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SYNTHETIC DRYING OILS

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This invention relates to a new class of drying oils of improved drying characteristics and to their preparation. More particularly, it relates to improved drying oils resulting from the esterification of polyallyl alcohols containing at least 5 esterifiable primary hydroxyl groups with fatty acids and mixtures thereof containing a relatively high percentage of unsaturated fatty acids and having an iodine value of at least 100.

The naturally occurring drying oils most commonly employed in the arts heretofore, particularly in the manufacture of paints and varnishes, have consisted essentially of a mixture of triglycerides of higher fatty acids the larger proportion of which are unsaturated. The drying characteristics as well as the heat-bodying or varnish-making qualities of these oils have generally been considered to depend primarily upon the degree and nature of their unsaturation.

The degree of unsaturation is dependent upon the ratio of linoleic, linolenic, eleostearic or other of the polyenic acid radicals of the glycerides to the oleic and the saturated acid radicals present in the oil and is commonly determined by halogen absorption measurements such as the iodine value. The nature of the unsaturation is also important inasmuch as conjugated unsaturation normally leads to appreciably faster drying and to faster heat-bodying oils than does non-conjugated unsaturation. I have taken advantage of this fact in my isomerization process disclosed and claimed in my copending application Serial No. 378,060, filed February 8, 1941, whereby unconjugated double bonds of fatty acids are caused to enter into conjugation.

It has generally been considered that the iodine value of a drying oil is the best criterion of its drying qualities and most textbooks therefore classify oils as "non-drying," "semi-drying" and "drying" in accordance with their iodine values. A recognized exception is the case of oils in which the unsaturation is of the conjugated rather than unconjugated form. Because halogens tend to react incompletely with conjugated double bonds the ordinary methods of analysis yield iodine values which are abnormally low and erroneous because they no longer provide a true measure of the degree of unsaturation. Hydrogen can be made to fully saturate conjugated double bonds and the degree of unsaturation of the conjugated oils has been accurately measured by a determination of the amount of hydrogen required to saturate these oils. To provide a uniform basis of measurement and a uniform standard these hydrogen values are generally calculated in terms of their iodine equivalent. These "hydrogen-iodine values" are therefore analogous to ordinary iodine values and both measure the unsaturation of the oils in terms of the percentage of iodine absorbed per unit weight of an oil. In other words the common idea has been to estimate the worth of an oil for varnish and paint purposes in terms of the amount of its unsaturation per unit of weight.

I have found that the iodine value of an oil is a misleading measure of its drying qualities since it is actually the amount and kind of unsaturation per molecule of oil rather than the unsaturation per unit weight that determines drying speed and heat gelation. This follows from the general theories of polymerization described by me in Industrial & Engineering Chemistry, vol. 229, pp. 440, 579 (1937) and is a special case of the broader concept that the number of functional groups of each molecule determines the gelation and drying characteristics of the oil.

In accordance with the present invention I compensate for the lack of an adequate amount of unsaturation in the majority of the drying oils, not by the customary means of trying to increase the amount of unsaturation per unit of weight, i. e. the iodine value, but by increasing the number of double bonds per molecule of the oil. The present invention accomplishes these theoretical and practical objectives, and others as will appear hereinafter, by the synthesis of esters in which at least 5 fatty acid radicals have been combined with one molecule of a polyallyl alcohol having at least five esterifiable primary hydroxyl groups. According to the principles of this invention the larger the number of the combined fatty acid radicals, the faster the rate of drying or of heat-gelation and the smaller may be the ratio of polyunsaturated acid radicals to the oleic or saturated acid radicals of the oil without inhibition of the drying or gelation characteristics. Therefore, I am able to utilize the mixed fatty acids of very poor drying oils such as cottonseed, corn and soya bean oils and convert these into esters which dry better than ordinary linseed oil without wasting or rejecting any of their constituent fatty acids.

I have found that oils produced by esterifying unsaturated higher fatty acids with polyallyl alcohols containing at least five and preferably considerably more than five primary hydroxyl groups possess improved drying properties as compared with glyceride oils prepared from the same higher fatty acids.

The polyallyl alcohols employed by me in the preparation of my improved drying oils may be prepared by blowing a stream of oxygen through heated allyl alcohol in a suitable vessel. 3080 parts by weight of allyl alcohol purified by distillation from NaOH were heated and maintained near the refluxing temperature in a closed vessel fitted with a reflux condenser. Oxygen was blown through the alcohol for a period of 240 hours at which time the acid number of the reaction mixture had increased to 18.0. The light yellow vis-

cous reaction product was freed of monomeric allyl alcohol by heating under reduced pressure. 1445 parts by weight of a clear, pale yellow, allyl alcohol polymer were obtained having a hydroxyl number of 600, acid number of 23.7, saponification number of 91, an iodine number of 78.7 and having approximately 10 primary hydroxyl groups per molecule. Other polyallyl alcohols prepared by a similar process were found to have from 5 to 16, and more, primary hydroxyl groups per molecule depending upon the condition of the polymerization reaction.

Fatty acids employed by me to provide drying oils of improved characteristics include those fatty acids derived from drying and semi-drying oils as well as the higher unsaturated fatty acids in more or less pure state. Since the iodine value of fatty acids is a measure of their degree of unsaturation per unit of weight and the molecular weights of the oil acids are closely equivalent it has been found that it can be conveniently employed to demarcate those fatty acids and fatty acid mixtures which may be reacted with the polyallyl alcohols of this invention to yield drying oils of improved properties. Accordingly I have found that those fatty acids and mixtures thereof having an iodine value of at least 100 may be employed in practicing my invention herein described.

Although it is possible to employ the straight unsaturated fatty acids, for example linoleic acid which has an iodine value of about 181, I prefer to use the fatty acids ordinarily commercially obtainable in the form of mixtures of fatty acids obtained by the hydrolysis of animal and vegetable oils. When using fatty acid mixtures obtained from semi-drying oils, such as cottonseed oil, sunflower seed oil, corn oil, sesame oil, etc., which fatty acid mixtures have iodine values of over 100, with polyallyl alcohols having at least 5 esterifiable primary hydroxy groups, the oil thus obtained has greatly superior drying properties when compared with its corresponding fatty acid triglyceride. This improvement, I believe, is due to the increased number of double bonds per molecule, i. e. the increased functionality of the new polyallyl alcohol esters in comparison with the glycerol ester which has but three ester linkages thus limiting the number of unsaturated functional groups obtainable in the molecule. These improved drying oils may be employed as such or may be blended with linseed oil, oiticica oil, tung oil, etc. to good advantage.

When I react polyallyl alcohols having at least 5 esterifiable primary hydroxyl groups with fatty acids derived from drying oils such as linseed oil, soya bean oil, oiticica oil, perilla oil, dehydrated castor oil, and the like, which have hydrogen-iodine values of 130 or more, the products possess greatly superior drying properties as compared to the corresponding glycerol-fatty acid esters. These improved oils show many of the characteristics of tung oil in time of drying, hardness of the film and water-resistance and may be used in place thereof for many purposes. Data showing more specifically the drying characteristics of such improved oils are given in the examples and tables which follow.

When preparing my improved drying oils I ordinarily employ substantially stoichiometrical proportions of the fatty acids and the polyallyl alcohols, that is, one molecule of fatty acid is added to the reaction mixture for each esterifiable primary hydroxyl group in the polyallyl alcohol employed. I do not intend to restrict my invention, however, to the use of substantially stoichiometrical quantities since it may be desirable in some cases to employ larger quantities of the alcohol or acid constituent.

The reaction whereby the drying oils of the present invention are produced takes place at elevated temperatures within the range 180–250° C. and preferably between 195–215° C. The time required for completing the reaction varies considerably and depends upon the particular reactants employed, the temperature, the catalysts (if any), the viscosity of the product desired, etc. Accordingly it is most convenient to measure the course of the reaction by the acid number of the reaction mixture which may be reduced to about 10 or even less when employing stoichiometric quantities of fatty acid and alcohol. However, because of possible excessive polymerization of the oil during the heating period I frequently stop the reaction when the reaction mixture has been reduced to an acid number of about 20. When an excess of fatty acid has been employed these values do not hold and allowance must be made for the excess of acid. When it is desired to obtain an oil of particularly low viscosity characteristics I react the mixture under milder conditions and stop the heating at acid values of the order of 35.

In some cases, and particularly when easily polymerizable higher fatty acids are employed such as those derived from linseed oil, soya bean oil or oiticica oil, or where isomerized fatty acids having a high content of conjugated double bonds are used such as the isomerized acids of soya bean oil, linseed oil and dehydrated castor oil, some difficulty may be experienced in obtaining an oil having a low hydroxyl value. When this difficulty is encountered it can be overcome by adding relatively small amounts of a reactive monocarboxylic acid of relatively low molecular weight or its anhydride, near the end of the heating period, in order to esterify any hydroxyl groups of the polyhydroxyl alcohol that may not have been esterified by the higher fatty acid. Thus, for example, in preparing synthetic drying oils consisting of esters of higher unsaturated fatty acids with polyallyl alcohol having at least 5 esterifiable primary hydroxyl groups, stoichiometric quantities of the fatty acid and alcohol may be heated together in the manner previously described until a product having a hydroxyl number of 20–50 is obtained, whereupon the calculated amount or an excess of a lower fatty acid or its anhydride such as acetic acid, propionic acid, butyric acid, acetic anhydride, ketene or other monocarboxylic acid of relatively low molecular weight such as benzoic acid, abietic acid, rosin or hydrogenated rosin is added. The heating is then continued, with distillation of excess lower fatty acid if necessary, until the oil has a suitably low hydroxyl value.

During the reaction period and while the product is at elevated temperatures it is advisable to keep it under an inert atmosphere such as CO_2 or N_2 to avoid oxygen induced polymerization. Catalysts such as p-toluene sulfonic acid, zinc chloride, HCl, litharge etc. in amounts of about .1% to 1% may be employed to speed up the reaction if desired but I have found that their use is not ordinarily necessary.

Upon completion of the esterification the reaction mixture usually contains small percentages of unreacted fatty acids, alcohol and only partially esterified alcohols which may be re-

moved to reduce the acid number and improve the drying properties of the oil. These materials may be readily removed by washing the product with ethyl alcohol as described in the examples which follow. It is also possible to remove the excess fatty acids by blowing steam through the oil, preferably under partially reduced pressure, in the manner of a steam distillation but care should be taken that the additional heating does not cause excessive polymerization of the oil. Still another method is to distill off the undesired constituents under a vacuum of a few millimeters pressure. The alcohol extraction method is most useful in those cases where a very low viscosity oil, as for paints, is to be produced and the reaction has been stopped while substantial quantities of unreacted fatty acids and polyhydroxy alcohols remain. In higher viscosity products such as used in varnishes an alcohol extraction or other means of reducing the acid value below 10 is not usually necessary.

My new drying oils may be used in the same manner and for the same purposes as drying oils heretofore used in the art such as in the manufacture of paints, varnishes, enamels and other coating compositions, alkyd resins, linoleum, printing inks, and many other products. The examples which follow illustrate in a degree some of these uses as well as the preparation of many different types of esters but are intended to be illustrative rather than in limitation of my invention which is to be construed as broadly as the appended claims permit. All parts given are by weight.

EXAMPLE 1

180 parts by weight of polyallyl alcohol containing approximately 10 primary OH groups in each molecule and 560 parts by weight of linseed fatty acids were charged into a reaction vessel fitted with a stirrer, thermometer, and CO_2 inlet tube leading to the bottom of the reaction mixture. The mixture was heated on an oil bath and the temperature brought to 200° C. in one hour. The water formed was distilled out through an outlet tube provided for the purpose and a good stream of CO_2 was maintained during all of the heating. After heating for 6 hours at 200–210° C. the heating was stopped and the product cooled and washed three times by extraction with ethyl alcohol. The final traces of alcohol were removed by blowing CO_2 through the oil at 120–130° C.

EXAMPLE 2

An oil was prepared from 180 parts by weight of polyallyl alcohol and 560 parts by weight of isomerized linseed fatty acids in the manner described above. The isomerized linseed fatty acids contained 36.8% of fatty acids having two double bonds in conjugation and 4.6% of fatty acids having three double bonds in conjugation.

Some of the more important chemical and physical characteristics of the oils prepared in Examples 1 and 2 are given in the following table. The properties of tung oil, oiticica oil, and dehydrated castor oil are also included for purposes of comparison. Viscosity values are given on the Gardner-Holdt scale and color is indicated on the Varnish Color System of the Institute of Paint and Varnish Research.

Table 1

Oil	Color	Viscosity	Acid No.	Ester value	Sap. No.	Iodine value (Wijs 2-hr.)	OH value
Linseed fatty acids+							
Glycerol	7	A	5.2	183.6	188.8	174.8	12.7
Polyallyl alcohol	11	S	8.0	168.2	176.2	162.1	10.6
Isomerized linseed fatty acids+							
Glycerol	1	F	6.0	185.4	191.4	137.6	14.5
Polyallyl alcohol	8	Z_3	6.1	172.8	178.9	122.0	6.2
Tung oil	10	J	7.7	184.9	192.6	164.2	-------
Oiticica oil	11	T	7.1	185.7	192.8	161.4	-------
Dehydrated castor oil	4	G	8.3	188.6	191.9	143.7	25.3

The above described drying oils were thinned to practically the same viscosity with mineral spirits and then there was added 0.02% cobalt and 0.16% lead as drier. Tin and glass panels were cleaned with toluene and the various oils applied. The panels were then inclined at approximately the same angle and the oil allowed to dry in a room at a constant temperature of 24° C. and relative humidity of 50%. Throughout these tests and in the preparation of the oils it was attempted to maintain uniform conditions so that the drying qualities of the oils could be compared directly.

Table 2

Oil	Tin panels			Glass panels		
	Set, hrs.	Tack-free, hrs.	Order of relative hardness after 24 hours	Set, hrs.	Tack-free, hrs.	Order of relative hardness after 24 hours
Linseed fatty acids+						
Glycerol	3.5	5.5+	9	3	24+	7
Polyallyl alcohol	1.5	3.5	3	1.5	5.5	1
Isomerized linseed fatty acids+						
Glycerol	4.5	5.5	9	3	5.5	7
Polyallyl alcohol	3.5	4.5	6	3	5.5	4
Tung oil	3.5	3.5	2	3	3	1
Oiticica oil	5.5	5.5	4	3	3	1
Dehydrated castor oil	2.5	4.5	8	3	3	6

It will be noted from the above that my drying oils compare favorably with tung oil and in most cases are superior to oiticica oil and dehydrated castor oil in drying time and hardness and show distinct improvement over the results obtained with similar oils prepared with glycerol as the alcohol.

These same oils were also tested for heat gelation time and water resistance of their films. The heat gelation test was made by a modified A. S. T. M. procedure and consisted in determining the time in minutes necessary for 5 cc. of the oil to gel in a 6 inch test tube at a temperature of 282° C., ±2° C. In the water resistance test a tin panel carrying a film of oil dried for at least 48 hours was immersed in water at 28° C. and examined at periods of 24 hours and 72 hours. The degree of whitening of the films was noted. In the table "1" represents no whitening; "2," very slight trace; "3," trace; "4," considerable; "5," severe; and "6," very severe. The panels were then removed from the water, exposed to the air, and their relative order of recovery noted. The results of these tests are as follows:

Table 3

Oil	Gelation time, minutes	Water resistance		
		24 hr.	72 hr.	Recovery
Linseed fatty acids+ Glycerol	>760	5	6	3
Polyallyl alcohol	205	2	3	1
Isomerized linseed fatty acids+ Glycerol	>600	4	5	3
Polyallyl alcohol	35	3	3	1
Tung oil	12	1	2	1
Oiticica oil	39	2	4	2
Dehydrated castor oil	410	4	4	2

These results show the striking improvement in my new oils over the corresponding fatty acid triglycerides and further show the closeness with which they approach the gelling time and film forming properties of tung oil.

EXAMPLE 3

193 parts by weight of polyallyl alcohol and 600 parts by weight of soya bean fatty acids were mixed and heated in a suitable reaction vessel at 200–210° C. until the acid number had dropped to 32.8. The product was then washed 4 times with ethyl alcohol whereupon the acid number was reduced to 4.5. The viscosity of the oil was reduced with acetone and it was then filtered through a paint strainer to remove a small amount of jelled particles which had formed. Alcohol and acetone were then removed by blowing with CO_2.

EXAMPLE 4

90 parts by weight of polyallyl alcohol and 282 parts by weight of cottonseed fatty acids were heated at approximately 200° C. The reaction mixture was stirred and a stream of CO_2 blown through it throughout the heating period. The acid number had been reduced to 35.8. The product was cooled and washed 4 times with ethyl alcohol whereby the acid number was reduced to 5.4. The viscosity of the oil was reduced with acetone and the material filtered through a paint strainer as above. The alcohol and acetone were then removed by blowing with a stream of CO_2.

What I claim is:

1. A method of preparing drying oils with improved drying properties which comprises esterifying a polyallyl alcohol having at least 5 esterifiable primary OH groups with fatty acids having an iodine value of at least 100 derived from an oil of the group consisting of dehydrated castor oil, soya bean oil, linseed oil and their conjugated isomers until at least 5 of the esterifiable primary OH groups have been esterified.

2. A method of preparing drying oils of improved drying properties which comprises esterifying substantially completely a polyallyl alcohol having at least 5 esterifiable primary OH groups with linseed oil fatty acids.

3. A method of preparing drying oils of improved drying properties which comprises esterifying substantially completely a polyallyl alcohol having at least 5 esterifiable primary OH groups with isomerized linseed oil fatty acids.

4. A method of preparing drying oils of improved drying properties which comprises esterifying substantially completely a polyallyl alcohol having at least 5 esterifiable primary OH groups with dehydrated castor oil fatty acids.

5. A drying oil consisting of a polyallyl alcohol having at least five esterifiable primary hydroxy groups esterified with higher fatty acids having an iodine value of at least 100, said oil having better drying characteristics than a triglyceride of the same fatty acids.

6. A method of producing drying oils of improved drying properties which comprises esterifying a polyallyl alcohol having at least five esterifiable primary hydroxy groups with higher fatty acids having an iodine value of at least 100 until at least five of the esterifiable primary hydroxy groups of the alcohol have been esterified.

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