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PRODUCTION OF DRYING OILS

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6 Claims. (Cl. 260—410.6)

This invention relates to a method of improving the drying characteristics of drying and semi-drying oils and particularly to those drying oils obtained by the esterification of pentaerythritol and dipentaerythritol with higher fatty acids and higher fatty acid glycerides.

The esters of pentaerythritol with such higher fatty acids as those obtainable from linseed oil, tung oil and soya bean oil are known to possess good properties for use in the manufacture of paints and varnishes. By esterifying unsaturated fatty acids of this type with pentaerythritol, which contains four primary hydroxyl groups, products are obtained having improved drying properties and water-resistance as compared with the corresponding fatty acid triglycerides.

In my copending application Serial No. 363,495, filed October 30, 1940, of which this is a continuation-in-part, I disclosed a method of preparing drying oils of improved characteristics by the esterification of dipentaerythritol with higher fatty acids. Esters of higher fatty acids with dipentaerythritol are prepared in accordance with the disclosure of that application by heating the alcohol with from 1–6 moles of a higher aliphatic saturated or unsaturated monocarboxylic acid having 6 or more carbon atoms or mixtures thereof. Representative of the various higher fatty acids contemplated by the new process are lauric, palmitic, stearic, oleic, linoleic, linolenic, ricinoleic, eleostearic, n-caproic, n-caprylic, n-capric, myristic, etc., as well as the mixed fatty acids obtained by hydrolysis of oils such as cottonseed, palm, olive, castor, peanut, soya bean, linseed, tung, perilla, safflower, sunflower and the like.

In the copending application of William B. Johnston, Serial No. 378,418, filed February 11, 1941, there is disclosed an improved process for preparing dipentaerythritol-fatty acid esters of the type described in my copending application referred to above. The improvement described in the Johnston application resides in heating the triglycerides of the higher fatty acids with dipentaerythritol, with concurrent removal from the reaction zone of glycerol formed during the reaction, whereby the intermediate step of liberating the fatty acids from their glycerides is eliminated.

In preparing the drying and semi-drying oils of the above-described classes, both by esterification of the free fatty acids with pentaerythritol and dipentaerythritol and by the ester interchange method, considerable difficulty has been experienced in obtaining a neutral product of low hydroxyl and acid numbers. This difficulty is occasioned by the increased polyfunctionality of the normal esters of pentaetrythritol and dipentaerythritol with unsaturated higher fatty acids, as compared with the triesters of these acids with glycerol, which causes excessive polymerization or heat-embodying of the oil before the esterification reaction is completed. The present application is directed specifically to a method of overcoming this difficulty during the manufacture of these oils.

I have found that the above-mentioned difficulties may be overcome and a better product obtained by extracting the crude penta- or dipentaerythritol esters formed by the reaction of penta- or dipentaerythritol with higher fatty acids or their triglycerides with an aliphatic alcohol of from 1 to 3 carbon atoms. I believe that the superior drying properties of the pentaerythritol and dipentaerythritol fatty acid esters produced by my process are due to the removal therefrom of the more highly hydroxylated esters such as the mono- and diesters of penta- and dipentaerythritol. These highly hydroxylated esters have poor drying properties and the water resistance of their films is poor. The mono-, di and tri- fatty acid esters of penta- and dipentaerythritol are soluble in lower aliphatic monohydric alcohols such as methyl, ethyl and isopropyl and are accordingly removed from the crude reaction mixture in the alcoholic extraction process. The alcoholic extraction also removes unreacted fatty acids employed in the direct esterification process and glycerol formed in the ester interchange process and the removal of either of these materials improves the drying characteristics of the product. In preparing the drying oil esters I therefore discontinue the heating before excessive polymerization or heat-bodying has taken place and I am enabled to obtain a drying oil of good color, low viscosity and, by virtue of the alcoholic extraction step, free from highly hydroxylated esters, unreacted fatty acids, glycerol, oils and other materials which may exert a deleterious effect upon the drying properties of the ester.

Of the lower aliphatic alcohols I prefer to use ethyl alcohol since it is readily available at a comparatively low cost and appears to have the best balanced solvent action upon the various constituents of the crude reaction mixture. Methyl alcohol and isopropyl alcohol may be employed as solvents if desired but do not yield

such a satisfactory product. Other solvents do not have the proper solubilizing effect upon the constituents desired to be removed or, on the other hand, they dissolve the poly- fatty acid esters of penta- and dipentaerythritol.

In carrying out my process penta- or dipentaerythritol is reacted with a higher fatty acid or a higher fatty acid triglyceride until the desired stage of esterification has been reached. The reaction is stopped before excessive polymerization and heat-bodying of the oil has taken place. The crude reaction mixture is then extracted with alcohol which is preferably of 95–100% strength. The alcoholic extraction step may be merely a mixing of the crude ester with alcohol. Upon allowing the mixture to stand the extracted ester will form as a lower layer and the alcohol solution of the highly hydroxylated esters of the mixture will form as a top layer and may be removed by decantation. The extraction process may be repeated as many times as desired. Other methods of extracting or washing the crude ester product with alcohol may also be employed.

The improved drying oil produced by the process just described may be used in the preparation of paints, varnishes, printing inks and other compositions as will be apparent from the following specific examples which are given by way of illustration and not in limitation of the broader aspects of my invention. Parts given are by weight.

Example 1

672 parts by weight of soya bean oil acids and 106 parts (5% excess over theory) of dipentaerythritol having a melting point of about 220° C. and a hydroxyl value of about 1300 were heated together in a flask provided with an agitator, a carbon dioxide inlet tube for the exclusion of air, and a condenser for the collection of water. The heating cycle was as follows:

Time	Temp.	Total water condensed	Remarks
Hours	°C.		
0.5	170		
0.75	190		
1.75	204	24 parts by wt.	Reaction mixture cleared
2.75	208	29 parts	
3.75	217	30 parts	Acid No.=27.5
4.75	220		
5.75	220	31 parts	Acid No.=13.8

After about 8 hours' heating it was evident from the rate of water evolution that higher temperatures or a very long reaction period would be necessary to obtain a neutral ester, and this would probably result in excessive polymerization or heat-bodying of the oil. Accordingly the contents of the reaction flask were cooled and shaken with twice their volume of anhydrous ethyl alcohol. An emulsion was formed which quickly separated into an upper layer, containing the unreacted fatty acids and monoesters, and a lower layer containing the desired reaction product.

The lower layer was drawn off and heated in an inert atmosphere at 120° C. until all the residual ethyl alcohol was expelled. The product was a clear, viscous yellow oil having an acid number of 4.5, a hydroxyl number of 16.8, a viscosity of G (Gardner-Holdt) and a color of 7–8 on the I. P. V. R. scale. When given a second extraction with alsolute alcohol as before the acid number was reduced to 3.4.

Comparison of the product with K. V. O. linseed oil showed it to have a faster drying time, better water resistance and better original color, as well as better color retention in exterior paint formulation. It also heat-bodied faster than linseed oil at 600° F.

A typical mixed pigment exterior paint was made in which the soya and dipentaerythritol ester was compared with alkali refined K. V. O. linseed oil. The following formulation was used.

	Parts by weight
White lead	735
Titanium oxide	428
Zinc oxide	213
"Asbestine" talc	87
Oil	645

Drier: 0.5% Pb+0.05% Mn+0.005% Co as metal to oil.

The pigments were ground on a roller mill with part of the oil and the remainder of the oil was added together with the drier. The paint containing the dipentaerythritol-soya acid oil had a somewhat higher consistency than that of the linseed oil paint, but no increase in consistency was noted after ageing for one week.

The paints were brushed on steel panels. Both panels air dried overnight to a tack-free condition, although the films had the characteristic softness of this type of paint. A portion of each panel was then covered and the panels were exposed to sunlight. The linseed oil film yellowed slightly after one day and considerably after one week while no yellowing occurred on the film containing the dipentaerythritol ester.

Example 2

672 parts of linseed fatty acids and 110 parts of dipentaerythritol were heated together as in Example 1, the temperature of the mixture being carried to 190° C. during the first 25 minutes and maintained at about 204° C. for the next 4.75 hours. The acid number of the batch was then 17.7.

After cooling and extraction with anhydrous ethanol as in Example 1 the product had an acid number of 5, a hydroxy number of 27.3, viscosity of F and color of 9. Upon adding driers in the amount of 0.5% Pb+0.05% Mn+0.005% Co as metal to oil and flowing on a tin panel the oil dried much more rapidly than linseed oil containing similar amounts of drier. It was only slightly tacky in 4 hours, very slightly tacky in 6 hours, and completely tack-free in 24 hours.

Example 3

106 parts of dipentaerythritol and 672 parts of dehydrated castor oil acids were reacted as in Example 1, being heated to 190° C. in 1 hour and held at 190–207° C. for 4.25 hours longer. At this time 34 cc. of water had been collected and the acid number of the batch was 21.3.

The ester was extracted with absolute alcohol as in previous examples and was found to have an acid number of 7.9, a hydroxyl number of 32.1, a viscosity of L and a color of 8. Preliminary tests showed faster drying of this ester than of the soya bean ester described in Example 1.

Example 4

Linseed oil fatty acids were isomerized as described in my copending application Serial No. 378,060, filed February 8, 1941, by stirring together 100 parts by weight of the acids, 100 parts of water, and 25 g. of 85% potassium hydroxide

until a soap paste was formed and heating in an agitated autoclave at 225° C. for 3.75 hours. The soaps were then hydrolyzed with hydrochloric acid at the boiling point of the aqueous solution and the fatty acids were separated, washed and dehydrated. The acids were then found to contain 33.1% of doubly conjugated and 11.5% of triply conjugated acids, whereas the original material had contained 1.81% and 0.253% respectively.

62 parts of these acids were mixed with 10.1 parts of dipentaerythritol and heated with agitation in an atmosphere of carbon dioxide. The temperature was carried to 180° C. in one hour, then to 200° C. during the second hour and maintained at this point for 5 hours longer, when the acid number was found to be 11.3. The ester was then extracted twice with anhydrous ethanol, recovered and dried. It had an acid number of 2.1, viscosity of Y (Gardner) and color of 4 (Hellige).

Upon addition of driers containing 0.5% Pb+0.05% Mn+0.005% Co as metal to oil and flowing out on a tin plate the ester was medium set in one hour, had a very slight tack for the next 4 hours, and was tack-free in 6 hours. After air-drying for 24 hours it showed only a very slight whitening when immersed in distilled water.

A varnish was prepared by cold mixing the oil with a 50% toluene solution of a varnish type resin containing about 15% of phenol-formaldehyde resin and about 85% ester gum on the basis of 25 gallons of oil to 100 pounds of the solid resin. When flowed on a tin plate and tested by heating a sample of this varnish gas checked like a tung oil varnish. A drier was added in the amount of 0.2% Pb+0.04% Co as metal to total solids and tin panels were coated and tested for drying rate and water-resistance. The varnish showed a strong tack after 3 hours, considerable tack after 6 hours, only slight tack after 8 hours and was tack-free in 24 hours. The water resistance was identical with that of a heat-bodied tung oil varnish of similar composition.

Example 5

560 parts of soya bean fatty acids and 72 parts of pentaerythritol were heated to 190–200° C. in 45 minutes and held at this temperature for 6.5 hours. A stream of inert gas was blown through the mixture during the reaction period. The reacted mixture having an acid number of 18.0 was extracted with an equal volume of absolute alcohol, the lower layer removed and extracted again with half its volume of absolute alcohol. The lower layer, consisting essentially of pentaerythritol-soya bean fatty acid esters was then heated to 130° C. under a blanket of inert gas to remove all of the alcohol used in the extraction. The extracted ester at this point had an acid number of 3.6, a color of 2L on the Hellige color scale and a viscosity of E–F' on the Gardner-Holdt scale.

This material was an improvement over the unextracted pentaerythritol-soya bean fatty acid ester in rate of drying and water resistance of the dried film but was not as good as the ester prepared from dipentaerythritol-soya bean fatty acids in either of these characteristics.

Example 6

552 parts cottonseed oil, 80 parts dipentaerythritol, and 2.5 parts $Na_3PO_4.12H_2O$ were heated under CO_2 to 250° C. in 45 minutes and held at this temperature for 45 minutes more. At this point all of the dipentaerythritol was dissolved in the cottonseed oil and the reaction mixture was a clear solution. The temperature of the reaction mixture was then raised rapidly to 290° C. and kept at 290° C. for 2 hours, meanwhile blowing a strong stream of CO_2 through the solution to assist in volatilizing glycerol formed in the reaction of the dipentaerythritol with cottonseed oil glycerides. The product was then cooled and filtered to given an oil having a viscosity of I (Gardner-Holdt) and a color of 8 on the I. P. V. R. color scale.

A portion of the reaction mixture was washed twice with alcohol as described above. The air-drying properties of the washed and unwashed esters were compared with bodied linseed oil of comparable viscosity. With 0.4% lead and 0.04% cobalt drier (percentage as metal to oil) the film of the unwashed dipentaerythritol cottonseed fatty acid ester after 24 hours air-drying at room temperature was tack-free whereas the linseed oil film under like conditions was tacky. The ester which had been washed with alcohol was found to dry faster and give a more water-resistant film than that of the unwashed ester.

What I claim is:

1. A method of improving the drying characteristics of crude esters of the group consisting of higher unsaturated fatty acid esters of pentaerythritol and higher unsaturated fatty acid esters of dipentaerythritol which comprises extracting said crude esters with an aliphatic mono-hydric alcohol of from 1 to 3 carbon atoms to remove alcohol soluble mono-, di- and tri- fatty acid esters, thereby lowering the hydroxyl number and improving the drying characteristics of the crude ester.

2. A method of improving the drying characteristics of crude esters of the group consisting of higher unsaturated fatty acid esters of pentaerythritol and higher unsaturated fatty acid esters of dipentaerythritol which comprises extracting said crude esters with ethyl alcohol to remove alcohol soluble mono- di- and tri- fatty acid esters, thereby lowering the hydroxyl number and improving the drying characteristics of the crude ester.

3. A method of improving the drying characteristics of crude higher unsaturated fatty acid esters of dipentaerythritol which comprises extracting said crude esters with an aliphatic monohydric alcohol of from 1 to 3 carbon atoms to remove alcohol soluble mono-, di- and tri- fatty acid esters of dipentaerythritol, thereby lowering the hydroxyl number and improving the drying characteristics of the crude ester.

4. A method of preparing a dipentaerythritol ester of relatively low acid number and improved drying properties which comprises heating dipentaerythritol with higher unsaturated fatty acids to obtain crude mixed dipentaerythritol esters and thereafter extracting the product with an aliphatic mono-hydric alcohol of from 1 to 3 carbon atoms to remove mono-, di- and tri- fatty acid esters of dipentaerythritol and unreacted higher unsaturated fatty acids, thereby lowering the acid number and hydroxyl number and improving the drying properties of the crude ester.

5. A method of preparing a dipentaerythritol ester of relatively low acid number, low hydroxyl number and improved drying properties which comprises heating dipentaerythritol with higher fatty acid triglycerides to obtain crude mixed dipentaerythritol esters and thereafter extracting

the product with an aliphatic mono-hydric alcohol of from 1 to 3 carbon atoms to remove alcohol soluble mono-, di- and tri- fatty acid esters of dipentaerythritol and glycerol thereby lowering the hydroxyl number and improving the drying characteristics of the crude ester.

6. A method of improving the drying characteristics of crude soya bean fatty acid esters of dipentaerythritol which comprises extracting said crude esters with ethyl alcohol to remove alcohol soluble mono-, di- and tri- fatty acid esters of dipentaerythritol thereby lowering the hydroxyl number and improving the drying characteristics of the crude ester.

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