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NEW SOLVENT-TYPE VARNISHES

Vinylacetate and butylmethacrylate polymers have been used in conservation for about twenty-five years. These and other synthetic resins are perhaps still not well known and may be considered to be 'new' in the sense that many conservators have had little experience with them. The types of synthetic thermoplastic resins of special interest to conservators are limited and are much the same wherever in the world they are manufactured. Therefore, although these remarks will refer primarily to products sold in America, it is hoped that the examples will provide a general outline of the subject and its major problems. The pertinent material that has already appeared in the book *On Picture Varnishes and Their Solvents* will not be reviewed in detail, but will merely be referred to[1].

Picture varnish is of the solvent type, consisting simply of a volatile solvent and a non-volatile thermoplastic substance. A varnish may be 'new' with respect to either component.

Solvents

Only brief mention will be made of solvents. There is available a certain amount of new knowledge concerning 'solvent power' and the 'balance' of solvent properties which is of assistance in the selection of new solvents. The fundamental principles of solvent action have been reviewed by Stolow and applied in his detailed investigation of the action of solvents on oil paint[2].

New facts are known about the properties of petroleum. In the matter of new materials, it might be mentioned that, because of the variety of petroleum fractions available and the tendency of turpentine to oxidize, turpentine is becoming less frequently used in the conservation laboratory. The propellant-solvent methylene dichloride is now frequently encountered in the pressurized spray cans found in artists' supply stores[3].

Characterization of polymers

A statement of the chemical nature of a polymer is a key specification: polyethylene, poly(vinylchloride-acetate), polystyrene. In addition, the essential properties of any resin may be characterized by specifying at least three parameters: average molecular weight, hardness and solubility type. It is obviously of importance to specify whether a resin is soluble in a 'strong' solvent or a 'mild' one*. Hardness, although poorly defined, appears to be related to Young's modulus[4] or to the stiffness of a film. The polymers of chief interest to the conservator are those that are internally plasticized (reference 1, p. 110); that is, the films do not need the addition of plasticizers such as dibutylphthalate to give them flexibility†.

A protective coating must have reasonable toughness in order to be successful. In other words, it must possess a certain minimum strength and it must be able to stretch somewhat

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* In the case of methacrylate polymers, it has been found possible to define a precise scale of solubility grade (reference 1, p. 46).

† Plasticizers that are fluid, such as dibutylphthalate, have been avoided in picture varnishes primarily to guard against the possibility that the plasticizer might migrate into the paint and thereby soften or otherwise affect it.

without cracking (reference 1, p. 135). It is known that, up to a certain point, increasing the average molecular weight of a polymer will increase the strength of the films and give them greater ability to elongate. Therefore, the characterization of polymers through some measurement that indicates the average molecular weight is an important specification.

The viscosity of a solution of resin at 20 per cent solids concentration in toluene has been taken as a rough indication
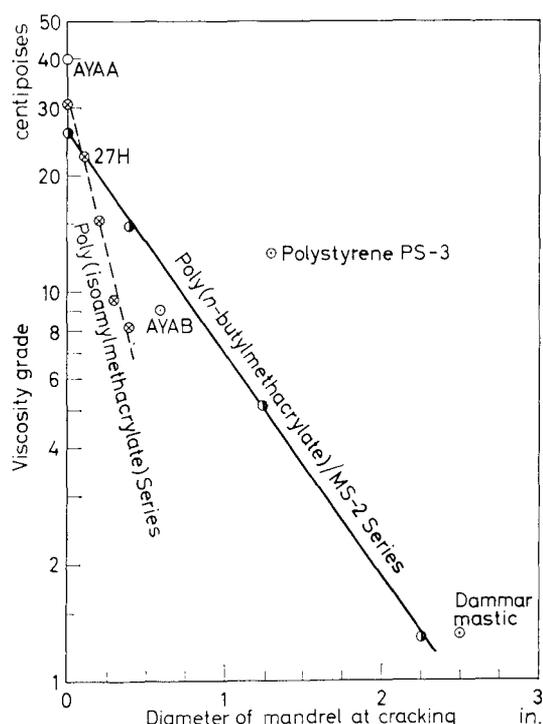

Figure 1. Brittleness of films at 70°F and 50 per cent relative humidity as a function of their viscosity grade (1·5-mil thick films on 1-mil aluminium foil).

of the average molecular weight. This measurement has been designated in our laboratory as the 'viscosity grade' of the resin (reference 1, p. 106). Data in *Table 1* show the relationship between viscosity grade and the brittleness of the baked-dry films as measured by the mandrel bending test. The data on mixtures of resin MS-2 (Howards of Ilford, Ltd) and the du Pont n-butylmethacrylate polymer 'Lucite' 44 illustrate the effect of adding the tough methacrylate polymer to the brittle MS-2.

The data in *Table 1* (with those in Table II, p. 108, of reference 1) are plotted in *Figure 1*. From consideration of this diagram, it is apparent that a resin, or mixture of resins, must have a viscosity grade of about 20 centipoises to produce films that are able to withstand a bend of 0·1 in. (2·54 mm) or less in this test. Many of the tough coatings used in commerce are

based on resins of considerably higher viscosity grade than this (reference 1, p. 111).

The selection of suitable viscosity grades for the resin in solvent-type varnishes remains open to question and discussion.

Table 1

Viscosity grade vs. cracking of baked-dry films

Test conditions: 70°F, 50 per cent relative humidity

Resin formulation in film	Viscosity grade (centipoises)	Sward hard-ness*	Diameter of mandrel at cracking (in.)
Lucite 44	48	32	<0·1
Lucite 44/MS-2 80/20	26	53	<0·1
Lucite 44/MS-2 60/40	14·8	60	0·6
Lucite 44/MS-2 20/80	5·2	77	1·3
Lucite 44/MS-2 10/90	1·3	—	2·3
Lucite 44/AW-2 10/90	1·3	—	1·6
AW-2	1·2	91	4·0
Dammar, Mastic	1·5	81	2·5

* Hardness of windowglass base equals 100.

From an analysis of the data in *Figure 1*, however, it does not seem necessary to select grades much higher than 25 centipoises for most protective coatings. In our research, we have been especially interested in types between 9 and 25 centipoises.

Synthetic polymers in solvent-type varnishes

A brief history of the introduction of synthetic thermoplastics in conservation has been presented elsewhere (reference 1, p. 104). Polyvinyl acetate was described in the early 1930s by Stout and Gettens. In view of the importance of this polymer, the National Gallery of Art Research Project at Mellon Institute undertook the preparation of a list of the different molecular weight grades available in various countries (reference 1, p. 218). Lower molecular weight varieties, particularly resin AYAB, have been introduced in recent years in a number of applications where higher fluidity and gloss were desired*.

Because they are available as granular powders and because of their solubility in 'mild' solvents, the butylmethacrylate polymers from the du Pont company have attracted much attention: the n-butyl polymer, 'Lucite' 44†, the isobutyl, 'Lucite' 45, and the 50–50 copolymer of these, 'Lucite' 46. Most conservators have found it convenient to use mixtures of 'Lucite' 44 and 45, varied according to the need. 'Lucite' 44 is one of the toughest thermoplastic resins available: literature from the du Pont company states that test samples will stretch three times their original length before breaking. Poly(n-butylmethacrylate) is readily identified by its hardness and solubility characteristics‡.

Resin AW-2, a resin in the viscosity-grade class of dammar and mastic, has received considerable attention abroad and is now available in the solid form in America. The data in *Table 1* show that AW-2 is considerably brittle when used alone. A number of proprietary varnishes are said to be prepared with

* Polymer AYAB exhibits cold flow in bulk, but in thin films it seems to be satisfactory in tests thus far. If used as the final coating, it may have a slight tendency to become dirty, for the reasons noted (reference 1, p. 134) in the case of poly(n-butylmethacrylate).

† Bedacryl 112 X (Imperial Chemical Industries) is similar in viscosity grade (reference 1, p. 217).

‡ We have identified in proprietary varnishes a second variety of the n-butyl polymer, having a viscosity grade of 27 centipoises. This is supplied by an American manufacturer other than du Pont and is not available in the solid form.

resin AW-2 and additions of stand oil. Howards of Ilford (England) markets a variety of AW-2, designated as MS-2. They have also produced a fully hydrogenated type, MS-2A, which has been evaluated by G. Thomson (see p. 176) at the National Gallery, London. Resins AW-2 and MS-2A are of high quality, but the author has had little experience with them in comparison to polymers of higher molecular weight.

Artists' supply stores in America offer a variety of paints and varnishes put up in spray cans. Dammar resin is available in this form, but it is believed that most of the coatings are based on cellulose acetate-butyrate and the Rohm and Haas acrylate-methacrylate copolymer 'Acryloid' B-72 ('Paraloid' in Europe). These proprietary formulations are seldom used on fine paintings. Tests show, however, that many of them are based on excellent materials and have their use in the conservation laboratory. As mentioned above, the development of pressurized containers has introduced methylene dichloride and related solvents.

Table 2

Selected resins for solvent-type varnishes

In order of decreasing fluidity, brittleness and penetration in porous areas:

Resin	Viscosity grade	Sward hardness
AW-2	1·3	86
Dammar	1·4	81
Polyvinyl acetate AYAB	9·0	63
27H (experimental varnish)	23·0	49
Poly(n-butylmethacrylate)	27·0	25
Acryloid B-72	29·0	65
Lucite 44 poly(n-butylmethacrylate)	48·0	30
Lucite 46 (n-butyl/isobutylmethacrylate copolymer)	50·0	61
Polyvinyl acetate AYAF	80·0	63

In order of increasing strength of solvent needed to formulate the varnish:

Resin	Solubility grade*
27H (experimental varnish)	8
AW-2	10 (?)
Lucite 44, 45 and 46	25
Dammar	—†
Acryloid B-72	80
Polyvinyl acetate AYAF, AYAB	89

* Percentage toluene by weight in n-dodecane necessary to make a clear solution at 25°C.

† Soluble in 'mild' petroleum fractions when fresh, requires toluene or 'stronger' solvent when aged.

An experimental varnish known as 27H was developed at Mellon Institute in 1953*. This polymer was unique in that it was specially prepared with selected film strength, high resistance to yellowing and solubility in a petroleum solvent having no aromatic compounds (reference 1, p. 200). Extensive studies of this and related polymers led to the discovery and investigation of the tendency of thermoplastic polymers to cross-link under the effect of light, a problem of fundamental interest that will be discussed below.

Table 2 summarizes the properties of the resins of principal interest to conservators in America.

Application of varnish

A number of problems is associated with the introduction of new and unfamiliar materials. In the application of a varnish,

* Varnish 27H was made only in limited quantities in the laboratory at the time and samples are no longer available.

perhaps the central problem has been the selection of a solvent sufficiently 'mild' to be used with little danger of attacking the paint during application, and, at a later time, during the removal. The risk of attack, of course, depends on the character of the paint or other material directly beneath the varnish. In certain cases, the ability of the substrate to withstand solvents of the 'strength' of toluene and cellosolve ($C_2H_5O(CH_2)_2OH$) has made the application of polyvinyl acetate possible. The Rohm and Haas 'Acryloid' B-72 is also soluble in toluene and forms a slightly cloudy solution in xylene. The butyl-methacrylate polymers are soluble in turpentine and in petroleum fractions having about 25 to 35 per cent aromatics. The experimental polymer 27H was designed to be soluble in paraffin and cycloparaffin hydrocarbons. Resin AW-2 is soluble in similar solvents. *Table 2* lists these polymers in order of their solubility grade (reference 1, p. 45).

In our research, polymers that may be applied and removed in xylene have been sought as a standard of the maximum solubility parameter or 'strength' of solvent to be used. To establish such a specification, the investigator must bear in mind that stronger solvents are generally required to remove aged resins than to dissolve them originally. More information is needed on the removal of aged coatings before this question can be properly considered. Miss Elizabeth Jones' re-forming process, for example, represents one of the many facets of the problem that should be further explored. Certain new facts regarding the aging and removal of polymers are discussed below.

The polymers listed in *Table 2* require solvents no 'stronger' than toluene to dissolve them. Yet, having thus limited the number, one still has the problem of learning to apply these materials, particularly if their molecular weight is significantly higher than mastic, dammar and AW-2 resins (reference 1, p. 120). High viscosity grade is, of course, associated with the desirable properties of increased strength and reduced brittle-ness. In order to take full advantage of these properties, American conservators have learned to apply the coatings by spray application. A discussion of the relative merits of brushing and spraying will not be undertaken here. Suffice it to say that many conservators have found spraying to be highly satisfactory once they have learned the technique. The use of spraying equipment requires skill and experience, however, just as does successful brushing.

To furnish additional information concerning the application of these materials, the National Gallery of Art Research Project undertook a study of the relationship of viscosity grade to film-forming properties. This led to data of the type shown in *Figure 1*. Commercial resins of lower viscosity grade than those which were in general use in 1950 were also sought out. For example, the use of polyvinyl acetate AYAB, AYAA and several other polymers in the 20–30 centipoise range of viscosity grade has been suggested.

While the spraying of coatings has introduced problems in the selection of solvents, the desire to brush solutions of high poly-mers in certain applications has also required special con-sideration. A sound review of petroleum chemistry was required in order to select solvents of a given solubility parameter and with varying evaporation rate (reference 1, p. 17). This subject was briefly reviewed in the *Application of Science in the Examination of Works of Art*, Museum of Fine Arts, Boston, Mass., 1959, pp. 70–72. Attention has been drawn to the wide variety of proprietary solvents described in the *Petroleum Thinner Index* of the National Paint, Varnish, and Lacquer Association, Washington 5, D.C.

Problems in removal of coatings

A fundamental problem associated with materials used in conservation involves their ease of removal. The use of thermo-plastic polymers in the viscosity-grade range of 9 to 80 centi-poises has raised a problem of basic interest: among the ways that such a substance may become altered in time, one manner is through the formation of cross-links. Although this phenomenon is not of major importance with materials of the average molecular weight of dammar, mastic and AW-2 resins, it is one the chemist must face if he wishes to use thermoplastic polymers of much higher molecular weight. As has been pointed out, it does not take very many chemical cross-links to cause such a polymer to become insoluble (reference 1, p. 203).

The tendency for thermoplastic polymers to cross-link upon aging has been found to be more the general rule, and the lack of this tendency the exception, than one might at first expect. Activation of certain chemical bonds by light and heat imparts the tendency to form new chemical bonds. Bond formation, of course, may take place with neighbouring molecular chains in the polymer. If this proceeds, the chains may become so linked together that they eventually fail to be dispersed in solvents. Thus, our investigation of polymers of the higher alkylmetha-crylate esters traced the tendency to lose solubility particularly to the presence of tertiary hydrogen atoms in the side-chain (reference 1, p. 152). The tendency to cross-link has also been observed in poly(vinylstearate-acetate) copolymers, poly(vinyl-butyral) and cellulose acetate-butyrate.

Table 3

Average rate of cross-linking of poly(n-butylmethacrylate) and poly(isoamylmethacrylate) on aluminium foil, under various filters in the fadeometer at 62°C

Filter	Filter, wavelength at 50% transmission	Relative rate for films to reach 50% insolubility	Relative rate calculated by the equation
Corex D glass	305	1·0	0·97
Window glass	330	0·44	0·49
Uvinul M-40 filter	358	0·19	0·21
Plexiglas UF-1	396	0·05	0·05

The first phase of an extensive investigation of cross-linking was to determine the structures in the methacrylate side-chain that possessed the greatest tendency to become insoluble. This led to the conclusion just stated and to the selection of mater-ials with a reduced tendency. The second phase was to determine the nature of the radiation that caused cross-linking. Data in *Table 3* demonstrate that ultra-violet radiation is primarily responsible. The influence of wavelength upon the rate is almost precisely that predicted by the probable damage factor for a given wavelength (D_λ), described in the Harrison report of the Metropolitan Museum of Art*. The rate at which the films reached 50 per cent insolubility was found to follow the equation

$$\text{Rate} = 1/T_{50} = 0\cdot16D_\lambda - 0\cdot05$$

where T_{50} is the time required to attain 50 per cent insolubility. Investigation also showed that an increase in the temperature of the samples increased the rate of cross-linking.

How important is this phenomenon under museum con-ditions? Most of the accelerated-aging tests first used to detect

* The results of these experiments were reported to The British Group, IIC, at their meeting of September 29, 1960.

and study the problem involved both elevated temperatures and ultra-violet radiation not normally encountered in a picture gallery. To minimize the effect of temperature, our laboratory conducted tests under 'daylight' fluorescent lamps in an air-conditioned room at 80°F and 50 per cent relative humidity. Under these conditions, the butylmethacrylate polymers from du Pont were found to develop 50 to 80 per cent insolubility in 8 to 10 million footcandle-hours of exposure. (After this exposure, the polymers could still be removed easily with toluene.) Such a degree of insolubility might be expected to develop in a matter of 50 to 100 years if the objects were to be

the polymers from a viscosity grade of 27 centipoises to about 10 centipoises. The possibility of inhibiting cross-linking has also been mentioned (reference 1, pp. 159 and 161).

To conclude these remarks, it should be said first that the problem of cross-linking is a general one in the aging of thermo-plastic polymers of reasonably high molecular weight. Research has shown, however, that certain chemical structures have greater tendency than others and that ultra-violet radiations are primarily responsible for the phenomenon. Moreover, the ability of a film to swell, rather than the actual insoluble matter present, controls in large measure the ease of removal.

Table 4

Ease of removal of pairs of films in relationship to their ability to be swollen by toluene

Aged film	Percentage insoluble in toluene	Fadeometer exposure (hours)	Percentage gain in weight (absorbed toluene after 3 days)	Time (sec) required to remove film with swabs dipped in:	
				Toluene	Acetone
Isobutyl MA* polymer	89·1	111	598	105	65
n-Butyl MA* polymer	100	228	77·2	>180	220
1/1 AW-2/n-propyl MA* polymer	96·2	416	91·4	75	6
1/1 MS-2/n-propyl MA* polymer	95·0	416	43·3	>180	25

*MA = methacrylate

illuminated at a level of about 50 footcandles during the day. From this first estimate, we may conclude that the phenomenon is not one to cause immediate alarm. Nevertheless, cross-linking can take place during exposure in museums and the possibility warrants particular attention wherever ordinary fluorescent lamps are to be used without ultra-violet filters or wherever daylight enters through ordinary window glass*.

Since practically all films become more difficult to remove in time, the laboratory is prompted to return again to funda-mental problems regarding the removal of films and the rate at which films, once soluble in solvents such as toluene, come to require 'stronger' solvents for removal. This led to studies which suggested that the ability of a film to swell under the action of solvents was important in facilitating its removal (reference 1, p. 200). Recent data, given in *Table 4*, demon-strate that the amount of insoluble material present in a film is not necessarily the major indication of its ability to be removed. Even though cross-linking may proceed to the extent that 50 to 95 per cent of the film becomes insoluble, this does not mean that the film cannot be removed with considerable ease as a soft swollen jelly. These preliminary findings concerning the role that swelling plays in removal draw special attention to the techniques used by Stolow in his studies of solvent action.

Polymers of low molecular weight might be expected to become insoluble at a lower rate. We have thus far found little benefit, however, in lowering the average molecular weight of

* There are ways of detecting the onset of cross-linking. Thomson's test is simple and highly sensitive (*Nature*, 178 (1956) 807; reference 1, p. 205). Measurements of the degree of soluble matter in samples picked up on a cotton swab have been used in our laboratory to follow the course of cross-linking in a quantitative way. A chromato-graphic leaching method has also been used (reference 1, p. 115). The conservator can detect the presence of cross-linked material by the tendency of a film to swell considerably under the action of solvents, and by the presence of a jelly-like mass. Such behaviour is considerably different from that observed when a fresh film of a polymer is dissolved with solvents.

The investigations continue and new information is being gained about cross-linking. From what has been learned so far, however, the author believes that, with proper supervision and keeping of records, coatings such as poly(butylmeth-acrylate) may still be used in the conservation of many objects.

Polymers with little tendency to cross-link

The search for high polymers which have little or no tendency to cross-link continues. Polyvinyl acetate has an extremely low tendency to cross-link in the fadeometer and in sunlight, if it does so at all. This fact was first pointed out by Thomson and has been confirmed in our experiments. Polyvinyl acetate, there-fore, retains its important place in the conservation laboratory.

Table 5

Percentage insolubility of Acryloid B-82 and Rhoplex AC-33 upon exposure on aluminium foil in fadeometer at 62°C

Insolubility in: Exposure time:	Toluene 394 h	Toluene 1045 h	Toluene 2027 h	Acetone 2027 h
B-82*	4·2	22·4	62·0	4·4
AC-33	10·6	43·8	77·4	4·8

* Rohm and Haas polymer similar to B-72.

Our search for structures in the methacrylate family that have little tendency to cross-link led us to the prediction that a copolymer of ethylmethacrylate and methylacrylate should possess this property. Tests in the fadeometer revealed that after 2000 hours on aluminium foil at 62°C such a polymer was still soluble in acetone to the extent of 95 per cent or better. This exposure is equivalent to over 40 million footcandle-hours. Although originally soluble in toluene, the polymer developed a certain degree of insolubility in this solvent as time went on. This change is apparently due to partial oxidation of the poly-mer and not to cross-linking, since otherwise the high solubility in acetone would not have occurred.

Following these tests of durability, we have suggested the consideration of this type of copolymer for certain applications. Commercially available polymers that are similar are the Rohm and Haas resin 'Acryloid' B-72 and their emulsion of a related polymer, 'Rhoplex' AC-33. The results of the exposure of these proprietary polymers in the fadeometer are given in *Table 5*. The conclusions from these data are the same as those made concerning the behaviour of the related polymers prepared in the laboratory. 'Acryloid' B-72 may be applied in xylene; evaporation may be retarded by the addition of solvents such as diethylbenzene or all-aromatic petroleum fractions. Varnish formulated with these solvents is slightly cloudy, but the films are satisfactory in appearance*.

Conclusions

We have learned much about the properties of solvent-type coatings in recent years, yet much remains to be investigated.

Thus far, research has discovered two thermoplastic polymers of reasonably high molecular weight which are soluble in solvents as 'mild' as toluene and xylene, and which form films that remain strong, colourless and soluble for extremely long periods of time. It is hoped that ever-increasing experience with these polymers in applications where they are suitable will strengthen the conservator's confidence and satisfaction in their use. In the range of viscosity grade similar to dammar and mastic resins, resins AW-2 and MS-2A also appear to be sound additions to the conservator's stock of materials.

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* The use of 'Acryloid' B-72 in the conservation of metal objects dates back a number of years: See *Rohm and Haas Reporter*, 8, No. 3 (1950) 14.