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Studies in Shellac Etch Primers: Part II — Shellac-Malic Acid-Zinc Tetroxy Chromate

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Stable single-pack etch primers have been developed from shellac, malic acid and zinc tetroxychromate which do not exhibit any gelling tendency. A composition containing dewaxed shellac 100; methylated spirit 100; *n*-butanol 82; zinc tetroxychromate 95; talc 5; and malic acid 20 parts is similar in performance to the conventional shellac etch primer using zinc chromate and phosphoric acid, with the additional advantage of outstanding adherence to and elasticity on steel.

ZINC tetroxychromate is the accepted pigment in the two-pack wash primer system. This pigment, ground in a solution of polyvinyl butyral, forms the pigment base in one pack, and a solution of phosphoric acid as the accelerator or etching agent in the other. Zinc tetroxychromate has a much higher corrosion resistance compared to other chromate pigments.

In the case of shellac etch primer, even a two-pack system of the conventional type is not possible, because shellac varnishes gel rapidly when ground with zinc tetroxychromate, obviously due to the acidic nature of lac. This difficulty can be overcome[1,2] by neutralizing the acidity by prior treatment of lac with magnesium oxide. A two-pack shellac etch primer can be formulated by grinding zinc tetroxychromate into this modified varnish to produce the pigment base. Alternatively, a 'reverse' primer was also proposed with zinc tetroxychromate ground into the alcoholic solvent alone being in one pack, and keeping the binder (shellac) in solution along with the phosphoric acid in the second pack. Neither of these formulations was, however, entirely satisfactory.

It has been reported earlier[3] that the gelling of shellac varnish on grinding it with certain grades of zinc chrome can be prevented by including about 2 per cent malic, tartaric or citric acid in the composition and that stable single-pack shellac wash primers of satisfactory performance can be prepared, even without phosphoric acid, by including, in its place, 20-25 per cent of any of these acids on the weight of lac in the composition. The possibility of using these acids to prevent the gelling of shellac varnishes, when ground with zinc tetroxychromate, has now been investigated. The results obtained are presented in this communication.

Experimental Procedure

The standardized etch primer based on shellac, malic acid and zinc chromate has the following composition[3]: dewaxed shellac, 100; spirit, 100; *n*-butyl alcohol, 82; malic acid, 20; zinc chrome, 95; and talc, 5 parts.

For the present study zinc tetroxychromate was used in place of zinc chrome and the proportions of malic, citric and tartaric acids were varied. Wash primers were prepared of different compositions and their storage behaviour investigated. After storage for different periods, films were prepared on cleaned aluminium panels by brushing and their scratch hardness determined after air drying for 24 hr. For preparing etch primers, the acid was dissolved in alcohol and then milled with the remaining ingredients for 8 hr or more till properly dispersed. For studying the storage behaviour, the primer samples were stored in bright (tin) plate containers.

Results and Discussion

The compositions prepared using citric acid and tartaric acid were found to thicken, irrespective of the quantity of acid used. Gelling also occurred within a few days in the case of the composition containing up to 5 per cent malic acid, but in the case of compositions containing higher proportions of malic acid, there was no gelling. Stable primers were obtained when the proportion of malic acid was 20-25 per cent on the weight of lac (Fig. 1). The optimum proportions of different constituents for obtaining a satisfactory primer were found to be as follows: dewaxed shellac, 100; methylated spirit, 100; *n*-butanol, 82; zinc tetroxychromate, 95; talc, 5; and malic acid, 20 parts. Even after 6 months' storage, the

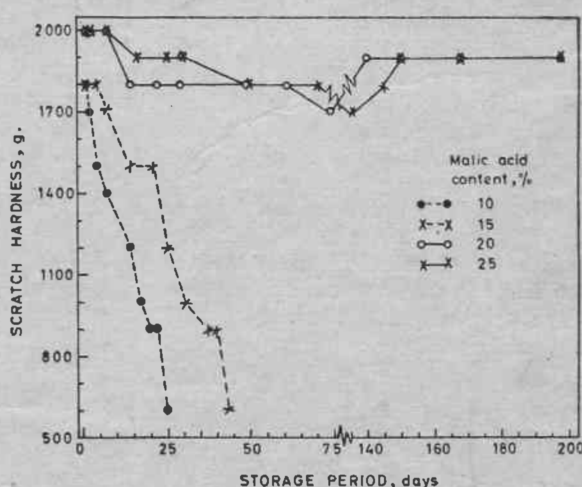

Fig. 1 — Effect of malic acid content on the storage stability of shellac wash primers

TABLE 1 — EFFECT OF MALIC ACID CONTENT ON THE VISCOSITY OF SHELLAC WASH PRIMERS

(Viscosity measured in B4 Ford cup.)

Storage period days	Viscosity, sec.		
Malic acid, %:	15	20	25
Freshly made	34·5	37·0	39·4
7	35·0	37·4	40·0
15	35·0	37·8	40·5
21	35·8	38·0	41·0
30	36·0	38·2	41·4
90	36·0	38·5	42·0
180	—	39·0	42·5

TABLE 2 — ADHESION (SCRATCH HARDNESS OF FILMS) OF SHELLAC-MALIC ACID-ZINC TETROXYCHROMATE ETCH PRIMER ON DIFFERENT METALS

(Metal panels of size 15×7·5 cm. were used)

Metal	Dry wt of film g.	Scratch hardness*† g.
Aluminium	0·3214	1900
Copper	0·3346	1600
Brass	0·3157	1600
GI sheet	0·3277	1600
Steel	0·3899	>2000

*Scratch hardness determined on brushed films after 24 hr air drying.

†The panels with paint films showed no cracks on bending over a conical mandrel (min. diam., 0·125 cm.).

primer was free from thickening and there was no deterioration in the film properties (Table 1). The pigment settling at the bottom could be easily redispersed.

Characteristics of the primer — Etch primer of the above composition was found to have excellent adhesion on different metal surfaces, and particularly on steel (Table 2). It also possessed satisfactory adhesion to finishing coats of oil paints, synthetic enamels and nitrocellulose lacquers. Films of the composition on light metals, such as aluminium, showed no cracks when bent over a conical mandrel (of minimum diameter 0·125 cm.), although on bending double, fine cracks did appear. On steel, however, even double folding did not rupture the film.

Films of the etch primer on all surfaces were resistant to all solvents to which shellac is inherently resistant. On steel surface, after a short interval, the films became resistant to spirit also, in which it was originally dissolved.

Metal panels coated with the etch primer, with and without finishing coats of oil paints, synthetic enamels and nitrocellulose lacquers, exposed to natural weathering gave satisfactory results.

The etch primer films could be baked, when desired, at 150°C. for 30 min. without any adverse effect.

Plasticizers — The possibility of improving the elasticity of the films on light metals by incorporating plasticizers or using modified lacs was investigated. Synthetic plasticizers like dibutyl phthalate, tricresyl phosphate and sextol phthalate (5, 10 and 25 per cent on the weight of lac) were tried and found to be ineffective. In fact, the scratch hardness on aluminium panels dropped from 1900 to about 700 g.

Modified shellacs — Saponified lac, esterified lac (ethyl ester) and etherified lac were tried as substitutes for dewaxed lac. In the case of the first two, although adhesion was adequate, there was hardly any improvement in flexibility. With ethylene glycol ether of lac, however, there was improved flexibility, with no deterioration in adhesion (scratch hardness). Films on aluminium could be bent double without cracking or lifting of the film.

Unlike the conventional etch primers, in the primer developed, no phosphoric or other mineral acid has been used; rather an organic acid (malic acid) has been used. The use of malic acid for increasing the adhesion of shellac films has been reported by some earlier workers[4]. Preliminary experiments have shown that if the chromate pigment in the primer composition is replaced by any inert pigment, such as titanium oxide, adhesion becomes poor and the resulting films flake off on the slightest bending of the panel. This indicates that the chromate pigment has an essential part to play in the adhesion of these primers to the substrate. The precise manner in which malic acid (and other acids) and the chromate pigments function in these primer compositions is under detailed investigation and will form the subject of a future communication.

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References

1. SANKARANARAYANAN, Y., *Research Memorandum No.* 206, *Paint Research Station, Teddington, England,* 1958, 158; *Indian Lac Res. Inst., Bull. No.* 93, 1958, 6.
2. SANKARANARAYANAN, Y. & RAO, V. S., *Paintindia* (*Lac Suppl.*) (1962), 26.
3. GUPTA, P. C. & SANKARANARAYANAN, Y., *Indian J. Technol.*, **4** (1966),
4. VENUGOPALAN, M., *Curr. Sci.*, **8** (1939), 16.