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Studies on Shellac Etch Primers: Part I—Shellac-Malic Acid-Zinc Chrome Compositions with & without Phosphoric Acid

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For the production of single-pack shellac etch primer, many commercial zinc chromes, especially those containing high percentages of chromic oxide, prove unsuitable because shellac varnishes gel when ground with these pigments. It has been found that the gelling is prevented by the incorporation of 2 per cent of malic, tartaric or citric acid into the shellac varnish before grinding with the pigments. By increasing the proportion of malic acid to 20 per cent on the weight of lac, it has been found possible to eliminate phosphoric acid from the composition. A single-pack primer made up of dewaxed shellac, 100; methylated spirit, 100; *n*-butyl alcohol, 82; malic acid, 20-25; zinc chrome, 95; and talc, 5 parts has been found to show excellent shelf-life, adhesion and flexibility.

ETCH primers, developed comparatively recently, find particular use on light metals and their alloys. The most commonly used composition is a two-pack system, polyvinyl butyral dissolved in alcohol and ground with zinc tetroxy chromate being in one pack, and a solution of phosphoric acid in alcohol in the other. These are mixed in appropriate proportions immediately before use, the shelf-life of the mixed material being about 8 hr. In view of their obvious advantages, the development of single-pack etch primers has also been attempted, generally making use of the less reactive zinc chromes and strontium chromes, although they do not exactly measure up to the performance of the two-pack system.

A satisfactory single-pack shellac etch primer was developed at this institute and is already in commercial production. Its composition, film properties and service trials on a variety of surfaces, particularly aluminium, have been described earlier[1-4].

This etch primer consists of a solution of dewaxed lac in alcohol and butyl alcohol into which are incorporated zinc chrome as the anticorrosive pigment and phosphoric acid as the etching agent. One of the limitations of this formulation is that the composition of zinc chrome has to be very specific, i.e. its chromic anhydride and zinc oxide contents should be within a very narrow range (about 38·6 and 40·4 per cent respectively). Many of the commercial samples conforming to the latest Indian specifications are unsuitable for the purpose, as, with these, the primer often gels in the mill within a few hours of grinding. The object of the present study was to find a means of eliminating this drawback, so that any commercial zinc chrome conforming to the latest specifications may be used for the production of this etch primer.

The first essential step is obviously to prevent the thickening and gelling of the composition during grinding in the mill and then, later, during storage.

Shellac varnishes rapidly thicken and finally gel when ground with alkaline or metallic pigments like zinc oxide, bronze powder, etc. Gardner[5] observed that hydroxy acids like malic, tartaric and citric, prevent this thickening. These acids were, therefore, investigated to see if they would prevent the gelling of shellac varnish when ground with zinc chrome, without adversely affecting the properties of the resulting etch primers.

Experimental Procedure

The etch primer used for the present study had the following composition: dewaxed shellac, 100; methylated spirit, 100; *n*-butyl alcohol, 82; zinc chrome, 95; talc, 5; phosphoric acid (85 per cent), 30; and spirit, 120 parts.

The shellac was dissolved in the methylated spirit in the cold and butyl alcohol added. The solution was ground in a ball mill with the zinc chrome and the talc for 8 hr. The phosphoric acid, diluted with spirit and cooled, was then added and the mixture ball milled for a further period of 4 hr.

The zinc chrome used was a commercial sample conforming to the current ISI specification (chromic oxide, 43·5; zinc oxide, 38·5; and K_2O, 10·1 per cent). Malic acid (0·1, 0·2, 0·5, 1·0, 1·5 and 2 per cent on the weight of lac) was added, dissolved in a small quantity of alcohol to the shellac varnish before incorporating the other ingredients.

Results and Discussion

In the absence of the hydroxy acid, the composition was found to gel within 3 hr, but gelling was retarded with increasing proportions of the hydroxy acid. The gelling period with 0·1, 0·2, 0·5, 1·0 and 1·5 g. malic acid per 100 g. lac was 2, 3, 4, 6 and 8 hr respectively. With 2 per cent malic acid (on the weight of lac), the composition could be ground to the requisite fineness and for the requisite period (8 hr) without any thickening and the material could be further processed by the addition of phosphoric acid and given a final grinding to produce etch primers of satisfactory performance, and comparable, in every respect, with the standard primer.

Identical results were obtained with various samples of zinc chrome obtained from different manufacturers.

Similar results were also obtained when other hydroxy acids, such as tartaric and citric acids were used. However, the use of nonhydroxy polyacids, such as succinic and oxalic, nonhydroxy mono acid, such as acetic, or hydroxy monocarboxylic acid, such as lactic or salicylic acid did not help to suppress the gelling tendency.

Etch primer without phosphoric acid — Phosphoric acid is the acid (etching) constituent used in the vast majority of wash primer formulations[6], although the use of hydrofluoric acid[7] has also been recommended. Ammonia and substituted ammonium phosphates[8] and mineral acids[9], in small amounts, have been reported to improve the phosphating action.

In the present study the possibility of using malic acid itself as the acid (etching) constituent, thereby eliminating phosphoric acid altogether, was investigated. Etch primers of standard composition, but containing different proportions of malic acid and no phosphoric acid were prepared. These were applied to clean aluminium panels by brushing and, after air drying for 24 hr, the scratch hardness of the resulting films was determined.

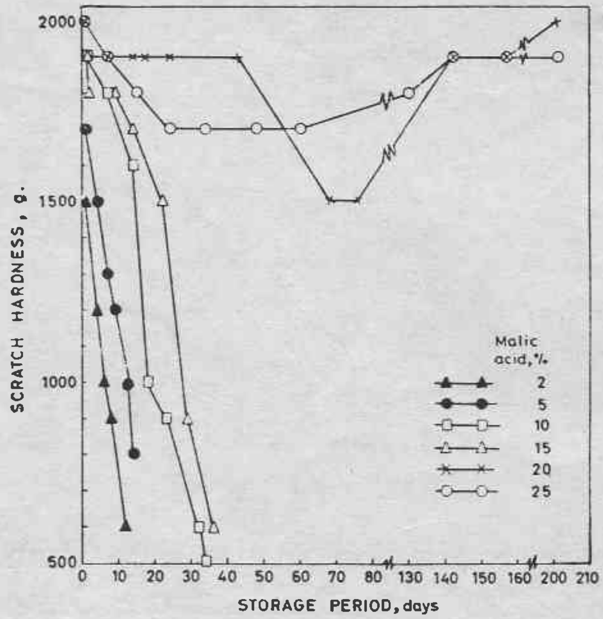

Fig. 1 — Effect of malic acid content on the scratch hardness of films from etch primers [film thickness, 1-1·3 mils]

TABLE 1 — VISCOSITIES OF PHOSPHORIC ACID-FREE SHELLAC WASH PRIMERS

(Viscosities measured in B_4 Ford cup are given in sec.)

Duration of storage days	Viscosity of sample containing		
	15% malic acid	20% malic acid	25% malic acid
Freshly made	29·0	32·5	34·0
7	29·2	32·5	34·2
15	29·6	33·0	34·5
22	30·0	33·6	34·8
30	30·6	34·0	35·2
90	31·5	34·9	35·5
180	—	36·5	37·8

Data obtained for compositions prepared without phosphoric acid are presented in Fig. 1. It is seen that although adhesion of the primers is high (1500-2000 g.) when freshly prepared, it falls off on storage in the case of samples containing 15 per cent or less malic acid. With 20-25 per cent malic acid, the adhesion remains steady up to 6 months, indicating good shelf-life. The viscosities of these primers do not also change appreciably during storage (Table 1).

Optimum composition — The optimum proportions of different constituents for obtaining a satisfactory single-pack etch primer without phosphoric acid has been found to be as follows: dewaxed shellac, 100; methylated spirit, 100; *n*-butyl alcohol, 82; malic acid, 20-25; zinc chrome, 95·00; and talc, 5·00 parts.

TABLE 2 — ADHESION CHARACTERISTICS OF PHOSPHORIC ACID-FREE WASH PRIMERS

(The primer contained 20 per cent malic acid; storage period, 6 months)

Metal panel	Dry weight of film* g.	Scratch hardness† g.
Aluminium	0·3198	2000
Copper	0·3212	2000
Brass	0·3106	2000
GI sheet	0·3256	1900
Steel	0·3542	2000

*Wt of film on 15×7·5 cm. panel.

†There was no crack on bending over a conical mandrel of min. diam. ⅛ in.

Malic acid is first dissolved in the methylated spirit into which lac is dissolved. The rest of the ingredients are then added and the mass ball milled for 8 hr.

This primer, like other shellac wash primers, is suitable for application by brush or spray.

Shelf-life — Etch primers of the above composition prepared and stored in bright plate friction-top containers exhibited no thickening, deterioration in film properties or caking of the pigment after over 6 months' storage.

The primer exhibited excellent adhesion on ferrous and non-ferrous metals (Table 2). Their adhesion to finishing coats, such as oil paints, synthetic enamels or nitrocellulose lacquers was equally good. Elasticity of the films of these etch primers is somewhat better than those of the primer using phosphoric acid.

Panels of different metals coated with this etch primer, with and without finishing coats, on exposure to natural weathering conditions, gave encouraging results.

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