

THE DEVELOPMENT OF MS2A REDUCED KETONE RESIN AND ITS APPLICATION IN PAINTINGS CONSERVATION

HISTORICAL DEVELOPMENT ⁽¹⁾

Ketone Resins based on condensation reactions involving methylcyclohexanone and/or cyclohexanone were first patented in the 1920's ⁽²⁾ and were produced commercially as AW2 (BASF, Germany) and MS2 (Howards, UK) from the 1930's.

By the late 1930's several hundred tonnes per annum of these resins were sold into the textiles and coatings industries. They were used particularly in a range of speciality paints and varnishes as light-fast additives that improved gloss and hardness.

The resins have a high solubility in low polarity solvents (hydrocarbons) coupled with a high refractive index. This enabled the formulation of high solids, low viscosity varnishes that were fairly easy to apply by brush or spray and provided attractive optical properties in terms of gloss/saturation. As a consequence of these properties, during the 1950's, ketone resins were evaluated as a more stable alternative to dammar in conservation varnishes for Works of Art. Whilst fast drying rate was an advantage, in many cases (though not all) the varnish films were found to break down even under museum conditions. A major problem associated with these ketone resins is the tendency of the ketone groups and double bonds to degrade in light, resulting in yellowing and a loss of solubility over time.

In 1959 Howards, with the support of Garry Thomson, Scientific Advisor at the London National Gallery, developed a reduced form of MS2 in which the double bonds and ketone groups were chemically removed by reduction with borohydride. The reduced product, designated MS2A, was evaluated extensively as a conservation varnish and was enthusiastically accepted. Handling characteristics and stability were superior to MS2 and to the natural resin varnishes, and the optical appearance of the applied varnish was described as being beautifully soft and silky. From 1962 Howards produced MS2A specifically for the conservation of Works of Art.

As general demand for the unmodified ketone resin MS2 increased, the plant process was changed to permit an increased production rate. The new MS2 product was no longer suitable for reduction to MS2A. In 1963 the BASF AW2 product was examined as an alternative source of ketone resin for reduction, and was found to be entirely acceptable. Because of its different chemical composition (being produced from a mixture of cyclohexanone and methyl cyclohexanone, as opposed to MS2, which was produced from methyl cyclohexanone only) the reduced AW2 was subtly different to MS2A in terms of its properties and appearance, and was designated MS2B. MS2B was produced for painting conservation until 1967. In 1967 BASF ceased production of their AW2 resin, and replaced it with a new resin derived solely from cyclohexanone, and designated as Ketone N. The reduction product of Ketone N was useless as a conservation varnish. (BASF later replaced their batch process for Ketone N by a continuous process, and this 'equivalent' resin was designated as Laropal K80).

In view of the continuing demand for MS2A/B in painting conservation, Howards agreed, in 1967, to install a small dedicated unit which used the traditional process and components to provide limited quantities of MS2A specifically for Art Conservation. When Howards was taken over by Laporte it was decided that MS2A production was not viable, and would be phased out. However, persuasion from a number of important sources safeguarded its continuation, albeit on a non-profit basis. The Howards/Laporte site was closed down in 1973 and a quantity of MS2A was stockpiled to satisfy ongoing demand. The material was not promoted, and it was expected that demand would subside. By 1983, when MS2A stocks were exhausted, demand for the product remained, and Laporte resumed limited production from dedicated equipment at its Widnes, UK, pilot plant facility. Again, the MS2A was not promoted, but was produced on an 'on-demand' basis and sold at its production cost. In 1984 the price of MS2A was £225 GBP/Kg, and by 1992 this had risen to £375 GBP/Kg. In 1993 the Widnes pilot plant facility was closed down and the know-how and production equipment were transferred to Linden Chemicals, a company

founded by two ex-employees of Laporte. Linden Chemicals promoted MS2A, and the increased demand, leading to increased scale of production, has enabled further price rises to be minimised.

MS2A COMPOSITION AND PROPERTIES

MS2A is the chemical reduction product of a complex mixture of methylation and condensation products formed from reactions involving methyl cyclohexanone, methanol and their derivatives. 'Typical' MS2A resin has a weight average molecular weight of 1800 and a number average molecular weight of 800, and contains approximately 8 ring units per molecule. Low boiling, lower molecular weight impurities are removed during processing by steam and vacuum distillation, whilst ketone groups and double bonds are removed by chemical reduction. The purified product has the following 'typical' properties:

Softening Temperature	: >85°C (Ring and Ball Method)				
OH Value	: >190 mg KOH/g (Acetic Anhydride Determination)				
Ketone Content	: <0.4 groups/100 gms (Hydroxylamine Hydrochloride)				
Acid Value	: Practically Zero				
Colour	: <0.2 red, <1.0 yellow Lovibond units (50% soln, 4 cm cell)				
Density	: 1.08				
Refractive Index	: 1.505				
Molecular Weight	: MS2A ⁽³⁾	c.f.	Mastic ⁽⁴⁾	c.f..	Dammar ⁽⁴⁾
	Mw	1776	1929		1361
	Mn	769	460		488
	Polydispersity	2.3	4.2		2.8

MS2A is produced as pale yellow granules having a high solubility (>50% w/w) in mineral spirit (White Spirit). The high solids, low viscosity varnish, which appears colourless once applied as a thin film, rapidly reaches gel (no flow) point. As a chemically reduced resin, the main colour forming bodies have, in effect, been removed. Accelerated ageing trials have shown that MS2A can be additionally stabilised by the use of HALS stabilisers (Tinuvin 292™, Ciba Geigy) ⁽⁵⁾. Even under abnormal ageing conditions and in cases where oxidative crosslinking is favoured, the low molecular weight resin is unlikely to become insoluble ⁽⁶⁾. It has been reported that unstabilised MS2A varnishes applied to Works of Art almost 40 years ago have shown no signs of ageing, and remain fully soluble in White Spirit ⁽⁷⁾.

Synthetic microcrystalline wax (Cosmolloid 80H) has been incorporated into MS2A varnishes to enable gloss to be modified across the extremes, from high gloss to an almost unvarnished appearance. The addition of wax also provides a plasticising effect to MS2A varnishes, which have a brittle nature attributable to hydrogen bonding between the many hydroxyl groups present in the product. These aspects of MS2A varnishes are described more fully in the following section.

PREPARATION, APPLICATION AND PROPERTIES OF MS2A VARNISHES

MS2A varnish recipes are commonly based on compositions devised by Mr Herbert Lank, reported in published articles and in personal communications ^(7,8). Sarah L. Fisher (National Gallery of Art, Washington, USA), has provided a comprehensive review of MS2A varnish formulations in the Paintings Conservation Catalog ⁽⁹⁾. A frequently used varnish formulation is as follows: ⁽¹⁰⁾

(A) Basic varnish for brushing or spraying:

50 g MS2A Resin broken down to small granules and suspended in a muslin bag is dissolved in 110 mls Stoddards Solvent (White Spirit to BS 245 having <20% aromatics content). The resin dissolves overnight, or more quickly with frequent stirring and a little heating.

This varnish may be used from a spray gun as prepared, or diluted with White Spirit or odourless kerosene (4 parts to 1 part diluent) to provide a more slowly drying varnish solution suitable for use as a brushed isolating layer.

(B) Basic matt varnish solution:

7 g Cosmolloid 80H microcrystalline wax is dissolved, with the aid of heating, in 150 mls White Spirit, followed by the addition of 18 mls basic varnish solution (A). The wax reduces brittleness in the dried varnish and enables the gloss to be varied. (Note that whilst bleached beeswax has also been used as a plasticiser/matting agent in MS2A varnishes, it is not recommended due to its tendency to degrade and colour with age).

(C) Diluted matt varnish as a finishing layer.

3 parts basic solution (A) are mixed with 1 part basic matt varnish (B). This formulation diminishes the brittleness of the applied varnish without affecting the gloss. By increasing the proportion of (B) to (A) the matt effect is introduced and heightened. This is further controlled by adjusting the spray aperture and distance from the painting, and can be modified again to increase gloss by gently polishing the dried varnish with a soft cloth.

Open/working time

MS2A may be easily worked with a brush following application. Dried varnish may be reworked with additional varnish application by brush to build up uneven areas. The silky soft optical appearance is optimum in the thinnest coats.

Cleaning

Dust which may accumulate as a surface film, often over a number of years and particularly on paintings frequently transported for exhibitions, is easily removed by gently washing with distilled water, followed by gentle polishing with a soft cloth. Varnishes most affected by dust accumulation have been reported to be those containing the higher levels of wax.

Ageing

Accelerated ageing trials have shown that oxidation/cross-linking can occur to induce slight yellowing and reduced solubility in White Spirit⁽¹¹⁾. Such effects should occur much more slowly than in the case of natural or ketone resins, and should be further limited by the addition of 2% Tinuvin 292™ (a Ciba Geigy HALS). Particularly conservators in the USA commonly use Tinuvin 292 stabilisation.

In practice MS2A varnishes examined to date, and applied up to 40 years ago without the addition of Tinuvin light stabilisers, have remained unchanged to the naked eye in terms of gloss and clarity, and have remained soluble in White Spirit with no evidence of discolouration in the removed varnish.

References:

- (1) Information taken from the archives of Howards of Ilford and Laporte Industries Ltd
- (2) I G Farbenindustrie (1929). See A.W.Hill, *Modern Plastics*, **25(12)** 119 (1947).
- (3) MS2A Batch 15021, GPC determination carried out by R.A.Evans (Solvay, Interox), against polystyrene standards using a MAXIMA(c) 820 GPC Analysis report.
- (4) 'Typical' data as reported by E.R.de la Rie in *Studies in Conservation* **32** 1-13 (1987)
- (5) E. R. de la Rie, C. W. McGlinchey in 'Cleaning, Retouching and Coatings' eds J. S. Mills and P. Smith, *Int. Inst. For Cons. Of Historic Works*, London 1990, P 168
- (6) E .R. de la Rie, 'Stability and Function of Coatings used in Conservation', from 'polymers in Conservation', eds. N. S. Allen, M. Edge, C. V. Horie, RSC Publication, 1992, P 75
- (7) H.Lank, Personal communications to Linden Chemicals and to S.L.Fisher (see(9)), and H.Lank, *Chemistry and Industry*, July 1992, P484-487.
- (8) H.Lank, Information presented in the 1972 Lisbon Conference, published 1976 (See (9))
- (9) S.L.Fisher, from 'Paintings Conservation Catalog' P81-91 *Nat. Gall. Of Art* 1997
- (10) Based on information supplied by M.Twist, C.Booth-Jones, M.Roberts, R.Woudhuysen-Keller.
- (11) E.R. de la Rie, A.M.Shadrinsky, *Studies in Conservation*, **34**, 9-19,(1989)