Resins from Hydroxyphenylstearic Acid[1]

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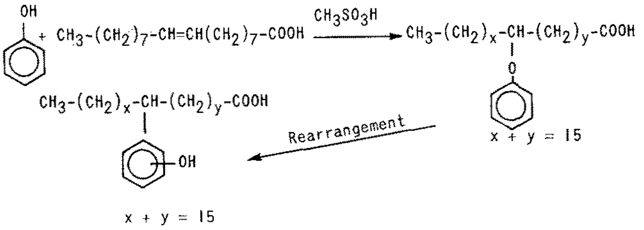
Abstract

Hydroxyphenylstearic acid, prepared by addition of phenol to oleic acid, has been condensed with excess formaldehyde using acidic and alkaline catalysts. The resulting resins have mol wt corresponding to 2–3 phenolic units and are readily soluble in alcohols. Films cast from these solutions are soft even after baking at 205C. In order to achieve greater hardness, solutions of the phenol-formaldehyde resins were coreacted with a solution of a commercial epoxy resin. Baked films cast from these systems were hard, flexible and chemically resistant.

Introduction

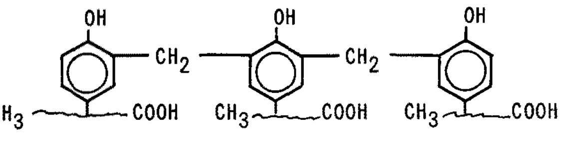
The acid-catalyzed addition of phenols to oleic acid has been studied recently in this laboratory (1–3). It was demonstrated that phenol and its derivatives could be added to oleic acid or methyl oleate in yields approximating 80% when methanesulfonic acid was used as catalyst-solvent. Thus, hydroxyphenylstearic acid is formed by the following reaction:



The reaction product can be conveniently purified by distillation of its methyl ester and subsequent saponification.

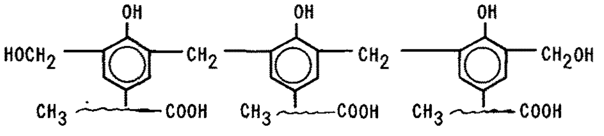
Hydroxyphenylstearic acid appeared to offer a likely source for novel phenol-formaldehyde resins containing fatty acid chains. It was expected that these resins would exhibit greater flexibility than those prepared from unsubstituted phenol. Hydroxyphenylstearic acid was reacted with formaldehyde in the presence of alkaline or acidic catalysts, and the resulting resins were tested for application as coating materials.

When an excess of phenol is condensed with formaldehyde under acid catalysis, novolac resins are usually formed. Such resins are believed to consist of phenolic nuclei connected through ortho and para positions by methylene bridges (4). A novolac resin prepared from hydroxyphenylstearic acid would be expected to have a structure resembling [1]:



[1]

On the other hand, when phenolic resins are prepared using an excess of formaldehyde and an alkaline catalyst, the resulting products, often called resoles, contain methylol end groups (5) as illustrated in structure [2].



[2]

In order to prepare resins with maximum functionality as in resoles, excess formaldehyde was used with either alkaline or acidic catalysts. The resulting condensates possessed mol wt corresponding to 2–3 phenolic units. The resins were readily soluble in alcohols, but films cast from these solutions were found to be soft even after baking at 205C.

In order to attain greater hardness in films obtained from formaldehyde condensates of hydroxyphenylstearic acid, these resins were reacted with a commercially available epoxy resin. Thus cross-linking could occur by reaction of the carboxyl and hydroxyl functions of the fat-derived resins with the epoxy and hydroxyl groups present in the epoxy resin. It was found that films prepared from such a mixture exhibited a better combination of hardness, flexibility and chemical resistance that films obtained from either component alone.

Experimental and Discussion

Starting Materials. Methyl oleate (98 + %) essentially free of polyunsaturated esters and containing not more than 1.0% saturated esters was used. Methanesulfonic acid was distilled prior to use in order to remove colored material. The phenol, formaldehyde and epoxy resins were the best commercial grades available and were used as received.

Hydroxyphenylstearic Acid. Although hydroxyphenylstearic acid can be prepared directly by acid-catalyzed addition of phenol to oleic acid, it was deemed advisable to first prepare methyl hydroxyphenylstearate which could then be purified by distillation and subsequently saponified.

The procedure used was essentially that of Ault and Eisner (1) except that a mixture of 148.3 g (0.50 mole) of methyl oleate and 188.2 g (2.0 moles) of phenol was added at room temp with stirring over a period of 1 hr to 336.2 g (3.5 moles) of methanesulfonic acid. After 6 hr additional stirring, the mixture was poured onto cracked ice and allowed to stand overnight. The organic layer was extracted with toluene, washed free of acid with 20% sodium sulfate, then with several portions of hot water to remove most of the excess phenol. After drying over magnesium sulfate, the solution was concd and the solvent-free residue distilled under reduced pressure. The portion boiling at 248–260C/2.0 mm weighed 95.5 g (48.7% yield).

It was found that methyl hydroxyphenylstearate as well as its derivatives could be analyzed by Wijs

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TABLE I

Formulation of Phenolic—Epoxy Resin Coating Material

Component	Amount	
Phenol-formaldehyde resin	1.08 g	Solution A
Solvent[a]	5.40 g	
Epoxy resin (Epoxide equiv. 1600–2000)	2.52 g	Solution B
Solvent[a]	5.40 g	
Benzyldimethylamine catalyst	0.10 ml	

[a] Solvent: 67% (wt) Butyl cellosolve; 33% (wt) Xylene.

iodine value (I.V.) as well as by conventional saponification value and hydroxyl determinations. Each mole of substituted phenol was expected to react with two moles of iodine monochloride, and this was indeed found to be the case when no contamination by unreacted phenol or oleic acid was present. I.V. (calc. for substitution by 2 iodine atoms) 65.0, found 68.1; sap. val. calc. 144.0, found 142.1.

Saponification of the distilled methyl hydroxyphenylstearate was carried out using standard procedures and a yield of 96.4% was obtained.

I.V., calc. 67.4, found 66.9; acid val., calc. 149.0, found 134.6.

Formaldehyde Resins of Hydroxyphenylstearic Acid. A) *Alkali-Catalyzed.* A mixture of 15.1 g of hydroxyphenylstearic acid (0.04 mole), 6.5 g of 37% formaldehyde (0.08 mole) and 0.032 g of sodium hydroxide (0.0008 mole) was refluxed with stirring under nitrogen. After 48 hr, the mixture was cooled, extracted with ether, and the ether extract acidified with dilute (10%) HCl. The ether was washed with water until neutral, dried over magnesium sulfate, and the solvent removed. I.V., found 55.6; % OH, found 4.77; mol wt (Rast Method), found 923.

B) *Acid-Catalyzed.* The reaction mixture described above was used, except that 0.05 g of oxalic acid dihydrate (0.0004 mole) was used as the catalyst. After 24 hr reflux, an additional 0.05 g of catalyst was added and the reaction allowed to continue a total of 48 hr. The mixture was then extracted with ether and the extracts washed with water. After drying over magnesium sulfate, the solvent was removed. I.V., found 42.6; % OH, found 4.79; mol wt (Rast Method), found 1006.

Formulation of Phenolic-Epoxy Resin Coating Material. The following conditions were found best for reaction of the new phenol-formaldehyde resins with an epoxy resin. A solution of the fat-based resin in an appropriate solvent or mixture of solvents (Solution A) was blended with a solution of the epoxy resin (epoxide equivalent 1600–2000) in the same solvent (Solution B). Since such blends had inadequate solution stability, it was found necessary to coreact the components; a catalytic amt of benzyldimethylamine was added and the mixture heated at 100C for 1 hr. The proportions of reactants and solvents are given in Table I. The phenol-formaldehyde resin comprised 30% of the total resin content, and the total solids was 25% by wt of the final mixture. This formulation was found to give optimum solution clarity and film performance. It was found that complete miscibility and clarity of solution was of utmost importance in obtaining good films.

Preparation of Test Panels. The clear solution of resin components described above was applied to 4 x 6 in. phosphate-treated steel panels using a 3-ml (wet film thickness) Bird film applicator. The panels were baked at 205C (400F) for 30 min and the properties of the resulting films were then determined.

Determination of Film Properties. Selected film properties were measured, as reported in Table II.

TABLE II

Comparison of Film Properties

Property tested	(A) Phenol-formal-dehyde resin alone	(B) Epoxy resin alone	A + B Core-acted (Table I)
Sward hardness	<20	60	50
Flexibility			
Conical mandrel (⅛ in.)	Pass	Pass	Pass
G.E. Flexibility Impact Test	Pass	Fail	Pass
Chemical resistance			
Acetone—25C, 90 days	Pass	Pass	Pass
Benzene—25C, 90 days	Pass	Pass	Pass
Sodium hydroxide—(5%) 25C, 90 days	Pass	Pass	Pass
Water (100C), 1 hr	Pass	Fail	Pass
Water (100C), 7 hr	Pass		Pass

1) Hardness was determined using the Sward rocker test, and films prepared from hydroxyphenylstearic acid resins coreacted with an epoxy resin gave values of 50 or higher, comparing favorably with those obtained from the epoxy alone. (It was noted that use of resins from the methyl esters of hydroxyphenylstearic acid led to marked softening of films, apparently because of the decreased functionality caused by the lack of free carboxylic acid groups.)

2) Flexibility was measured using the conical mandrel test with a ⅛-in. mandrel. All of the films passed this test. In an attempt to differentiate between the flexibility of the blended films and those from epoxy resins alone, a G.E. flexibility impact tester was employed. It was found that neither type of film cracked obviously or grossly when subjected to the test, and films prepared from a blend of an epoxy with the hydroxyphenylstearic acid—formaldehyde resin showed no evidence of stress even when examined under a microscope. However, films obtained from the unblended epoxy were visibly affected, becoming opaque, with fine stress lines radiating from the center of impact.

3) Films prepared from the present blends displayed excellent resistance to solvents such as acetone and benzene, being unaffected after immersion in these solvents for three months. Dilute (5%) sodium hydroxide showed little effect during a similar period of time, although a 10% solution caused marring within 30 days. Substantial improvement in resistance to boiling water was achieved by incorporation of the phenol-formaldehyde resin into the blend as illustrated by the data in Table II.

Conclusion

Protective coatings were prepared from phenol-formaldehyde resins of hydroxyphenylstearic acid coreacted with an epoxy resin. Resistance to solvents such as acetone or benzene was excellent. These coatings displayed greater flexibility than coatings from unblended epoxies as well as superior resistance to boiling water. The improvement in properties is attributable to the presence of fatty acid chains in the resulting mixture.

REFERENCES

1. Ault, W. C., and A. Eisner, JAOCS *39*, 132–3 (1962).
2. Eisner, A., T. Perlstein and W. C. Ault, *Ibid. 39*, 290–2 (1962).
3. Eisner, A., T. Perlstein and W. C. Ault, *Ibid. 40*, 594–6 (1963).
4. Martin, R. W., "The Chemistry of Phenolic Resins," John Wiley & Sons, Inc., New York, 1956, p. 99.
5. Martin, R. W., *Ibid.*, p. 88.

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