Synthetic Oils From Residual Dimerized Fat Acids

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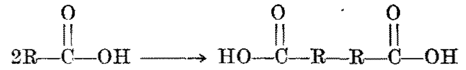
Surface coatings, i.e., paints and varnishes, prepared from semi-drying oils such as corn, cottonseed, or soybean, are generally inferior to coatings prepared from drying oils such as tung, linseed, or dehydrated castor. One major factor responsible for this difference is the high proportion of "non-drying" constituents present in the semi-drying oils. For example, each of these oils contains appreciable quantities of saturated and mono-unsaturated acids such as palmitic, stearic, and oleic.

The coatings prepared from unmodified semi-drying oils are much slower to dry, becoming tack-free only after long periods of time. They are softer and less resistant than coatings made from "drying" oils. By suitable modification of the semi-drying oils, it is possible to obtain coatings either equal to or superior to coatings made from linseed oil. Although several different modifications of semi-drying oils enhance their properties, our discussion will be limited to one method of modification, namely, polymerization of the fat acid constituents of the oil to form dimeric and trimeric acids, the removal from the polymerization mixture of the unpolymerized fraction, and the subsequent synthesis of the glycerol, pentaerythritol, or other esters of the polymerized acids. This method has received some attention by Hill and Walker (6) and Voorheen Noury (7). Their work was directed toward the improvement of linseed oil, which is a drying oil, rather than corn or soybean oils, which are semi-drying. As a part of a general program designed to increase the industrial utilization of certain semi-drying vegetable oils normally produced in excess in this country, the Oil and Protein Division of the Northern Regional Research Laboratory initiated a study of synthetic oils prepared from residual dimerized fat acids (2).

The enhancement of the properties obtained by this method is primarily obtained by the formation of dimeric and trimeric acids from the fat acids and their separation from the unpolymerized fat acids. The unpolymerized fat acids contain most of the non-drying fraction of the oil, and consequently their separation constitutes an actual removal of the non-drying from the drying constituents. The residue, i.e., the drying constituent, now differs from its original form. It contains dimeric and trimeric fat acids (3) which were formed from linoleic and linolenic acids. The mechanism of the formation of these acids is not known, but it can be represented graphically (see Equations A and B).

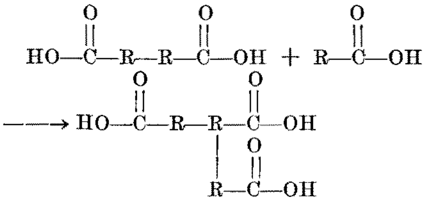
Equation A:



$$2R-\overset{\overset{O}{\|}}{C}-OH \longrightarrow HO-\overset{\overset{O}{\|}}{C}-R-R-\overset{\overset{O}{\|}}{C}-OH$$

Linoleic acid   Dimeric fat acid I

Equation B:



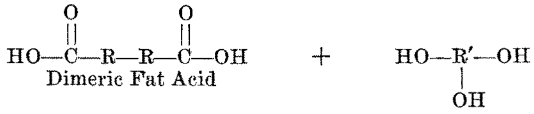
$$HO-\overset{\overset{O}{\|}}{C}-R-R-\overset{\overset{O}{\|}}{C}-OH + R-\overset{\overset{O}{\|}}{C}-OH \longrightarrow HO-\overset{\overset{O}{\|}}{C}-R-\underset{\underset{R-\overset{\overset{O}{\|}}{C}-OH}{|}}{R}-\overset{\overset{O}{\|}}{C}-OH$$

Trimeric fat acid II

As shown in the equations, these acids may be considered to be a dibasic fat acid, having a molecular weight of 560, and a tribasic fat acid having a molecular weight of 840.

Experimental details of the polymerization of methyl esters of fat acids from a number of different oils and the separation of the polymerized from the non-polymerized fraction have been described by Bradley and Johnston (2). Unpublished work (5) at the Northern Regional Research Laboratory has shown that the dimerized fat acids obtained from polymerized corn, cottonseed, soybean, and dehydrated castor oil are very similar, if not identical. This similarity also persists in the trimerized fat acids.[2]

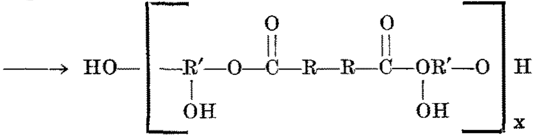
Synthetic oils were prepared from the residual dimerized fat acids with polyalcohols in conjunction with soybean and linseed fat acids. The synthesis was effected in a manner similar to that used in the preparation of alkyd resins. Equations C and D give a graphical representation of how the preparation of the oils was effected.



$$HO-\overset{\overset{O}{\|}}{C}-R-R-\overset{\overset{O}{\|}}{C}-OH + HO-\underset{\underset{OH}{|}}{R'}-OH$$

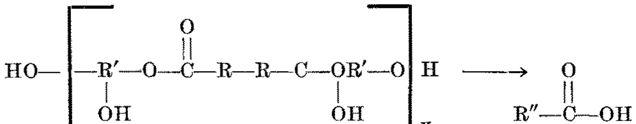
Dimeric Fat Acid   Polyalcohol

Equation C:



$$\longrightarrow HO-\left[-\underset{\underset{OH}{|}}{R'}-O-\overset{\overset{O}{\|}}{C}-R-R-\overset{\overset{O}{\|}}{C}-O\underset{\underset{OH}{|}}{R'}-O\right]_x H$$

Polymeric Ester III



$$HO-\left[-\underset{\underset{OH}{|}}{R'}-O-\overset{\overset{O}{\|}}{C}-R-R-C-O\underset{\underset{OH}{|}}{R'}-O\right]_x H \longrightarrow R''-\overset{\overset{O}{\|}}{C}-OH$$

Fat Acid

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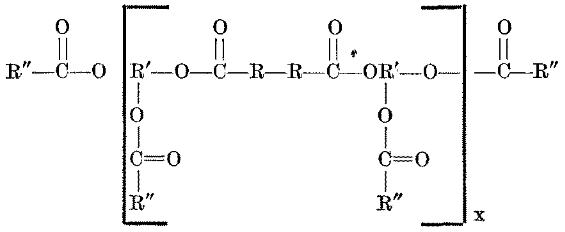
[1] The Northern Regional Research Laboratory is one of four Regional Laboratories authorized by Congress in the Agricultural Research Act of 1938 for the purpose of conducting research to develop new uses and outlets for agricultural commodities. These Laboratories are administered and operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Residual dimerized fat acids from soybean oil are somewhat different, since soybean oil contains a small amount of linolenic acid which gives different polymerized products than linoleic acid.

Equation D:



$$R''-\overset{O}{\overset{\|}{C}}-O\left[\begin{array}{c}R'-O-\overset{O}{\overset{\|}{C}}-R-R-\overset{O}{\overset{\|}{C}}-OR'-O-\\ \quad O\qquad\qquad\qquad\qquad O\\ \quad C{=}O\qquad\qquad\qquad C{=}O\\ \quad R''\qquad\qquad\qquad\qquad R''\end{array}\right]_x-\overset{O}{\overset{\|}{C}}-R''$$

Synthetic Oil IV

The residual dimerized fat acids were heated with the polyalcohol to form the polymeric ester (III). The ester was then reacted with fat acids to give a synthetic oil (IV). Since trimerized fat acids were present, these equations give only a partial picture of the synthetic oil preparation. In addition, the ratios of the polyalcohol, residual dimerized fat acids, and fat acids such as soybean fat acids which were used, determine the average value of x. Two groups of oils were prepared by use of proper ratio of reactants. In the first, the ratios were controlled to give an average value for x of 1, and in the second to give an average for x of 3.

Experimental

PREPARATION OF SYNTHETIC OILS:

The two general compositions of reactants were tried as follows: The first used equal parts of residual dimerized fat acids and soybean or linseed oil acids (x = 3 in Formula IV), and the second, two parts of soybean or linseed oil acids to one part of residual dimerized fat acid (x = 1, Formula IV). In some preparations, small percentages of maleic or phthalic anhydride were added in an attempt to enhance the properties. The following is a detailed description of the preparation of one synthetic oil: 275 gm. of residual dimerized fat acids, 91.2 gm. of glycerol (5 per cent excess), and 0.5 gm. of PbO catalyst were placed in a three-neck flask, fitted with stirrer, thermometer, inlet tube for carbon dioxide, and reflux condenser which was heated with steam. The heated condenser allowed water to escape but retained glycerol in the reaction flask. The mixture was heated at 185° to 195° C. for one hour with stirring. At the end of this period, 550 gm. of linseed oil fat acids were added. The mixture was then heated for 9 to 10 hours more with a slow but gradual increase in temperature to 230° C. The reaction was usually stopped at this stage provided a low acidity was obtained. The oil was cooled and stored under carbon dioxide until such time as it was used for tests or varnish formulation.

Table 1 gives the composition of the reactants used in the preparation of the synthetic oils and contains physical constants of the final products. The viscosity of the synthetic oils could be varied by the amount of vegetable oil acids used in their preparation. Gelation was encountered in some attempts when tetrahydric or hexahydric alcohols, or maleic anhydride, were used in the preparations. The time required to obtain low acid values could be readily shortened by the use of reduced pressure after the initial reaction had occurred.

Varnishes From Synthetic Oils. Ester gum varnishes of a 33⅓-gallon oil length were prepared from the synthetic oils and from bodied linseed oil, using the following formula and procedure:

31.9 g.	Ester Gum
4.0 g.	Rosin (W W.)
100.0 ml.	Oil
100.0 ml.	Mineral Spirits
1.1 ml.	Cobalt Naphthenate (6 per cent Co)
2.3 ml.	Lead Naphthenate (24 per cent Pb)

TABLE 1

Synthetic Oils from Residual Dimerized Fat Acids

Oil No.	Designation of Oil	Amounts of Fat Acid and Source	Amounts of Polyalcohol	Amounts of Additional Dibasic Acid	Time of Reaction	Final Product Acid No.	Final Product Color Gardner	Final Product Viscosity Gardner
		Per 100 Parts of Residual Dimerized Fat Acid			Hours			
1	1SG[2]	100 Soybean	22 Glycerol	....	11.5	8.8	11	Z_5
2	2SG	200 Soybean	33.1 Glycerol	....	11.5	8.0	12	
3	1LG	100 Linseed	22 Glycerol					
4	2LG	200 Linseed	33.1 Glycerol	....	12.5	5.0	10	T
5	2SPE	200 Soybean	35.1 Pentaerythritol	....	12.5	7.6	11	Z_2
6	1SM	100 Soybean	35.5 Mannitol	....	16	....	....	Almost a gel
7	2SM	200 Soybean	50.3 Mannitol	....	18	4.0	11	Z_4
8	2SM	200 Soybean	50.3 Mannitol	....	19	8.7	10	Z_6
9	2CSG	200 Soybean[1]	33.1 Glycerol	....	12	5.7	11	X
10	2SG PA	200 Soybean	46.3 Glycerol	30 Phthalic Anhydride	14	3.0	13	Z_1
11	2SG MA	200 Soybean	37.1 Glycerol	5.9 Maleic Anhydride	13	8.4	11	Z
12	2SG MA	200 Soybean	39.2 Glycerol	Maleic Anhydride	11.5	24.0	11	Z_6
13	2LG MA	200 Linseed	37.4 Glycerol	Maleic Anhydride	10	8.5	11	Z_1
14	2SPE MA	200 Soybean	38.8 Pentaerythritol	5.8 Maleic Anhydride	12	12	10	Z_6

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[1] Alkali conjugated soybean oil acids (4).

[2] The oils have been designated by symbols for ease in referring from table to table: For example, 2SPE designates the oil made from 1 part residual dimerized fat acids, 2 parts soybean fat acids with pentaerythritol; 1SG designates the oil made from 1 part residual dimerized fat acids, 1 part soybean fat acids with glycerol.

The oil and ester gum were heated in a 600 ml. beaker to 296-299° C. (565-570° F.). This temperature was held until a 5- to 8-inch string from a cold plate was obtained. The heat was removed and the rosin added to check any further reaction. The cook was cooled rapidly by vigorous stirring and when the temperature had dropped to 149° C. (300° F.), the varnish was reduced with mineral spirits. Finally, at room temperature, driers were added in amounts sufficient to give approximately 0.05 per cent cobalt metal and 0.5 per cent lead, based on the weight of oil used. Later, if necessary, the varnish was reduced to viscosity of D, with additional solvent. Table 2 gives a resumé of fifteen varnishes prepared in this manner.

TABLE 2

Varnishes from Synthetic Oils

Oil No.	Designation of Oil	Cooking Time (Min.)	Viscosity (Gardner)	Color (Gardner)	Additional Solvent to Reduce to Viscosity of D (Gardner)
1	ISG[2]	17	E	15	8
2	2SG	72	D	17	....
3	1LB	16	E	14	8
4	2LG	60	D	15	....
5	2SPE	20	E	15	10
6	1SM	13	U	13	90
7	2SM	18	F	15	15
8	2SM	14	J	13	42
9	2CSG	47	D	15	....
10	2SG PA	111	D	17	....
11	2SG MA	53	D	16	....
12	2SG MA	24	E	14	11
13	2LG MA	23	E	14	8
14	2SPE MA	9	L	12	49
15	Linseed Oil X	60	D	13	....

EVALUATION:

Oil Films. The synthetic oils were compared directly with three different linseed oils: a commercial bodied oil of "X" viscosity, a laboratory bodied oil of "Y" viscosity, and a commercial alkali-refined oil of "A" viscosity. All oils were reduced to viscosity of "A" with Skellysolve C, except the linseed oil A, and 0.1 per cent cobalt naphthenate drier was added. Table 3 gives the times required for obtaining initial sets, dust-free and dry surfaces. Observations on water and alkali resistance of the oil films are also given in this table. Films used for water and alkali resistance were prepared from oils reduced to a viscosity of "A". The films used in tests with water were flowed on tin panels, while those used in tests with alkali were obtained by dipping test tubes into the oils. Prior to testing, oil films were allowed to dry for 72 hours. The films were immersed in water, and the amount of blushing at 24, 48, and 72 hours was noted; also, the time required for the film to recover to its initial appearance was measured. For alkali resistance, the oil films were dipped in 0.1 N sodium hydroxide, and the time required for failure of the film was noted.

Varnish Films. The varnishes were flowed on glass plates and allowed to stand in a vertical position. The temperature of the drying cabinet was maintained at 27° C. ± 1° C., and a relative humidity of 45 to 50 per cent. Results of the drying tests are given in Table 4.

TABLE 4

Drying of Varnishes from Synthetic Oils

Varnish from Oil No.	Designation of Oil	Time Required for: Initial Set	Time Required for: Dust-free	Film Condition After: Eight Hours	Film Condition After: Twenty-four Hours
1	1SG[2]	150-180	270-300	Tacky	Sl. Tacky
2	2SG	120-150	330-360	Tacky	Tacky
3	1LG	120-150	300-330	Sl. Tacky	Sl. Tacky
4	2LG	90-120	210-240	Sl. Tacky	V. Sl. Tacky
5	2SPE	90-120	210-240	V. Sl. Tacky	V. Sl. Tacky
6	1SM	30-60	150-180	Not Tacky	Not Tacky
7	2SM	90-120	150-180	Not Tacky	Not Tacky
8	2SM	120-150	270-300	Sl. Tacky	V. Sl. Tacky
9	2CSMG	120-150	330-360	V. Tacky	V. Tacky
10	2SG PA	150-180	330-360	Tacky	Tacky
11	2SG MA	120-150	240-270	Sl. Tacky	V. Sl. Tacky
12	2SG MA	210-240	330-360	V. Sl. Tacky	V. Sl. Tacky
13	2LG MA	60-90	240-270	V. Sl. Tacky	Not Tacky
14	2SPE MA	60-90	210-240	V. Sl. Tacky	Not Tacky
15	Linseed X	60-90	240-270	V. Sl. Tacky	Not Tacky

[2] (See footnote,[2] Table 1.)

For the water resistance tests, films were obtained by flowing on tin panels and allowing to dry for 72 hours. Tests with cold water were run by immersing one-half of the film panels in distilled water and examining the films at regular intervals. For hot water resistance tests, one-half of each film panel was immersed in boiling distilled water for one hour. Table 5 gives the results of these tests.

Alkali resistance of the varnishes was determined by noting the time required for a film to fail on exposure to a 3 per cent sodium hydroxide solution. The films were prepared by dipping test tubes into varnishes, inverting the tubes, and allowing the films to dry for 72 hours. The films were immersed in the 3 per cent alkali and the time required for the film

TABLE 3

Evaluation of Oil Films, Including Drying Rate, Water and Alkali Resistance

Oil No.	Designation	Time Required for Drying (Min.): Initial Set	Time Required for Drying (Min.): Dust Free	Time Required for Drying (Min.): Dry	Appearance of Film After Immersion in Water for: 24 Hrs.	Appearance of Film After Immersion in Water for: 48 Hrs.	Appearance of Film After Immersion in Water for: 72 Hrs.	Recovery After Immersion (Min.)	Time Required for Film to Fail in 0.1 N-Sodium Hydroxide (Min.)
1	1SG[2]	30-40	50-65	75-105	V. Sl. Blush	Sl. Blush	Sl. Blush	20	> 8
2	2SG	60-90	120-150	180-210	S. Blush	B. Blush	B. Blush	>60	>10
3	1LG	30-40	50-70	75-120	V. Sl. Blush	Sl. Blush	Blush	30	4
4	2LG	50-70	75-105	135-180	V. Sl. Blush	Blush	B. Blush	20	3
5	2SPE	30-45	50-65	75-105	V. Sl. Blush	Sl. Blush	Blush	>60	>10
6	1SM	10-20	30-40	75-105	V. Sl. Blush	Sl. Blush	Sl. Blush	>60	1
7	2SM	20-30	45-60	105-150	V. Sl. Blush	Sl. Blush	Sl. Blush	20	5
8	2SM	45-60	105-135	165-205	V. Sl. Blush	Sl. Blush	Blushed	30	2
9	2CSG	180-210	210-240	240-270	Sl. Blush	B. Blush	V. B. Blush	60	>15
10	2SG PA	60-90	90-120	75-180	V. Sl. Blush	B. Blush	V. B. Blush	120	5
11	2SG MA	60-75	90-105	120-165	V. Sl. Blush	Sl. Blush	Blushed	30	2
12	2SG MA	20	45-75	90-135	V. Sl. Blush	Sl. Blush	Sl. Blush	30	2
13	2LG MA	50-60	70-90	120-150	V. Sl. Blush	V. Sl. Blush	Sl. Blush	30	2
14	2SPE MA	20	45-60	75-105	V. Sl. Blush	V. Sl. Blush	Sl. Blush	20	3
Linseed X		90-120	150-180	210-270	Sl. Blush	Blush	B. Blush	30	1
Linseed Y		90-120	150-180	210-270	Blush	V. B. Blush	V. B. Blush	>60	1
Linseed A		120-150	165-195	225-285	B. Blush	V. B. Blush	V. B. Blush	>120	1

[2] (See footnote,[2] Table 1.)

TABLE 5

Water Resistance of Varnish Films

Varnish No.	Designation	Appearance of Film After Exposure to Cold Water for			Recovery After 48 Hours Immersion (Min.)	75 Hours	Recovery After 75 Hours Immersion (Min.)	Film Condition After 1 Hour in Boiling Water	Recovery (Min.)
		6 Hours	24 Hours	48 Hours					
1	1SG[2]	V. Sl. Blush	Blush	Blush	30-35	B. Blush	35-40	Badly Whitened—No Pin Holes	15-20
2	2SG	Blush	B. Blush	B. Blush	30-35	V. B. Blush	35-40	Badly Whitened—No Pin Holes	35-40
3	1LG	Sl. Blush	Blush	B. Blush	30-35	V. B. Blush	35-40	Badly Whitened—No Pin Holes	30-35
4	2LG	Blush	Blush	B. Blush	30-40	B. Blush	35-40	Badly Whitened—No Pin Holes	30
5	2SPE	V. Sl. Blush	Sl. Blush	Sl. Blush	15-20	Sl. Blush	20-25	V. Sl. Whitened Pin Holes at Water Line	5-10
6	1SM	V. Sl. Blush	V. Sl. Blush	V. Sl. Blush	5-10	V. Sl. Blush	15-20	V. Sl. Whitened Pin Holes at Water Line	5-10
7	2SM	V. Sl. Blush	Sl. Blush	Blush	30-35	Blush	35-40	Sl. Whitened Pin Holes at Water Line	5-10
8	2SM	V. Sl. Blush	Sl. Blush	Blush	15-20	Blush	20-25	Whitened—No Pin Holes	15-20
9	2CSG	B. Blush	B. Blush	V. B. Blush	>60	V. B. Blush	>60	V. Badly Whitened Pin Holes	80-90
10	2SG PA	B. Blush	B. Blush	V. B. Blush	>60	V. B. Blush	>60	V. Badly Whitened Pin Holes	50-60
11	2SG MA	B. Blush	B. Blush	V. B. Blush	30-35	V. B. Blush	35-40	V. Badly Whitened Pin Holes	30
12	2SG MA	V. Sl. Blush	V. Sl. Blush	Blush	15-20	Blush	20-25	Whitened Pin Holes	5-10
13	2LG MA	V. Sl. Blush	Sl. Blush	Blush	25-30	Blush	30-35	Whitened—No Pin Holes	5-10
14	2SPE MA	V. V. Sl. Blush	V. Sl. Blush	V. Sl. Blush	5-10	V. Sl. Blush	15-20	V. V. Sl. Whitened—No Pin Holes	5
15	Linseed X	Blush	B. Blush	B. Blush	30-35	V. B. Blush	35-40	Badly Whitened—No Pin Holes	30-35

[2] (See footnote,[2] Table 1.)

to dissolve or break was recorded as failure. Table 6 gives the hardness of the varnish films as well as the alkali resistance data.

TABLE 6

Alkali Resistance and Hardness of Varnish Films

Varnish Number	Designation of Oil	Rocker Hardness of Varnish Films		Time Required for Film Failure in 3% NaOH in Minutes
		24 Hours	72 Hours	
1	1SG[2]	8	10	65
2	2SG	10	14	50
3	1LG	8	10	55
4	2LG	8	12	60
5	2SPE	10	14	135
6	1SM	26	30	60
7	2SM	16	23	120
8	2SM	23	28	50
9	2CSG	2	2	40
10	2SG PA	6	10	50
11	2SG MA	8	12	50
12	2SG MA	8	10	55
13	2LG MA	12	15	65
14	2SPE MA	10	16	90
15	Linseed X	8	14	45
Plate Glass		100		

[2] (See footnote,[2] Table 1.)

Discussion and Conclusions

In the chemical sense, "drying" of oils and some resinous materials is a phenomenon which is directly related to functionality and polymerization. It is a mechanism whereby essentially linear molecules, usually liquid in nature, are converted into a cross-linked or three-dimensional polymeric molecule (1). Usually oil films are produced by oxidative polymerization or by a combination of thermal and oxidative polymerization. Since the residual dimerized fat acids are polymeric, i.e., dimeric and trimeric (3, 4) and give cross-linked, three-dimensional polymers with difunctional molecules (3), these acids may be considered to be "drying" constituents.

The synthetic oils prepared from residual dimerized fat acids and soybean and linseed fat acids should be superior to the original oils, i.e., soybean and linseed. The total amount of available "drying" constituents has been increased. The amount of this increase is proportional to the amount of residual dimerized fat acids used in the preparation of the synthetic oils.

For example, soybean oil, which has approximately 60 per cent linoleic and linolenic acids, is converted to residual dimerized fat acids. Estimates based on Bradley's and Johnston's work (2) would indicate that polymerization gives 50 parts by weight of residual dimerized fat acids and 50 parts of nonpolymerized fat acids.

$$\begin{array}{c} \text{Soybean Oil Acids} \\ \text{100 parts} \end{array} \longrightarrow \begin{array}{c} \text{Residual Dimerized Fat Acids} \\ \text{50 parts} \\ + \\ \text{Non-polymeric Fat Acids} \\ \text{50 parts} \end{array}$$

If 50 parts of residual dimerized fat acids are reacted with polyalcohol and 100 parts of soybean fat acids, the proportion of drying constituents has been increased from 60 per cent in the original soybean oil to 73.3 per cent in the synthetic oil. If equal parts by weight are used, an increase of drying constituents to 80 per cent is achieved. Table 7 shows the manner of this increase more clearly.

TABLE 7

Increase in Drying Constituents—Soybean Oil

		"Drying" Constituents
		Percent
Soybean Oil		60
50—Residual Dimerized Fat Acids 50—Soybean Fat Acids	Synthetic Oil (1-1)	80
50—Residual Dimerized Fat Acids 100—Soybean Fat Acids	Synthetic Oil (1-2)	73

If linseed fat acids are used in a 1-1 ratio, the drying constituents are increased from 75 to 88 per cent; if a 1-2 ratio is used, an increase to 83 per cent is effected. Table 8 shows these relationships more clearly.

At comparable viscosities, a synthetic oil should be superior to a bodied oil of equal viscosity. During the polymerization required in the heat bodying of the oil, the viscosity increases by the dimerization of the "drying" fat acid present. This reaction reduces the proportion of "drying" fat acid in the remaining monomeric fat acids. In the synthetic oil, the same viscosity can be achieved without reducing the proportion of "drying" fat acids remaining in the monomeric fat acids. Of course, some polymerization may occur during the preparation of the synthetic oils, but since the temperature was usually kept below 225° C., the amount would be small.

TABLE 8

Increase in Drying Constituents—Linseed Oil

		"Drying" Constituents
		Percent
Linseed Oil		75
50—Residual Dimerized Fat Acids 50—Linseed Fat Acids	Synthetic Oil (1-1)	88
50—Residual Dimerized Fat Acids 100—Linseed Fat Acids	Synthetic Oil (1-2)	83

The experimental results support the belief that these synthetic oils are superior. For example, the synthetic oils dried faster and were more water- and alkali-resistant than linseed oils used as test controls. The drying time was reduced as much as one-third using glycerol, soybean fat acids, and residual dimerized fat acids. The oils containing equal portions of residual dimerized fat acids and of vegetable fat acids (Formula IV, average value of $x = 3$), i.e., oils 1 and 3 dried faster and possessed better water and alkali resistance than when a 1-2 ratio was used (Formula IV, average value of x is 1), i.e., oils 2 and 4. The use of polyalcohols, such as mannitol and pentaerythritol, gave better oils (see oils 5, 6, 7, and 8), but the improvement over the synthetic oils prepared from equal parts of residual dimerized fat acids and vegetable fat acids was not marked. Indeed, in some tests, the oils from polyalcohols were inferior, but the higher polyalcohols improved all synthetic oils where a 1-2 ratio of residual dimerized fat acids to soybean or linseed fat acids was used in the preparation. The use of maleic anhydride reduced the drying times of oils having the 1-2 ratio of acids, increased water resistance, and apparently reduced alkali resistance (see oils 11, 14).

The alkali resistance of the synthetic oils studied depended on the amount of residual dimerized fat acids used. Roughly, the alkali resistance was proportioned to the amount of residual dimerized fat acids and inversely proportional to the amount of vegetable fat acids. Of course, the ratio of residual dimerized fat acids used would determine the initial concentration of C-C bond. Apparently, alkali resistance is some function of amount of C-C bonds present. The superior alkali resistance of films from conjugated oils supports this observation since it is believed that more C-C bonds are formed in these films than in films from non-conjugated oils. Also, heat polymerized oils like bodied linseed, perilla, and tung have greater alkali resistance in oil films and varnishes than do unbodied linseed, perilla, and tung oils, respectively. It is interesting to note that the synthetic oil prepared from one part residual dimerized fat acids and two parts conjugated soybean fat acids, oil No. 9, had the best alkali resistance of any of the oils tested.

By the incorporation of the synthetic oils into ester gum varnishes, the time required for drying as compared to the oils alone was increased, the water resistance only slightly improved, and the alkali resistance measurably improved. While the oil films made from the synthetic oils were definitely superior to the oil films from the linseed oils, this superiority in properties of films was not evident in the ester-gum varnishes. It appears that the formulation of the oils with ester gum had an equalizing effect on the films, i.e., the varnish films prepared from the oils were more nearly equal in drying rate, water and alkali resistance than the films made from the original oils. It is quite evident that the method of varnish formulation used was not satisfactory for these oils. It is believed that varnishes prepared from the residual dimerized fat acids rather than from oils containing these acids will show definite superiority over the parent oils, i.e., soybean and linseed, as constituents of varnishes. Further investigation is in progress.

Summary

Synthetic oils have been prepared from residual dimerized fat acids with soybean and linseed fat acids by esterification with polyalcohols, and with or without maleic anhydride or phthalic anhydride. Preliminary evaluation indicates that these oils give films which dry faster and are more resistant to water and alkali than linseed oil films. This enhancement of water and alkali resistance may result from an increase in C-C bonds present in the films. Ester gum varnishes made from these oils were not markedly superior to similar varnishes made from linseed oil.

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