term "tall oil fatty acids" does not adequately describe the simple chemical nature of the material with which they are dealing. Furthermore hydrogenation of these tall oil fatty acids yields octadecanoic (stearic) acid in a high state of purity; this product and any of its derivatives should certainly be named in accordance with this. In our own work we have found "tall oil fatty acids" names to be cumbersome when applied to many derivatives, unsuitable for modern chemical indexing, and inadequate for use in technical reports.

In an attempt to systematize the nomenclature, we are showing in Table II a comparison between a) "tall oil fatty acid" nomenclature, b) names derived from trivial fatty acid names, c) names based on an adaptation of IUPAC nomenclature, and d) an alternate system based on the use of the word "octadeca(sesqui)enoic acid" to describe the tall oil fatty acid fraction. The derivation of this word may be explained as follows:

$CH_3(CH_2)_{16}COOH$	octadecanoic acid (0 double bonds)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	octadecenoic acid (1 double bond)
$CH_3(CH_2)_7CH{=}CH{-}$ $CH_2CH{=}CH(CH_2)_4COOH$	octadecadienoic acid (2 double bonds)
$R{-}(CH{=}CH)_{1.5}{-}R'{-}COOH$ (where R plus $R'{=}C_{15}$)	octadeca(sesqui)enoic acid

Octadeca(sesqui)enoic acid thus indicates an 18-carbon acid having 1.5 ethylenic double bonds. It lends itself readily to a succinct description of its derivatives, and it is shorter than any of the other systems, as can be seen from Table II.

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Monomer and Amino Resin Modified Tall Oil Fatty Acid Alkyds

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TALL OIL FATTY ACIDS have gained an increasing area of utilization in alkyd resins for surface coatings because of their low cost, high quality, and availability. The use of these materials with the newer polyols, such as trimethylolethane, has resulted in advantages in compatibility and resistance qualities over the more conventional resins. The High Polymer Alkyd Technique (1) has also contributed to the utilization of these acids, minimizing their previously experienced limitation of slower dry.

In general, the modification of alkyd resins for use in air drying and baking systems has extended the utility of these materials. Thus urea and melamine formaldehyde resins have been combined with medium and short oil alkyds for several decades to provide materials showing desirable color and gloss retention, chemical resistance, and improved durability in a variety of applications. More recently, alkyd resins have also been modified with vinyl monomers to result in compositions which have been termed copolymer or, in certain quarters, mixed polymer vehicles (2). Monomers of interest have included styrene, vinyltoluene, and methyl methacrylate. Through their use alkyd resins have led to vehicles showing light color, fast dry, good adhesion to metals, and resistance to water and chemicals.

The purpose of this paper is to describe the results of investigations of the use of tall oil fatty acids in medium and short oil resins based on trimethylolethane, prepared by a conventional and the High Polymer Technique. In turn, some of these systems were treated with styrene and methyl methacrylate monomers [1] or else mixed with urea formaldehyde or melamine formaldehyde resins.

Experimental Preparation and Evaluation Results

I. *Alkyd Resin Preparations.* All resins were prepared by the solvent (3) process in one liter, three-necked flasks with a thermometer, stirrer, and Dean Stark trap, surmounted by a water-cooled condenser attached. Heating was done with an electrical mantle connected to a variable transformer.

1. *High Polymer Technique. Medium alkyd—Molar ratio PA/TME/FA—1/1/0.7 (70% initial esterification level)* (4). To the flask were charged 222 g. (1.50 moles) of pthalic anhydride, 181 g. (1.50 moles) of trimethylolethane, 210 g. (0.73 moles) of low-rosin-content tall oil fatty acids, and 25 g. of xylol as azeotrope-former. The system was heated with stirring over a 2-hr. period to 245°C. and held for an acid number of 10.

An additional portion of tall oil fatty acids, 90 g. (0.31 moles), was introduced to the flask below the surface of the resin, and the system was again brought to 245°C. and maintained at this temperature until an acid number of 10 was reached. The resin was cooled to 140°C. and diluted to 50% nonvolatile content with xylol. The viscosity (Gardner Holdt) of the resin solution was B+. The viscosity-solids reaction for the various alkyds used in the study are summarized in Figure 1.

% Initial esterification	Gardner viscosity 50% NV in xylol	Acid number (on solids)
Medium oil (mole ratio = 1/1/.7 = PA/TME/FA)		
100	A	8.3
70	B+	10.0
50	A+	10.1
Short oil (mole ratio = 1/1/.42)		
100	U	9.7
70	V+	8.3
60	Z_3	7.7

FIG. 1. Tall oil fatty acid alkyds.

2. *Conventional Procedure Alkyd.* The conventional alkyd preparation, shown as the 100% initial esterification type in Figure 1, involved similar equipment and procedures except that all of the fatty acid was added at the beginning of the reaction.

II. *Monomer Modification (Styrene and Methyl Methacrylate).* Two hundred grams of the alkyd solution (50% nonvolatile) were charged to a one-

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[1] A previous paper by one of the authors (WMK) described the advantages of using trimethylolethane in monomer modified alkyd resins—ACS Division of Paint, Plastics, and Printing Ink Chem. Preprint Book, September, 1954.

TABLE I
Monomer Modification of Tall Oil Fatty Acid Alkyds
Molar Ratio PA/Polyol/FA = 1/1/0.7
Monomer Alkyd 1/1

Alkyd resin % initial esterification	Modifying monomer	Viscosity at 50% in xylol	Dry times			Sward hardness	Mar R.	Flexible ⅛ in. mandrel
			Set to touch	Kleenex tack-free	Aluminum foil dry			
100 (Conventional)	Styrene	W	:05	:08	:31	18	Fair	Slight cracking
70	Styrene	Z_1	:04	:07	:28	18	Very good	Pass
50	Styrene	Z_2	:04	:05	:25	22	Good	Pass
100 (Conventional)	Methyl methacrylate	U	:05	:07	:22	20	Good	Slight cracking
70	Methyl methacrylate	Z_2	:04	:05	:16	26	Very good	Pass
50	Methyl methacrylate	Z	:04	:05	:12	16	Very good	Pass

liter flask with a thermometer, addition funnel, stirrer, and reflux condenser attached. The system was heated to 140°C., and over a 3-hr. period a solution of 2.5 g. of ditertiary butyl peroxide in 100 g. of styrene was added. The heating was continued to the reflux temperature (160°C.) and maintained for 3 hrs. after the addition had been completed. The resin was cooled and diluted to 50% nonvolatile content with xylol.

The modification with methyl methacrylate was performed in a similar manner but at 130°C. to avoid loss of monomer.

In each case the unreacted monomer was less than 2%, based on the amount initially charged. (This could be further minimized by a longer reaction cycle with an additional portion of peroxide catalyst).

III. Amino Resin Modification. The alkyds prepared in Section I were cold-mixed with sufficient solutions of urea formaldehyde resin (Uformite F200E, Rohm and Haas) or melamine formaldehyde resin (Cymel 248-8, American Cyanamid) to result in levels of 10, 20, and 30% of amino resin based on the total solids of the system. Film property evaluations were made by the usual techniques.

Results

Table I summarizes the data regarding monomer modification of the medium type of alkyds. The drying properties show a trend to faster times for the High Polymer alkyds. Specific improvements are noted in both flexibility and mar resistances in which the conventional preparative approaches have frequently given less than satisfactory results.

These improvements are not unexpected in terms of the experience gained in other areas of application for High Polymer alkyds. Better flexibilities have generally been obtained, possibly as the result of a more "linear" structure in the resin.

TABLE II
Short Alkyd Resins (Mole Ratio PA/Polyol/FA = 1/1/0.42)
Modified with Urea Formaldehyde Resin

Alkyd resin % initial esterification	Amino resin content	Sward hardness	Rating[1] after 16 hr., 205°C.	Hot water[2]	Resistance	
					3% NaOH R.T. initial attack[3]	1% Tide 70°C. denude
	%				*hr.*	*hr.*
100 (Conventional)	10	42	4	SO	93	186
	20	44	4	SO	200	105
	30	36	4	SL	309	186
70	10	32	4	SL	141	98
	20	38	4	SO	240	186
	30	30	4	SO	300	98
60	10	48	3	SL	165	>2000
	20	50	3	SL	310	1400
	30	52	3	SL	310	1280

[1] Ratings in the heat resistance test were: 0 = no effect, 1 = slight, 2 = somewhat, 3 = considerable, 4 = extensive darkening.
[2] Water resistance: SL = slight, SO = somewhat.
[3] Denude times in the caustic resistance test were >2000 hrs.

TABLE III
Short Alkyd Resins—Modified with Melamine Formaldehyde Resin

Alkyd resin % initial esterification	Amino resin content	Sward hardness	Rating after 16 hr., 205°C.	Hot water	Resistance	
					3% NaOH R.T. initial attack	1% Tide 70°C. denude
	%				*hr.*	*hr.*
100 (Conventional)	10	42	3	SL	309	168
	20	54	3	SL	309	480
	30	56	3	SL	309	624
70	10	44	3	SL	141	186
	20	58	3	SL	333	800
	30	54	3	V. SL	333	1400
60	10	56	2	SO	>2000	>2000
	20	62	2	SL	>2000	>2000
	30	72	2	SL	>2000	>2000

A more extensive study was made of the effects of different levels of initial esterification for the High Polymer Alkyd Technique in the amino resin combinations. The purpose of this was to determine the possible existence of an optimum level.

Table II describes the combinations made with a commercial urea formaldehyde resin. It is apparent from the data that the short type of resins made by the High Polymer Technique at the 60% initial esterification have greater hardness, better resistance to extended periods at high temperature, and better resistance to chemical attack.

Particular advantage of the better heat resistance might be made in furniture finishes. To test this premise, an alkyd-urea resin (80–20) system was baked for 15 min. at 250°F. with 0.5% butyl phosphoric acid. The coating when made with the 60% initial esterification High Polymer alkyd had better burning-cigarette-scorch-resistance than did the modified conventional resin.

Table III deals with the same alkyds but modified with a commercial melamine formaldehyde resin. Similar observations are made as noted previously for Table II.

Summary

Monomer modified tall oil fatty acid trimethylolethane medium type of phthalic alkyds made by the High Polymer Alkyd Technique show improved properties in dry time, mar resistance, and flexibility as compared with monomer modified conventional prepared systems.

Greater hardness, less color degradation, greater resistance to extended periods at high temperature, and alkali and detergent resistances result from the urea and melamine resin modifications of tall oil fatty acid High Polymer alkyds than is obtained with similarly modified conventional alkyds.

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Tall Oil Fatty Acid Mixtures as a New Approach to Quality Alkyds

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THE HIGH QUALITY and low cost of fractionated tall oil fatty acids of low rosin content together with their favorable availability have captured the interest of alkyd and paint chemists. The historic, slower-drying characteristics of the tall oil acids have been overcome to a large extent by the High Polymer Technique (1). The door is therefore open to wider utilization of the tall oil fatty acids alone or in conjunction with the spectrum of oils and fatty acids used in alkyd resin production.

This paper deals with alkyds containing tall oil fatty acids admixed with varying proportions of soya fatty acids and soya oil as well as with linseed fatty acids and linseed oil both by conventional and High Polymer procedures and offers comparison of properties of the vehicles prepared.

Experimental

Since long oil alkyds comprise such a large proportion of the current resin production for trade sales paints, this type of alkyd was selected as the basis of our study. As a method of formulation of a representative resin, the molar approach to alkyd structure (2) was applied to a 23% phthalic alkyd and a mol ratio of 1.035/1/1.41 (phthalic anhydride/technical pentaerythritol/fatty acid) was evolved. Because the contribution of the fatty acid portion was our main interest, various combinations were made with tall oil fatty acids and soy or linseed fatty acids.

The High Polymer Alkyd Technique was used in addition to the conventional methods of alkyd preparation to determine the extent of improvement in properties in those combinations studied. Solvent processing (3) was used in the resin preparations to take advantage of its greater reproducibility and minimum losses.

To prepare a High Polymer alkyd having the 1.035/1/1.41 formulation and 70% initial esterification, in which the ratio of soya fatty acids to tall oil fatty acids was 75/25, the following formulation and procedure were used.

To a three-necked, 3-liter, round-bottomed flask with thermometer, stirrer, and a Dean-Stark trap surmounted by a water condenser attached, were added 365 g. (1.26 moles) of soya fatty acids, 121 g. (0.42 mole) of tall oil fatty acids,[1] 246 g. (1.70 moles) of technical pentaerythritol, and 261 g. (1.76 moles) of phthalic anhydride.

The system was heated to 210°C. with sufficient agitation and xylol for reflux. The temperature was held at 210°C. until an acid number of 10 was achieved. Then 156 g. (0.54 mole) of soya fatty acids and 51 g. (0.18 mole) of tall oil fatty acids were added.

The temperature was raised again to 245°C. and held at this temperature until an acid number of *ca.* 8 was reached. After cooling to 160°C., the system was diluted to 50% nonvolatile in mineral spirits. The conventional method of cooking this alkyd was to charge all the materials, heat to 245°C. with agitation and xylol for reflux, and hold at 245°C. until an acid number of *ca.* 8 was reached.

To prepare the soybean oil-tall oil fatty acid alkyds by the High Polymer Alkyd Technique in which the ratio of soya fatty acids to tall oil fatty acids was also 75/25, 25% of the oil was withheld and replaced with glycerol or pentaerythritol and tall oil fatty acids. Thus the formulation and procedure were as follows.

To a three-necked, 3-liter, round-bottomed flask with thermometer, stirrer, and inert gas inlet tube attached were added 620 g. (0.70 mole) of alkali-refined soybean oil, 188 g. (1.30 moles) of pentaerythritol, and 0.0620 g. of litharge.

The system was heated to 230°C. with adequate agitation and a CO_2 blanket and was held at this temperature until a methanol solubility of 2½ parts of methanol to 1 part of alcoholysate was achieved. The system was then changed to a solvent type of cook. Next 306 g. (2.07 moles) of phthalic anhydride were added, and the system was esterified at 210°C. with xylol reflux until an acid number of 10 was achieved. Then

TABLE I
Soya Fatty Acid-Tall Oil Fatty Acid Alkyds Conventional Preparation *vs.* High Polymer Technique

Soya/tall ratio	Method	Color @ 50 M	Viscosity @ 50 M	Acid No. (solids)	Drying times			Sward hardness			
					Set to touch hr.: min.	Tack-free hr.: min.	Foil-dry hr.: min.	days			
								1	7	14	28
100/0	Conv.	5+	A	7.3	2:01	4:15	9:00	10	24	26	38
100/0	HPT	5−	G	7.4	2:56	4:56	7:00	8	20	24	30
75/25	Conv.	5+	A	7.5	3:29	5:30	9:30	8	24	24	32
75/25	HPT	5	I	7.0	2:48	4:03	8:40	10	20	34	40
50/50	Conv.	5+	A	8.0	3:27	5:57	12–15	10	18	20	26
50/50	HPT	5–6	F	8.0	2:47	4:17	9:17	10	22	22	30
25/75	Conv.	5+	A	7.5	3:25	6:05	12–15	8	20	22	30
25/75	HPT	5	G	8.2	2:46	4:46	10:00	8	20	20	32
0/100	Conv.	5+	A	8.1	3:23	6:07	12–15	8	18	20	32
0/100	HPT	5	H	7.6	2:54	4:54	9:30	8	16	16	22

Notes. 1. Cold- and hot-water resistances of all films in the same range.
2. 1% Tide resistance (167°F.) of all films in the same range (1–2 hr.).
3. 3% NaOH resistance (RT) of all films in the same range (2–4 hr.).

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[1] Aconew Extra tall oil fatty acids from Newport Industries.