THERMAL DEGRADATION PLOTS

Fig. 15. Temperature vs heating rate (ln) thermal degradation plot for Dymax 4-20638 calculated from Thermogravimetric Analysis (TGA) results based on a comparative 75% weight loss - Polymer Characterization Lab, Queen's University.

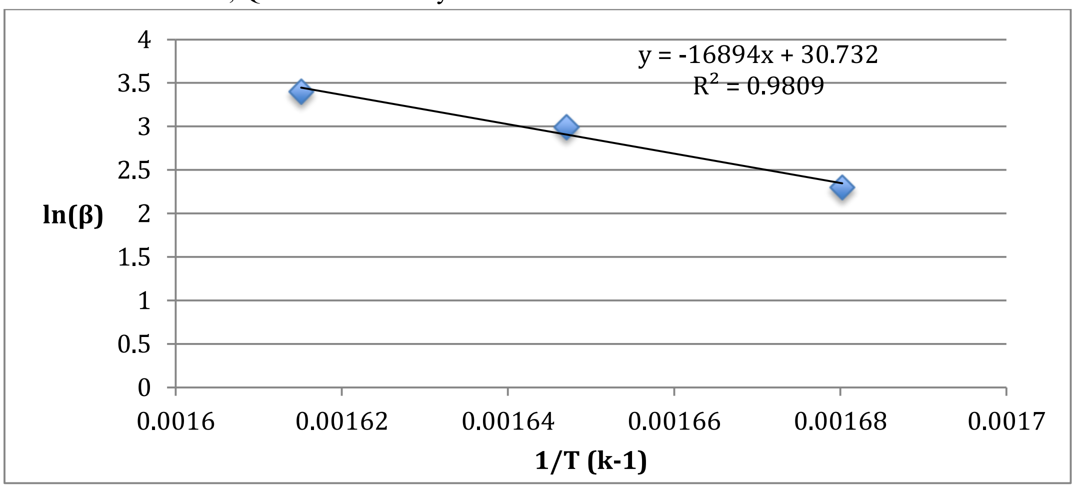
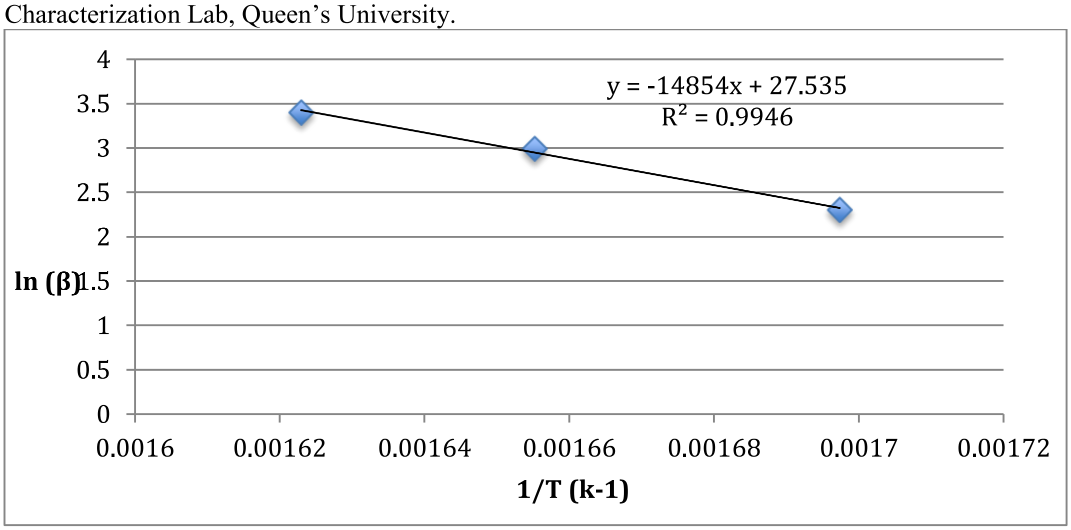


Fig. 16. Temperature vs heating rate (ln) thermal degradation plot for Hxtal NYL-1 calculated from Thermogravimetric Analysis (TGA) results based on a comparative 80 % weight loss - Polymer Characterization Lab, Queen's University.



Appendix 2. EQUIPMENT AND MATERIAL SPECIFICATIONS

Microscope: Nikon S-Kt stereomicroscope and Olympus microscope imaging system
Manufacturer: Nikon and Olympus respectively

Rub-Test Machine: Custom-designed rub-test machine supporting small weight of 760g (with 80 garnet sandpaper) attached to rotating arm on small motor. Rotation speed: 50 passes of the weight in 60 seconds.
Manufacturer: See Beauchamp 2014

Polymer Characterization Lab: Thermogravimetric Analysis (TA) Instrument G500 equipped with a 16-sample pan carousel auto-sampler.
Manufacturer: TA Instruments

Infrared Spectroscopy: Avatar 320 ™ E.S.P.™ with Transmission E.S.P. baseplate
Manufacturer: Nicolet Instrument Corp., 5225 Verona Rd., Madison, WI 53711-4495

Surface Modification Tool: MashIR Flattening Tool
Manufacturer: Kevley Technologies

Spectrophotometer: Minolta CM-700D Spectrophotometer with CIE 1976 L*a*b* color space
Manufacturer: Konica Minolta

Glossmeter: BYK Gardner Micro-Tri-gloss 20/60/85° Glossmeter
Geometry application measurement area: 20°: high gloss 10x10 mm (0.4x0.4 in); 60°: semi-gloss 9x15 mm (0.35x0.6 in); 85°: low gloss 5x38 mm (0.2x1.5 in)
Manufacturer: BYK

Aging Oven: Despatch Industrial Humidity oven LEA 1-69 oven at a) 95°C and 50% RH; b) 85°C and 50% RH.
Manufacturer: Despatch Industries

Light Box: (2) Custom-designed sealed LED accelerated light fading chambers with adjustable lux settings
Manufacturer: Michael Doutre (Queen's University)

Appendix 3. SPECTROPHOTOMETER RESULTS

Table 11. The b* values of coupons before adhesive application (BA) and after accelerated ageing (AL) as well as the change (Δ) in b*. These values, along with the L* and a* values (unlisted) were used to calculate the change in E (overall color change) for the coupons.

		b* BA			b* AL	Δb* from
Unscratched PMMA control	Mean	6.26	Unscratched PMMA control AL	Mean	6.40	0.14
	St. Dev.	0.04		St. Dev.	0.16	
Scratched PMMA control	Mean	6.17	Scratched PMMA control AL	Mean	6.28	0.11
	St. Dev.	0.06		St. Dev.	0.18	
B72 BA	Mean	6.16	B72 AL	Mean	5.83	-0.33
	St. Dev.	0.07		St. Dev.	0.06	
Dymax BA	Mean	6.16	Dymax AL	Mean	5.82	-0.35
	St. Dev.	0.06		St. Dev.	0.04	
Hxtal BA	Mean	6.20	Hxtal AL	Mean	5.87	-0.33
	St. Dev.	0.06		St. Dev.	0.07	
FB BA	Mean	6.24	FB AL	Mean	5.78	-0.46
	St. Dev.	0.08		St. Dev.	0.06	
FH BA	Mean	6.14	FH AL	Mean	5.88	-0.25
	St. Dev.	0.07		St. Dev.	0.07	
FD BA	Mean	6.20	FD AL	Mean	5.83	-0.37
	St. Dev.	0.10		St. Dev.	0.05	
SB BA	Mean	6.09	SB AL	Mean	5.76	-0.33
	St. Dev.	0.09		St. Dev.	0.07	
SD BA	Mean	6.15	SD AL	Mean	5.78	-0.37
	St. Dev.	0.06		St. Dev.	0.07	
SH BA	Mean	6.14	SH AL	Mean	5.85	-0.29
	St. Dev.	0.10		St. Dev.	0.05	

Fig. 17. The b* values for Dymax 4-20638 and various modification methods. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

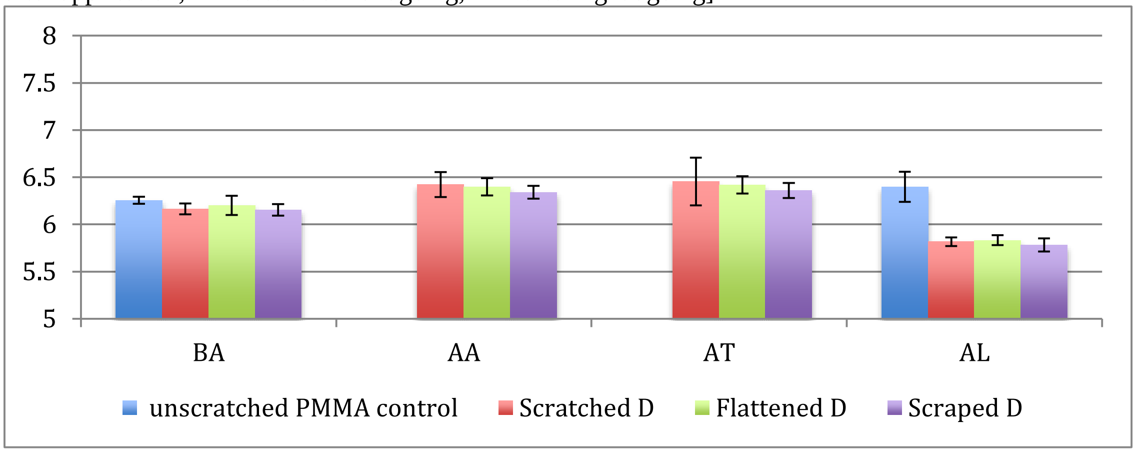


Fig. 18. The b* values for Paraloid B-72 and various modification methods. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

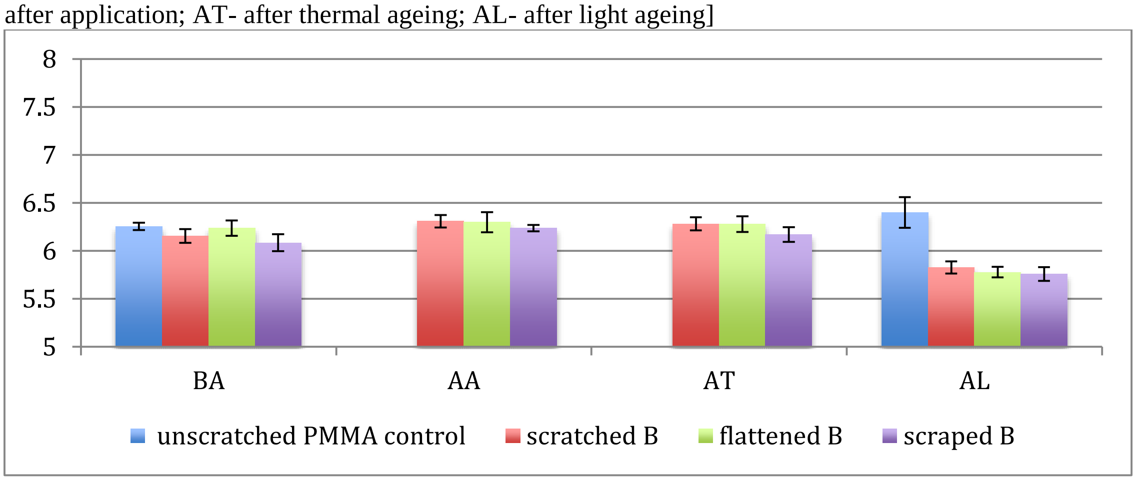
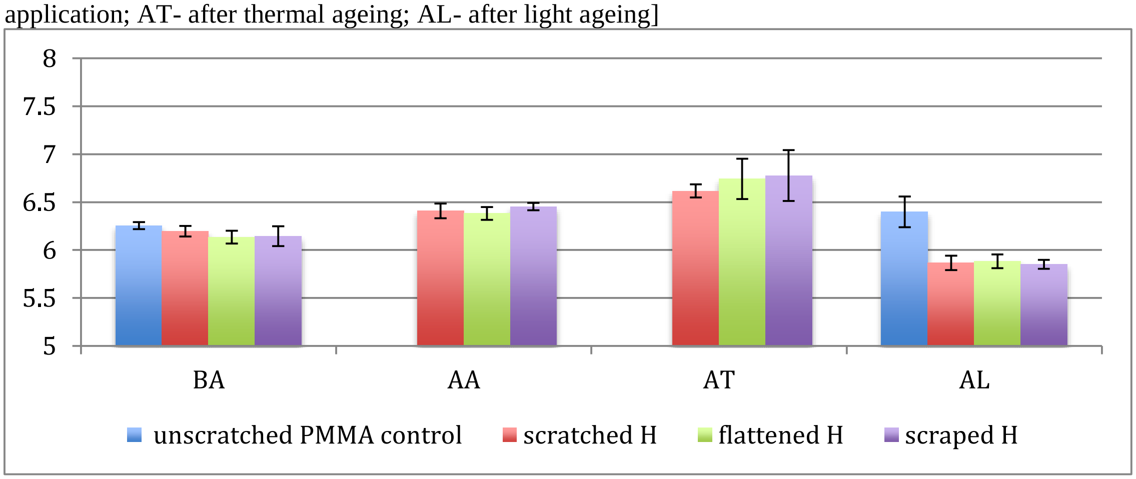


Fig. 19. The b* values for Hxtal and various modification methods. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]



Appendix 4. GLOSSMETER RESULTS

Table 12. Glossmeter results on all coupons before adhesive application (BA) and after accelerated ageing (AL) demonstrating the change in surface gloss. Negative values indicate a more matte surface, while positive values identify a gloss increase.

		60° BA			60° AL	Δ gloss 60 degrees
Unscratched PMMA control	Mean	165.06	Unscratched PMMA control AL	Mean	148.81	-16.25
	St. Dev.	3.96		St. Dev.	13.96	
Scratched PMMA control	Mean	142.11	Scratched PMMA control AL	Mean	140.12	-1.99
	St. Dev.	10.63		St. Dev.	10.64	
Dymax BA	Mean	147.98	Dymax AL	Mean	140.31	-7.67
	St. Dev.	7.09		St. Dev.	4.049	
B72 BA	Mean	132.65	B72 AL	Mean	125.32	-7.33
	St. Dev.	7.66		St. Dev.	7.618	
Hxtal BA	Mean	146.11	Hxtal AL	Mean	149.16	3.05
	St. Dev.	10.01		St. Dev.	12.52	
FD BA	Mean	153.18	FD AL	Mean	130.63	-22.55
	St. Dev.	7.16		St. Dev.	6.39	
FB BA	Mean	142.37	FB AL	Mean	98.19	-44.18
	St. Dev.	8.78		St. Dev.	4.47	
FH BA	Mean	134.40	FH AL	Mean	147.44	13.04
	St. Dev.	8.89		St. Dev.	12.10	
SD BA	Mean	165.06	SD AL	Mean	147.38	-17.68
	St. Dev.	6.56		St. Dev.	4.95	
SB BA	Mean	133.46	SB AL	Mean	98.16	-35.30
	St. Dev.	11.56		St. Dev.	3.94	
SH BA	Mean	141.01	SH AL	Mean	149.64	8.63
	St. Dev.	9.55		St. Dev.	10.12	

Fig. 20. Change in surface gloss per modification technique from the control PMMA surface before adhesive application.

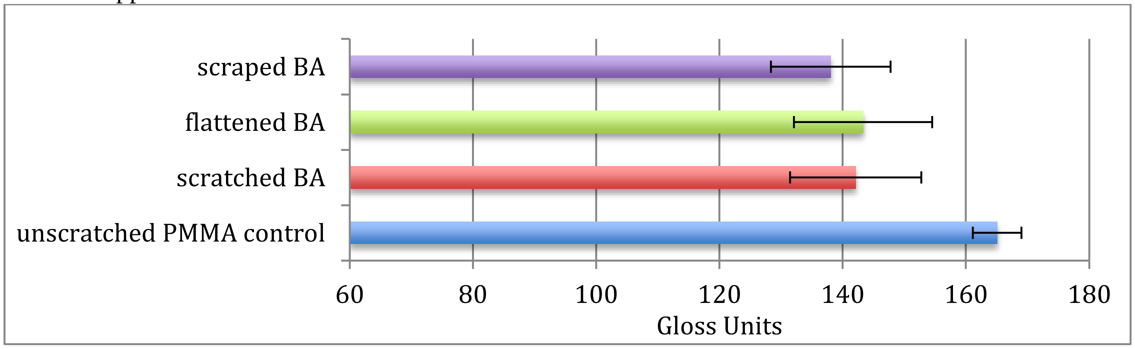


Fig. 21. The gloss values for scratched Dymax coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

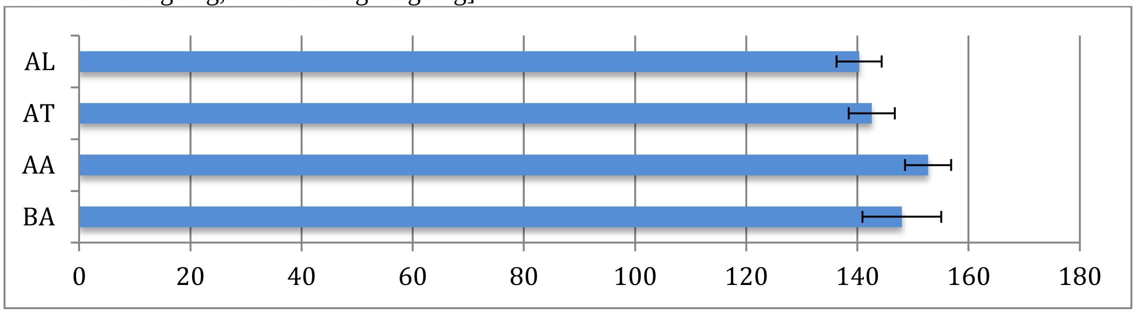


Fig. 22. The gloss values for scratched B72 coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

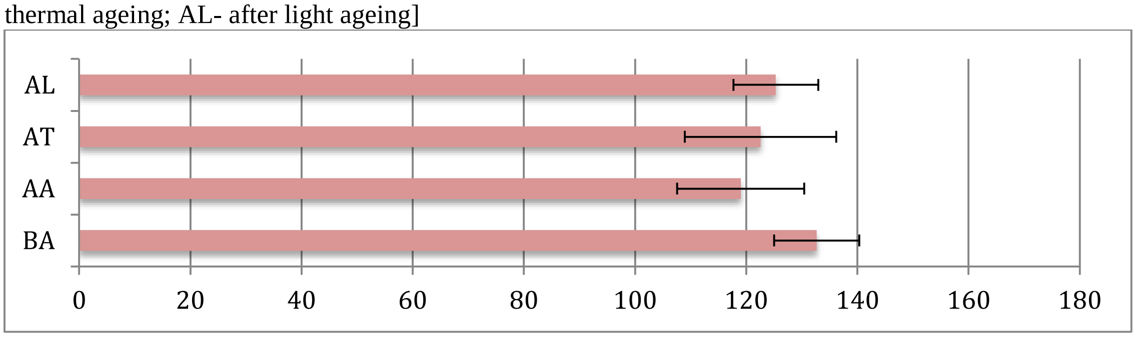


Fig. 23. The gloss values for scratched Hxtal coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

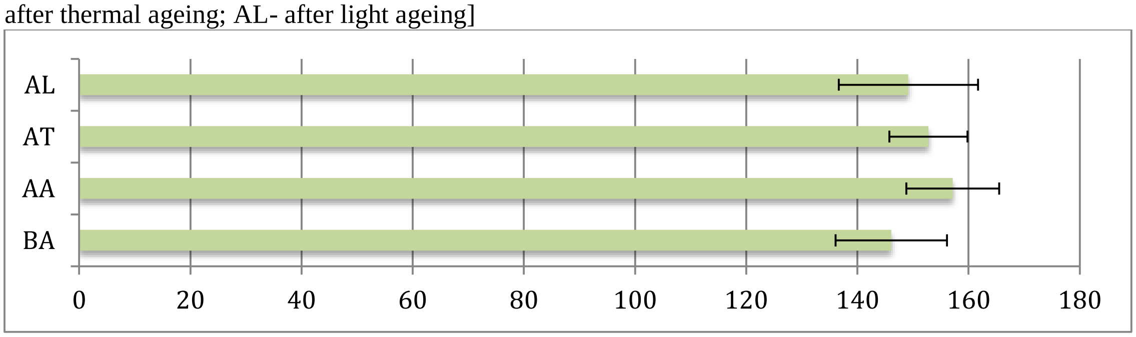


Fig. 24. Comparison: Fill materials over **scratched** PMMA surface.

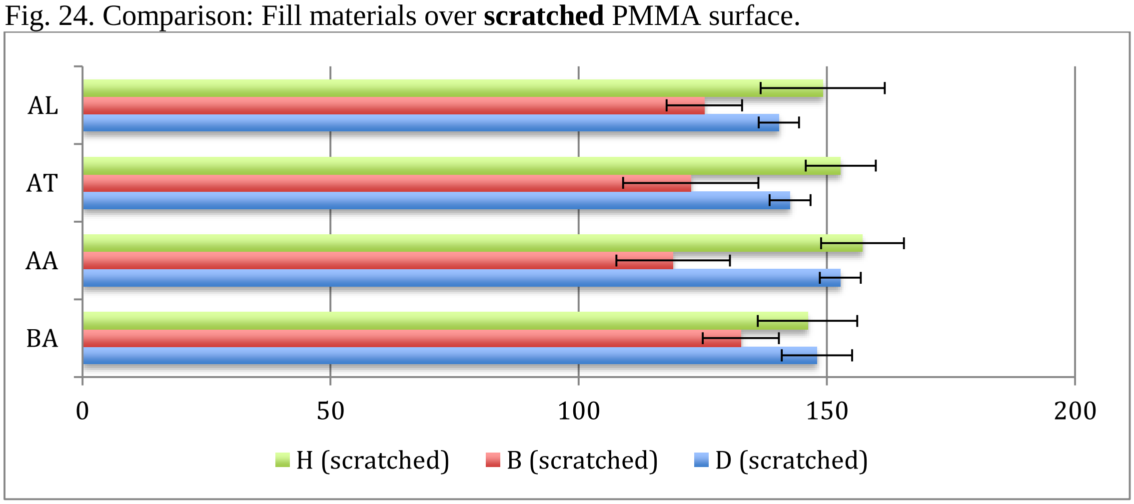


Fig. 25. The gloss values for scratch-flattened Dymax coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

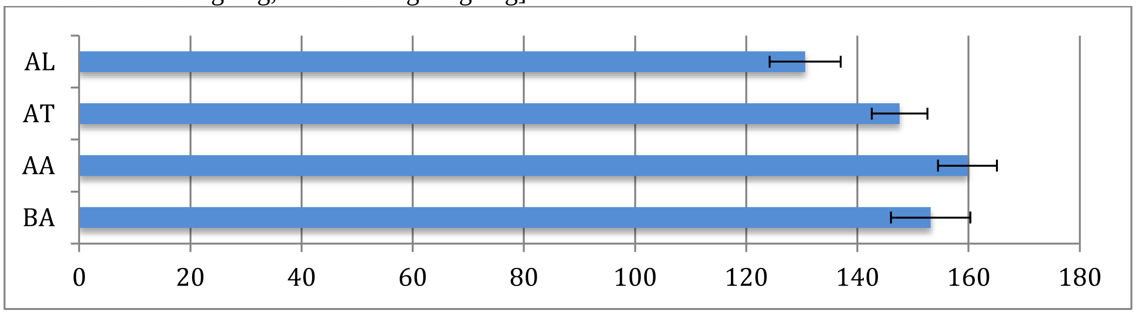


Fig. 26. The gloss values for scratch-flattened B72 coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

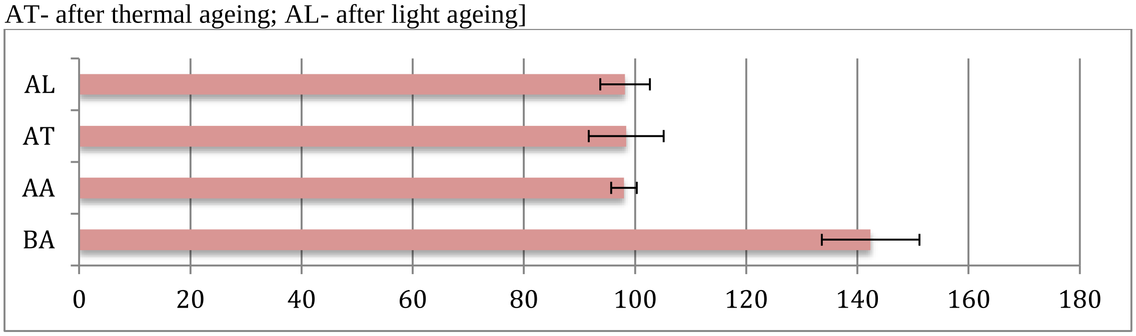


Fig. 27. The gloss values for scratch-flattened Hxtal coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

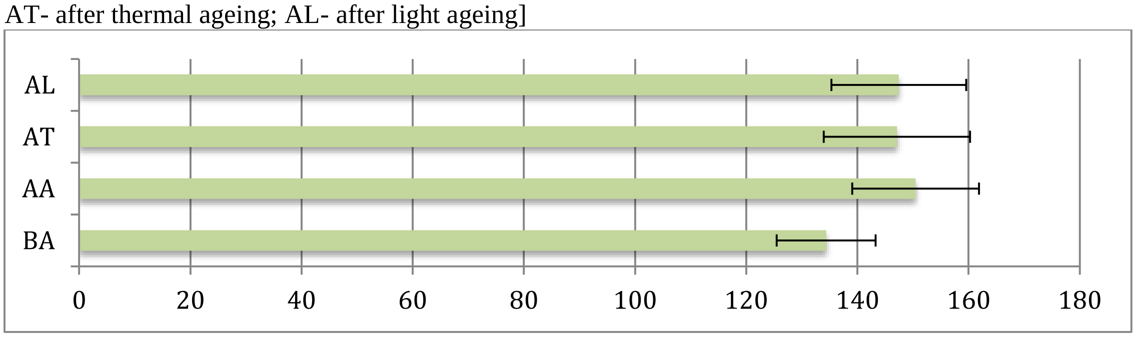


Fig. 28. Comparison: Fill materials over **scratch-flattened** PMMA surface

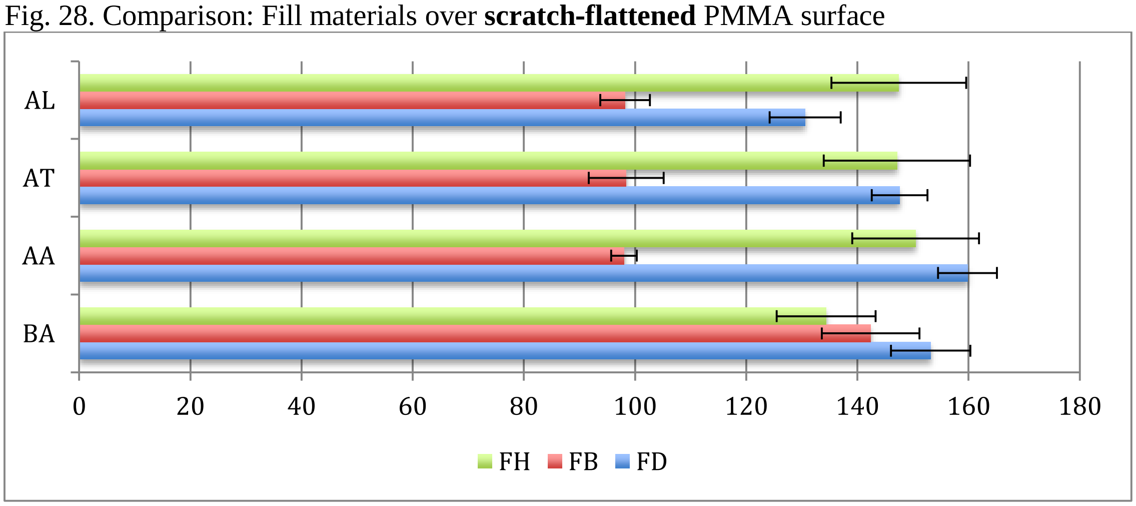


Fig. 29. The gloss values for scratch-scraped Dymax coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

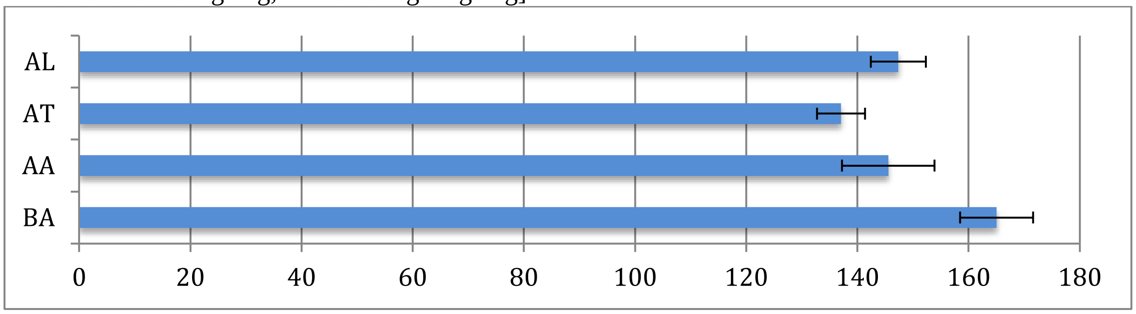


Fig. 30. The gloss values for scratch-scraped B72 coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

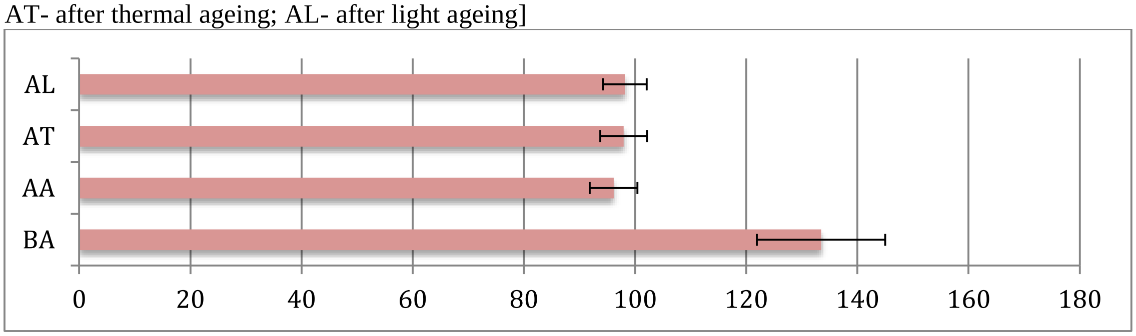


Fig. 31. The gloss values for scratch-scraped Hxtal coupon. [BA- before adhesive; AA- after application; AT- after thermal ageing; AL- after light ageing]

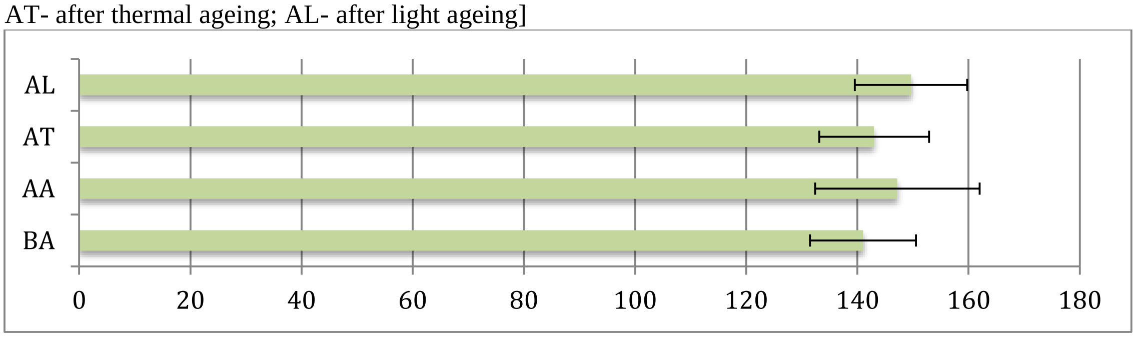
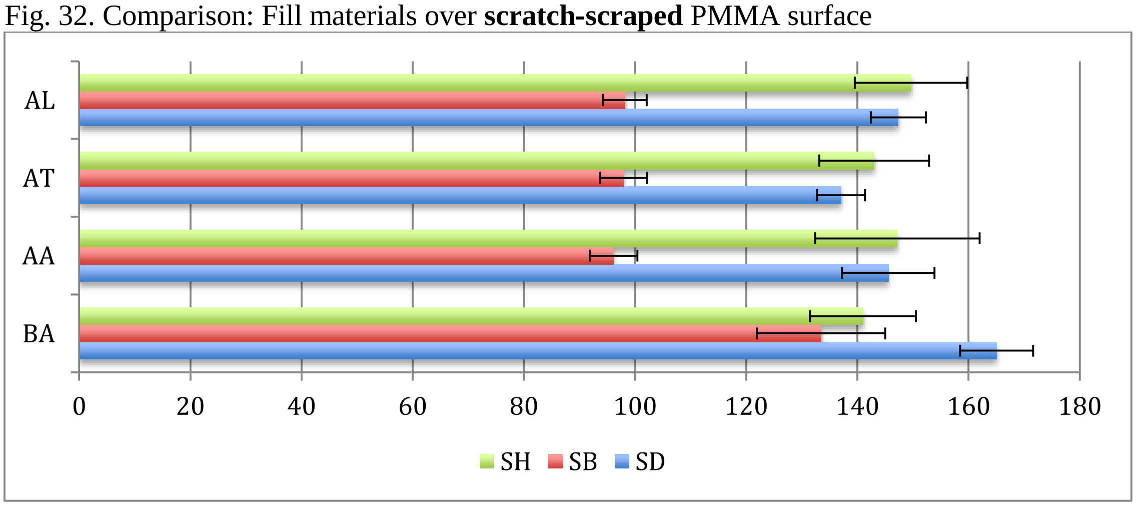


Fig. 32. Comparison: Fill materials over **scratch-scraped** PMMA surface



REFERENCES

Adobe. 2000. Technical Guides. Adobe Systems Incorporated. http://dba.med.sc.edu/price/irf/Adobe_tg/models/cielab.html (accessed 02/28/15)

ASTM. 2008. Standard test methods for viscosity of adhesives, D-1084. Philadelphia, American Society for Testing and Materials.

Allen, K. 1984. Fundamental aspects of adhesion. In Adhesives in Engineering and Design, ed. W.A. Lees. Berlin: Springer Verlag. 129-139.

Beauchamp, M.L. 2014. The use of cyclododecane as a temporary fixative for loose surface media on paper to allow mechanical conservation treatments. Master's thesis, Queen's University, Kingston, Ontario, Canada.

Blank, S. 1990. An introduction to plastics and rubber in collections. Studies in Conservation 35:53-63.

Breitung, E. 2007. Survey of abrasion resistant acrylics and polycarbonates for face-mounted photographs. Photographic materials group, Washington, DC: AIC. 12:114-125.

Chapman, S., and D. Mason. 2003. Literature Review: the use of Paraloid B-72 as a surface consolidant for stained glass. JAIC 42(2):381-392.

Cyro Industries. 2001. Working with Acrylite® Acrylic Sheet. Rockaway, NJ.

Down, J.L. 1984. The yellowing of epoxy resin adhesives: report on natural dark ageing. Studies in Conservation 29:63-76.

Dymax. 2002. Ultra Light-Weld® 4-20638 One-Part UV Curing Decorative Coating Product Data Sheet. Torrington, CT.

Evonik Industries. 2013. Acrylite® Technical Information: Light transmission and reflectance. Evonik Cyro LLC. Parsippany, New Jersey.

Evonik Industries. 2014. Sales Handbook: Acrylite®. 7.1 Reactive adhesives. Evonik Cyro LLC. Parsippany, New Jersey.

Fenn, J. 1993. Labeling plastic artefacts. In Saving the 20th century: the Conservation of Modern Materials, ed. D. Grattan. Ottawa: Canadian Conservation Institute. 341-350.

Flynn, J.H. and L.A. Wall, 1966. A quick direct method for the determination of activation energy from thermogravimetric data. Polymer Lett., 4: 323-331.

Fuchs, O. 1989. Solvents and non-solvents for polymers. In Polymer Handbook 3rd edition. ed. J. Brandup and E.H. Immergut. New York: John Wiley & sons, Inc. VII/379-407.

Gambill, W.R. 1959. How to estimate mixtures viscosities. Chemical Engineering. 66: 151-152.

Granowski, C., A. Wise, C. Drover, and Z. Stachurski. 2007. A preliminary investigation into acrylic glazing deterioration. Topics in Photographic Preservation. Washington, DC: AIC. 12:99-113.

Grattan, D. 1993. Degradation rates for some historic polymers and the potential of various conservation measures for minimizing oxidative degradation. In Saving the 20th century: the conservation of modern materials, ed. D. Grattan. Ottawa: Canadian Conservation Institute. 351-359.

Haddon, M.R., and T.J. Smith. 1991. The chemistry and application of UV-cured adhesives. International Journal of Adhesion and Adhesives 11(3):183-186.

Hamid, S. Halim, M. B. Amin, and A. G. Maadhah, eds. 1992. Handbook of polymer degradation. In Environmental Science and Pollution Control series Volume 2. New York: M. Dekker.

Hess Norris, Debra. 2015. Personal communication. ANAGPIC, Winterthur Museum, University of Delaware, Delaware.

Horie, C.V. 1982. Reversibility of polymer treatments. Resins in Conservation, Scottish society for conservation and restoration, Proceedings of the Symposium University of Edinburgh extra mural Department, Edinburgh, Scotland. 3-1 to 3-6.

Hxtal Adhesive, LLC. 2010. Material safety data sheet – HXTAL NYL-1 Part A and Part B. November 10.

Johnsen, J.S. 1996. Accelerated aging: changes in swelling and melting point of photographic gelatin. ICOM committee for conservation. 11th Triennial Meeting, Edinburgh. Scotland: ICOM. 2:586-590.

Jürgens, M. 2001. Silicon rubber face-mounting of photographs to poly(methyl methacrylate): process, structure, materials, and long-term dark stability. Master's thesis, Queen's University, Kingston, Ontario, Canada.

Jürgens, M. 2015. Personal communication. Photographic Materials Group Meeting (PMG), AIC. Boston, Massachusetts.

Karnes, C. and K. Jennings. 2005. Contemporary artists' perspectives on coating, lamination and face-mounting. In Coatings on photographs: materials, technique and conservation. ed. C. McCabe. Washington, DC: American institute for conservation. 347-357.

Kim, E., and E. Breitung. 2007. Scratch repair on acrylics used in face-mounting photographs: a survey of materials and techniques. Topics in Photographic Preservation. Washington, DC: AIC. 12:144-159.

Koob, S. 1986. The use of Paraloid B-72 as an adhesive: its applications for archaeological ceramics and other materials. Studies in Conservation 31: 7-14.
Pénichon, S., and M. Jürgens. 2001. Two finishing techniques for contemporary photographs. Topics in Photographic Preservation, Washington, DC: AIC. 9:85-96.

Pénichon, S., Jürgens, M., and A. Murray. 2002. Light and dark stability of laminates and face-mounted photographs: a preliminary investigation. In Works of art on paper, books, documents, and photographs: Techniques and conservation, ed. V. Daniels et al. London: The international Institute for Conservation. 154-159.

Pénichon, S., and M. Jürgens. 2005. Plastic Lamination and face-mounting of contemporary photographs. In Coatings on photographs: materials, techniques, and conservation, ed. C. McCabe. Washington. DC: American Institute for Conservation. 219-233.

Phenix, A. 1992. Solvents for Paraloid B-72. Conservation News 48:21–3.

Sale, D. 1993. An evaluation of 11 adhesives for repairing poly(methyl methacrylate) objects and sculpture. In Saving the 20th century: the conservation of modern materials, ed. D. Grattan. Ottawa: Canadian Conservation Institute. 325-339.

Sale, D. 1995. An evaluation of six adhesives for repairing poly(methyl methacrylate) objects and sculpture: changes in tensile strength and colour after accelerated ageing. In Preprints of the conference Resins Ancient and Modern in the University of Aberdeen 13-14 September 1995, ed. J.H. Townsend and M. Wright. Edinburgh: Scottish Society for Conservation and Restoration. 17-32.

Sale, D. 2011. Yellowing and appearance of conservation adhesives for poly(methyl methacrylate): A reappraisal of 20-year old samples and methods. CCI Symposium ICC, Adhesives and Consolidants for Conservation: Research and Applications, Symposium 2011. Ottawa, Canada. 17-21.

Seferis, J. C. 1989. Refractive indices of polymers. In Polymer Handbook, 3rd edition. ed. J. Brandup and E.H. Immergut. New York: John Wiley & sons, Inc. VI/451-461.

Shashoua, Y. 2008. Conservation of plastics: Materials science, degradation and preservation. Amsterdam: Elsevier/Butterworth-Heinemann.

Swanson, R. 1965. Plastics technology: basic materials and processes. Bloomington, Illinois: McKnight & McKnight Publishing Company.

Talas. Year Unknown. Hxtal NYL-1 Instructions. Brooklyn, NY.

Tennent, N.H., and J. H. Townsend. 1984. The significance of the refractive index of adhesives for glass repair. In Adhesives and Consolidants. Preprints of the contributions to the Paris Congress, 2-8 September 1984. ed. N.S. Brommelle et al. London: International Institute for Conservation. 205-212.

van Oosten, T.B. 2002. Crystals and crazes: degradation in plastics due to microclimates. In Plastics in art: history, technology, and conservation. ed. T.B. van Oosten et al. Munchen: Restaurierung und Konservierung von Kunstund Kulturgut. 80-89.

Zorn, S., and S. Dobrusskin. 2011. ‘Diasec’ and other finishing techniques, investigation of accelerated light fading. Studies in Conservation 56: 257-266.

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