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RESEARCH ARTICLE



The Next Generation of MS2A Resin: MS3

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ABSTRACT

MS2A was a reduced ketone resin and a preferred varnish for many painting conservators but ceased production in 2014. To remedy this, a new, more consistent manufacturing process has recently been developed and the next generation of resin designed with replicated chemistry is called MS3. Direct comparison between MS3 and MS2A is limited as no fresh samples of MS2A exist, so work presented here focuses primarily on the performance and characteristics of MS3 compared to literature reports of MS2A, and comparisons to older reference samples of MS2A. Refractive index, gloss, glass transition temperature, and molecular weight are presented. MS3 and comparative low molecular weight varnish resins were artificially aged and examined using FTIR and color measurements. Practical handling and performance were evaluated by varnishing two oil paintings. This study has shown that new MS3 resin demonstrates consistency with older samples of MS2A alongside improvements in keto-reduction, color, flow, and batch to batch consistency.

RÉSUMÉ

Le MS2A était une résine cétonique réduite et un vernis de prédilection pour de nombreux conservateurs-restaurateurs de peinture jusqu'à l'arrêt de sa production en 2014. Afin d'y remédier, un nouveau procédé de fabrication plus cohérent a récemment été développé ; la nouvelle génération de résines conçue avec une chimie répliquée s'appelle MS3. La comparaison directe entre la MS3 et la MS2A est limitée puisque aucun échantillon récent de la résine MS2A n'existe, de ce fait le travail présenté ici se concentre principalement sur les performances et les caractéristiques de la résine MS3 en comparaison avec la documentation écrite sur la MS2A et des échantillons plus anciens de MS2A. L'indice de réfraction, la brillance, la température de transition vitreuse et le poids moléculaire sont présentés ici. La MS3 et d'autres résines à faible poids moléculaire ont été artificiellement vieillies et par la suite examinées à l'aide de mesures IRTF et colorimétriques. La maniabilité et la performance ont été évaluées en vernissant deux peintures à l'huile. Cette étude a démontré que la nouvelle résine MS3 montre une cohérence avec les anciens échantillons de MS2A ainsi que des améliorations dans la réduction des cétones, la couleur, le débit et la cohérence d'un lot à l'autre. Traduit par Lucile Berthelot.

RESUMO

MS2A era uma resina de acetona reduzida e um verniz preferido para muitos conservadores de pintura, mas teve a produção interrompida em 2014. Para remediar isso, um novo processo de fabricação mais consistente foi desenvolvido recentemente e a próxima geração de resina projetada com química replicada, chamada MS3. A comparação direta entre MS3 e MS2A é limitada, pois não existem amostras novas de MS2A, portanto, o trabalho apresentado aqui se concentra principalmente no desempenho e nas características do MS3 em comparação com relatórios da literatura de MS2A e comparações com amostras de referência mais antigas de MS2A. Índice de refração, brilho, temperatura de transição vítrea e peso molecular são apresentados. MS3 e resinas de verniz comparativas de baixo peso molecular foram envelhecidas artificialmente e examinadas usando FTIR e medições de cor. O manuseio prático e o desempenho foram avaliados envernizando duas pinturas a óleo. Este estudo mostrou que a nova resina MS3 demonstra consistência com amostras mais antigas de MS2A, juntamente com melhorias na redução de ceto, cor, fluxo e consistência de lote para lote. Traduzido por Beatriz Haspo.

RESUMEN

MS2A era una resina con bajo contenido de cetonas y un barniz preferido por muchos conservadores de pintura, pero su producción cesó en el 2014. Para remediar esto,

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recientemente se desarrolló un nuevo proceso de fabricación más consistente y la próxima generación de resina diseñada replicando la química se llama MS3. La comparación directa entre las resinas MS3 y MS2A es limitada ya que no existen muestras frescas de MS2A, por lo que el trabajo presentado aquí se centra principalmente en el rendimiento y las características de MS3 en comparación con informes sobre MS2A en la literatura y en comparaciones con muestras de referencia antiguas de MS2A. Se presentan el índice de refracción, el brillo, la temperatura de transición vítrea y el peso molecular. Muestras de MS3 y de resinas de barniz de bajo peso molecular comparativas se envejecieron artificialmente y se examinaron usando mediciones de color y de espectroscopía infrarroja por transformada de Fourier (FTIR). El manejo práctico y el rendimiento se evaluaron mediante el barnizado de dos pinturas al óleo. Este estudio ha demostrado que la nueva resina MS3 es consistente con las muestras más antiguas de MS2A junto con mejoras en la reducción del grupo ceto, el color, el flujo y la consistencia de lote a lote. Traducción: Silvia Centeno.

1. Introduction

1.1. Background

MS2A poly-cyclohexanone resin was the first, and until recently the only, synthetic picture varnish developed specifically for the painting conservation profession. It first went into production in 1962 after Garry Thomson, then a research chemist at London's National Gallery, had earlier approached resin manufacturer Howards about modifying an existing ketone resin called MS2 to improve its visual, handling, and aging properties. The resulting product, created by subjecting the MS2 resin to a borohydride reduction process, proved to be enormously popular for generations of painting conservators, who found the varnish provided an ideal surface sheen to paintings with its balance of saturation and gloss that proved optimal for oil paintings. Due to the reduction step in the manufacturing process, MS2A was also more resistant to oxidative color change than unreduced ketone resins or natural resins such as dammar and mastic. Over the following decades, MS2A became periodically unavailable as resin manufacturers merged, ceased production or encountered difficulties in sourcing the suitable base materials. With the closure of Linden Nazareth Chemicals in 2014 the production of MS2A was halted for good, despite ongoing demand from the conservation profession. In response to this, the conservation department of National Gallery of Victoria and CSIRO Australia joined forces in 2016 to explore the feasibility of making MS2A available once

more. The outcome of this project is MS3, a next-generation successor to MS2A.

1.2. Chemistry

The chemistry of keto-resins has been extensively reviewed by de la Rie and Shedrinsky (1989). Later, Routledge (2000) described MS2A as complex mixture of methylation and condensation products formed from methyl cyclohexanone, methanol, and their derivatives, and has proposed it is comprised of a range of dimers and trimers, some of which are keto-reduced while others are not.

Broadly, the two mechanistic pathways that have been proposed are depicted in Figure 1. In *Path a*, the methylcyclohexanone **1** condenses with itself under basic conditions to give the dimer **2**. Subsequent repeating condensation with dimer **2**, thus giving longer oligomeric species. In *Path b*, methanol is proposed to be reduced to formaldehyde, which then participates in the polymerization to give species **3**.

In our hands, the intermediate keto-resin material was found to be unstable, which hindered full structural characterization. Thus, the keto-resin was immediately reduced to give the fully reduced keto-resin MS3.

1.3. Evaluation

It is important for conservation professionals to understand the material composition and physical properties

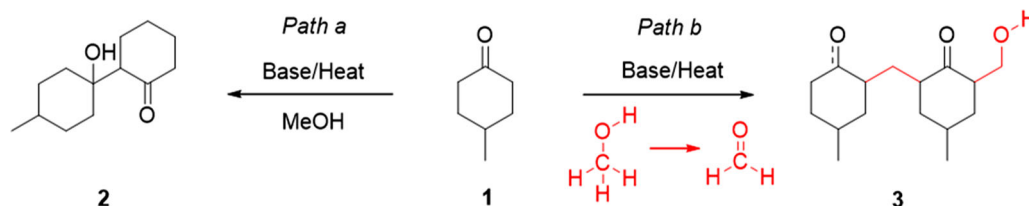


Figure 1. Proposed synthetic pathway in keto-resin chemistry.

of the materials used in conservation treatments. This paper describes some of the fundamental properties of MS3 resin and additionally compares it with properties of MS2A that have been reported in the literature, and against reference samples of MS2A manufactured by Linden Chemicals using the original method.

Foundational work was performed by Maines and de la Rie (2005) on the aging of low molecular weight resins used as varnishes for paintings and focussed on two critical parameters for evaluation: molecular weight distributions and glass transition temperatures. Properties measured in this work include refractive index (RI), gloss, glass transition temperature (measured by DSC), and molecular weight (measured by GPC). The properties of chemical structure (measured by FTIR), color change, solubility/reversibility, and practical workability/handling/performance were measured before and after accelerated aging.

A summary of evaluation is as follows:

- (1) Physical properties
 - (a) Refractive index (RI)
 - (b) Gloss
 - (c) Glass transition temperature (DSC)
 - (d) Molecular weight (GPC)
- (2) Chemical structure (FTIR) before and after accelerated aging
- (3) Color before and after accelerated aging
- (4) Solubility and reversibility before and after accelerated aging
- (5) Practical handling, visual observations, and performance

2. Experimental

2.1. Resin samples

Three different reference samples of MS2A resin, each from different time periods, were provided by the National Gallery of Victoria Conservation Department:

MS2A-NGV-01: Linden Nazareth MS2A dated from December 2001 (NGV Conservation department supplies and records)

MS2A-NGV-06: Linden Nazareth MS2A purchased in November 2006 (NGV Conservation department supplies and records)

MS2A-NGV-11: Linden Nazareth MS2A dated January 2011 (NGV Conservation department supplies and records)

Three different reference samples of MS3 resin were provided by CSIRO and Boron Molecular:

MS3-CSIRO-16: Samples of MS3 resin were obtained from CSIRO (2016), at the end of the lab scale development period.

MS3-BM-18: Samples of MS3 resin were obtained from Boron Molecular (2018), chemical manufacturer, Melbourne, Australia, produced using their standardized proprietary production method.

MS3-BM-19: Samples of MS3 resin were obtained from Boron Molecular (2019), chemical manufacturer, Melbourne, Australia, produced using their standardized proprietary production method.

Resin samples were evaluated either directly in bulk form or solubilized and dried. To prepare solubilized resin for aging and handling evaluation, samples were prepared by grinding into powder form and made up to a 25% w/v solution with odorless mineral spirits with an additional 5 ml of acetone, using a magnetic stirrer.

2.2. Accelerated aging

MS3 was compared with a group of low molecular weight (LMW) synthetic and natural resins before and after being artificially aged: (Note: B-72 and A-81 are not categorized as LMW)

- MS3 (MS3-BM-19)
- MS2A (MS2A-NGV-11)
- Laropal K-80 (BASF, undated)
- Dammar (Dipterocarpaceae, Indonesia, supplied by Langridge Artist Materials, Australia)
- Paraloid B-72 (Rohm and Haas, undated)
- Laropal A-81 (BASF, supplied by Talas, c.2015)
- Regalrez 1094 (Eastman, supplied by Talas c.2015)

Each of the above resins were painted in a thin stripe onto two playing card-sized substrates: pre-primed artist board and glass. Samples were artificially aged using ASTM G154-2006 Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Non-metallic Materials, Cycle Conditions 8 hrs UV at 45°C, Lamp Type UVA 340, Irradiance 0.89 W/m²/nm, Black Panel Temperature 45 °C, with exposure times of 0, 168, 336, 672 and 1344 h.

Detailed methodologies for instrumental analyses are provided in the Appendix.

3. Results and discussion

Low molecular weight (LMW) varnish resins are reported to have relatively high glass transition temperatures, have relatively high refractive indices, and appear glossier than longer chain polymers (de la Rie et al. 2010, Whitten et al. 1997).

Table 1. Glass transition temperature of MS2A and MS3.

Sample	T_g (Av) (°C)	Date of manufacture	Literature reference
MS3-BM-18	52 ± 1	2018	Sourced from Boron Molecular
MS2A	49 ± 2	2002	Maines and de la Rie (2005)
MS2A	57	unknown	de la Rie and Shedrinsky (1989)

3.1. Glass transition temperature

Maines and de la Rie (2005) reported the glass transition temperature (T_g) of MS2A to be 49°C while another sample was reported by de la Rie and Shedrinsky (1989) to be 57°C. Differences are perhaps attributable to variability in batch composition of MS2A, or perhaps analysis procedures between measuring laboratories. The glass transition temperature of MS3 was found to be 52°C, between the two reported values for samples of MS2A, as shown in Table 1.

A detailed study on the kinetics of thermal decomposition of ketonic resins prepared from cyclohexanone and cyclopentanone was published by Uttaravalli and Dinda (2017) and showed that the apparent activation energy of the resins studied increased, corresponding with an increase of resin average molecular weight. This observation may be useful to explore further at a later stage whereby glass transition temperature may be an indicator of molecular degradation.

Table 2. Gloss measurements of MS3.

Angle (Degrees)	Gloss units (GU)
20	79.3
60	93.3
80	97.0

3.2. Gloss

Gloss measurements indicate the amount of light reflected on the surface relative to a reference standard, measured in gloss units (GU). The amount of light that is reflected on the surface is dependent on the angle of incidence and the properties of the surface.

As shown in Table 2, MS3 demonstrates high gloss values as expected for a low molecular weight resin.

The appearance of MS2A has been described as satin or silky, being less glossy than dammar or Laropal A81, and much less glossy compared to Regalrez (Stoner and Rushfield 2012). It should be noted that lower molecular weight resins result in higher specular reflectance compared to high molecular weight resins. Low molecular weight resins, with weight-average molecular weights in the range 800–6500, including natural resins, produce smoother surfaces by flowing into and leveling the substrate, thereby eliminating both high-frequency and low-frequency roughness (de la Rie and Shedrinsky 1989).

3.3. Refractive index

While it is often reported as a physical parameter of resins, the refractive index (RI) of varnish has been shown to have little impact on the appearance of a varnished painting. The ability of a resin coating to level out or replicate surface roughness is dependent on its molecular weight, and molecular weight is the more dominant parameter in determining the appearance of an oil painting (Berns and de la Rie 2003).

Historically, MS2A has been reported to have an RI of 1.505 (CAMEO 2016). The refractive index was measured as a dissolved sample dried, and as shown in Figure 2, was found to have a very similar value of $n_D^{20} = 1.50452$.

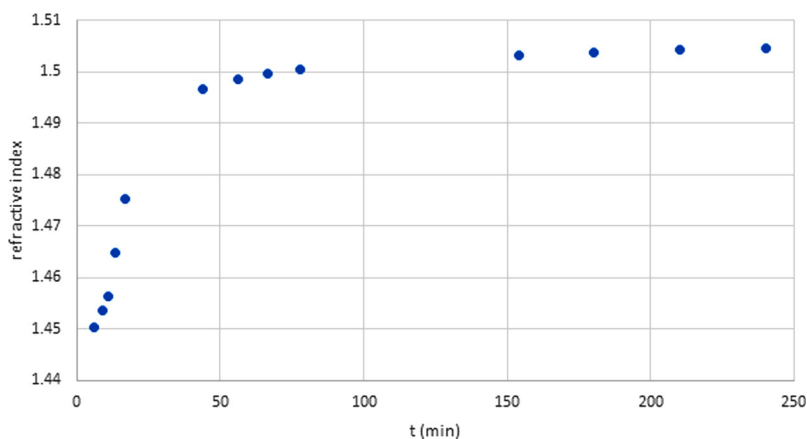
**Figure 2.** Refractive index of MS3.

Table 3. Comparative GPC Data on MS2A and MS3.

Entry	Sample	Number average (M_n)	Weight average (M_w)	Polydispersity (D)	Date of manufacture	Literature reference
1	MS3-BM-19	573 ± 19	1195 ± 31	2.08 (n = 3)	2018	Sample sourced from Boron Molecular
2	MS2A-NGV-06	528	1903	3.6	2006	Sample sourced from NGV
3	MS2A	586	1561	2.67	2002	Maines and de la Rie (2005)
4	MS2A	769	1776	2.31	Batch 15021 (un-dated)	Routledge 2000

3.4. Molecular weight

The molecular weight of a polymer is measured using gel permeation chromatography (GPC), sometimes also referred to as size exclusion chromatography (SEC). The molecular weight of MS2A and MS3 is shown in Table 3. The molecular weight of polymers and oligomers is defined as a distribution, as polymerization leads to a range of different chain lengths. Weight average molecular weight (M_w) is calculated from the weight fraction distribution of different sized molecules and number average molecular weight (M_n) is calculated from the mole fraction distribution of different sized molecules. Larger molecules weigh more than smaller molecules, so M_w is a higher value, and always greater than M_n . The ratio of (M_w/M_n) defines polymer polydispersity.

MS3-BM-19 (Entry 1) is a similar M_n to the MS2A resins (Entries 2-4), but lower M_w , which reflects a narrower range of oligomeric species and hence tighter polydispersity. MS3-BM-19 (Entry 1) represents the average of three samples (n = 3) taken at different points during the production run and indicates the consistency and reproducibility of the new production method.

3.5. FTIR

Comparison of MS3 with MS2A

MS3 was compared with two reference samples of MS2A obtained from the conservation materials store of the NGV, which were purchased from Linden Chemicals in 2001 and 2011. An overlay of FTIR spectra is shown in Figure 3. All three samples were individually searched as unknowns in the Infrared and Raman Users Group (IRUG) spectral database (Price, Pretzel, and Lomax 2009). The highest library match scores were with spectra with IRUG filenames: *ISR00005* and *ISR00006* which are both reduced poly-cyclohexanone resins, confirming sample composition and chemistry.

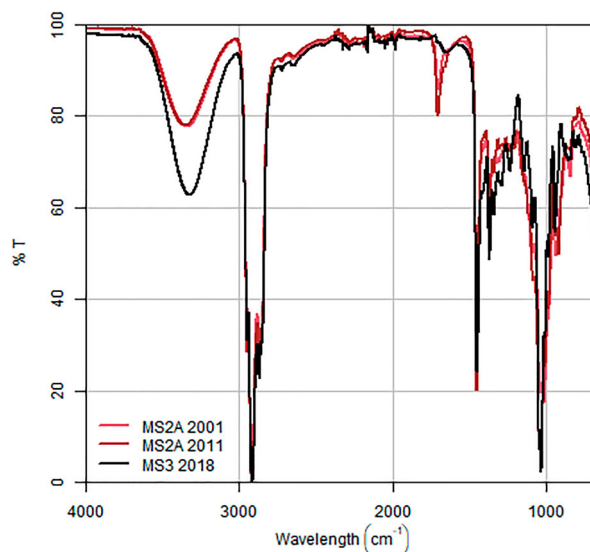
A visual comparison of the two MS2A samples found the 2001 sample to be a pale-yellow color while the more recent 2011 sample was a darker yellow. The MS3 sample was almost clear in color. Because the difference in color was not consistent with the age of the samples, it is believed that the color difference is less a

consequence of aging than a result of variability in manufacturing conditions.

The intensity of the carbonyl band at 1708 cm^{-1} in the two MS2A 2001 and MS2A 2011 samples corresponds with their greater yellow coloration, with the visually darker resin exhibiting a stronger carbonyl peak. The band is almost absent in the MS3 spectrum indicating effective reduction of the carbonyl functional group. MS3 exhibits a more intense OH band at $\sim 3500\text{ cm}^{-1}$ in comparison to both MS2A samples, in agreement with more complete chemical reduction of the carbonyl groups to OH functional groups.

The band observed at 1372 cm^{-1} is attributed to symmetric bending vibration of $-\text{CH}_3$ group and is present in both the MS2A and MS3 spectra. It is absent in IRUG and reference sample spectra of Ketone N and Laropal K80 shown in Figure 4 (Mills and White 1994).

Symmetric bending vibration of $-\text{CH}_2$ groups at 1453 cm^{-1} , attributable to alkanes, is present in all spectra. CH bands observed at 2915 cm^{-1} are identical in MS2A and MS3 with a shoulder at 2948 cm^{-1} due to $-\text{CH}_3$ stretch. Ketone N and Laropal K80 do not exhibit a shoulder due to the absence of $-\text{CH}_3$ which is consistent with both Ketone N and Laropal K80 being produced using non-methylated cyclohexanone as the precursor monomer.

**Figure 3.** FTIR Spectra of MS3 and MS2A.

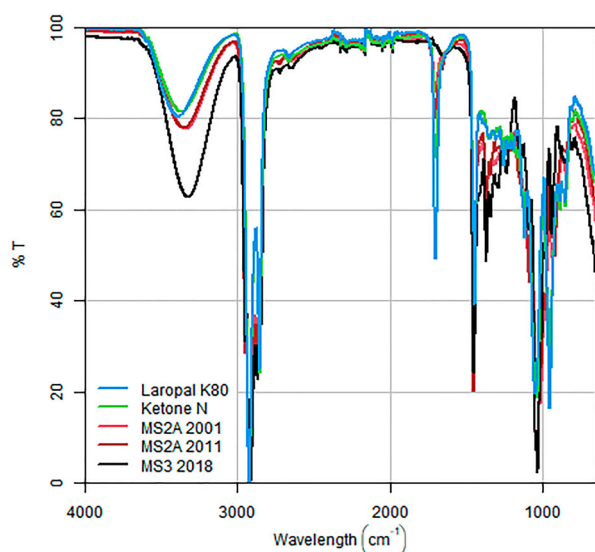


Figure 4. FTIR Spectra of MS3 and low molecular weight resins.

3.6. Aging of MS3 and MS2A

Normalized FTIR spectra collected from the MS3 samples aged for 168, 336 and 672 h shown in [Figure 5](#) demonstrate an increasing presence of the carbonyl band at 1708 cm^{-1} , where the initial unaged sample (control) has almost none, indicating oxidation of the resin due to aging. For samples aged for 1344 h, the intensity of the carbonyl stretch has reduced and shifted slightly to 1729 cm^{-1} , which could indicate additional decomposition has occurred.

FTIR spectra collected from the MS2A samples over the same time periods also show this trend, but whereas the initial MS3 sample (control) begins with no carbonyl stretch, the initial MS2A sample (control) already has a small carbonyl stretch present. This is due either to residual carbonyl functionality being present from the original manufacturing process, or some initial oxidation having already occurred because of the age of the resin. The normalized MS2A FTIR spectrum at 1344 h also has the carbonyl stretch shifted to a higher wavelength.

3.7. Color

The CIE 1976 $L^*a^*b^*$ color space (also referred to as CIELAB) is one of the most popular color spaces for measuring object colors. Of the three axes ($L^*a^*b^*$), L^* indicates lightness and a^* and b^* are chromaticity coordinates; a^* and b^* are color directions: $+a^*$ is the red axis, $-a^*$ is the green axis, $+b^*$ is the yellow axis and $-b^*$ is the blue axis.

Prior studies ([Doménech-Carbó et al. 2008](#)) indicate photo-aging contributes more to degradation than thermal effects or those of gas (SO_2) so accelerated aging was

undertaken with photo-aging with a slightly elevated temperature throughout. Each color coordinate was measured for samples at each time interval, however only b^* is reported here to illustrate comparative yellowing.

Development of yellowing (b^*) with artificial aging for MS3 and other low molecular weight resins is shown in [Figure 6](#). All b^* values are positive, indicating samples exhibit some yellow color. Dammar changed the most and earliest, followed by Laropal K80, which reached its greatest change after 672 h. These two varnishes became less yellow after reaching their peak which is assumed to be attributable to photooxidative degradation of the chemical structure, and subsequent lightening. MS2A and MS3 responded in a similar manner and both changed considerably, but more gradually,

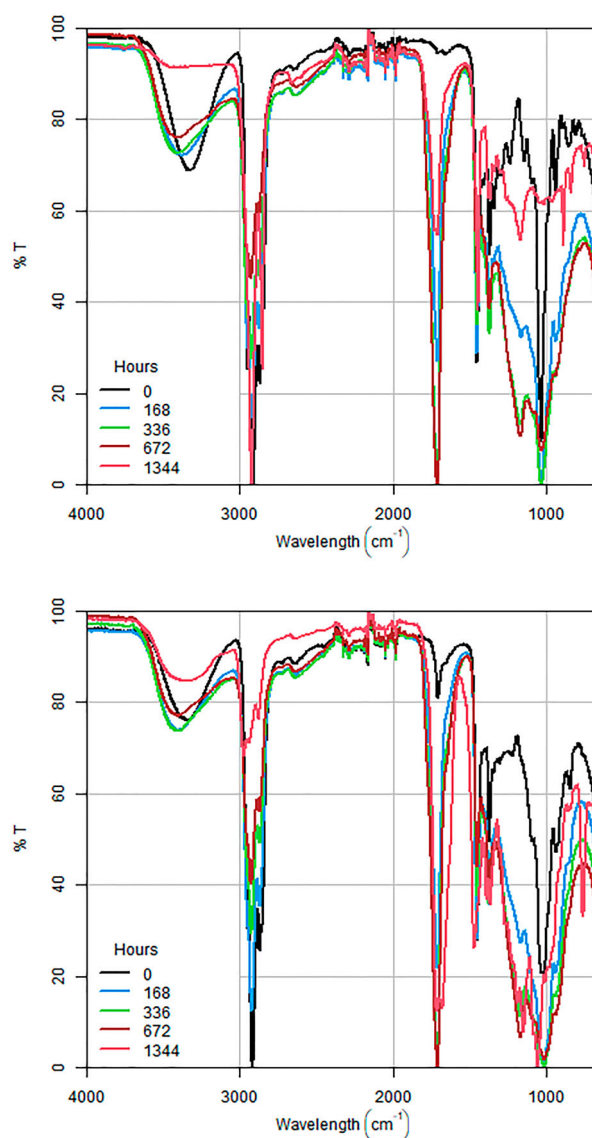


Figure 5. FTIR Spectra of aged MS3 (above) and MS2A (below).

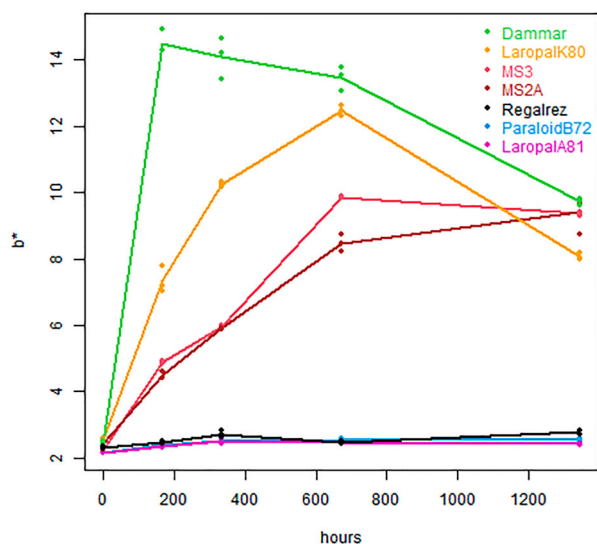


Figure 6. Development of yellowing (b^*) with artificial aging for MS3 and other low molecular weight resins.

and plateaued at similar colors to Dammar and Laropal K80 by the end of the exposure period.

Regalrez, Paraloid B-72, and Laropal A-81 became only slightly yellowed over the entire eight weeks. The changes in Regalrez, Paraloid B-72, and Laropal A-81 were not noticeable to the human eye, but the others became noticeably yellower. MS3 and MS2A were indistinguishable from each other but yellowed less rapidly compared to Dammar and Laropal K-80.

In practice, MS2A varnishes have been examined almost 40 years after the first application, and in the absence of Tinuvin 292, have remained unchanged to the naked eye in terms of gloss and clarity with no evidence of discoloration in removed varnish (Routledge 2000).

3.8. Solubility and reversibility

The practical evaluation of polymer solubility after ageing is critical (Smith and Johnson 2008). Solubility testing showed that MS3 and MS2A have very similar solubility characteristics under conditions of artificial aging. The solvent composition needed to solubilize aged resin

films is shown in Table 4. Both resins shared the same starting solubilities, but as the light exposure increased MS2A required slightly higher concentrations of the more polar solvent (acetone). The final reading after 1344 h of exposure showed that both resins required a 65% proportion of acetone to achieve solubility. Laropal K-80 displayed a relatively rapid transition to solubility only in 100% acetone, demonstrating that it was even less effective than Dammar in resisting light-induced degradation. It also revealed the effectiveness of the carbonyl reduction process in significantly improving the aging properties of a poly-cyclohexanone resin.

As expected, Regalrez 1094, Paraloid B-72, and Laropal A-81 all showed greater resistance to photo-oxidative degradation by remaining soluble in the lower-polarity solvents after 1344 h of exposure. This demonstrates that ketone resins, regardless of the degree of reduction, are more prone to degradation than those formed with hydrogenated hydrocarbon, methacrylate, or aldehyde oligomers. However, it has been demonstrated that hindered amine light stabilizers (HALS) can improve the light stability performance of resins, compensating for this relative shortcoming. Future testing of the performance of MS3 with the addition of a HALS is an area for future research.

4. Practical handling, visual observations and performance

MS3 (MS3-CSIRO-16) was tested for its physical and handling properties in comparison with two archived samples of MS2A (MS2A-NGV-01 and MS2A-NGV-06). Specifically, the tests assessed the resins according to their appearance in crystalline form; their dispersal into solution; and their viscosity, handling properties and surface appearance. An additional sample, labeled X in Figure 7, of Linden Nazareth MS2A dates from January 2011 and is presented for visual comparison but was not used for this test due to insufficient quantities.

Observations in solid form: The Linden resins were distinctly yellower in color, with some large (20 mm+) crystals and fractures the predominant shape of the

Table 4. Solvent compositions needed for resin reversibility.

Resin Sample	Exposure (hours)				
	0	168	336	672	1344
MS3	80C: 20T	90 T: 10A	80 T: 20A	65T: 35A	35 T: 65A
MS2A	80C: 20T	85 T: 15A	80 T: 20A	60 T: 40A	35 T: 65A
Laropal K-80	100C	70 T: 30A	100A	100A	100A
Dammar	50C: 50T	70 T: 30A	60 T: 40A	50 T: 50A	100A
Paraloid B-72	60C: 40T	60C: 40T	50C: 50T	60C: 40T	100T
Laropal A-81	80C: 20T	60C: 40T	100T	100T	90 T: 10A
Regalrez 1094	100C	100C	100C	100C	80C: 20T

Note: Soluble in (%) C = cyclohexane, T = toluene, A = acetone.

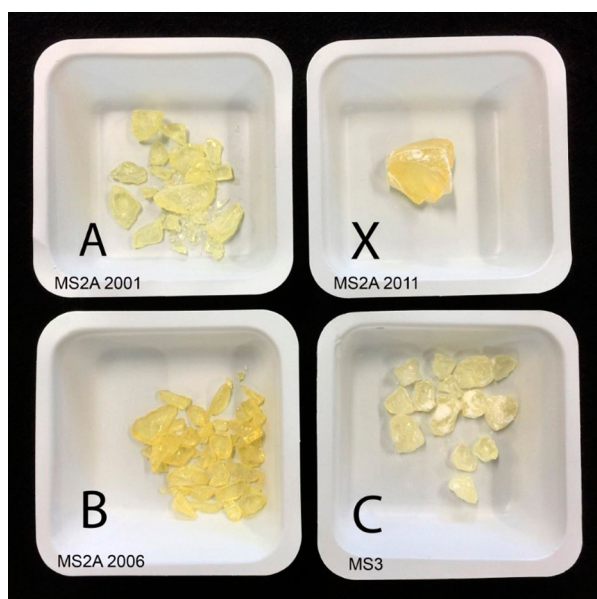


Figure 7. Photograph of 3 solid form MS2A resins and MS3.

crystals. Significantly, each of the 3 Linden MS2A resins differed in color from the others, with the 2006 batch the most discolored. This relatively light color of the 2001 batch suggests that the discoloration was caused by variability in production rather than aging. The CSIRO resin was largely ground into powder, though the larger crystals were pebble-like and less than 10 mm in length.

Dispersal into solution: Each resin was ground into powder form and put into 25% w/v solution with odorless mineral spirits with an additional 5 ml of acetone, using a magnetic stirrer. All three went into solution readily and were completely solubilized within 30 min. Shown in [Figure 8](#), the same color difference that was noted with the resins in solid form was also evident when put into solution, with both MS2A resins notably yellower than MS3.

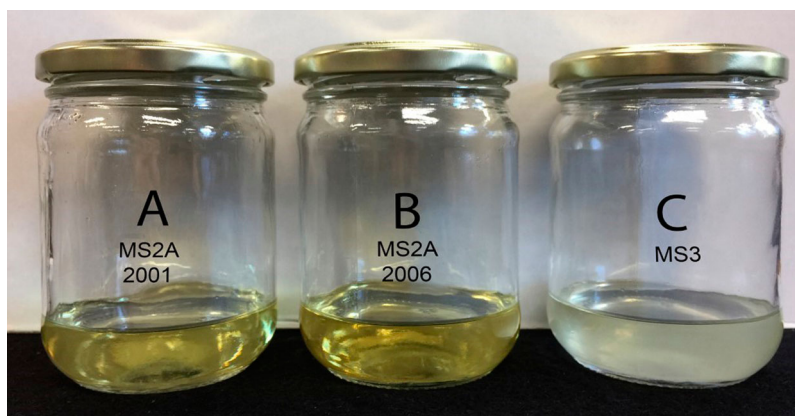


Figure 8. Photograph of the test MS2A resins in solution, with MS3 at right.

Two nineteenth-century paintings from the National Gallery of Victoria collection were chosen for the test: *Dreadnought* by Frederic Sheldon (oil on canvas, 1890), and *Naworth Castle, Cumberland* by a British painter in the manner of John Constable (oil on oak panel, before 1900). Both paintings were cleaned prior to the test, with their old and highly discolored varnishes removed using solvent mixtures of acetone in mineral spirits. Each painting was divided into three equal vertical bands by means of fine white threads so that each varnish could be tested and viewed alongside the others ([Figure 9](#)).

4.1. Application

Before each application, the varnish brush was rinsed in a solution of acetone in mineral spirits, wiped dry and then saturated in the varnish solution. The varnish was then applied to each painting in its vertical band. The brush was then rinsed and dried again ahead of the next application with the second varnish, and so on with the third. There was little or no difference apparent in the brushing application process, with each varnish appearing to have a similar viscosity and brushing/feathering characteristics.

4.2. Drying

MS3 appeared to dry slightly more quickly than either of the MS2A samples. Once dried, there was no apparent surface difference between the three varnishes on the canvas, though on the panel MS3 appeared marginally less glossy and the 2006 Linden varnish the glossiest. Conservators working in the NGV painting conservation studio were asked to examine the paintings without

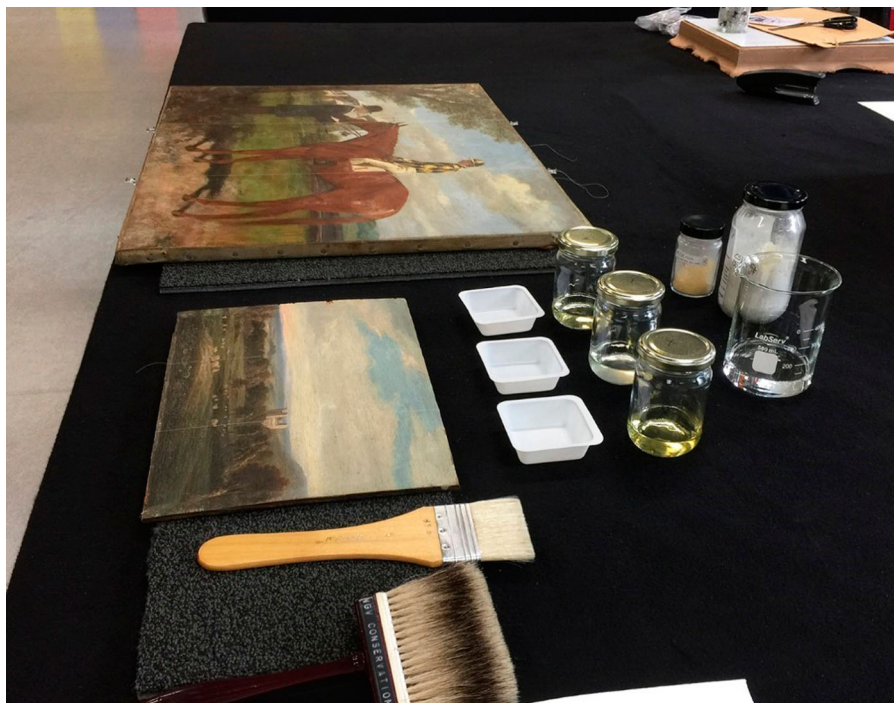


Figure 9. The two paintings prior to application of the three varnishes.

knowing which varnishes they were looking at. They were unable to make any distinction between the three varnishes. A second brush coat was applied 24 h later. Again, the three varnishes were indistinguishable from another.

4.3. Brittleness

One of the distinguishing features of MS2A and dammar resin is its characteristic brittleness, which is often used to advantage when modifying the surface effect of the painting by rubbing back the smooth, newly applied surface by hand with powder made from crushed dry resin. This technique is not possible with longer chain polymer resins such as Paraloid B-72 or Laropal A-81.

The three varnished sections were rubbed back with their respective solid resins. There was no discernible difference in brittleness between the three, and no discernible difference in the surface of the painting after the rubbing.

4.4. Spray varnishing

The final part of the testing process was to finish the varnish process by observing how each varnish performed when sprayed. Each section was sprayed with a Binks Bullows L920 compressed air spray gun, with the gun cleared with acetone/methylated spirits before each varnish was introduced. Of the three, the 2001 Linden resin

appeared to leave a marginally glossier surface than MS3 or Linden 2006 resins, both of which needed extra spraying to bring them up to the same level of gloss. This may have been the result of other variable factors. With the final appearance, there was little if any difference in characteristics between MS3 and the two MS2A resins.

4.5. Retouching

A key advantage of MS2A which also sets it apart from almost all other varnish resins is its usefulness as a retouching medium because it does not require strongly odorous solvents for retouching. Most other retouching media require diluents containing aromatic solvents such as xylene or solvents such as polyglycol monoether, which gives off unpleasant vapors. Others such as ethanol have evaporation rates which are less suitable for inpainting purposes. By contrast, MS2A can be repeatedly solubilized in odorless mineral spirits with a small quantity of added acetone.

Retouching tests were carried out at the NGV over a period of months, using both Linden and MS3 with no difference in handling qualities noted.

5. Conclusion

This study reports physical properties, performance, and handling of newly developed MS3 resin, with a

focus on comparison with MS2A for which production has ceased. Refractive index, gloss, glass transition temperature, and molecular weight were presented and compared with samples of MS2A or reported measurements. Changes in chemical composition, color, solubility, and reversibility of MS3 and MS2A, both aged and unaged, indicate the newly developed resin is extremely similar in chemistry to its predecessor.

The study of performance and handling characteristics found that MS3 performed in a similar if not identical way to samples of MS2A in terms of visual and handling properties, specifically in relation to solubility, surface appearance, viscosity, brittleness, and spraying capability.

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Disclosure statement

Boron Molecular is the manufacturer and vendor of MS3.

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Appendix. Instrumental methods

Refractive index (RI): Resin (20 mg) was dissolved in dichloromethane (300 μ l) and applied to the cell of a Mettler-Toledo RM50 refractometer. The solvent was evaporated by means of hot air from a heat gun, leaving a sticky gum. Refractive index was measured until a steady value was observed over 4 h, during which time the resin had hardened.

Gloss: Gloss was evaluated according to Australian Standard 1580.600 Cured coatings – Determination of visual properties. The sample was coated onto black and white Lenata Card and dried to a thickness of 150 microns. Specular reflectance was measured at 3 angles.

Glass transition temperature (DSC): Samples were analyzed using a Mettler Toledo Differential Scanning Calorimetry (DSC) DSC-3 connected to a Huber TC100 intra-cooler. Samples were prepared in sealed Aluminum (pierced) 40 μ l crucibles, with sample mass 6–9 mg. Samples heated from -20 $^{\circ}$ C to 150 $^{\circ}$ C at 10 K per minute under inert N_2 atmosphere (gas flow rate 50 mL/min) and repeated through 3 heat/cool cycles. Data were analyzed by Mettler Toledo Star-e, version 15.00 software. Glass transition temperature (T_g) was determined from the third melt of the DSC report and average from three production runs.

Molecular weight (GPC): Gel permeation chromatography (GPC) was performed on a Waters Alliance system equipped with an Alliance 2695 Separations Module (integrated quaternary solvent delivery, solvent degasser and autosampler system), a Waters column heater module, a Waters 2414 RDI refractive index detector, a Waters PDA 2996 photodiode array detector (210–400 nm at 1.2 nm) and 4 \times Agilent PL-Gel columns (3 \times PL-Gel Mixed C (5 μ m) and 1 \times PL-Gel Mixed E (3 μ m) columns), each 300 mm \times 7.8 mm², providing an effective molar mass range of 200– 2×10^6 . Tetrahydrofuran (THF) high purity solvent (HPLC grade) was pre-filtered through aluminum oxide (90 active neutral, 70–230 mesh) with 0.45

μ m filter, and 0.1 L-1 2,6-di-tert-butyl-4-methylphenol (BHT) was added as an inhibitor. The filtered THF containing BHT was purged slowly with nitrogen gas and used as an eluent with a flow rate of 1 mL/min at 30 BOC. Number (M_n) and weight average (M_w) molar masses were evaluated using Waters Empower-3 software. The GPC columns were calibrated with low dispersity polystyrene (PSt) standards (Polymer Laboratories) ranging from 580 to 7,500,000 g mol⁻¹, and molar masses are reported as PSt equivalents. A 3rd-order polynomial was used to fit the log Mp vs. time calibration curve, which was near linear across the molar mass ranges.

Chemical structure (FTIR): Samples were measured using a Perkin Elmer Spectrum 400 FTIR spectrometer with an ATR sampling accessory. Small samples were crushed to a fine powder and placed directly onto the Universal ATR sampling crystal (DATR 1 bounce Diamond/ZnSe) and measured across the range 4000–650 cm⁻¹ with number of co-added scans 8, resolution 4 cm⁻¹. Data were processed with Perkin Elmer Spectrum 10 software, version 10.6.1 and normalized to the most intense peak (2915 cm⁻¹). No smoothing or baseline corrections were applied.

Color: Samples of resin were painted on artists' board and color was measured using a Konica Minolta CM-700d spectrophotometer with a measurement aperture having a diameter of 10 mm. Each recorded measurement consisted of an average of seven color measurements ($L^*a^*b^*$). Each resin was measured at 3 separate points in the stripe. Identical measurements were made on unaged and artificially aged samples.

Solubility and reversibility: The solubility testing methods used for this project were based on those first proposed by Feller and Baillie (1972, 72). They advocated the use of three solvents (cyclohexane, toluene and acetone) used in mixtures, representing a gradual increase in polarity to determine the point of solubility of a low molecular weight resin. The experiment method for solubility tests using swabs was based on de la Rie's method (1988, 67–68).

Glass plates were purchased and cut to the dimensions specified by the Australian Wool Testing Authority Ltd: 6 Slides 7 \times 11 cm, 2.5 mm thick. The plates were washed, rinsed and dried prior to the application of the resins. The resins were put into solution and applied by brush in regular stripes on the plates.

Solubility testing was performed using small cotton swabs, rolling the solvent or mixture over a surface approximately one square centimeter, using only a small amount of pressure. If, after 4 or 5 rolls of the swabs the surface was judged not to have changed after evaporation of the solvent, the film was deemed insoluble in that solvent or mixture. Determination of solubility however was not unambiguous, particularly with the more exposed samples where the surfaces typically blanched and became matte before they became completely solubilized in a more polar solvent.

Solvent mixtures were made up to 1 mL in a 10 mL measuring cylinder with Pasteur pipettes. The solutions were shaken and mixed before the swabs were dipped into them.