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SYNTHETIC ESTERS

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4 Claims. (Cl. 260—410.6)

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The present invention relates to improved synthetic drying oils and other esters derived from the esterification of polyhydric alcohols resulting from the condensation of glycerol dichlorhydrin with glycerol or pentaerythritol.

It is therefore a primary object of the present invention to provide drying oils and other esters having new and unusual properties, resulting from the esterification of the condensation product of glycerol or pentaerythritol with glycerol dichlorhydrin.

The polyhydric alcohol condensation products which are employed for esterification in the present invention are those derived from glycerol dichlorhydrin and either glycerol or pentaerythritol and can be made as disclosed in our copending application Serial No. 705,489, filed October 24, 1946, entitled Polyhydric Alcohols. As will be apparent from the examples herein and in the above identified application, the condensation is effected between the glycerol dichlorhydrin and the glycerol or pentaerythritol within the approximate range of ½ to 2 moles of the glycerol dichlorhydrin per mole of glycerol or pentaerythritol. This condensation probably results in a certain amount of cross-linking between molecules of the polyhydroxy compounds, and produces a different type of polyhydric alcohol. When these polyhydric alcohols are esterified with fatty acids from drying or semi-drying oils, the resultant esters are far superior to other available drying oils. In general, for this purpose any unsaturated acid or mixture of acids, either natural or synthetic, may be employed, such as acids obtained from linseed, soybean, perilla, oiticica, cottonseed, corn, palm, dehydrated castor, tung, olive, peanut, safflower, and sunflower oils, and fish oils such as sardine, menhaden, and the like.

The esterification proceeds readily according to the usual esterification techniques. Thus stoichiometric quantities of the condensation product and the fatty acid may be mixed and heated with stirring, preferably in an inert atmosphere, with agitation, at 180° C.–300° C. until a low acid number has been attained. If desired, a stream of inert gas may be bubbled into the reaction mixture, as through the stirrer, in order to carry off the water of reaction more efficiently. Similarly, an azeotropic method of water removal may be employed, using high boiling material such as triisopropylbenzene. More conveniently, an azeotropic solvent such as xylene may be used in sufficiently small quantity so that a high temperature is maintained.

Likewise the esters may be obtained by a trans-

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esterification reaction between the condensation product and the glyceride or other esters of the fatty acids. Here again a temperature of 180–300° C. with stirring may be employed and there may be added a transesterification catalyst such as the oil soluble salts of calcium, strontium, barium, zinc, lithium, and the like. The glycerol or other alcohol formed in the process may, of course, be removed.

The esterifications proceed with unexpected ease considering the size of the molecules. If a catalyst such as zinc stearate is employed, it is possible to obtain products with very low acid numbers in four to five hours. The resulting oils are light in color and have a high viscosity.

The synthetic oils of the present invention may be readily compounded into paints, and may also be cooked into varnishes with resins and gums in accordance with the usual varnish procedure. By combining fatty acids of oils ordinarily considered too "soft" for varnish making (such as soybean oil) with the new polyhydric alcohol, oils result which require a short cooking time for varnish formulation, and yield varnishes whose films are extremely tough and abrasion resistant.

The oils, when cast as films, dry within 2–3 hours to hard resistant films whose properties are in every way superior to films from other reconstituted oils employing polyhydric alcohols, such as pentaerythritol. In some instances these films compared favorably with those of a "long oil" alkyd. A good way to demonstrate the superiority of the present drying oils is by comparison of their Brown heat times with commercially available drying oils. For example, a linseed ester of the condensation product of pentaerythritol and glycerol dichlorohydrin had a Brown heat time of 92 minutes, whereas a linseed ester of pentaerythritol had a Brown heat time, under identical conditions, of 207 minutes. This demonstrates the superiority of the present drying oils inasmuch as a low Brown heat time indicates rapid drying characteristics, superior film characteristics, and good behavior in varnish making. This proved to be true in actual varnish formulation.

Example 1

Pentaerythritol (272 parts) was mixed with aqueous sodium hydroxide (50%, 704 parts) after which the mixture was heated at 90° C. for thirty minutes. Glycerol dichlorohydrin (516 parts) was added with stirring over a period of four and one-half hours at a temperature which did not exceed 105° C. Thereafter, the reaction mixture

was heated and stirred for one-half hour longer, after which the reaction mixture was diluted with methanol, neutralized with dilute hydrochloric acid and filtered. The filtrate was desolvated under reduced pressure and a product was obtained by methanol extraction. The resulting syrup had a hydroxyl content of 29.0%.

A mixture of 50 parts of this condensation product with 242 parts of linseed acids and 2.2 parts of zinc stearate was heated and stirred for five and one-half hours at 235° C. The water of reaction was removed azeotropically by xylene and was collected in a Dean-Stark type of water trap. At the end of this time slightly more than the theoretical quantity of water had collected and the acid number was 7.9. There resulted after removal of the xylene a light colored oil with the following properties:

Acid number	7.9
Hydroxyl number	5.3
Specific gravity $\frac{25}{25}$	0.951
Sap. eq.	316.9, 316.9
Iodine number	160.9
Viscosity (Gardner)	K–L at 25° C.

A film cast from this oil into which had been incorporated 0.1% manganese and 0.05% cobalt driers, dried tack-free in less than three hours.

The resulting film was extremely hard and abrasion resistant and resisted with great tenacity the corrosive action of water and dilute alkali.

Example 2

Aqueous sodium hydroxide (50%, 352 parts) was heated to 95° C., after which glycerol dichlorohydrin (258 parts) was added with stirring at such a rate that the internal temperature did not at any time exceed 115° C. The addition was effected in three and one-half hours after which stirring and heating at 95° C. was continued for four hours. The reaction mixture was then diluted with methanol, neutralized with dilute hydrochloric acid and filtered, after which the filtrate was concentrated under reduced pressure. The resulting material was extracted with absolute methanol, after which the solvent was evaporated to obtain a syrup with a hydroxyl content of 27.5%.

A mixture of 50 parts of this condensation product was reacted with linseed acids (226.5 parts) and zinc stearate (2.2 parts) as described in Example 1. The reaction mixture was heated for nine hours at 235° C., at the end of which time the theoretical quantity of water had collected. The oil had the following properties:

Specific gravity $\frac{25}{25}$	0.950
Sap. eq.	322.2
Iodine number	153.8
Viscosity (Gardner)	E–F at 25° C.

This oil likewise possessed excellent film forming properties and dried in less than three hours.

Example 3

Glycerol (95%, 129 parts) was mixed with aqueous sodium hydroxide (50%, 332 parts) and cooled externally. Thereafter, the mixture was heated to 90–95° C. and glycerol dichlorohydrin (258 parts) was added dropwise over a period of two hours while the mixture was stirred vigorously. Thereafter, stirring and heating at 90–95° C. was continued for five hours, after which the reaction mixture was neutralized with hydrochloric acid, diluted with methanol and filtered. The filtrate was evaporated under reduced pressure to yield a mixture of product and inorganic material from which the product was extracted with methanol. The solvent was removed under reduced pressure to yield a thick syrup with a hydroxyl content of 30.0%.

A mixture of this product (50 parts), linseed acids (245 parts) and zinc stearate (1.7 parts) was reacted as described in Example 1. The mixture was heated for six hours at 235° C., at the end of which time slightly more than the theoretical quantity of water had collected. The product which was light in color had the following properties:

Acid number	6.2
Hydroxyl number	0
Specific gravity $\frac{25}{25}$	0.9467
Sap. eq.	302.7
Iodine number	163.1
Viscosity (Gardner)	E–F at 25° C.

It likewise yielded an excellent tack-free film in less than three hours.

Example 4

Glycerol (95%, 776 parts) was mixed with aqueous sodium hydroxide (50%, 704 parts) and cooled externally. The mixture was heated to 90° C. and glycerol dichlorohydrin (516 parts) was added with stirring over a period of four and one-half hours. The reaction was continued at 90–95° C. with stirring for a total reaction time of seven hours. The condensation mixture was neutralized and the product was isolated as described in the preceding example. From this product excess glycerol (305 parts) was removed by distillation at reduced pressure. The residue was taken up in methanol, filtered, and the filtrate was concentrated to yield 675 parts of product with a hydroxyl content of 33.2%.

This condensation product (50 parts) was esterified with linseed acids (247 parts) in the presence of zinc stearate (2.2 parts) according to the procedure described in preceding examples. At the end of three hours the theoretical quantity of water had collected. The oil which yielded a hard film in less than three hours, had the following properties:

Acid number	6.2
Hydroxyl number	5.5
Specific gravity $\frac{25}{25}$	0.949
Sap. eq.	307.7
Iodine number	160.6
Viscosity (Gardner)	E–F at 25° C.

Example 5

The condensation product described in Example 1 (50 parts) was esterified with soybean acids (238 parts) in the presence of zinc stearate (2.2 parts). The esterification was conducted at 235° C. as indicated in previous examples for a period of six hours. The oil had the following properties and dried to a hard film within four hours.

Specific gravity $\frac{25}{25}$	0.9451
Sap. eq.	321.2
Iodine number	118.7
Viscosity (Gardner)	J–K at 25° C.

Example 6

The condensation product described in Example 2 (50 parts) was esterified with soybean acids (225.7 parts) in the presence of zinc stearate (2.2 parts. The esterification proceeded as in previous examples for seven hours at 235° C. The oil had the following properties. It likewise dried to a hard film within four hours.

Specific gravity $\frac{25}{25}$	0.9443
Sap. eq.	318.0
Iodine number	115.1
Viscosity (Gardner)	G–H at 25° C.

Example 7

Glycerol (95%, 485 parts) aqueous sodium hydroxide (50%, 880 parts) and glycerol dichlorohydrin (645 parts) were reacted as indicated in Example 4. The excess glycerol was removed from the product by distillation under reduced pressure to yield a syrup with a hydroxyl content of 27.4%.

Fifty parts of this condensation product was esterified with soybean acids (225 parts) in the presence of zinc stearate (2.2 parts) according to the procedure described in previous examples. After six hours at 235° C. there resulted an extremely viscous product which dried to a hard film within four hours and which possessed the following properties:

Acid number	3.8
Hydroxyl number	7.7
Iodine number	117.3
Sap. eq.	326.8
Specific gravity $\frac{25}{25}$	0.9471

Example 8

A mixture of the condensation product described in Example 7 (50 parts) and acetic anhydride (200 parts) was treated with a few drops of concentrated sulfuric acid. Complete solution resulted after one hour on the steam bath. The volatile material was then removed under reduced pressure to yield a syrupy product with a saponification equivalent of 138.2.

Example 9

The condensation product described in Example 4 (10 parts) suspended in dry pyridine (200 parts), was treated with 51.8 parts of palmityl chloride while being cooled externally. After fourteen hours, the mixture was added slowly to ice water, and the product was allowed to precipitate from ethanol. There resulted a hard, white wax with a saponification equivalent of 285.1 and a melting point of 66° C.

Example 10

The condensation product described in Example 1 (10 parts) was heated with stearic acid (48.3 parts) and with zinc stearate (0.44 part)

for two hours at 150° C. The water of reaction was removed azeotropically with xylene. There resulted a hard white wax with a melting point of 65–8° C.

While various modifications of the above invention have been described, it is to be understood that this invention is not limited thereto, but may be varied within the scope of the following claims.

We claim as our invention:

1. A mixed soybean oil fatty acid ester of a polyhydric alcohol, said polyhydric alcohol resulting from the condensation, under alkaline conditions, of glycerol dichlorhydrin with a polyhydroxy compound selected from the group consisting of pentaerythritol and glycerol, the glycerol dichlorhydrin being employed in the relative proportion of from one-half to two moles per mole of polyhydroxy compound, said polyhydric alcohol being substantially completely esterified.

2. A mixed linseed oil fatty acid ester of a polyhydric alcohol, said polyhydric alcohol resulting from the condensation, under alkaline conditions, of glycerol dichlorhydrin with a polyhydroxy compound selected from the group consisting of pentaerythritol and glycerol, the glycerol dichlorhydrin being employed in the relative proportion of from one-half to two moles per mole of polyhydroxy compound, said polyhydric alcohol being substantially completely esterified.

3. An unsaturated higher fatty acid ester of a polyhydric alcohol, said polyhydric alcohol resulting from the condensation, under alkaline conditions, of glycerol dichlorhydrin with a polyhydroxy compound selected from the group consisting of pentaerythritol and glycerol, the glycerol dichlorhydrin being employed in the relative proportion of from one-half to two moles per mole of polyhydroxy compound, said polyhydric alcohol being substantially completely esterified.

4. A fatty acid ester of a polyhydric alcohol, said polyhydric alcohol resulting from the condensation, under alkaline conditions, of glycerol dichlorhydrin with a polyhydroxy compound selected from the group consisting of pentaerythritol and glycerol, the glycerol dichlorhydrin being employed in the relative proportion of from one-half to two moles per mole of polyhydroxy compound, the polyhydric alcohol being substantially completely esterified with a mixture of unsaturated acids derived from a fatty oil.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
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Certificate of Correction

Patent No. 2,527,870 October 31, 1950

HAROLD WITTCOFF ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 4, line 46, for "(247 parts)" read *(274 parts)*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of January, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.