United States Patent Office 2,754,307 Patented July 10, 1956

2,754,307

DRYING OILS

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No Drawing. Application September 24, 1952, Serial No. 311,332

10 Claims. (Cl. 260—404.8)

The present invention relates to drying oils and more particularly provides new and improved rapidly drying oils and methods of producing the same.

According to the invention, the drying rate of fatty oils is accelerated by first condensing them with a certain proportion of fumaric acid, whereby there are formed fatty oil-fumaric acid adducts containing free carboxy radicals, and then esterifying said adducts with pentaerythritol. Fatty oils suitably used for the preparation of the present improved drying oils are non-conjugated, unsaturated, non-hydroxylated fatty oils having from 10 to 24 carbon atoms in the carbon chain of the fatty acids of the oils. As examples of useful oils may be mentioned soybean, linseed, olive, perilla, safflower, codliver, whale, sardine, rape seed, sunflower, corn, grape seed and cotton seed oils. The fatty oils may be of a non-drying, semi-drying or drying type.

It is old in the art to condense such oils with acyclic olefinic dicarboxylic acids or anhydrides thereof, usually maleic anhydride, to form addition products which may be esterified to give viscous to solid resinous materials, e. g., as described broadly in the Clocker Patents Nos. 2,188,882–890 and 2,275,843. Now we have found that when the fatty oils are reacted with from 3 per cent to less than 10 per cent by weight of fumaric acid, based on the weight of the oil, and the resulting addition products are esterified with pentaerythritol, there are obtained oily reaction products possessing improved drying characteristics. Oils of poor drying properties are particularly modified. Thus, by the present treatment, soybean oil or safflower oil, which are oils of the semi-drying type, are converted into oils having a drying rate which far exceeds that of some drying oils, e. g., bodied linseed oil, and is substantially equal to that of the similarly treated linseed oil, i. e., the pentaerythritol ester of linseed oil-fumaric acid adduct. We have found, for example, that whether one starts with linseed oil or safflower oil, reaction of the oil with fumaric acid in the proportions shown above, and subsequent esterification of the oil-fumaric acid adduct gives in each case an oil which dries tack-free in six hours. This is unexpected from prior art knowledge of esterified fatty-oil-maleic anhydride adducts, wherein the drying rates of products prepared from drying oils were generally more rapid than the drying rates of products obtained from the semi-drying oils. We have also found that the use of fumaric acid, specifically, as the dicarboxylic adduct-forming component and pentaerythritol, specifically, as the esterifying alcohol is critical in obtaining the significant improvement in drying rate attained by the present invention. Contrary to results produced with maleic anhydride, reaction of the fatty oil with fumaric acid results in little, if any change in drying properties of the oil. Thus, the fumaric acid adducts of soybean, linseed, cotton seed or safflower oil all have drying times which are greater than 48 hours; whereas, as is known in the art, reaction of the same oils with maleic anhydride results

in products of considerably improved drying properties. In order to obtain a significant change in drying time when employing fumaric acid instead of maleic anhydride, there must be employed only from 3 per cent to less than 10 per cent of fumaric acid in preparing the adducts, and the resulting adducts must be further reacted with an esterifying agent. Here again, however, the effect of the esterifying agent on drying time improvement is unexpectedly critical. The glycerine ester of soybean oil-fumaric acid adduct has substantially the drying rate possessed by the glycerine ester of soybean oil-maleic anhydride adduct; the pentaerythritol ester of soybean oil-fumaric acid adduct has a drying rate which is much more rapid than that of the pentaerythritol ester of soybean oil-maleic anhydride adduct, although the soybean oil-maleic anhydride adduct, before esterification, has a drying rate which is considerably higher than the drying rate of the soybean oil-fumaric acid adduct before esterification.

The present invention provides a new and very efficient method for improving the drying rates of non-conjugated, unsaturated, non-hydroxylated fatty oils, generally. It further provides for the coating industries a new paint and varnish vehicle of superior drying properties and great economic value. The present invention also serves the agricultural industry in providing for it transformation of such readily available, but poorly drying, oils, as soybean oil, safflower oil and cotton seed oil into highly desirable technical commodities.

In improving the drying rates of the fatty oils, it is preferred to operate substantially as follows:

A mixture consisting of the fatty oil and from 3.0 per cent to less than 10 per cent by weight of fumaric acid is processed with agitation and in an inert atmosphere at a temperature of from 300° F. to 500° F. until completion of the addition reaction. Depending upon the reaction conditions used, i. e., the quantities involved, agitation, and temperature, the processing time may vary from a period of several minutes to several hours. Progress of the addition reaction may be followed by noting the acid value of the reaction mixture at intervals. To the clear reaction mixture so obtained, which reaction mixture comprises the fatty oil-fumaric acid adduct, there is then added pentaerythritol in an amount calculated to esterify the free carboxy groups of the adduct. The mixture of adduct and pentaerythritol is then heated until esterification has been substantially completed. This may be gauged either by noting the quantity of water involved or by determining the viscosity and/or acid value changes in samples taken at intervals from the reaction mixture. Temperatures employed in the esterification reaction are generally of the same order used for the preparation of the adduct.

In preparing the present rapid drying oils, it is imperative that the proportion of fumaric acid to fatty oil be adhered to within the limits defined above. The use of amounts of fumaric acid which are less than 3 per cent by weight of the fatty oil does not result in substantial modification of the drying rate of the oil and the use of 10 per cent or more of the fumaric acid based on the weight of the fatty oil is not desirable in that products of poor viscosity, and even of a gel-like to solid, resinous nature, may be thereby obtained. When employing at least 3 per cent but less than 10 per cent of the fumaric acid, however, and reacting the resulting adducts with pentaerythritol to substantially complete esterification, there are obtained highly viscous, clear, yellow to colorless oils having low acid values, very good thermal stability and excellent drying properties. The present drying oils are thus of outstanding usefulness in the formulation of rapid-drying paints, varnishes and enamels.

The invention is further illustrated but not limited by the following examples:

Example 1

Two-hundred g. of soybean oil was charged to a three-necked 500 cc. flask which was provided with a constant feed of carbon dioxide. The oil was heated to a temperature of 250° F. and 10 g. of fumaric acid (5% by weight of the oil) was added to it. The resulting mixture was then heated, with mechanical agitation and in a carbon dioxide atmosphere, for about 1.2 hours at a temperature of 500° F. A sample taken from the reaction mixture at this point had an acid value of 21.6. External heating was then discontinued and to the reaction mixture there was added 6.46 g. of technical pentaerythritol, and heating of the whole was resumed at a temperature of 525° F. for 1.5 hours. At the end of that time determination of the acid value of the reaction mixture showed substantially complete esterification. The esterified adduct had a color of 6 (Gardner), and viscosity L–N (Gardner-Holdt), and an acid value of 9.8.

Example 2

Employing the procedure described in the preceding example, soybean oil was processed with maleic anhydride and the resulting reaction product esterified with pentaerythritol. The pentaerythritol ester of the soybean oil-maleic anhydride adduct thus obtained was reddish pale; it had a color of 8 (Gardner), viscosity J (Gardner-Holdt), and an acid value of 6.6.

Example 3

A mixture consisting of 300 g. of soybean oil and 17.0 g. of fumaric acid was processed, in a carbon dioxide atmosphere at a temperature of 520° F. A sample taken from the reaction mixture at the end of 45 minutes of heating had an acid value of 32.0. After heating for a total of one hour at 520° F., external heating was discontinued and the temperature of the reaction mixture was allowed to fall to 400° F. 105 g. of glycerine was then added, and heating was resumed at 500° F. for about 107 minutes. The product thus obtained had an acid value of 10, color 8–9 (Gardner), and viscosity J–K (Gardner-Holdt).

Example 4

A mixture consisting of 300 g. soybean oil and 14.4 g. of maleic anhydride was heated for one hour at a temperature of 520° F. At the end of that time the acid value of the reaction mixture was 21.1. The reaction mixture was allowed to cool to 400° F. and 10.5 g. of glycerine was then added. After heating the resulting mixture for one hour at 500° F., there was obtained a product which had an acid value of 10.2, a color of 8–9 (Gardner) and viscosity F (Gardner-Holdt).

Example 5

A mixture consisting of 300 g. of soybean oil, and 17.0 g. of maleic acid was heated for one hour at a temperature of 520° F. At the end of that time the acid value of the reaction mixture was 21.5. After cooling to 400° F., 10.5 g. of glycerine was added to the reaction mixture and the whole was then heated for about one hour at a temperature of 500° F. The product thus obtained had an acid value of 9.5, a color of 6–7 (Gardner) and viscosity E–F (Gardner-Holdt).

Example 6

Three-hundred g. of refined cotton seed oil was heated with 15 g. of fumaric acid in a carbon dioxide atmosphere and with mechanical stirring to a temperature of 500° F. within 30 minutes and then maintained at that temperature for 1.5 hours. A sample taken from the reaction mixture at this point had an acid value of 29.0. External heating was then discontinued and to 109 g. of the reaction mixture thus obtained (a cotton seed oil-fumaric acid adduct), there was added 3.2 g. of pentaerythritol. The whole was then brought to a temperature of 525° F. within 15 minutes and kept at this temperature for 1.5 hours. The esterified adduct thus obtained had a color of 6 (Gardner) and a viscosity of I (Gardner-Holdt).

For purposes of comparison, to 105 g. of the above fumaric acid-cotton seed oil adduct there was added 3.1 g. of glycerine at a temperature of 400° F., the mixture was heated to 525° F. within 15 minutes and then maintained at that temperature for 1.5 hours. There was thus obtained the glycerine ester of cotton seed oil-fumaric acid adduct having a color of 6–7 (Gardner) and viscosity G (Gardner-Holdt).

Example 7

To 300 g. of linseed oil, heated to 300° F., there was added 15 g. of fumaric acid. The resulting mixture was brought to a temperature of 500° F. during 15 minutes and held at about this temperature for another 1.5 hours. The linseed oil-fumaric acid adduct thus obtained had a color of 6 on the Gardner scale and viscosity F (Gardner-Holdt).

105 g. of the above adduct was heated to 480° F. and there was then added to it 3.2 g. of pentaerythritol. The mixture was brought to a temperature of 520° F. and held at 520–530° F. for 1.5 hours. The pentaerythritol ester of linseed oil-fumaric acid adduct thus obtained had a color of 7 on the Gardner scale and viscosity X (Gardner-Holdt).

For purposes of comparison, 105 g. of the above linseed oil-fumaric acid adduct was brought to a temperature of 350° F. and there was then added to it 3.09 g. of glycerine. The mixture was brought to a temperature of 530° F. within 30 minutes and maintained at this temperature for another 1.5 hours. The glycerine ester of linseed oil-fumaric acid adduct had a color of 7 on the Gardner scale and viscosity of U (Gardner-Holdt).

Example 8

Three-hundred g. of safflower oil was heated to 360° F. and there was added to the heated oil 15 g. of fumaric acid, in a carbon dioxide atmosphere and with mechanical stirring. The temperature of the reaction mixture gradually was brought to 500° F. and then held at this temperature for about 1.5 hours. The safflower oil-fumaric acid adduct thus obtained had a color of 6 on the Gardner scale and viscosity of E (Gardner-Holdt).

To 105 g. of the adduct thus obtained there was added, at a temperature of 400° F., 3.2 g. of pentaerythritol, and the resulting mixture was gradually brought to 525° F. and held at approximately this temperature for 1.5 hours. The pentaerythritol ester of safflower oil-fumaric acid adduct thus obtained had a color of 6–7 on the Gardner scale and viscosity P (Gardner-Holdt).

For purposes of comparison, 105 g. of the safflower oil-fumaric acid adduct obtained above was mixed with 3.09 g. of glycerine at a temperature of 400° F., the resulting mixture was brought to 520° F. within 25 minutes and held at 520°–530° F. for 1.5 hours. The glycerine ester of safflower oil-fumaric acid adduct thus obtained had a color of 5–6 on the Gardner scale and viscosity K (Gardner-Holdt).

Example 9

This example shows the drying properties of the esterified adducts of Examples 1 to 8. Each of the products was incorporated with 0.5 per cent lead—0.05 per cent cobalt drier and films were cast from each without em-

ploying a solvent. The drying times of each of the films were found to be as follows:

Film Tested	Drying Time, Hours	
	Set to touch	Tack-free
Pentaerythritol ester of soybean oil-fumaric acid adduct (Example 1)	2.75	6.5.
Pentaerythritol ester of soybean oil-maleic anhydride adduct (Example 2)	5.80	not in 8 hours.
Glycerine ester of soybean oil-fumaric acid adduct (Example 3)	4.50	24.0.
Glycerine ester of soybean oil-maleic anhydride adduct (Example 4)	6.00	not in 24 hours.
Glycerine ester of soybean oil-maleic acid adduct (Example 5)	6.50	Do.
Linseed oil-fumaric acid adduct (Example 7)	4	Do.
Pentaerythritol ester of linseed oil-fumaric acid adduct (Example 7)	1.5	6.
Glycerine ester of linseed oil-fumaric acid adduct (Example 7)	2	not in 24 hours.
Safflower oil-fumaric acid adduct (Example 8)	6	Do.
Pentaerythritol ester of safflower oil-fumaric acid adduct (Example 8)	2.5	6.
Glycerine ester of safflower oil-fumaric acid adduct (Example 8)	3	not in 24 hours.
Cotton seed oil-fumaric acid adduct (Example 6)	6	not in 48 hours.
Pentaerythritol ester of cotton seed oil-fumaric acid adduct (Example 6)	4	18.
Glycerine ester of cotton seed oil-fumaric acid adduct (Example 6)	5	not in 48 hours.

As herein stated, the quantity of fumaric acid employed in the preparation of the present drying oils may be varied. While the above examples all show the use of about 5 per cent by weight of the acid component in order to present comparable data, fumaric acid in amounts as low as 3 per cent may be employed to obtain an oil of improved drying properties. The use of 10 per cent or more of the fumaric acid is not desirable. While the optimum quantity of fumaric acid employed is a function of processing time and temperature, we have found that from, say, 3 per cent to 9 per cent of fumaric acid generally results in improvement of the fatty oil. Oils of best drying properties, color and viscosity are obtained when employing an even more narrow range of concentration, say, from 4 per cent to 7 per cent of fumaric acid based on the weight of the fatty oil.

The processing of the oils is advantageously effected in an inert atmosphere, e. g., in an atmosphere of nitrogen or carbon dioxide. However, formation of the present esterified adducts may also be effected in air. While varying temperatures may be used, we have found that very little addition reaction takes place when the mixture of fatty oil and fumaric acid is processed at a temperature of below 200° C. (329° F.). Optimum conversion is obtained at temperatures of from, say, 230° C. to 280° C. (446° F. to 536° F.).

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

This is a continuation-in-part of our application, Serial No. 181,946, filed August 28, 1950.

What we claim is:

1. A drying oil comprising the pentaerythritol ester of an adduct of fumaric acid and a non-conjugated, unsaturated, non-hydroxylated fatty oil having from 10 to 24 carbon atoms in the carbon chains of the fatty acids of the oil, said adduct being obtainable by heating the fatty oil with from 3 per cent to less than 10 per cent by weight of fumaric acid.

2. A drying oil comprising the pentaerythritol ester of an adduct of soybean oil and fumaric acid, said adduct being obtainable by heating the fatty oil with from 3 per cent to less than 10 per cent by weight of fumaric acid.

3. A drying oil comprising the pentaerythritol ester of an adduct of linseed oil and fumaric acid, said adduct being obtainable by heating the fatty oil with from 3 per cent to less than 10 per cent by weight of fumaric acid.

4. A drying oil comprising the pentaerythritol ester of an adduct of cotton seed oil and fumaric acid, said adduct being obtainable by heating the fatty oil with from 3 per cent to less than 10 per cent by weight of fumaric acid.

5. A drying oil comprising the pentaerythritol ester of an adduct of safflower oil and fumaric acid, said adduct being obtainable by heating the fatty oil with from 3 per cent to less than 10 per cent by weight of fumaric acid.

6. The method of improving the drying ability of a non-conjugated, unsaturated, non-hydroxylated fatty oil having from 10 to 24 carbon atoms in the carbon chains of the fatty acids of the oil which comprises heating said oil with from 3 per cent to less than 10 per cent of fumaric acid, based on the weight of said oil until formation of an adduct of the oil and fumaric acid, and then esterifying said adduct with pentaerythritol.

7. The method of improving the drying rate of soybean oil which comprises heating said oil with from 3 per cent to less than 10 per cent of fumaric acid based on the weight of said oil until formation of an adduct of the oil and fumaric acid, and then esterifying said adduct with pentaerythritol.

8. The method of improving the drying rate of linseed oil which comprises heating said oil with from 3 per cent to less than 10 per cent of fumaric acid based on the weight of said oil until formation of an adduct of the oil and fumaric acid, and then esterifying said adduct with pentaerythritol.

9. The method of improving the drying rate of cotton seed oil which comprises heating said oil with from 3 per cent to less than 10 per cent of fumaric acid based on the weight of said oil until formation of an adduct of the oil and fumaric acid, and then esterifying said adduct with pentaerythritol.

10. The method of improving the drying rate of safflower oil which comprises heating said oil with from 3 per cent to less than 10 per cent of fumaric acid based on the weight of said oil until formation of an adduct of the oil and fumaric acid, and then esterifying said adduct with pentaerythritol.

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