Partial butyl ether/ester of shellac

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PARTIAL butyl ether/esters of shellac have been prepared by boiling under reflux dewaxed shellac (100) in n-butyl alcohol (200) with an azeotropic leg, with or without catalyst. The ether/ester (A.V. 45-50) dissolves in the usual shellac solvents and in aqueous ammonia to form clear solutions. It shows greater tolerance for aromatic hydrocarbons, esters and ketones than shellac itself and its films are more adherent and elastic both from solvent and aqueous varnishes, in both of which it behaves as an internally plasticised shellac. If the acid values are higher, the films do not have adequate elasticity and, if lower, the ether/ester does not produce clear solutions in aqueous ammonia and the films also do not become tack free.

SHELLAC alkyl esters are easily prepared from simple dervatives of shellac of very interesting properties. Unlike shellac itself, they are sticky, balsam like materials easily and completely soluble in aromatic hydrocarbons, esters and ketones and also possess a much longer life under heat which consequently make them more suitable for further modification with other chemicals by azeotropic distillation of fusion. These esters have been recommended for use as resin plasticisers in nitro-cellulose lacquers[1] and their polymerised products for incorporation with rubber[2]. By themselves, however, they are poor film formers.

The methyl[2–5] ethyl[2,4,5] n-butyl[6], amyl (fusel oil)[5,7] allyl[8] ethylene glycol[9] and [9,10] esters have been reported in literature. They have all been prepared, with the exception of the last two, using mineral acid as catalyst which is later removed by washing with water or under vacuum[6] or by treatment with calcium or barium carbonate. Elimination of the catalyst removal would obviously be an advantage.

A systematic study was therefore taken upto investigate the possibility of the preparation of shellac alkyl esters without the use of any catalyst. For this study, *n*-butyl alcohol was preferred as the alcohol because water separates easily from an azeotropic mixture and drying of the alcohol consequently poses no problem. Further, because of its higher boiling point a higher reaction temperature is also possible than with the cheaper ethyl and methyl alcohols and, consequently, more rapid esterification. In the course of these studies, a partial ether/ester of very interesting properties has been obtained. This paper describes the preparation and properties of this partial butyl ether/ester.

Preparation of the ether/ester

A solution of dewaxed shellac (100 g) in *n*-butyl alcohol (200 g) is boiled under reflux with a Dean and Stark separator, till the acid value drops to about 50 (about 20 hours). The solvent is then distilled off as much as possible and the last traces removed by heating the product in an open dish to 120°C.

Properties

The solvent free ether/ester is a tough non tacky resin with practically no odour at room temperature. It dissolves readily in the usual shellac solvents and solutions in alcohol withstand considerably more dilution with aromatic hydrocarbons, esters and ketones than a similar solution of straight shellac. It does not give a clear solution in toluene alone. A 25 per cent solution in a solvent mixture of 1 part of *n*-butyl alcohol and 2-4 parts of toluene is clear and bright and is easily brushable. The ether/ester is also soluble in aqueous ammonia and other alkalies to form clear solutions.

A typical sample with an acid value 50 had a hydroxyl value of 181, a butoxyl content of 13.81 per cent, carbonyl value of 10.20 and a molecular weight (by Rast's method) of 1082. From the above chemical constants, it can easily be calculated that 30.55 per cent of the carboxyl has been esterified and 31.69 per cent of the hydroxyl etherified which would account for 2.86 and 10.91 per cent butoxyls, respectively, thus accounting for a total of 13.77 per cent butoxyl content which is well within the limits of experimental error of the observed figure 13.81 per cent. The molecular weight of 1082 as against 950-1000 for straight shellac would indicate that the resin did not undergo any breakdown in molecular size during the treatment. The product is thus a partial ether/ester of shellac and both esterification and etherification had taken place during the treatment with the alcohol, a phenomenon already observed in the case of esterification with allyl alcohol.[11] Etherification presumably accounts for the low hydroxyl values (and solubility in aromatic hydrocarbon solvents) of fuller alkyl esters[5] reported in literature.

Varnishes of this ether/ester may be prepared either in alcohol, alcohol/toluene (2:1), *n*-butyl alcohol/toluene (1:4) or in aqueous ammonia. For use in surface coatings, the material need not also be completely freed from solvent. The solvent needs only to be distilled to leave a solution containing 66

per cent non-volatiles (similar to other commercial resins) which is easier to handle and can be diluted with alcohol or toluene or poured into aqueous ammonia to obtain clear solutions.

Film properties

Solvent and aqueous varnishes both yield clear homogenous films. The air dried films are hard, glossy and flexible but of poor water resistance. Baking of this film (at 150°C for 30 minutes) improves the water resistance also (Table I). Thus, the material is only very similar to dewaxed lac in solvent based varnishes whereas in aqueous varnishes it is distinctly superior, because of its outstanding adhesion and elasticity. This improved adhesion and elasticity of the aqueous varnishes is retained even after pigmentation, baked films being hard, elastic and water resistant. The baked films are also resistant to alcohol, acetone, ethyl acetate and toluene and remain unaffected even upto 48 hours immersion.

This ether/ester thus behaves as an internally plasticised shellac both in solvent based as well as in aqueous finishes.

Improving the water resistance

As mentioned above, this ether/ester is deficient in water resistance as far as air dried films are concerned. It has already been shown that heat and water resistance of air dried shellac films are considerably enhanced by modifying the varnish with butylated melamine/formaldehyde resin[12,13]. Similar improvement has been noticed with this ether/ester also, the optimum proportion of the melamine resin being 40 per cent on the weight of lac (Table II) similar to the case of shellac.

Alternate method of preparation

It will be noted that preparation of this ether/ester involves boiling under reflux for a period of 20 hours. As this is too long a period for practical working, the possibility of reducing it to a 8 hour schedule was investigated with the use of catalysts although this might introduce the necessity of one additional step of having to remove the catalyst. *Para*-toluene sulphonic acid was tried as this need not be removed for use in surface coatings but the product invariably gelled dur-

TABLE — I

FILM PROPERTIES OF CLEAR VARNISHES

		Film properties						
		Film air dried for 7 days			Film baked at 150°C for 30 minutes.			
Sl. No.	Varnish	Scratch hardness (gm)	Flexibility	Impact resistance	Water resistance Condition after 24 (hours) immersion	Scratch hardness (gm)	Flexibility	Impact resistance	Water resistance condition after 24 hours immersion
1.	In n-butyl-toluene	600	Passes	Passes	Bad blush	800 900	Passes	Fails	No. blush
2.	In aqueous ammonia	500	-do-	-do-	-do-	400	-do-	Passes	-do-

TABLE — II

FILM PROPERTIES OF CLEAR VARNISHES WITH DIFFERENT PROPORTION OF MELAMINE RESIN AFTER AIR DRYING FOR 7 DAYS

			Water resistance								
Sl. No.	Melamine resin taken on the weight of ether/ester (per cent.)	Gloss (per cent)	Flexibility	Initial blushing (hours)	condition blushing after 24 hrs. immersion	Time for removing the blushed surface (Hrs.)	Impact resistance	Solvent resistance in 50% diluted alcohol	Heat resistance Resistance to boiling water temp. (minutes)	Scratch hardness (gm)
1.*	0	76	Passes	2-3	Bad	—	Passes	Fails	Fails	600
2.	20	62	-do-	Over night	Blush	Less than	-do-	-do-	2	800
3.	30	65	-do-	-do-	-do-	an hour	-do-	-do-	10	800 900
4.	40	69	-do-	-do-	-do-	-do-	-do-	Passes	10	900
5.	50	42	-do-	-do-	Negligible blush	-do- -do-	-do-	Fails	5	900

* A Control i.e. partial ether/ester alone.

ing distillation of the surplus alcohol even when the catalyst used was only 0.5 per cent. Hydrochloric acid was the most satisfactory catalyst. An ether/ester of acid value in the range of 45-50 could be obtained by boiling under reflux, with a Dean and Stark separator, a solution of 100 g dewaxed lac in 200 g butyl alcohol for four hours in the presence of 2 ml of the acid, removal of the acid by boiling the reaction mixture for another one and a half hours with excess barium carbonate and filtering before distilling off surplus solvent to produce a 66 per cent solution. The ether/ester so obtained had almost the same chemical constants as the product obtained without using the catalyst and the same film properties. Therefore the ether/ester can be made by either method according to one's choice.

Optimum degree of esterification

It will be noted that by suitable adjustment of time of treatment and amount of catalyst used, ether/esters of a range of acid values can be produced. But it has been found that when the acid value is much more than 50, the films are not adequately elastic and when lower than 40, the ether/ester does not form clear solutions in aqueous ammonia and tackiness persists in the films even after prolonged baking. A product with an acid value in the range of 45 to 50 is the most suitable. The methyl or ethyl ester of this range of acid value does not serve as well.

The obvious use for this ether/ester is in aqueous finishes of the baking type, both clear as well as pigmented, where the brittleness and poor adhesion of shellac make it unsuitable. The ether/ester has also been found to be a suitable vehicle for red oxide primers for steel for application by conventional technique as well as by electrodeposition. The coatings are hard, adherent and elastic and resisted corrosion in a salt spray cabinet for two days. Studies are in progress to improve the corrosion resistance.

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