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RAPID DRYING OIL, HAVING CONJUGATED SYSTEM FROM SOY BEAN OIL

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11 Claims. (Cl. 260—406)

This invention relates to oils possessing drying properties having conjugated double bonds and to methods of preparing such oils from soy bean oil or soy bean oils from which the saturated glycerides have been partially to completely removed or from which also a part of the glyceride esters of oleic acid have been removed.

It is an object of my invention to prepare oils having quick drying properties by first oxidizing soy bean oil whereby oxygen is introduced at the point or points of the unsaturated C to C bonds in the unsaturated fatty acids of the glycerides, then eliminating water from the molecule without thermal decomposition whereby conjugated double bonds are formed in the higher fatty acid nucleus. Accordingly it is the particular object of my invention to synthesize from soy bean oil artificial drying oils having diene and triene and such polyene linkages by introducing OH groups into the carboxylic acid nucleus, then eliminating the OH groups and H atoms connected to different carbon atoms thereby securing this conjugated type of unsaturation. It is a further object to treat soy bean oils with oxygen gas or oxygen containing gas below a temperature sufficient substantially to promote polymerization of the oil and stopping the oxidation before body gelation takes place to introduce the OH groups into the carboxylic acid nucleus, then to eliminate H_2O thereby securing these conjugated type oils having properties closely akin to China wood oil. Oils made by my invention are oxidized, non-coagulated products. Restricted temperature ranges are used so that there is no substantial polymerization.

Soy bean oil has been used to a limited extent in paints admixed with larger proportions of linseed oil. Both these oils have the non-conjugated double bonds. It has been appreciated for years that an oil such as China wood oil having a conjugated system of double bonds is preferable to the oils having the isolated system because of the readiness of the first type to form films. Several years ago it was discovered that castor oil which has as a major constituent the glycerides of ricinoleic acid

$$CH_3(CH_2)_5\underset{\underset{OH}{|}}{CH}.CH_2CH=CH.(CH_2)_7COOH$$

could by heating under various conditions be converted into an oil having properties somewhat like China wood oil because of the elimination of water to give the ester of

$$CH_3(CH_2)_5CH=CHCH=CH(CH_2)_7COOH$$

This is characterized as a diene. Such a process and a description of the resulting oil is to be found in German Patent No. 555,496 and several other patents and in literature. Tung oil i. e. China wood oil contains eleostearic acid glycerides which have three double bonds in the conjugated positions and is referred to as a triene. And whereas this diene type dehydrated castor oil is not an equivalent of tung oil, because the last is faster in speed of drying, jelling and bodying, it does have places where it can be used in the place of or independently of China wood oil because it exceeds in speed of drying and bodying, linseed and perilla oils which have linolenic acid esters predominantly.

Soy bean oil has been classed by some authorities as a drying oil but more often as a semi-drying oil. Because of the relatively high cost of castor oil, the conversion of the unsaturated glycerides of soy bean oil into a drying oil of the unsaturated conjugated type admirably adapted to paint, varnish and other liquid coating compositions by the formation of polyhydroxy acid esters followed by dehydration fulfills a need. Because of wars in the Orient which cause both high prices and unavailability of China wood oil, serviceable substitutes are welcome.

Soy bean oil is characterized by an iodine number (Hanus) of about 128, with esters of saturated acid totaling about 11.2%, the glycerides of oleic acid 33.4%, of linoleic acid 51.5% and of linolenic acid 2.3%. Oleic acid has one double bond, linoleic two non-conjugated double bonds and linolenic acid three.

When an unsaturated oil is blown or oxidized by air hydroxyl groups are formed at the ethylene linkage. This is especially true if the oxidation is carried out with moist air. It is believed that oxygen is first absorbed so as to saturate the ethylene linkage, and that further reaction takes place with water to produce two hydroxyl groups. While this is the theory, it is known that hydroxyl groups are formed. Southcombe "Chem. of the Oil Industry" 1926, p. 181 refers to this in these terms: "Hydroxyl groups are unquestion-

ably formed as the considerable rise in acetyl value proves."

There are several ways by which the oxidation of fatty oils to secure hydroxy glycerides may be achieved, from which the dehydrated oils are then prepared. Several treatments will be given. These several methods of oxidation outlined herein do not yield the same product.

Refined soy bean oil is oxidized by air preferably moist air at 120° C. in presence of lead and calcium oxides and pyrolusite to yield an oil of an iodine number ⅔ to ½ of the value before blowing and a rise in acetyl value or absorption of oxygen corresponding to the drop in iodine value. Unheated soy bean oil whose composition I have set out above has an iodine value of 128 (Hanus method of determination). Other temperatures between 70°–150° C. preferably not above 125° C. and conveniently 80°–90° C. can be used. The pressure employed varies from 25–125# gauge pressure, usually 45#, but these limits can be varied. Dangers of using temperatures 150° C. and above is that polymerization results. Oxidation is stopped before gelation or coagulation of the body of oil takes place. There is during blowing a gradual diminution in solubility of the oil in the usual soy bean oil solvents such as petroleum spirits, carbon tetrachloride, and proportionately an increase in the solubility in ethyl alcohol and other lower alcohols. The unoxidized portion can be removed as explained later.

Another method is to blow soy bean oil by the method set out in Patent No. 2,059,259 using temperatures not above 70° C. A longer time is required than in the former method. The test as set out in Patent No. 2,059,259 is that "this end point lies within the range of where the oil will form a solid gel on standing, either immediately upon cooling to room temperature, or after several weeks but not beyond the point where the oil will be fluid at a temperature of about 160° F. when the treatment is first finished."

Another method is to blow at temperatures from 40°–70° C. refined soy bean oil, with humid air. The humid air produces the hydroxy glycerides quicker than the dry air.

In all these cases, a soy bean oil which has been treated with selective solvents to remove the saturated glycerides and non-esters may be used instead of the refined oils containing the saturated glycerides. Lecithin and other phosphatides should be absent because the presence thereof slows down the oxidation. Of course if one chooses, the mono or diglycerides from soy bean oil or other esters thereof could be used.

Auto catalysts can be employed of course. Some of these are set out in the following U. S. De Groote patents: Nos. 2,025,806 through 2,025,809.

Another method of oxidation is that set out in U. S. Patents No. 2,072,151 and 1,968,243. In the former soy bean oil has added to it 0.1–2% of maleic acid (or anhydride) or equivalent acid. The oil is blown with air at 80° C. for 25–30 hours but not until a gel or congealed product is formed. Before the product fails to dissolve in ethyl ether the oxidation is stopped. The unoxidized and unoxidizable oil is then removed by treatment with petroleum ether or petroleum naphtha or other like solvent having little solvating action on the desired components of the oxidized uncoagulated oil. The desired uncoagulated components are in the lower layer. This extraction may well be repeated once or more. A temperature of 60–110° C. can be used in this aforesaid oxidation. I prefer to use humid air because this does shorten the operation. Instead of maleic acid, then as in U. S. No. 1,968,243 cobalt linoleate or equivalent can be added in 0.4% to the soy bean oil and like blowing and subsequent operations carried out.

These various oxidized oils containing two or more OH groups in each acid residue part of the glyceride are heated to effect removal of water from the compound. Various methods can be used, the efficiency of which varies. I prefer to achieve the dehydration by using as catalysts or aids the following compounds: clays, oxides of certain metals, acid derivatives of sulfuric acid, phosphoric acid. When clays were used, the degree of dehydration increased approximately with the amount used. Rather large amounts were required to obtain products with the highest iodine numbers. There were other methods than these but these are exceedingly efficient and particularly the clays. The use of the aforesaid materials on these synthetic hydroxylated oils from soy beans can even be considered an invention within an invention.

The general method of procedure of dehydration is this:

50 g. oxidized soy bean oil is put in 500 ml. round bottom flask. The selected catalyst is added to the oil in the flask through a delivery tube in a stopper. Inert gas is admitted through another tube. A thermometer is inserted in the flask. The flask was heated by molten metal or other heating medium. The delivery tube was connected to an air condenser which is connected to a graduate. From the acetyl and iodine numbers the theoretical amount of water which would be formed in complete dehydration can be calculated. This is one way of following the reaction by determining from the amount of water distilled, the extent of dehydration.

As a rule the temperature was increased rapidly to about 200° C., after which it was allowed to increase to a more moderate rate. The active range was usually below 250° C. Of course a vacuum can be employed to supplement this whereby lower temperatures can be used. In any event there should never be attained such a high temperature as to produce thermal decomposition and yield shorter carbon chain compounds except in minor incidental traces.

Kaolin was used in amounts of 20%, 16%, 10%, 4% and 1%, the upper range being best, yielding oil products of greatest increase of I number and decrease of acetyl value. The time of heating was 30–60 minutes. Sodium acid sulfate in amounts of 2% gave oil products of almost as great an increase in I number. Phosphoric acid 2% of 85% strength on 2 g. coke yielded oil product of somewhat less I number than the acid sulfate. Tungsten oxide 1% of the weight of the treated oil as reprecipitated powder gave a drying oil upon removal of the catalyst which had almost as great an increase of I number as the 16% kaolin treatment. Al_2O_3 with and without Zn can be used, in a similar range up to 275–280° C.; the amount of Al_2O_3 and Zn is a few percent. Zn can be used with kaolin too. The function of the Zn is to prevent polymerization. Solid catalysts have to be removed from the oil of course.

After the above described dehydration operation, it may be expedient to remove the esters of hydroxy acids, olein acid and other impurities. One way is the use of acetone or lower alcohols. Another way, the reverse of alcohol in solubility

is the use of petroleum solvents as petroleum naphtha.

The drying oils of conjugated double bonds produced from oxygen gas oxidation and dehydration have long life of films, excellent color retention, pronounced water resistance and good pigment wetting characteristics. They have such uses as: making odorless and colorless oil varnishes, printing inks, "baking" varnish for tin, textile check-back oils, for China wood oil cook-in varnish, outside varnish, linoleum and factics, lacquers, synthetic fibers, for plastification instead of castor oil, various chemical syntheses.

These dehydrated oils supra can be blended with China wood oil, linseed oil, synthetic resins, etc. Thickening by heat polymerization (stand oil) or blowing with air is easy. The addition of 1–2% dryer solution speeds drying.

To polymerize this dehydrated pre-oxidized soy bean oil, it is heated at a uniform rate, air excluded while the oil is gently agitated by a current of CO_2. Temperatures of 500° F. to 590° F. are suitable. The rate of polymerization depends on the temperature. In one series of runs, the dehydrated oil was bodied to a viscosity of 46 poises in a vacuum of 15–25 mm. at 535° F., 575° F. and 625° F. The time was shorter for the highest temperatures.

Blowing dehydrated pre-oxidized soy bean oil with air or oxygen at elevated temperatures gives viscous products which are quick setting.

The dehydrated oil secured from the oxygen containing gas pre-treated soy bean oil can be bodied with linseed and tung oils.

Such driers as cobalt naphthenate 0.1%, lead naphthenate 0.2%, manganese naphthenate 0.03% are adaptable for shortening the drying of the oil, whether bodied or not.

Alkyd type resins can be made from its fatty acids by heating and agitating it with phthalic anhydride, glycerine at conventional temperatures and amounts, such temperatures being such as 470° F. (until a daub at room temperature gives a long silk which is about 8 hours, stirring at 100 R. P. M.) then cooling whereupon a thinner is added and small amounts of lead or cobalt dryer.

Also for further unsaturation, the "enol" oils (dehydrated soy bean oil after oxidation—see supra) are treated with aqueous hypochlorous acid. This chloroxy oil itself has good drying properties. Then both water and hydrogen chloride are split off to yield "enol" oils of greater unsaturation than the starting materials respectively. Both treatments are done according to conventional procedures.

It is to be understood that I do not commit myself to any theory except that water is split off from the hydroxylated soy bean oil or other esters of soy bean acids such as the monohydric alcohol esters of low molecular weight or the esters of sorbitol, or other polyhydric alcohols of 4–6 C atoms.

It is thought, that as in the case of the hydrogenation of fatty oils containing unsaturated glycerides of various degrees under proper conditions the more unsaturated esters are hydrogenated before the oleates, so also that in the case of oxidation by methods herein, the more unsaturated glycerides are oxidized first and the oleates last. This may be termed selective oxidation and whereas it may not be entirely true, the analogy to selective hydrogenation of oils exists.

When oleates are blown, because there is only one double bond present, the oily body is characterized by hydroxyl groups like the esters of dihydroxy stearic acid. The linoleic acid nucleus would, after linolenic acid nucleus was partially oxidized, seem to be first oxidized with the attendant introduction of two "OH" groups on adjacent carbon atoms. By blowing linoleates or oils containing the same and other highly unsaturated esters, the resulting product when the double bonds have been partially saturated is characterized by the presence of both a hydroxyl radical and an ethylene linkage. Then with attaining the same degree of unsaturation thus as the oleic acid glycerides both would oxidize simultaneously. These materials because of the presence of OH groups can be converted into diene and other higher polyenes characterized by conjugated system of double bonds. It will be seen upon considering the structure of linoleic acid (some question, but given by Righter's Org. Chem. vol. 1, p. 354, 6th ed.)

$$CH_3(CH_2)_4CH{=}CH.CH_2CH{=}CH(CH_2)_7COOH$$

that it is possible to have four double bonds in conjugated position upon full oxidation and dehydration. Oleic acid would give two double bonds in conjugated position similarly. Whether the product has "enes" beyond the di or tri, I am not certain but I think so. There would seem to be; and when the hypochlorous acid treatment with subsequent HCl and H_2O elimination (sometimes when referring to castor oil dienol designated the Swiss treatment because used in Switzerland to secure the trienol) is used after the initial dehydration certainly at least trienol oil constituents are present just as in the case of the "Swiss treated castor oil" i. e. trienol castor oil.

I am aware that the type of reactions employed herein are not new but the employment of these reactions in series on soy bean oil or esters of these mixed acids thereof is new and the products are new. The preparation of olefines having conjugated double bonds from glycols such as

$$(CH_3)_2.C(OH).C(OH)(CH_3)_2$$

by the removal of water by means of zinc chloride, potassium hydrogen sulfate or oxalic acid or by distilling them over heated alumina is disclosed in J. A. C. S. 1914, 36, 980. And the use of dry and moist air or oxygen gases to introduce OH groups into unsaturated oils is not broadly new, using non-conjugated fatty oils as the initial material. Mention has been made of this previously. My invention resides in the selection of the initial material, applying proper reactants and reactions thereto in series with the result that valuable new products have been synthesized.

It is to be understood that while I have illustrated several methods, both in the introduction of hydroxy groups and in the elimination of water from the intermediate product to secure a conjugated system or systems, I do not intend to be limited except as defined in the claims. The fact that my dehydrated oils react with maleic anhydride is the indication that my oils possess the conjugated system or systems.

I claim:

1. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a gas containing free oxygen below a temperature sufficient to promote any material polymerization and without gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil ester nucleus, then eliminating

water of composition from the hydroxlated esters by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting esters is produced.

2. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a gas containing free oxygen below 150° C. and without gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil nucleus, then eliminating water of composition from the hydroxylated esters by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting esters is produced.

3. The process of producing a rapid drying oil from soy bean oil comprising reacting soy bean oil freed from at least a portion of the saturated fatty acid esters, by contacting it with a gas containing free oxygen below a temperature sufficient to promote any material polymerization and gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil ester nucleus, then eliminating water of composition from the hydroxylated oil by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting oil is produced.

4. The process of producing a rapid drying oil from soy bean oil comprising reacting soy bean oil freed from at least a portion of the oleates, by contacting it with a gas containing free oxygen below a temperature sufficient to promote any material polymerization and gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil, then eliminating water of composition from the hydroxylated oil by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting oil is produced.

5. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with oxygen below a temperature sufficient to promote any material polymerization and without gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil ester nucleus, then eliminating water of composition from the hydroxylated esters by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting esters is produced.

6. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a water-moist gas containing free oxygen below a temperature sufficient to promote any material polymerization and without gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil ester nucleus, then eliminating water of composition from the hydroxylated esters by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting esters is produced.

7. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a gas containing free oxygen at a pressure substantially above atmospheric pressure and below a temperature sufficient to promote any material polymerization and without gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil nucleus, then eliminating water of composition from the hydroxylated esters by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting esters is produced.

8. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a water-moist gas containing free oxygen below a temperature sufficient to promote any material polymerization and without gelation or coagulation of the oil mass, and at a pressure substantially above atmospheric pressure, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil nucleus, then eliminating water of composition from the hydroxylated esters by heating the same in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting esters is produced.

9. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a humid gas containing free oxygen at a temperature lying between about 40° C. and 70° C. whereby OH groups are introduced into the unsaturated carboxylic acid radical part of the soy bean oil nucleus without gelation of the oily mass, then eliminating water of composition from the hydroxylated esters by heating the same without substantial pyrolysis in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and faster drying properties than the original esters is produced.

10. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a gas containing free oxygen in the presence of a small amount of non-volatile alkaline agent while maintaining a temperature insufficiently high to promote any material polymerization and without gelation or coagulation of the oil mass, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil ester nucleus, then eliminating water by composition from the hydroxylated esters by heating the same without substantial pyrolysis

in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and faster drying properties than the original esters is produced.

11. The process of producing a rapid drying oil from soy bean oil esters comprising reacting the soy bean oil esters by contacting these esters with a moisture laden gas containing free oxygen below a temperature of 150° C. and without gelation or coagulation of the oil mass, and at a pressure substantially above atmospheric pressure, to introduce OH groups into the unsaturated carboxylic acid radical part of the soy bean oil nucleus, said oxidized oil having an iodine number at least about one-third less than the starting oil before the gas contacting operation, then eliminating water of composition from the hydroxylated esters by heating the same in the presence of a catalyst promoting the elimination of water and removing the said water by distilling it off whereby an oil having conjugated double bonds and drying faster than the starting esters is produced.

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