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THE INFLUENCE OF ORPIMENT IN SHELLAC ON THE PROTECTIVE PROPERTIES OF THE VARNISH.

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Introduction.

Small amounts of orpiment are usually added in the manufacture of dark grades of shellac in order to render these samples light-coloured and therefore more attractive. In recent times, however, objection is raised to this practice on the ground that the presence of orpiment adversely affects the properties of the shellac and interferes in the process of its application, e.g., in the bleaching industry. Views are at the same time held by some that orpiment imparts some beneficial properties to the shellac. It was, therefore, intended to test the accuracy of these statements and determine exactly the effect of orpiment addition on the resulting shellac. In this paper an attempt has been made to find out the extent to which orpiment affects, beneficially or adversely, the protective properties of the shellac film as is obtained with a coating varnish.

Experimental.

Samples of shellac containing varying quantities of orpiment were prepared by the country method in the experimental lac factory attached to the Lac Research Institute ; control samples, free from orpiment, were also prepared from the same seed lacs. The orpiment content of the samples was determined by a modification of the Gooch-Browning method.[1]

50% varnishes were prepared in the cold, using as solvent a mixture of 100 parts of 95% ethyl alcohol and 5 parts of pure methyl alcohol. Films were prepared on glass slides by the spinning method regulating the time and duration of spinning to get films of approximately the same thickness in each case. In the absence of a constant temperature-humidity chamber, drying was carried out at room temperature and humidity. As the tests are relative, however, and as all the films for any particular test were prepared at the same time, this would not detract from the value of the tests in any way.

Colour of Varnish.

Addition of orpiment renders the varnish lemon-yellow in colour when sufficient quantity of orpiment is present. When the shellac is particularly dark, however, the resulting varnish looks greenish. A number of varnishes from orpiment-containing shellacs were filtered free from suspended orpiment. These were compared with varnishes from their control, orpiment-free shellacs treated in the same way. In the majority of cases the colours of solutions of corresponding arsenicated and non-arsenicated shellacs were identical. In a few cases differences in colour were noted but these were only extremely small. It is indicated, therefore, that the orpiment has not chemically affected the colouring matter of the resin during manufacture into shellac. The lighter colour of the varnish is, therefore, due to the optical effect of the dispersion of fine particles of orpiment in the solution.

Appearance of the Film.

Films with excess of orpiment in a coarse form have a rough uneven surface. If, however, only fine particles of orpiment are present in the varnish, the film will be yellowish but quite smooth, glossy and acceptable. Dark coloured woods will appear greenish when too much orpiment is present but when only small quantities are present, as is usually the case in commercial practice, even this defect will not be very apparent.

Effect of Water.

Tests were made to find out the effect of immersion in water.

In one series of experiments, the films were prepared on glass and, after drying and trimming to remove the thick portions at the edge, immersed in distilled water for 2 days. Partial blushing was observed in all cases and no distinct difference could be noticed in the behaviour of different films.

A quantitative test was also made to find out the amount of water absorbed by various films as a result of water immersion ; but again no definite, marked differences in the water absorbing capacity could be observed.

In a second set of experiments it was proposed to test the effect of water immersion on an absorbent material coated with the various varnishes under examination. Teak wood panels were coated by dipping and after the film was thoroughly dry, the specimens were kept immersed in water for a week.

Some of the test specimens were badly affected with chalking, others to a smaller extent ; but orpiment was found to have no effect either way. It was observed that a smooth and fine-grained surface would withstand the effect of moisture better than a rough, coarse-grained surface ; possibly, a continuous protective film would be obtained in the former case.

Scratch Hardness.

To determine the relative hardness of the films, tests were carried out with a scratch hardness tester of the weighted needle type made by Messrs. Griffin and Tatlock, London, according to the Air Ministry specification and similar in principle to that used by Mardles [2]. The end-point was determined in each case by noting the approximate weight required to scratch the entire thickness of the film and expose the glass surface under the greater part of the scratch. The thickness of the film close to the scratch was then measured with a film-guage and was found to be 20-25 microns in each case.

Films were prepared by the spinning method and in one series of experiments, the varnish was shaken before taking out for the preparation of the film. This method was, however, considered not strictly comparative as the very coarse particles of orpiment would render the films much more uneven than is found in practice. In the second series of tests, therefore, the coarser particles of orpiment were allowed to settle overnight leaving only a fine suspension of orpiment in the varnish. A large quantity of orpiment was, nevertheless, present in these tests as well.

The following tables indicate the results obtained.

TABLE I.

Scratch hardness of films without sedimentation of orpiment.

Sample No.	% As_2S_3	Wt. in kilos required for scratching.	
		After 3 days' drying.	After 2 weeks' drying.
1	Control	1.15-1.20	1.70-1.80
2	0.67	1.20-1.25	1.80-2.00
3	1.15	1.10-1.15	1.80-2.00
4	Control	1.20-1.25	2.00-2.20
5	2.34	1.05-1.10	1.80-2.00

TABLE II.

Scratch hardness of films with partial sedimentation of orpiment.

Sample No.	$\%As_2S_3$	Wt. in kilos required for scratching.	
		After 1 week's drying.	After 2 weeks' drying.
1	Control	2.60-2.70	2.60-2.70
2	0.67	1.90-2.00	2.30-2.40
3	1.15	1.80-1.90	2.10-2.20
4	Control	1.60-1.70	1.80-1.90
5	2.34	1.60-1.70	1.70-1.80
6	Control	2.20-2.30	2.50-2.60
7	0.30	2.30-2.40	2.30-2.40

It should be mentioned that one column of results cannot be compared with another as the tests were carried out under room conditions of temperature and humidity. All the tests in any one column were, however, done under identical conditions so that the values for orpiment samples and the corresponding controls are strictly comparable.

It will be seen from the above tables that the effect of orpiment, though not marked considering the difficulty of obtaining strictly uniform films of identical thickness, seems to be to lower the hardness of the film to a small extent. This is probably due to the particles of the orpiment interfering with the adhesion of the film.

Resistance to Abrasion.

The comparative resistance of the varnish films to abrasive action was next tested.

Films were prepared on glass as for hardness tests and tested with an apparatus similar to Gardner's arrangement[3]. Emery powder of 30-60 mesh size was used as abrasive and the flow of abrasive was checked when the film was just abraded enough to show up the glass surface at any point. The thickness of the film close to the point was measured and the abrasion factor $\frac{\text{Wt. of abrasive in grams}}{\text{film thickness in cm.} \times 1000.}$ was determined for each test. The mean values from four tests have been given in each case.

TABLE III.

Resistance of films to abrasion after 3 days' drying.

Sample No.	$\%As_2S_3$	Abrasion factor.	
		Without sedimentation.	With partial sedimentation.
1	Control	508	888
2	0.67	434	599
3	1.15	—	835
4	Control	475	550
5	2.34	440	519
6	Control	—	991
7	0.30	—	925

It is clear from the above table that, except in one instance, the tendency of orpiment has been to lower, to a small extent, the resistance of the film to abrasive action.

Exposure Tests.

The weathering properties of the varnish films were next taken up for investigation.

Teak wood panels were planed and sanded well to give a smooth surface. A primary coat of shellac varnish was then given to the entire panel in order to protect the unexposed sides and also serve as a filler for the side to be exposed. After drying, one face was rubbed down with sand-paper and coated with the test varnish by the method of spinning without sedimentation of orpiment. The specimens containing orpiment had a rough and uneven surface due to the large particles sticking out of the film. The test panels were exposed outside facing the sun at an angle of 45°. The temperature of solar radiation ranged from 90°-95° in the earlier part of the test.

No apparent change in the condition of the film was noticed for two weeks. A wet and windy day occurred, followed by a cloudy and breezy day with a heavy mist on the day after. Immediately afterwards, a break-down of the film was noticed in places in the case of all specimens. Later, when the effect of dry heat was felt, cracks developed

and a loss of gloss was also noticed. All the specimens were similarly affected but, in general, the orpiment samples had suffered slightly more than the controls.

In the second series of experiments, the panels were prepared in the same way but were coated with the test varnish after partial sedimentation of orpiment. The specimens were then exposed to the ultraviolet radiation from a mercury lamp under atmospheric conditions of humidity. The temperature obtained in the vicinity of the specimens was about 85°F. As the tests were comparative, no attempt was made to simulate the actual weather conditions but since it had been found[4] that the exposure of a wet film had the maximum deteriorating effect, the panels were sprayed with water at the commencement of each day's exposure with the view of accelerating the break-down.

In a few days blistering was observed to a variable extent, accompanied by a pronounced blushing at the lower edges where the specimens were in longer contact with the sprayed water. Very small patches of chalking were also to be noticed. After about four weeks' exposure the films lost their gloss, the dullness varying in different cases. The films were intact in all cases and satisfactory excepting for the slight defects mentioned above.

As regards the effect of orpiment, it was observed that it had no influence on the weathering properties of the film. It is to be concluded, therefore, that if the orpiment is in a sufficiently fine form not to interfere seriously with the adhesion of the film, it is possible that the varnish will not suffer in any way due to its presence. In the foregoing exposure tests, the coarse particles of orpiment were probably loosened from the film due to the expansion and contraction of the latter and were then taken away by the wind and rain.

In conclusion, it should be mentioned that the above tests have been made with considerably more orpiment than is actually met with in practice with the object of accentuating the effect. Except in rare cases, the orpiment actually present in the shellac of commerce would hardly exceed 0.5% and perhaps never 1%. The effect of orpiment can only be, therefore, at the worst, of the degree indicated in the foregoing tests.

Summary.

1. The influence of large quantities of orpiment in shellac on some of the properties of the resulting varnish has been studied by means of comparative tests made with and without the addition of orpiment in the manufacture of shellac.

2. Tests on the colour of filtered varnishes go to indicate that the lighter colour of orpimented shellac is due only to the optical effect as a result of the suspension of fine orpiment and not to any chemical action on the colour of the resin.

3. Varnishes containing orpiment give films which are of satisfactory colour and appearance, provided too much orpiment has not been used.

4. No distinct difference has been noticed in the behaviour of films towards water, either on glass or on wood.

5. An excess of orpiment tends to reduce the scratch-hardness of the film and its resistance to abrasion.

6. A large quantity of orpiment shortens, to a small extent, the life of the film on exposure to weather conditions. A fair amount present in a fine form may not, however, adversely affect the resistance of the film.

7. No useful purpose appears to be served by the use of orpiment from the point of view of the protective properties of the varnish film.

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