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OIL FROM HYDROXYLATED FATTY ACIDS

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Usual natural oils are glycerides of higher unsaturated fatty acids. In recent years, considerable study has been given to the preparation of synthetic oils and related compounds of the alkyd resin type and in such case the synthetic bodies produced ordinarily are glycerides or esters of comparatively low molecular weight polyhydric alcohols. At various times (as in times of war or threatened war) there are many demands for glycerine and its usual equivalents, and at the same time fatty acids are relatively plentiful. The present invention relates to the manufacture of oils from natural fatty acids without the use of glycerine or what are normally considered equivalent types of alcohol.

This invention is based on our discovery that if the fatty acids of drying oils are hydroxylated, they can readily be converted into substantially neutral oils in various manners. Thus if the hydroxylated acids are heated, they will undergo inter or intra esterification to form lactones or lactides or other substantially neutral molecules, or such hydroxylated acids can be esterified with other acid bodies which may themselves be fatty acids of drying oils or may be lower fatty acids, or which may be other acid bodies of a film-forming nature such as the acids of natural resins, or various carboxylic acids such as phthalic acid or maleic acid or the like. Since the hydroxylated drying oil acids will have both active hydroxyl groups and also carboxyl groups, the reaction may be somewhat controlled by first blocking the carboxyl groups. This can be accomplished by esterifying the hydroxylated fatty acids with a simple monohydric alcohol, and for this purpose we have found methyl alcohol particularly efficient, as the esterification can be conducted under conditions which will not cause substantial inter or intra esterification of the hydroxylated molecules, thus leaving the hydroxyl groups available for further reaction.

The degree of hydroxylation of the fatty acids will of course bear some relation to the degree of unsaturation of the oil treated, for of course oleic acid will develop fewer hydroxyl groups than a more unsaturated acid such as the drying oil acids. However the proportionate yield of hydroxylated acids tends to decrease as the iodine number of the acid to be treated increases, due to the development of oxidized by-products and products of degradation.

The hydroxylation may be accomplished by the use of various oxidizing agents such as potassium permanganate or hydrogen peroxide. The addition of hydroxyl groups to the various oil fatty acids gives rise to the formation of a number of isomers similar to those found in sugar chemistry. Generally speaking, we have found that the hydroxylated fatty acids prepared by the use of hydrogen peroxide have a lower melting point than those prepared by the permanganate method. This observation applied particularly to the treatment of mixed acids such as those obtained from natural oils. In the examples given hereafter the hydroxylation is carried out by the permanganate method except where the peroxide method is particularly indicated.

In our use of the hydrogen peroxide method, the unsaturated fatty acids to be hydroxylated were dissolved in glacial acetic acid to which a quantity of 30% hydrogen peroxide solution was added. The mixture was placed on a water bath and gently heated. After a few minutes the fatty acid layer disappeared and the whole solution became homogeneous. The solution bubbled, indicating the progress of the reaction. The major portion of the reaction took place in about 30 minutes as indicated by the frothing, but heating was continued for a total of at least 4 hours.

When treating oleic acid having an iodine number of about 89, satisfactory results were had when 280 parts of this acid were used with 800 parts of the glacial acetic acid and 292 parts of 30% peroxide.

With sunflower oil acids having an iodine number of between 135 and 145, 210 parts were employed, with the same amounts of acetic acid and peroxide as given above; in the case of linseed fatty acids having an iodine number of between 170 and 180, only 140 parts of the oil acids were used.

After the heating has been completed, the acetic acid solution was cooled and the hydroxylated acids crystallized out. They can be filtered off and freed of acetic acid by washing successively with water and petroleum ether. Acetic acid may be recovered by adding additional water to precipitate further acids and then distilling off the acetic acid, leaving a viscous residue insoluble in petroleum ether which gives tests for the presence of peroxide oxygen and the carbony' group.

The use of permanganate is illustrated by the following procedure:

For 168 grams of oleic acid of an iodine number of 89, 50 grams of potassium hydroxide in one liter of water were first used to saponify the acids. The solution of 168 grams of potassium permanganate in 6 liters of water was gradually added for a period of 2 to 3 hours to the potas-

sium oleate which was kept very cold and rapidly stirred during the reaction. Stirring was continued for one hour after the final addition of the permanganate solution. The mixture became mushy and attained a brown to black appearance. Sulphur dioxide was now passed into this mixture until it became white, thus liberating the hydroxylated acids. If desired, a small amount of hydrochloric acid may also be added at this point. The white hydroxylated acids are filtered, washed thoroughly with water and refluxed with textile spirits (aliphatic hydrocarbons with a boiling point of 65° to 100° C.) and filtered. The process is repeated twice. This removes stearic acid or unhydroxylated acids. The following table indicates proportions of reagents which we have employed with various types of oils:

Acid			KOH	$KMnO_4$	Water
Type	Iodine No.	Parts			
			Parts	*Parts*	*Parts*
Sunflower	135-145	168	58.2	252	9,000
Safflower	130-145	168	58.2	252	9,000
Linseed	170-180	168	66.4	332	12,000
Oleic	89-90	168	50.0	168	6,000
Castor	82-90	177	50.0	168	6,000

The hydroxylated acids prepared in this manner are saturated, that is, they contain substantially no ethenoid linkages.

Since these hydroxylated acids contain both carboxyl and hydroxyl groups, they can be subjected to both inter and intra esterification to form lactones and lactides by simple heating, but we have found that this reaction is best conducted in the presence of a solvent such for example as an aliphatic hydrocarbon type of solvent with a boiling range in the order of about 200° C.

It is to be understood that our reference to the formation of lactones and lactides is intended only to give an indication of the type of reaction that may go on and that other types of large molecules may be produced, but these are all substantially uniform as regards acidity and hydroxyl content, as after the reaction caused by heating, an unesterified hydroxyl group remains intact for each acid residue. As an alternative the hydroxylated acids may be subjected directly to esterification with other acids or they may first be given a self-esterification treatment and subsequently acidified with additional fatty acids. In such case if a solvent has been employed, it may be removed by distillation before the addition of further unhydroxylated fatty acids.

As illustrated by the examples which will be given hereafter, acids employed may either be other oil acids or simpler fatty acids such as acetic acid may be used, or we may employ other types of acid such as rosin acids or the resin-forming carboxylic acids such as phthalic acid and maleic acid and the like.

If esterification of the hydroxylated acids and other acids is to be accomplished with the aid of heat (as is usually the case) inter and intra esterification will tend to go on simultaneously. If this is not desired, it can be avoided by first blocking off the reactive carboxyl groups of the hydroxylated acids. Since self-esterification is to be avoided, this blocking off cannot be carried out by the usual esterification methods involving heat. However, we have found that this blocking off can be efficiently accomplished by the use of methyl alcohol following the following procedure:

About 25 parts of the hydroxylated acids were dissolved in 150 parts of methanol and made alkaline to phenolphthalein by the cautious addition of a 50% aqueous solution of potassium hydroxide. To the resulting alcoholic soap solution, an equal mol portion (the amount depending on the molecular weight of the acids) of dimethyl sulphate was added. After standing for 24 hours at room temperatures crystals of potassium methyl sulphate separated. Water was then added which precipitated the methyl ester of the hydroxy acids and dissolved the crystals. The ester was filtered off and washed with several portions of a 1 to 2% sodium carbonate solution followed by several washings with hot water. The ester was then dried by heating until it became a liquid and water was no longer evolved.

The resulting methyl esters of hydroxylated acids are white and wax-like possessing melting points ranging from 94° to 130° C., which is higher than the melting points of most commercial waxes. These products are not very soluble in organic solvents as single components but they have sufficient solubility so that they not only are available as intermediate products for the processes herein set forth, but they may also be employed in a mixture of solvents as lubricants for lacquers. These methyl esters of hydroxylated acids having free hydroxyl groups can be used for esterifying other types of acids as already referred to. We have found that the best results were accomplished at temperatures of between 230 and 240° C. using carbon dioxide to maintain agitation and remove water of reaction. Generally speaking, the secondary alcohol groups which are found in these hydroxylated acids require a higher temperature for esterification than do the simple alcohols.

During the esterification process the free hydroxyl groups that are uncombined are reduced to a small fraction of their original value and the final acid value is high. However, it has been found that the reaction mass tends to come to an equilibrium showing a definite acidity. It may be that this is the result of the compounds undergoing some slight dehydration within themselves so that the final alcohol in the oil possesses an ethenoid linkage, whereas, the original alcohol was saturated. In any event, when such acidity is found, it may be advisable to add sufficient alcohol to reduce or eliminate this acidity and thereby increase the complexity of the compound. For this purpose, glycerol has been found particularly advantageous, but other alcohols, particularly polyhydric alcohols, may be employed.

In the examples which follow, after the various types of drying oil esters were prepared, each was compared with an alkaline refined linseed oil in order to judge of the properties of the new product. The driers used in each case (except where otherwise specified) were: .3% Pb, .02% Mn and .02% Co. The film thicknesses were .02 of an inch. The oils were dried under standard conditions of light, 70° F. and 50% relative humidity. The drying time of the standard linseed oil was about 5 hours. In most cases, the prepared oils dried in time shorter than 5 hours and had a water resistance equal to or better than the natural oil. In all cases, the esters containing China-wood fatty acids were by far the superior. This evidence then points specifically to the very

definite influence of the type of acid radical, rather than the alcohol, on water resistance.

Example No. 1.—Sunflower oil fatty acids were hydroxylated by the permanganate process. The hydroxylated acid averages 3 hydroxyl groups per mol and had an iodine absorption of 6%. Of the hydroxylated sunflower acids, 17 parts were heated with 29 parts of linseed oil acids to a temperature of between 220° C. and 230° C. for 12 hours, and gently agitated with a stream of CO_2 gas. At the end of that time the acid value remained constant at 63.5 mg. KOH/g. The product was then washed several times with methanol to remove the greater portion of the free acid.

The finished product had the following constants:

Acid number_____ 25 mg. KOH/g.
Saponification value. 186 mg. KOH/g.
Acetyl value_____ 21 mg. KOH/g. original oil.

This oil dried to a smooth film with driers in about 3 hours. Its water resistance was about the same as linseed oil.

Example No. 2.—Linseed oil fatty acids were hydroxylated in accordance with the permanganate method giving rather poor yields. Due to decomposition, the resultant acids averaged 2 hydroxyl groups per molecule and had an iodine absorption of 3%. 25 parts of these hydroxylated acids were heated with 22 parts of additional linseed oil acids for 12 hours at a temperature of from 220 to 230° C. while being gently agitated with CO_2 gas. The acid value remained constant at 62 mg. KOH/g. After washing with methanol, the ester had the following constants:

Acid value_____ 26 mg. KOH/g.
Saponification value_____ 195.5 mg. KOH/g.
Acetyl value_____ Nil.

This oil dried to a smooth film in about 6 hours with driers. Its water resistance was about the same as that of linseed oil.

Example No. 3.—This example was exactly similar to Example No. 2, except that China-wood oil acids were combined with the hydroxylated linseed oil acids. The methanol washed product had the following constants:

Acid value_____ 34 mg. KOH/g.
Saponification value. 187 mg. KOH/g.
Acetyl value_____ 10 mg. KOH/g. original oil.

This product was very viscous and dried to a smooth film with driers in about 3 hours. Its water resistance was considerably better than that of linseed oil.

Example No. 4.—In this example the hydroxylated acids were produced from safflower oil and averaged 3.7 hydroxyl groups per molecule with an iodine absorption of 6%. 25 parts of these hydroxylated acids were mixed with 27 parts of linseed oil fatty acids and 27 parts of China-wood oil fatty acids in 100 parts of hydrocarbon solvent having a boiling point range of 192° to 207° C. This mixture was refluxed so that the evolved water was removed from the reaction mixture with the solvent and the solvent was returned. The refluxing was continued until no more water was evolved. The solvent was then distilled off and the last traces were removed under vacuum. The recovered viscous oil had the following constants:

Acid value_____ 33 mg. KOH/g.
Saponification value. 186.5 mg. KOH/g.
Acetyl value_____ 22 mg. KOH/g. original oil.

This oil dried to a smooth film with driers. Its water resistance was better than that of linseed oil.

Example No. 5.—In this example hydroxylated safflower acids were refluxed with methanol. In such case the highly hydroxylated acids remained insoluble and can be filtered from the alcoholic solution containing largely the dihydroxy acids. The particular fraction of hydroxylated acids used in this example average 2.5 hydroxyl groups per molecule. The iodine absorption was 6%. 20 parts of these hydroxylated acids were combined with 25.4 parts of China-wood oil acids using 60 parts of solvent as in Example No. 4. The recovered viscous oil had the following constants:

Acid value_____ 27.5 mg. KOH/g.
Saponification value_____ 188.5 mg. KOH/g.

It dried to a smooth tough film in 2½ hours. Its water resistance was considerably better than that of linseed oil.

Example No. 6.—Hydroxylated castor oil fatty acids were esterified with methyl alcohol as described above. The resulting product averaged 3.4 hydroxyl groups per molecule with an iodine absorption of 9%. 20 parts of these hydroxylated acids were heated with 54 parts of linseed acids for 15 hours at a temperature of from 230° to 240° C. while agitation was continued with a stream of CO_2. At the end of that time the acid value remained constant. The product was washed several times with methanol and had the following constants:

Acid value_____ 18 mg. KOH/g.
Saponification value_____ 197 mg. KOH/g.
Acetyl value_____ Nil.

This product dried to a smooth film in 4 hours and showed water resistance equivalent to that of linseed oil.

Example No. 7.—The methyl esters of hydroxylated sunflower acids were produced averaging 3 hydroxyl groups per molecule with an iodine absorption of 6%. 20 parts of these acids were heated with 49 parts of linseed acids for 15 hours as in Example No. 6. The product had the following constants:

Acid value_____ 23 mg. KOH/g.
Saponification value_____ 195 mg. KOH/g.
Acetyl value_____ Nil.

This oil dried to a smooth film with driers in about 5 hours. Its water resistance was about the same as linseed oil.

Example No. 8.—54 parts of hydroxylated sunflower acids averaging 3 hydroxyl groups per molecule with an iodine absorption of 6% were mixed with 120 parts of hydrocarbon solvent having a boiling point of from 192° to 207° C. This mixture was refluxed and the distillate received in a Bidwell & Stirling tube so that the solvent returned to the mixture while the water was captured, such refluxing continuing for 8 hours until the mixture was practically neutral. The solvent was removed by distilation and vacuum. The resultant product was very viscous and plastic and possessed the following constants:

Acid value_____ 2.7 mg. KOH/g.
Saponification value. 149 mg. KOH/g.
Acetyl value_____ 49 mg. KOH/g. original oil.
Iodine value_____ 3.4%.

Example No. 9.—A portion of the product produced as in Example No. 8 was further esterified

with linseed fatty acids. 20 parts of such product and 4.9 parts of linseed acids were heated together at a temperature of 230° to 240° C. for 8 hours while being agitated by a small stream of CO_2. The product then had the following constants:

Acid value	Nil.
Saponification value	164 mg. KOH/g.

This product dried to a soft plastic film with driers.

Example No. 10.—25 parts of hydroxylated linseed acids as in Example No. 2 were heated with 22 parts of ordinary linseed acids for 12 hours at a temperature of 220 to 230° C. while being gently agitated with CO_2 until the acid value remained substantially constant at 86 mg. KOH/g. 38.8 parts of this product was then mixed with 1.8 parts of glycerol and the mixture was heated for 6 hours at a temperature of 220 to 230° C. until the acid value reached 12.2 mg. KOH/g. This product had a saponification value of 188 mg. KOH/g. and an acetyl value of 25.5 mg. KOH/g. of original oil.

The oil dried to a smooth film in 3½ hours with drier. Its water resistance was about the same as that of linseed oil.

Example No. 11.—An ester, methyl dihydroxy stearate (containing 2 hydroxyl groups per molecule) was prepared. 14 parts of this stearate were heated with 22 parts of rosin (W. G.) at 240° C. for 10 hours when the acid value remained constant at 76 mg. KOH/g. The resultant product resembled ester gum in physical properties.

Example No. 12.—200 parts of safflower oil were mixed with 250 parts of 30% peroxide solution and 400 parts of glacial acetic acid. The mixture was refluxed on a water bath for 4 hours. As soon as the reaction mixture became warm the reaction became quite vigorous. This required about 45 minutes and continued for about 30 minutes. The heating was continued for between 2½ and 3 hours after this vigorous action ended. Water was then added and the product washed free of acetic acid and dried over anhydrous sodium sulphate. The oxidized product had an acetylation value of 165 mg. KOH/g. 50 parts of this oil were esterified with 41 parts of linseed oil fatty acids for 8 hours, at a temperature of 200° C. by passing carbon dioxide through the agitated reaction mixture. At the end of this time heating was discontinued because the mixture was becoming very viscous. The acid value at this point was 18.8 mg. KOH/g., whereas, the value of the original mixture was 81.4 mg. KOH/g.

The final product was very viscous and was diluted with an equal volume of toluene. When treated with .02% cobalt as a drier it dried to a smooth, tough film in 2½ to 3 hours.

Example No. 13.—The white methyl ester of mixed hydroxylated oleic, sunflower, safflower and linseed oil acids was refluxed for 2 hours with about twice its weight of acetic anhydride. A small quantity of anhydrous sodium acetate (about 6% of the weight of the anhydride) was added. The reaction mixture was poured into water and washed until the aqueous washings were neutral to litmus. This took four washings in hot water. The oily acetates of a yellowish brown color were then dried over anhydrous sodium sulphate.

These acetates were used as a plasticizer in nitrocellulose according to the following formulation:

	Parts
Nitrocellulose (5–6 sec.)	18.0
Toluol	34.5
Ethyl acetate	8.0
Butyl acetate	20.0
Butyl alcohol	7.0
Plasticizer	12.5

The resulting lacquer was diluted to spraying consistency and sprayed on aluminum and copper panels, in comparison with a similar lacquer made up with dibutyl phthalate as a plasticizer. The properties of the lacquer films as regards adhesion and hardness were practically identical. However, it was found that the plasticizing action of these novel esters per unit weight was greater than that of dibutyl phthalate and for that reason smaller quantities could be used to advantage.

It is understood that the foregoing examples are given only by way of illustration and may be modified in many particulars without departing from the spirit of our invention.

What we claim is:

1. A synthetic drying oil consisting of the reaction products of a hydroxylated compound of a drying oil acid having at least two hydroxyl groups esterified with at least two molecules of drying oil acid for each molecule of such hydroxylated compound, such product being characterized by the fact that it has a number of double bonds per molecule at least approximately equal to the aggregate number of double bonds in said last specified drying oil acid molecules.

2. An oil as specified in claim 1 in which the hydroxylated compound of the drying oil acid is esterified in the carboxyl end with a monohydric alcohol radical.

3. A method of producing a synthetic drying oil which comprises preparing the hydroxylated compound of a drying oil acid having at least two hydroxyl groups and esterifying such hydroxylated compound with at least two molecules of drying oil acid for each molecule of such hydroxylated compound while maintaining the double bonds of said last specified drying oil acid molecules substantially unsaturated.

4. A method as specified in claim 3 which includes the further step of neutralizing by esterifying at the carboxyl end with an alcohol.

5. The method of preparing synthetic drying oils which comprises reacting with unsaturated drying oil acids a hydroxylated compound represented by the formula $CH_3C_nH_{2n-x}(OH)_xCOOR$, in which n is at least 16 and x at least 2 and R is a member selected from the group consisting of hydrogen and the CH_3 radical, to produce a compound having a degree of unsaturation approximately corresponding with the number of double bonds of the drying oil acids.

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