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Robert L. Feller

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HARDNESS AND FLEXIBILITY OF NATURAL AND SYNTHETIC-RESIN VARNISHES

By Robert L. Feller, National Gallery of Art Fellowship, Mellon Institute, Pittsburgh, Pa.

The National Gallery of Art Fellowship, established at Mellon Institute in September, 1950, has been commissioned to investigate artists' materials, both for use in original work and in conservation. The development of a picture varnish has been chosen as the first subject for research. In view of the variety of durable synthetic resins which have been developed in recent years, museums everywhere have expressed the hope that a picture varnish might be formulated with a synthetic which would prove far superior to damar and mastic. Polyvinyl acetate and normal-butyl polymethacrylate have been used for this purpose for a number of years by prominent museums here and abroad. These synthetics are clear and highly resistant to cracking and yellowing. However, the commercially available synthetics were not developed with the artists' and conservators' requirements in mind. There is a need, therefore, for an investigation into the specific problem of formulating a protective coating for paintings.

In the development of a new substance there are two major avenues of approach. By one method the desirable properties of the old may be measured and then closely matched in the new. Or the problem may be approached much more fundamentally by first determining precisely what properties are required "to do the job" and then developing a material having exactly those properties. This last method, while much slower than the first, in general leads to the most significant improvements. Unfortunately, however, we are not at all positive of the exact properties desired in a protective coating for pictures. Although an international commission meeting in Rome in 1930 listed about a dozen requirements for such a coating, these specifications are very general; they are not scientifically explicit. It is therefore necessary to approach the problem of developing a new picture varnish from both points of view: measuring the properities of the old and, at the same time, investigating the fundamental requirements of a protective coating.

Concept of Hardness

Discussions of painting techniques often refer to copal resins as being "hard" and to damar and mastic as "soft." These remarks apply to a property which we all sense and yet find very difficult to describe. What, precisely, is referred to? Is it the stiffness of the varnishes, their brittleness, their resistance to marring, or perhaps something else? There are many machines currently in use in paint and varnish laboratories that purport to measure "hardness." The expression has never been exactly defined, however. It is customarily defined solely in terms of the apparatus, or method, used in measurement: indentation-hardness, penetration-hardness, scratch-hardness, rocker-hardness, etc. Each of these measures something slightly different. For this reason, it is best to apply several different methods to a problem.

The Fellowship planned, therefore, to measure this property by several methods and to establish a scale of relative hardnesses for the better-known resins. In this fashion a method of comparison would be available when new materials were developed for a picture varnish. The pencil-hardness test and the Walker-Steele rocker-hardness machine were selected. The resistance to cracking was also measured by bending films of varnish on aluminum foil around mandrels of decreasing diameter.

The pencil-hardness test (Organic Finishing *10*, 23 (1949)) is a simple one, in which the hardness of a paint or varnish is designated as the engineering drawing pencil that will just scratch the surface. Eagle "Turquoise" pencils in the range 2H to 5B were used for this purpose, with satisfactory results. The Walker-Steele hardness machine (J. Oil & Colour Chemists' Assoc., *21* 379 (1938)) is similar in principle to the better known Sward hardness rocker. The application of these instruments is based on the fact that the oscillations of a rocking object will be quickly damped out when rocking on a soft, rubbery surface, but will continue much longer on hard, rigid surfaces. The Walker-Steele instrument is a balance beam which rocks on two ½″-diameter steel balls. The hardness of a film is defined as the time necessary for the beam to be damped through 22.5° of arc when rocking on the supported film. This time is usually reported relative to the time of damping when the beam rocks on the unpainted surface of the support material, window glass in our case. The present instrument was found to rock on glass for approximately 400 seconds before being damped through the specified arc. All other times were reported as the decimal fraction of this value.

Preparation of Sample Varnishes

A very important question that must be answered when studying the "typical" properties of paints and varnishes is the following: "How long should a film be allowed to dry before measuring its properties?" A spirit varnish dries through the loss of solvent. It is generally dry to the touch within one to three days, but the film is by no means entirely free of solvent at this time. Our experiments show that the film contains as much as twenty per cent solvent at the end of a month's standing at 70° F. and 50% relative humidity. In this sense the varnish is not "dry." Indeed, its properties are still changing.

However, because of the inconvenience of waiting longer, it was decided to take measurements at the end of one month of drying at 70° F. and 50% relative humidity and also after the films had been baked for two days at 158° F. The two measurements provide a range in properties: those after one month "natural" drying and those after all the solvent has been driven off. The baking treatment may be considered as "accelerated aging." Our tests showed that, except perhaps for normal-butyl polymethacrylate in turpentine, two days at 158° F. was sufficient to drive off most of the solvent. This treatment apparently caused little if any deterioration of the films, although some oxidation occurred with the natural-resin varnishes both in the air and in the oven.

Since the natural resins, damar and mastic, are likely to vary in their properties from sample to sample, three different preparations of each were used for the tests. Two were proprietary varnishes and the third was prepared in the laboratory from the best grade of resin and turpentine. Polyvinyl acetate was purchased from the Union Carbide and Carbon Corporation and the iso- and normal-butyl polymethacrylate from E. I. du Pont de Nemours & Company. The resins were not plasticized by adding linseed oil or other agents. All varnishes were prepared in films 0.001 to 0.004" thick on glass or aluminum foil.

Experimental Results

The results of our experiments establish an order of scratch- and rocker-hardness for spirit varnishes as follows: Mastic; Damar; Isobutyl polymethacrylate; Polyvinyl acetate; Normal-butyl polymethacrylate. This list also represents a fair approximation of the order of brittleness. Mastic and damar are quite brittle. In an unplasticized condition, the isobutyl polymethacrylate resin that was used in these experiments could be cracked, although its films were not as brittle as those of the natural resins. The polyvinyl acetate resins which were purchased varied in their average molecular weight. Films of the higher molecular varieties and of the normal-butyl polymethacrylate resin did not crack even after baking. Some of the lower molecular weight types of polyvinyl acetate are brittle, however. Specifically, of course, the remarks regarding iso- and normal-butyl polymethacrylate are true only of the particular commercial products studied; they are the varieties now used by several museums in this country.

The results with damar and mastic were particularly interesting. After baking the films (i.e., driving off the turpentine solvent) both varnishes showed the same rocker-hardness. After drying for one month at 70° F. and 50% relative humidity, damar varnish definitely showed lower hardness values than mastic. In order to gain further insight into this difference, their brittleness was also measured. The varnishes were coated on 0.001"-thick aluminum foil and subjected to the same drying schedule as the samples on glass plates. Brittleness of the varnishes was then obtained by measuring the sharpness-of-bend necessary to crack the film. It was found that one-month-old damar was much less brittle than mastic, but, after baking, the two varnishes were very similar. This behavior correlates well with the hardness measurements. The conclusion, therefore, is that, when compared as a spirit varnish prepared with turpentine, mastic is more brittle than damar. In time, damar varnish is expected to approach the brittleness and rocker-hardness of mastic.

Conclusions

What general conclusions may be drawn from these experiments? Spirit varnishes made with the traditional resins are hard and brittle, whereas those made with polyvinyl acetate and normal-butyl polymethacrylate are soft and flexible. This difference is largely due to the size of the molecules in these materials. The synthetics possess an average molecular weight three to ten times that of the natural materials.

Additional tests, under ultraviolet light, indicate that the natural resins, yellow to begin with, tend to increase in yellowness with age. On the other hand, these particular synthetics are clear and are highly resistant to yellowing. Many samples of the varnishes prepared with synthetics did not yellow at all during the tests. Precisely speaking, of course, no organic material may be regarded as nonyellowing, in the same sense that no material is "permanent."

In seeking to develop a new varnish, the approach which attempts to duplicate the properties of the old material perhaps will play a minor role. Synthetics are capable of much greater toughness and resistance to yellowing than damar and mastic. Because of their high molecular weight, the synthetics thus far examined constitute an entirely different class of substances in comparison with the two natural resins.

They possess certain faults, however. In general, the synthetics have lower refractive indices. This is perhaps an undesirable feature which must be modified, because the refractive index of the varnish affects the values of the colors in the painting. There is another problem which must be solved: by virtue of their high molecular weights, the viscosity of their solutions runs higher than comparable concentrations of the natural resins. In this particular situation, however, we are working at opposite ends. As a general principle, larger molecules form tougher films. Unfortunately it is more difficult to dissolve such substances in mild solvents than it is to dissolve the smaller molecules. A compromise may be necessary. In addition to these problems, the Fellowship intends to investigate moisture permeability and resistance-to-blooming. New synthetic resins also will be prepared in the laboratory.

Summary

Our investigations have shown that the synthetics studied are remarkably more resistant to cracking and to yellowing than damar and mastic. This is so much so that they may be considered an entirely different class of materials. Experiments have also shown that, during its lifetime, a spirit varnish prepared with damar is expected to be more resistant to cracking than mastic. A scale of hardnesses has been established for the better known spirit varnishes used in protecting pictures. A fact already known in the field of commercial lacquers has been shown to be equally true in the case of the picture varnishes: the films retain considerable solvent long after they are dry to the touch. The retained solvent definitely affects the properties of the films, usually causing them to be more flexible than they will become in time.

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