SYMPOSIUM: TALL OIL. PART I

conducted by The American Oil Chemists' Society
at its 55th Annual Meeting, New Orleans, Louisiana
April 19-22, 1964

J. P. KRUMBEIN, PRESIDING
H. P. DUPUY, PROGRAM CHAIRMAN

Tall Oil Acids in Some New Coatings Systems

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Abstract

Tall oil fatty acids have been used in this study in the preparation of a number of new coatings resins. Formaldehyde modified pentaerythritol-tall oil acid alkyds and urethane-alkyds are described for use where fast drying, hard films are required.

In epoxy esters, compositions based on terpene-epoxy tall oil acid ester derivatives are evaluated in comparison with bisphenol based dehydrated castor esters. Such resins find use in maintenance and marine finishes where chemical resistances are required.

Introduction

THE USE OF TALL OIL fatty acids in coatings vehicles particularly based on alkyd resins has been well accepted for several years (1,2). The adequate performance features, ready availability, and low cost have been factors in the continued use and interest on the commercial scene for the demanding protective coatings industry.

There is a constant need for the improvement of even the best coatings as new environments and performance features are encountered. It is the purpose of this paper to describe several applications for tall oil acids of low rosin content which have been developed in the program of the Heyden Div. to assist the coatings industry.

Too often the prejudices of past poor experience may limit the trial and acceptance of a potentially useful material. The use of tall oil acids in alkyd formulations has led in some cases to slow drying coatings notwithstanding some recommendations which have demonstrated easy solutions (3). Since alkyd resins represent the greatest volume in coatings vehicles, additional means of improvement should be of interest. The method used in this paper to provide the gain in performance is based on the presence of cyclic acetal modified pentaerythritol groups recently described in a U.S. patent (4). Increased rates of dry, hardness development, and alkali and detergent resistances have been demonstrated.

Proceeding to specialty type resins, using some of the "miracle" resin structures available, a number of urethane-alkyd types have been prepared in which tall oil acids contribute significantly to performance. The use of the pentaerythritol-formaldehyde structure to gain ease of preparation, stability, and high quality in combination with the high abrasion and chemical resistance of the isocyanate leakage makes an unusual combination.

Epoxy tall oil acid esters based on a terpene-phenol glycidyl ether derivative (Terpenox®) (5) have been prepared for use in highly corrosive maintenance and marine areas. The low cost of tall oil acids is matched with high performance and application ease in meeting the critical demands of service.

Experimental

Alkyd Resins. Resins were prepared by the solvent method (6) in one liter, three-necked flasks, with a thermometer, stirrer and Dean-Stark trap surmounted by a water-cooled condenser. Heating was done with an electric mantle controlled by a variable transformer.

A typical procedure was: The ingredients were charged at room temp to the flask and heated to 245C in two hr. This temp was maintained with constant

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TABLE I

Alkyd Resins

Composition				Constants			Air dry films [0.05% Co + 0.5% Pb (3 mil wet)]						
							Dry time		Sward Hardness				
Moles TOFA	Moles PA	Moles polyol[a]	Moles CH_2O	Viscosity	Solids solvent	Acid No.	Tack free	Foil dry	1 day	3 days	28 days	Denude time 70C 1% Tide ®	R.T. 3% NaOH
A) Short oil													
0.5	1.0	1.0 Glycerol	......	U	50% Xylol	8.1	4:50	8:00	10	16	28	1:20	3:
0.5	1.0	1.0 TME	..	D	50% Xylol	9.7	2:50	6:50	12	22	30	2:45	7:
0.5	1.0	1.0 PE	0.55	Z_3	50% Xylol	14.1	0:30	2:30	16	24	30	28:30	24:
B) Medium oil													
0.8	1.0	1.0 Glycerol	.....	V	50% M.S.	8.4	6:30	11:30	4	8	18	2:	6:45
0.8	1.0	1.0 PE	0.55	X	50% M.S.	15.0	5:40	8:15	12	18	24	2:30	96:
0.8	1.0	0.5 PE—0.5 Et glycol		V	50% M.S.	9.7	6:10	10:20	14	20	24	2:	8:

[a] It is not possible to prepare an unmodified PE alkyd due to the higher functionality of this polyol.

Formaldehyde was charged as paraformaldehyde.

MS = Mineral spirits.

PE = Monopentaerythritol.

Times in hr : min.

reflux until an acid number of less than 15 was obtained. The resin was cooled to 140C and diluted with the appropriate solvent.

Resins were evaluated as clear films by the previously published procedures. Paints were prepared at pigment/binder ratio of 1/1 with TiO_2.

Table I describes the formulation constants and properties of the alkyd resins prepared in the study. It is evident that resistant coatings with excellent hardness, dry times and resistances may be prepared from tall oil acids and the penaterythritol-formaldehyde structure as the polyol. Table II shows that these improvements are maintained in paint systems. The noted advantages have practical application in trade sales vehicles, metal decorating and automobile refinishing enamels.

Urethane—Alkyd Resins. The replacement of part of the difunctional acids in alkyd resins (usually a phthalic type) by a diisocyanate as toluene diisocyanate has provided attractive resistant coatings with application in clear wood finishes and floor coatings. Although there are several references to preparative methods from natural oils and from tall oil acids, these may suffer from difficulties in providing clear resins which may be readily duplicated (7–9). The use of the pentaerythritol-formaldehyde modification of the alkyd resin eliminates this problem particularly in the medium and short oil ranges providing more readily soluble precursors for the subsequent toluene diisocyanate reaction. In essence, a "partial" alkyd is formed by the reaction of phthalic, pentaerythritol, formaldehyde and tall oil acids. The product is then cooled and subsequently reacted with toluene diisocyanate.

A typical procedure was: Into a similar set-up for the alkyd preparation were charged 0.5 mole of phthalic anhydride, 1.0 moles of pentaerythritol (MonoPentek®), 0.55 moles paraformaldehyde (Acodar®) and 0.8 moles of tall oil fatty acids. The system was heated at 220C in two hr and then held at this temp until an acid number of less than three was reached. Xylol was used as the reflux solvent.

The resin was cooled to 50C and the Dean-Stark trap was replaced with an addition tube surmounted by a dropping funnel. At 50C the dropwise addition (30 min) of 0.4 moles of TDI was begun, maintaining the temp no higher than 65C. A six-fold quantity (based on TDI) of xylol is used to moderate the reaction. The temp was then increased to 85C and 0.008% by wt (on solids) of 24% lead naphthenate was added. The system was then held at 85C until constant viscosity was achieved (ca. 10 hr).

Table III describes the resins made in the study.

It may be concluded from the data presented in Table III that fast drying resistant resins can be made from isocyanate modified tall oil acid alkyd resins. For comparative viewpoint only, an alkyd resin having similar stoichiometric composition to the long oil urethane alkyd has been included. (Improved performance of the alkyd resin can be achieved by increasing the diacid content to 1.03 moles.)

It is interesting to note that the performance features of the tall oil acid urethane-alkyd (A) are similar to those of the commercial urethane-alkyd at half the analyzed isocyanate content of the latter.

TABLE II

Paint Dry Times Tall Oil Alkyd Resins

Resin	Air dry tack free	Foil dry	TiO_2 Pigment/binder = 1/1 sward hardness		
			1 day	3 days	28 days
A) Short oil					
Glycerol	0:40	6:20	14	18	38
TME	0:35	3:20	14	18	38
PE—CH_2O	0:40	0:50	22	28	38
B) Medium oil					
Glycerol	10:50	38:00	4	18	28
PE—CH_2O	3:40	10:50	10	18	36
PE—glycol	1:15	13:45	8	16	32
Commercial glycerol-soy	4:00	13:45	8	18	28

Films were cast by means of a Bird applicator at 0.003 in. wet film thickness.

Driers used were 0.05% Co (tallate) and 0.5% Pb(tallate)metal content based on resin solids.

TABLE III

Urethane-Alkyd Resins

Composition					Constants		Dry times		Air dry films sward hardness		Denude 70C 1% Tide ®	Times R.T. 3% NaOH
Moles TOFA	Moles TDI	Moles PA	Moles PE	Moles CH_2O	Viscosity	Solids solvent	Tack free	Foil dry	7 days	28 days		
A)												
0.8	0.35	0.5	1.0	0.55	J	50% Xylol	:10	1:30	40	48	120:	16:
B)												
0.8	0.40	0.5	1.0	0.55	V	50% Xylol	:08	:40	56	64	216:	624:
1.8	0.9	....	1.0	......	K	50% M.S.	:35	2:15	40	48	1:30	16:
1.8	......	0.9 (alkyd)	1.0	......	A	50% M.S.	2:30	48:	16	24	1:30	0.10
Commercial oil modified isocyanate					E	50% M.S.	0:45	1:15	60	72	120:	16:

Films were catalyzed by 0.05% Co and 0.5% Pb (as tallates) on resin solids in a 0.003 inch wet film.

TABLE IV

Epoxy Esters Based on Tall Oil Acids

Composition					Constants		Air dry properties 0.04% Co 3 mil wet					
Epoxy type	Epoxy wt	DCOFA wt	TOFA wt	IPA	Viscosity	Solids solvent	Tack free	Foil dry	Sward hardness		Denude 70C 1% Tide ®	Times R.T. 3% NaOH
									3 days	28 days		
A) Terpene-epoxy.....	66.7	16.6	16.7	....	S	50% Xylol	1:00	2:30	50	70	2100	1900
B) Terpene-epoxy.....	65.3	...	32.6	2.1	V	50% Xylol	:45	3:00	30	72	550	1680
Bisphenol	60	40	...	.	U	50% Xylol	:55	2:30	22	64	550	890

DCOFA = dehydrated castor fatty acids (Baker 9–11 type).
TOFA = low rosin tall oil fatty acids (Acodar—Newport Industries).
IPA = isophthalic acid

Epoxy Esters. In order to provide highly resistant coatings systems necessary to meet the demands of premium applications, an epoxy resin "backbone" is frequently the answer. By incorporating tall oil acids into the formulation of esters, significant cost reduction can be achieved. Our laboratory has prepared a terpene-phenol glycidyl ether derivative (5) which in its esters has shown unusual chemical resistance, solvent miscibility and resin compatibilities as compared with the common bisphenol types.

Tall oil acids have been used in two ways in this segment of work: a) as partial replacement of the more costly dehydrated castor fatty acids, and b) as the sole fatty acid component. Table IV describes the formulations, resins and properties obtained.

The procedure used in the case of the split fatty acid cook was as follows: To a similar system used in the preparation of the alkyd resins were charged 66.7 parts of "T" resin (5), 16.6 parts of dehydrated castor fatty acids, four parts of xylol to maintain reflux as the azeotrope-former. The mixture was heated to 260C in two hr and held until the acid number reached 10. The remainder of fatty acid (16.7 parts of tall oil acids) was then added and the reaction continued at 260C to an acid number less than 10. The resin was cooled to 140C and then diluted with the appropriate solvent.

It appears from the data presented in Table IV that tall oil acid based epoxy esters may be made with high performance features. Resin B described in the above table has the unique balance of properties for use as a dip coating vehicle requiring stability of the resin at application temp of 125F with rapid conversion at 400F baking temp. A vehicle of these qualities may find use in washing machine primers and topcoats, electrical equipment finishes, etc.

Conclusions

Tall oil fatty acids have been used in the preparation of new types of alkyd, urethane alkyds and epoxy esters. Fast drying durable resins are provided for use in trade sales, metal decoration, primer and topcoat applications.

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[Received May 6, 1964—Accepted August 26, 1964]

Mechanically Aided Thin-Film Evaporation as a Tool for the Tall Oil Industry

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Abstract

This article describes the thin-film evaporation process and emphasizes its values in applications where heat sensitivity, high viscosity and low thermal conductivity are important processing factors.

Processing Tall Oil

MANY PRODUCTS in the tall oil industry can be processed efficiently by thin-film evaporators since there are literally hundreds of tall oil products which are viscous, or heat sensitive, or both.

But tall oil products vary a great deal in composition. Thus, it becomes difficult to generalize on the applicability of the thin-film evaporator to these products A number of tests which have been performed illustrate, however, the applicability of thin-film evaporation in tall oil processing.

One series of tests showed that valuable materials such as tall oil fatty acids could be recovered from waste tall oil pitch by thin-film evaporation. Since the residue becomes very viscous as products are separated, distillate rates are low in this operation, averaging 5–10 lb/hr/sq ft.

Tests have also been run on tall oil products whose yield rates and maximum Gardner colors were specified. Distillation rates here varied from 15–35 lb/hr/sq ft due mainly to the less viscous nature of the material. Similarly, work has been done on a tall oil fatty acid where the object was to remove color bodies to improve Gardner color from a No. 7 to a No. 3 or No. 4. Distillation rates ranged up to 38 lb/hr/sq ft.