REFERENCES

1. Kraft, W. M., Roberts, G. T., Janusz, E. G., and Weisfeld, J., Am. Paint J., *41*, No. 28, 96 (March 25, 1957).
2. Heavers, M. J., Paint Manufacture, *28*, No. 1, 5 (January 1958) and *28*, No. 2, 48 (February 1958).
3. Earhart, K. A., and Rabin, B., U. S. Patent 2,308,498.
4. Kraft, W. M., Official Digest, *29*, No. 391, 780 (August 1957).

[Received July 1, 1958]

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

GEORGE T. ROBERTS, WILLIAM M. KRAFT, DONALD A. STAFF, and PETER BELSKY,
Heyden Newport Chemical Corporation, Research Division, Garfield, New Jersey

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.).

---

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

TABLE II

Linseed Fatty Acid-Tall Oil Fatty Acid Alkyds Conventional Preparation *vs.* High Polymer Technique

Linseed/tall ratio	Method	Color @ 50 M	Viscosity @ 50 M	Acid No. (solids)	Dry times			Sward hardness days				3% NaOH (RT) Time to denude hr.:min.
					Set to touch hr.: min.	Tack-free hr.: min.	Foil-dry hr.: min.	1	7	14	28	
100/0	Conv.	6—	C	7.6	1:36	2:36	4:36	8	28	42	60	6:00
	HPT	7	P	12.4	1:23	1:58	4:00	12	28	36	50	8:30
75/25	Conv.	6—	C	8.2	1:34	2:34	5:04	10	36	34	48	2:45
	HPT	6	J	14.2	1:17	2:07	4:30	12	34	32	40	8:00
50/50	Conv.	5+	B	8.6	2:52	3:32	8:47	8	24	28	38	2:00
	HPT	6	M	7.5	1:35	3:20	5:05	12	30	32	42	7:30
25/75	Conv.	5+	B	7.6	3:00	3:45	10:00	10	20	28	40	2:30
	HPT	5	G	7.6	2:48	4:04	8:34	10	26	32	40	2:30
0/100	Conv.	5+	A	8.1	3:23	6:07	12–15	8	18	20	32	2:30
	HPT	5	H	7.6	2:54	4:54	9:30	8	16	16	22	3:15

Note: Cold- and hot-water resistance of all films in the same range.

202 g. (0.70 mole) of tall oil fatty acids were added and esterified at 245°C. until an acid number of *ca.* 8 was attained. After cooling, the system was diluted to 50% solids in mineral spirits.

The conventional method of cooking the all-soybean alkyd was to alcoholyze the oil and pentaerythritol, add the phthalic, and esterify until an acid number of *ca.* 8 was attained.

The soya type of fatty acids-tall oil fatty acids mixtures were made by both the conventional and High Polymer Technique in the following ratios: 100/0, 75/25, 50/50, 25/75, 0/100. The air-dried film data for these resins are presented in Table I. The data on the oil and oil:fatty acid mixtures are not presented because they do not lend themselves to comparison in a homologous series. They are described later.

The results of Table I indicate the advantages of High Polymer Technique in reducing dry times and resin color as well as in increasing viscosity. It is interesting to note that a 75/25 soya/tall ratio High Polymer Technique produces a slightly faster drying and equal-hardness film as compared with a 100% soy acid conventional resin. Table I also shows that alkyds based on mixtures of the two acids may in some cases give harder films than those based on each acid alone. The reason for this behavior is obscure at present.

Although the viscosity of comparable systems is not identical, work independent of the paper indicates that, even where these are made equal, the dry times of the conventional systems are longer than those based on the High Polymer Technique. Equal viscosities were generally achieved in such studies by processing the conventional alkyd to a lower acid number.

Table II describes the results of the study made with linseed fatty acids by using the same type of formulations previously described for the soybean series. Dry times increase markedly in these conventional alkyds beyond the 75/25 linseed/tall ratio. Caustic resistances and hardness of film show similar variations.

Table II indicates again the value of the High Polymer Technique. Mixtures of 75/25 and 50/50 linseed/tall show properties which are superior or equal to those of linseed fatty acid conventional alkyds.

Table III presents information on systems derived from linseed oil and soybean oil. When the High Polymer Technique is applied to oils, the amount of oil withheld is replaced by its molecular equivalent of fatty acid and polyol. In the preparation the main portion of the oil and the normal amount of polyol used in the alcoholysis is combined with the equivalent amount of polyol. After alcoholysis the phthalic anhydride is added; the resin is cooked to low acid number; the remainder of fatty acid is added and again processed to a resin of low acid number. The linseed oil data indicate that pentaerythritol is a

TABLE III

Oil-Fatty Acids Alkyds—Conventional *vs.* High Polymer

Modification	Color @ 50 M	Viscosity @ 50 M	Acid No. (solids)	Dry times			Sward hardness				1% Tide (167°F.) Time to denude hr.:min.	3% NaOH (RT) Time to denude hr.:min.
							Days					
				Set to touch hr.:min.	Tack-free hr.:min.	Foil-dry hr.:min.	1	7	14	28		
Linseed oil (conventional)	5	F	8.0	1:30	3:15	5:15	8	14	32	48	4:30	9:00
HPT [a] Linseed oil and tall oil fatty acids 75/25	5	E	8.5	1:34	3:30	5:30	10	28	36	48	3:00	7:45
HPT [b] Linseed oil and tall oil fatty acids 75/25	5	A	8.0	1:58	5:00	10:13	10	22	22	32	1:00	3:30
Soybean oil (conventional)	5	A	8.8	2:42	4:42	10:28	10	18	18	22	All films denuded in 1½–2 hr.	All films denuded in 1½–3 hr.
HPT [a] Soybean oil and tall oil fatty acids 75/25	4	B	8.6	2:41	4:41	9:40	10	20	20	30	All films denuded in 1½–2 hr.	All films denuded in 1½–3 hr.
HPT [b] Soybean oil and tall oil fatty acids 75/25	5	A	8.0	5:31	8:25	24–30	6	12	12	16	All films denuded in 1½–2 hr.	All films denuded in 1½–3 hr.

[a] PE reconstituted. [b] Glycerol reconstituted.

Notes: Cold- and hot-water resistance of all films in the same range.

better choice for dry time, hardness, and resistances than glycerol in this application.

From the soybean oil data it appears that the High Polymer Technique with pentaerythritol gives better dry times and hardness than the usual preparations.

Conclusions

Tall oil fatty acids may replace up to 50% of linseed or soya fatty acids, using the High Polymer Alkyd Technique, to obtain similar dry rates and resistances of conventional all-linseed or soy long-oil vehicles. Tall oil fatty acids also can be substituted for 25% of either linseed or soya fatty acids without adverse effects on the drying rates of conventionally prepared long-oil alkyds.

Tall oil fatty acids likewise may be used in conjunction with the alcoholysis type of alkyds by the use of the High Polymer Technique. These vehicles show properties similar to conventional resins prepared from linseed oil and improvements over resins based on soybean oil.

REFERENCES

1. Kraft, W. M., Roberts, G. T., Janusz, E. G., and Weisfeld, J., American Paint Journal, *41*, No. 28, 96–120 (March 25, 1957).
2. Kraft, W. M., Official Digest, *29*, No. 391, 780 (August 1957).
3. Earhart, K. A., and Rabin, B., to Devoe and Raynolds, U. S. Patent 2,308,498 (January 19, 1943).

[Received April 22, 1958]

The Fractionation of Lanolin With Urea [1]

ABNER EISNER, WILFRED R. NOBLE, and JOHN T. SCANLAN,
Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

WOOL WAX, the secretion product of the sebaceous glands of the sheep, is a complex mixture of high molecular weight esters. A large number of acids and alcohols have been isolated (10, 2, 6, 3) from the saponification products of wool wax. Some of the alcohols are dihydric, and some of the acids are hydroxy acids. Consequently the possible number of ester and diester combinations is very large. However it has been demonstrated that many of the components of both alcohol fraction and the acid fraction form urea adducts (7, 8). Some of the esters present should also possess the necessary requirements to form adducts with urea, but statements that wool grease does not form an adduct with urea have appeared in the literature (9).

In the course of an investigation of the transesterification of lanolin with methyl acetate, the formation of urea adducts was used as a measure of the extent of the transesterification reaction. As a check on the validity of this procedure, a blank run was made on the original lanolin. It was found that by applying the method for making urea adducts to lanolin, a urea adduct can be made. The fraction forming the complex is about 6–8% of the original lanolin. In addition to the hard, nontacky wax fraction recovered from the separated urea complex, a fluid fraction and a sticky semisolid were also obtained. The latter two fractions were obtained by the solvent extraction of the nonadduct-forming material from urea adducts.

The fluid fraction, a viscous liquid at room temperature, amounts to about 71% of the original lanolin. The properties of this fraction indicate that it may have considerable practical utility. Its analysis shows it to be practically of the same composition as lanolin. This and the ease with which it can be handled make it potentially valuable for use in formulations in place of ordinary lanolin. Furthermore it has better solubility than unmodified lanolin. At 25°C. a 10% solution of the fluid fraction in mineral oil remains clear while a similar solution made from ordinary lanolin is cloudy. As in the case of lanolin, a further improvement in the fluid properties of the fraction can be obtained by acetylation (1).

In the production of the complexes, *i.e.*, when lanolin was treated with urea and methanol, the solution of any one component in any other was only partial, and the result was a physical mixture in the form of a stiff paste. In order to separate the complexes from the portion of lanolin which does not form a complex, it was necessary to extract the latter with a solvent. Ether was used because the solubility of urea in ether is slight; consequently the possibility of destroying the complexes during the extraction is lessened. The bulk of the extraction was carried out by slurrying the mixture with cold ether and filtering. The filter cake was washed several times with cold ether. The batch-extraction did not remove all the noncomplex-forming material. Some of the nonadduct-forming material clung tenaciously to the complexes but could be recovered by extraction with ether in a Soxhlet apparatus. The three fractions thus obtained differ markedly in appearance. The noncomplex fraction most easily removed from the adducts was a viscous liquid. The second noncomplex fraction was a sticky semi-solid. The complex-forming fraction was a hard, white wax.

Experimental

Five hundred grams of U.S.P. lanolin were mixed with 1,500 ml. of methanol and 480 g. of urea while being heated on the steam bath. Heating was continued until sufficient methanol had boiled off to leave the mixture as a stiff paste. The mixture was then removed from the source of heat and stirred vigorously, using a mechanical stirrer, for 45 min. At the end of the stirring period the mixture was cooled to 2°C. and kept at this temperature over-night. Sufficient ether was added to form a thin slurry, and the resulting mixture was filtered. The material on the filter was washed with more cold ether. The ethereal filtrate and washings were combined, extracted with dilute HCl to remove any urea, and water-washed until neutral. The ether was then removed by distillation. The residue was a fluid product (Fraction I) amounting to 71% of the original lanolin. The filter cake was extracted with ether in a Soxhlet apparatus for 24 hr. The ether extract worked up in a manner similar to that described above, yielded a sticky, semi-solid material (Fraction

---

[1] Presented at the Fall Meeting, American Oil Chemists' Society, Chicago, Ill., October 20–22, 1958.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.