A Study of Eleostearic Acid-Containing Resins

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Abstract

A variety of polyesters, polyurethanes, and sulfonyl-polyurethanes containing eleostearic acid (ESA) have been prepared and evaluated. The film parameters under investigation usually included water absorption, tensile strength, elongation, density, permeability, and percentage of oxygen uptake.

The incorporation of ESA into polyester resin compositions results in such film properties as decreased water absorption, oxygen uptake, elongation, and permeability with a concomitant increase in tensile strength and density. Oxidative-polymerization of the polyesters containing ESA affords advantages in that their films show good tensile strength. Elongation is quite superior to that of the non-oxidatively polymerized ESA polyesters.

As a result of the advantages gained by the incorporation of ESA into polyester resins, its use (or tung oil) is recommended in these and similar resin systems.

Emphasized is the importance of employing ESA in vehicular compositions when coatings with excellent weathering resistance are required. Moreover oxidative-polymerization, a concept first introduced by C. H. Fisher, M. Zief, and R. C. Hockett, (U.S. Patent 2,594,303), is suggested for ESA-containing vehicles.

Introduction

THE IMPORTANCE OF PROTECTIVE COATINGS has continued to increase since thier inception; however the advances made in coating technology have not resulted in polymers that resist failure during long periods of exterior exposure. For some time now the compositions of alkyd resin vehicles have been altered in an effort to produce coatings which possess superior resistance to weather.

This paper will present data on the influence of chemical composition on a number of film parameters. The use of eleostearic acid (ESA), the principal fatty acid component of tung oil, is suggested. The incorporation of prescribed quantities of ESA into coating compositions has allowed advantageous alteration of various properties of a typical alkyd resin vehicle, notably water absorption, percentage of elongation, tensile strength, density, permeability, and percentage of oxygen uptake.

Perhaps the most striking and detrimental property of coatings is their tendency to absorb large quantities of water. The influence of water absorption on film failure was noted by Brown (1) and later by Brunt (2), who proposed that films absorbing less than 2% by weight of water would not be expected to fail by blistering and peeling. More recently the authors (3) have suggested solutions for the preparation of coatings, especially of the alkyd resin type, that show excellent durability as measured by accelerated weathering tests.

Experimental Procedure

All experimental operations, including weighings, were conducted in a constant temperature room at 25C and 40% relative humidity. In film preparation, the coatings were applied to gelatinized photographic paper with a constant thickness blade to give a dry-film thickness of 2 mils. After drying on the gelatin paper for 14 days, these pieces of paper and their films were soaked in distilled water until the films could be easily removed. The films were then washed carefully to ensure complete removal of any residual gelatin and dried in a constant temperature room by suspension from a wire for 6 days. (The washed films gave negative test for nitrogen.) The films were trimmed and weighed, and the weight was recorded as Weight No. 1. This weight had little significance however.

Samples of the dry films were than immersed in a large volume of water (4.0 liters) at pH's of 5, 7, and 9 for seven days in an effort to establish an equilibrium between the aqueous solution and films. These pH's were maintained by addition of a few drops of dilute acid or alkali whenever necessary to restore the solution to the chosen pH values of 5, 7, and 9. The films were then removed from the solutions, blotted between pads of tissue to remove all surface water, and weighed at once. A Sartorious balance was employed, and the time interval between removal of the films from the water and the weighing procedure was 63 ± 3 seconds. This weight is designated as Weight No. 2. The films were allowed to dry to a constant weight in the atmosphere of a constant temperature room with circulating air, at which time Weight No. 3 was obtained.

The difference between Weights No. 2 and No. 3 was calculated as the percentage gain in weight, based on the weight of the film. This value is not subject to the error on account of materials which dissolve from the film at the same time that the film is gaining weight by absorption of water. Such a process could result in obtaining negative water absorption values, as reported by Ashton (4).

The majority of the vehicles employed (Table I and II, Figures 1–7) were long oil alkyd resins of the base formula: 2 moles of mono-pentaerythritol, 2 moles of

TABLE I

Influence of Replacement of 20% of Tall Oil Fatty Acid in a 2:2:4 Alkyd by Eleostearic Acid and Stearic Acid, on Gain in Weight of Dried Film During Immersion[a]

Clear films, replacement of 20% of tall oil with	Gain in weight (g) immersed at pH = 9	% Elong.	Tensile strength kg/cm^2
Stearic acid	11.1	57	10.4
No replacement	4.7	65	36.0
Eleostearic acid	2.7	63	68.0

[a] % Lowering when eleostearic acid is incorporated = 42.5%.

TABLE II

Correlation of Water Absorption with Blister Resistance[a]

% Eleostearic acid	% Water absorption	Blister (A.S.T.M.) rating
0	11.7	5–6
5	9.8	5–6
10	5.9	9
15	5.3	9.5
20	5.2	9.5
25	4.7	10

[a] 18% PVC pentaerythritol-based alkyd: 7.14% TiO_2, 10.86% Burgess Clay. Nonoxidatively polymerized resins.

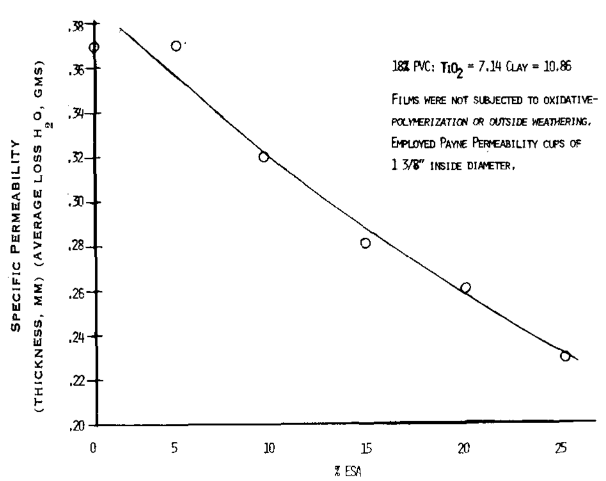

FIG. 1. Influence on permeability of increasing concentration of eleostearic acid.

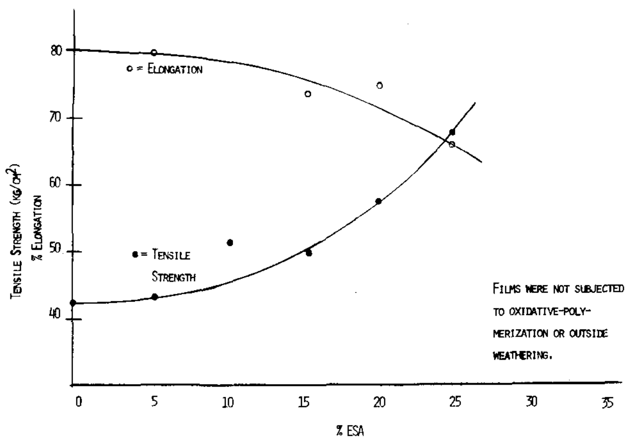

FIG. 3. Variations in tensile strength and elongation with increasing concentration of eleostearic acid.

phthalic anhydride, and 4 moles of unsaturated fatty acids.

The resins were synthesized according to the Kraft technique (5), in which all of the phthalic anhydride and a portion of the nonconjugated fatty acids were initially esterified with the pentaerythritol to an acid value of approximately 8 to 10. The remainder of the fatty acid to be employed (primarily ESA) was subsequently added, and the acid value was taken to 8 ± 2.

Preoxidation of alkyds was accomplished by blowing with air or oxygen (3). When the desired viscosity was attained, excess oxygen was removed with a nitrogen sparge and residual peroxides were destroyed with ca. 0.5% triphenyl phosphine. Polyurethanes resembling alkyds (urethane-alkyd hybrids) were prepared by substituting 2,4-toluene diisocyanate or p-isocyanatobenzenesulfonyl isocyanate for phthalic anhydride, according to the procedure described by Thames et al. (6). The p-isocyanatobenzenesulfonyl isocyanate was prepared by phosgenation of sulfanilamide in nitrobenzene, according to the procedure of Smith et al. (17). Film density was determined by the method of Clark and Tschentke (8). Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.

Discussion and Results

Data on only one conjugated acid, ESA, is reported in this paper. Other nonconjugated fatty acids or alcoholized oils were also used. Soy, safflower, and sunflower were found to be perfectly satisfactory in place of refined tall oil (rosin below 2%). Trimethylol ethane was at times employed rather than pentaerythritol, and diisocyanates were used as phthalic anhydride substitutes in a few cases. Both clear and pigmented films were studied.

An old concept is re-introduced, namely, preoxidation (oxidative-polymerization) of the alkyds by passing air through the resins at 50–70C until an appropriate viscosity is obtained, usually Z-6 to Z-7 Gardner. It should be emphasized that, subsequent to the preoxidative process, residual peroxide content must be reduced or this will result in resin instability with a tendency toward gelation.

This concept of preoxidation of the vehicle has been patented by Long and Ball, (United States Patent 2,059,259) in the 1930's. It is re-introduced at this time because of the reactivity of ESA-containing resins toward such a process. It is proposed that the presence of the acyclic conjugated triene system results in a lowering of the activation energy for free radical formation, which can by a variety of paths result in predominately resin polymerization (through the unsaturated center) rather than oxidation. It is therefore suggested that the term "oxidative-polymerization" is particularly relevant when resins so treated contain ESA. The films of polymers thus produced, subsequent to four months of weathering at 45 South, have been shown to contain less oxygen than their non-ESA-containing counterparts (Fig. 6).

The percentage of oxygen gained appears to have a correlation with water absorption; films containing low-oxygen content absorb less water and consequently show enhanced service life.

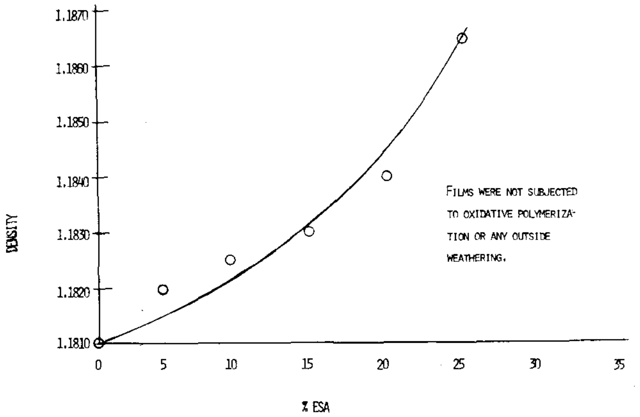

FIG. 2. Density variations with changes in eleostearic acid content.

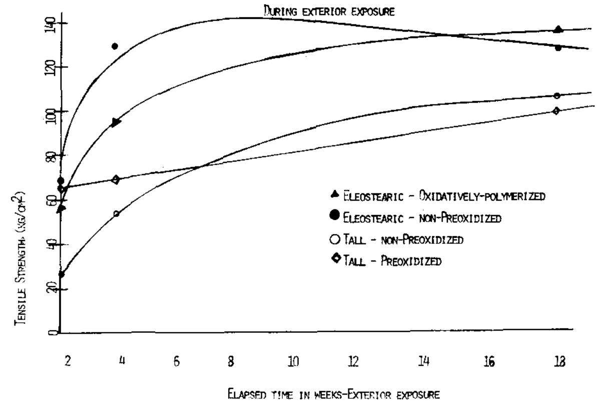

FIG. 4. Change in tensile strength of preoxidized and non-preoxidized resins during exterior exposure.

The replacement of 20% of the tall oil fatty acids (approximately 1:1 linoleic and oleic) by stearic acid resulted in films that absorbed 11.1% of water instead of 4.7% (Table I). Replacement of 20% of the tall oil by eleostearic acid lowered water absorption from 4.7 to 2.7% that is, by 42%.

The virtue of eleostearic acid chains in the polymer molecules lies in their tendency, either by heat or by oxidative-polymerization, to form polymer molecules of higher molecular weight. The resultant films from these are more dense and show lower water absorption. The films with stearic, rather than eleostearic, acid could not thus polymerize, hence were softer and less dense, absorbing a higher percentage of water.

The progressive replacement of tall oil by eleostearic acid in a 2:2:4 alkyd, pigmented at 18% PVC with nonalkaline pigments, lowered the water absorption from 11.7 to 4.7% (Table II). Resins containing more than 25% ESA did not show further significant decreases in water absorption. Thus it is suggested that, for such a resin system, further lowering of water absorption may be gained by a decrease in acid value.

The successful preparation of resins becomes progressively more difficult as higher concentrations of ESA are employed. Those resins containing 20 and particularly 25% ESA require much care to avoid gelation. The preparation of resins containing 10–15% ESA proceeds smoothly. Thus, because of the added experimental difficulties encountered with high ESA content and the relatively small H_2O absorption advantage at the higher content over that of the 10–15% ESA-containing resins, the use of 10–15% ESA is recommended.

Blister Box Test

A number of resins, the films of which exhibited either high or low gain in weight during immersion were applied to edge-grain redwood boards. Two coats, each of 2 mils dry-film thickness, were applied and dried three days between coats. Part of the final drying period was in direct sunlight on the roof of this laboratory. These panels were than tested on an Eagle Picher Blister Box by using a differential of 40C between the water in the inside and the air in the room outside. The ASTM rating system was employed (9) (Table II).

Film Density

The density of ESA-containing vehicles (Fig. 2) is greater than that of vehicles containing only tall oil fatty acids and shows, as well, a rise with increasing ESA content. Such data are consistent with those of Fig. 1, in which the specific permeability of alkyd films (18% PVC) decreases with an increase in ESA content.

Tensile Strength

The tensile strength and elongation were measured simultaneously on a Gardner-Parks film tester. The free film test samples were cut 1 cm wide and 10 cm long, and each end was taped with Scotch tape. The film thickness was measured with a Vernier caliper, and the smallest reading was recorded. The percentage of elongation was read directly from the film tester, and the tensile strength was calculated from the load in grams indicated by the spring at the moment of film rupture.

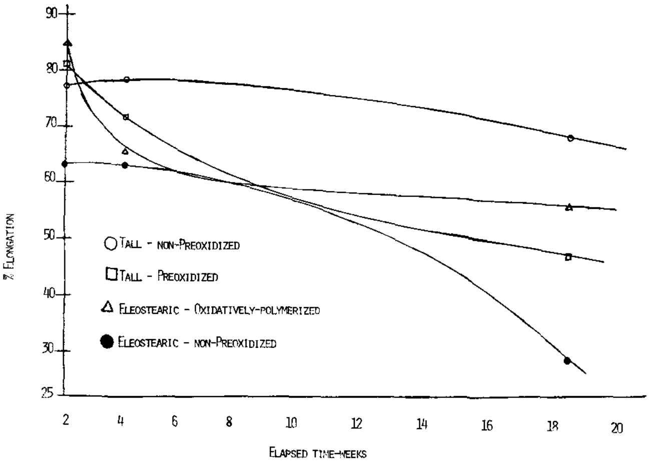

FIG. 5. Change in elongation of pre-oxidized and nonpreoxidized resins during exterior exposure.

The data for Fig. 4 and 5 were obtained as follows. Free films stripped from photographic (gelatin-coated) paper were taped with surgical tape onto boards and exposed at 45 South on the roof of the laboratory. At intervals a sheet of each composition was removed and cut into specimens 1 × 10 cm for the Gardner tester. Elemental analyses of these films were obtained (Fig. 6).

As the percentage of ESA increases, elongation decreases (Fig. 5) and ultimate tensile strength increases (Fig. 4). This would be expected if resin polymerization were occurring to a significant extent. High percentage of elongation in a film is important to permit it to follow expansions and contractions of the substrate. Thus there appears to be an optimum concentration of ESA in which a proper balance between tensile strength, elongation, and water absorption values are obtained. It is suggested that such a concentration would be 10–15% ESA or 15–20% tung oil.

The effect of exposure of preoxidized and nonpreoxidized films on tensile strength, elongation, and oxygen absorption was studied. The polymers investigated contained 2 moles of phthalic anhydride, 2 moles of pentaerythritol, and 4.0 moles of tall oil fatty acids except when ESA was present. In this event the total fatty acid content was made up of 3.2 moles of tall oil fatty acids and 0.8 moles of ESA. All films were exposed for 18 weeks at 45 South.

The tensile strength (Fig. 4) of ESA-containing resins is higher than that of the non-ESA-containing resins; both resin types show an increase with exposure time. The oxidatively-polymerized ESA resin exhibits the maximum tensile strength after 18 weeks of exposure. However elongation (Fig. 5) of these resins shows a decrease with exposure time; the most significant elongation decrease is exhibited by the non-preoxidized ESA resin.

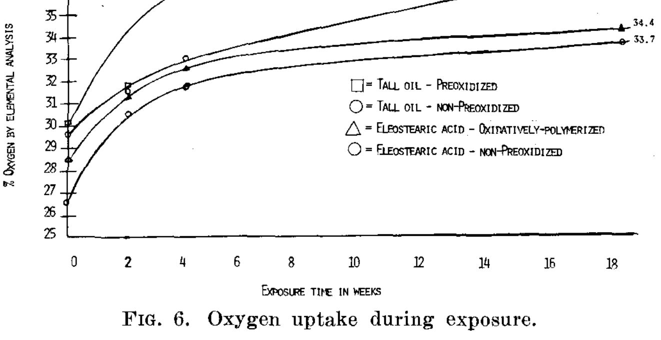

FIG. 6. Oxygen uptake during exposure.

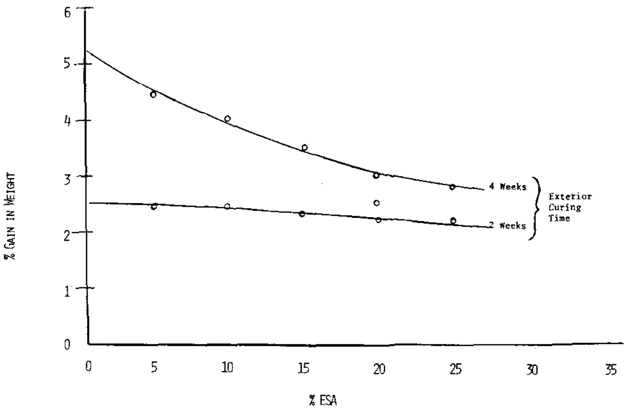

FIG. 7. Influence of eleostearic acid on the water absorption (nonpre-oxidized resins).

This can be rationalized by considering that the non-preoxidized resin, during solvent loss and film aging, is undergoing film modification owing to the polymerization and drying process. Such variations in film structure would result in strains within the film and consequently less elongation. In the case of the preoxidatively polymerized films much of the oxidation and polymerization has occurred prior to the film formation, with the result that less significant strains are encountered during film aging.

The oxygen content of ESA resins (whether oxidatively polymerized or not) is lower than that of its tall oil fatty acid counterparts (Fig. 6).

The percentage of water absorption of clear alkyd films, after four weeks of exterior exposure in addition to two weeks indoors (Fig. 7), shows that the percentage of gain in weight of the films during seven days of immersion in water decreases as the percentage of eleostearic acid increases to 25. This effect is more pronounced for the resin with the longer cure-time. This indicates a greater degree of polymerization for the ESA-containing resins. The resin cured four weeks and containing no ESA showed high water absorption. This suggests that oxidation to produce polar hydrophilic groups is occurring. In contrast, it is suggested that the ESA-containing films are polymerizing to produce impervious and water-resistant films during this stage of curing.

TABLE III

Influence of ESA on Water Absorption of Various Resins (Non-preoxidized)[a]

	Mole Equivalents		
Polyol	Difunctional cross-linking agent	Oil content	% Gain in weight
2 TME	1.5 A	2.4 TOFA; 0.6 ESA	2.50
2 TME	1.5 A	3.0 TOFA; no ESA	5.01
2 TME	1.5 B	2.4 TOFA; 0.6 ESA	6.40
2 TME	1.5 B	3.0 TOFA; no ESA	42.0
2 PE	2.0 A	3.2 TOFA; 0.8 ESA	.89
2 PE	2.0 A	4.0 TOFA; no ESA	2.00
2 PE	2.0 B	3.2 TOFA; 0.8 ESA	8.00
2 PE	2.0 B	4.0 TOFA; no ESA	9.8

[a] A = toluene diisocyanate; B = p-isocyanatobenzenesulfonyl isocyanate; TME = trimethylol ethane; PE = pentaerythritol; TOFA = tall oil fatty acids; ESA = eleostearic acid.

Although a variety of polyfunctional alcohols and difunctional cross-linking agents were employed, the use of ESA in coating compositions invariably resulted in a decrease in water absorption (Table III). The magnitude of this decrease does however appear to depend heavily on the nature of the cross-linking agent and polyol. For instance, the resin prepared from p-isocyanatobenzenesulfonyl isocyanate is highly polar and, as a result, shows 42% water absorption. The replacement of the trifunctional trimethylolethane by tetrafunctional pentaerythritol produces a water absorption decrease from 42 to 9.8%. The incorporation of ESA into the latter resin further reduces water absorption to 8.9%.

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