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DRYING OIL COMPOSITION

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The present invention relates to certain new resin-like products and to the method of preparing the same, such products being especially adapted for use as or in protective coating compositions and as or in binders for mouldable compositions. More particularly our invention contemplates certain new resin-like substances composed essentially of the reaction products obtained by interaction of certain constituents of oxidized drying or semi-drying oils with selected fatty acids.

We have discovered that when drying or semi-drying oils are subjected to oxidation limited substantially to the formation of uncoagulated products of oxidation and such products of oxidation are further treated to effect a separation therefrom of a substantial proportion of the unoxidized and non-hardening constituents, we obtain products of remarkable properties, particularly adapted for use in protective coating compositions and in binders for mouldable compositions of various sorts, such as linoleum. This subject matter is disclosed and claimed in our co-pending application Serial No. 773,305, filed June 30, 1934; and Serial No. 576,206, filed Nov. 19, 1931, which on July 31, 1934 matured into Patent No. 1,968,244. We have now further discovered that if this oxidized oil product, separated from a substantial proportion of unoxidized and non-hardening constituents, is caused to react with selected fatty acids of either the saturated or unsaturated series, there are obtained new resin-like substances which are even more valuable in many respects for use as or in the vehicle for enamels, paints, varnishes, and similar protective coating compositions and also in or as the binder for mouldable compositions. We have still further discovered that such novel resin-like products may also be obtained by subjecting a drying or semi-drying oil to an oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, simultaneously or subsequently causing interaction of the products of oxidation with selected fatty acids, and finally separating from the reaction products a substantial proportion of the unoxidized and non-hardening constituents. It is to these further discoveries that the present invention pertains.

Broadly, our process invention, whereby the novel resin-like substances of our product invention may be obtained, comprises the steps of subjecting a substance which contains a drying or semi-drying oil to an oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, simultaneously or subsequently causing interaction between certain constituents of the products of the oil oxidation and a fatty acid or fatty acids selected from that group or series of fatty acids characterized by 14 to 22 carbon atoms, and before or subsequent to such interaction of the fatty acids with constituents of the oxidized oil, treating such oil oxidation products, or the reaction products thereof with the fatty acid or acids, to remove therefrom a substantial proportion of the unoxidized oil constituents and non-hardening constituents. Our product invention contemplates certain new resin-like substances composed essentially of the reaction products of fluid oxidized glycerides of linoleic and linolenic acids which result from the oxidation of drying or semi-drying oils, with free fatty acids of 14 to 22 carbon atoms, such reaction products being separated from a substantial proportion of the unoxidized and non-hardening oil constituents of the product of the oil oxidation.

In preparing the novel products of our invention we prefer to employ linseed oil as the base. Other drying or semi-drying oils such as perilla oil, rubber seed oil, or soya bean oil may be used and, in general, any drying or semi-drying oil which, upon oxidation, yields a substantial amount of the oxidized glycerides of linoleic and/or linolenic acids in fluid phase will be found satisfactory.

The fatty acids which, according to our invention are combined with the oxidized but uncoagulated glycerides of linoleic and/or linolenic acids resulting from the oxidation treatment of the drying or semi-drying oil, may comprise both those designated as unsaturated fatty acids and those known as saturated and hydroxy saturated fatty acids. For the purposes of our invention, however, we propose to employ fatty acids selected from that group which includes the several fatty acid series characterized by 14 to 22 carbon atoms. Such group includes unsaturated fatty acids of the oleic acid series, $C_nH_{2n-2}O_2$ of which oleic acid $C_{18}H_{34}O_2$ and tetradecylenic acid

$C_{14}H_{28}O_2$ are typical examples; the linoleic acid series $C_NH_{2N-4}O_2$, of which linoleic acid $C_{18}H_{32}O_2$ is a typical example; the linolenic acid series $C_NH_{2N-6}O_2$ of which linolenic acid $C_{18}H_{30}O_2$ is a typical example; and the clupanodonic acid series $C_NH_{2N-10}O_2$, of which clupanodonic acid $C_{22}H_{34}O_2$ is a typical example. The group also includes saturated fatty acids of the series $C_NH_{2N}O_2$ of which palmitic acid $C_{16}H_{32}O_2$ and stearic acid $C_{18}H_{36}O_2$ are typical examples as well as the hydroxy unsaturated fatty acid $C_NH_{2N-2}O_3$ of which ricinoleic acid $C_{17}H_{32}(OH)COOH$ is a typical example. The selection of the particular fatty acid or mixture of fatty acids will of course be governed by the particular properties which are desired in the ultimate product as hereinafter more fully set forth. The amount and proportion of fatty acid which is combined with the oxidized oil constituents may vary within wide limits but will substantially exceed the amount normally found in drying or semi-drying oils. We prefer to limit the amount to somewhat less than the calculated reacting equivalent (based on the amount of the oxidized glycerides of linoleic and linolenic acids present in the prepared oil component) so that there will be a minimum of free fatty acid present in the ultimate reaction products. In general we propose to combine with the desired oxidized but uncoagulated glycerides of the drying or semi-drying oil 5% to 25%, by weight, of fatty acids.

The process of our invention may be practiced in several ways depending upon the sequence of the several essential steps thereof above recited. By way of illustrating various aspects of our invention we will describe in detail several alternative procedures in accordance therewith.

Method I

The preferred method involves first, the limited oxidation of the drying or semi-drying oil, second, the separation from the products of oxidation of a substantial proportion of unoxidized oil constituents and non-hardening oil constituents, and finally the refluxing of selected fatty acids with the oxidized and treated oil which may be held in solution in a solvent.

Example.—Linseed oil is heated to about 80° C. and a suitable drier, for instance, .04% cobalt linoleate, is added. The oil at a temperature of approximately 80° C. is then blown with air or is aerated with an equivalent oxygen containing gas for 10 to 25 hours. When a tested sample just fails to completely dissolve in ethyl ether, oxidation is discontinued. The batch is then cooled and treated to effect a separation of the unoxidized and non-hardening oil constituents. This separation may be effected by subjecting the oxidized oil to selective extraction with a solvent capable of dissolving the undesirable constituents but possessing little, if any, solvating action upon the oxidized but uncoagulated glycerides of linolenic and linoleic acids which are desirable as the oil base for the novel resinous products of our invention. The preferred solvent is petroleum ether (boiling range 30° to 75° C.) and about 3 to 4 volumes thereof to one volume of the oxidized oil should be employed. Petroleum naphtha (boiling range 60° to 160° C.) may be used as an equivalent extracting solvent. The oxidized but uncoagulated constitutents of the oil which are desirable constituents for the preparation of the novel reaction products of our invention form a lower layer while substantial proportions of the unoxidized and non-hardening oil constituents dissolve in the extracting solvent to form an upper layer. This upper layer is removed by decantation. The extraction process is preferably repeated two or three times to assure an adequate separation. The remaining portion of the oxidized oil, in fluid phase, is then subjected to low heat and preferably at reduced pressure to remove the last portion of the extracting solvent. For convenience in subsequent handling, the desired constituents of the oxidized oil obtained by the oxidizing and separating treatment above described are preferably dissolved in a suitable solvent, such as toluol, xylene, hi-flash coal tar naphtha, or any other similar water immiscible solvent, to provide a 60% to 80% solution.

To this solution of the desired oxidized but uncoagulated constituents of the drying or semi-drying oil, separated from a substantial proportion of the unoxidized and non-hardening oil constituents of the product of the oil oxidation, is added a fatty acid or a mixture of fatty acids selected from that group above described and characterized by 14 to 22 carbon atoms. Continuing the typical illustrative example, to 6 parts by weight of the oxidized and treated linseed oil, dissolved in toluol to form a 60% solution, is added 1 part by weight of the mixed fatty acids of linseed oil, comprising chiefly linoleic and linolenic fatty acids. This mixture is refluxed for 45 minutes in a standard type of refluxing unit equipped with a condenser designed to trap out any condensed water liberated by the reaction and prevent its return to the reaction chamber. The resinous product resulting from the refluxing operation, either in solution or freed of solvent, constitutes one embodiment of our product invention.

The refluxing operation may be effected with or without the aid of a catalytic agent. Among the catalysts that may be employed are aluminum chloride, hydrogen chloride and lactic acid, any one of which will facilitate reaction. The amount of catalyst may be varied but, in general, an amount equal to 0.1 to 1% by weight of the total solids in the reaction chamber will be found satisfactory.

Method II

The second method comprises, first, oxidizing the drying or semi-drying oil while limiting such oxidation to the formation of uncoagulated products of oxidation, second, refluxing such products of oxidation with selected fatty acids in the presence of a common solvent, and finally, treating the reaction products obtained by the refluxing operation to separate therefrom a substantial proportion of the unoxidized and non-hardening oil constituents.

Example.—Perilla oil is heated to about 80° C. and a suitable drier such as .02% of cobalt naphthenate is added. The oil at approximately 80° C. is then blown with air for 10 to 25 hours. When a tested sample just fails to dissolve in ethyl ether the oxidation is discontinued. To 10 parts by weight of this oxidized oil, dissolved in toluol or other equivalent solvent to form a 60% solution, is added 1 part by weight of palmitic acid and 1 part of stearic acid. This mixture is then refluxed for one hour in a standard type of refluxing unit equipped with a condenser designed to trap out any condensed water liberated by the reaction and prevent its return to the reaction chamber. A small amount of hydrochloric

acid (0.1% by weight) may be used if desired as a catalytic agent to hasten the reaction. At the end of the refluxing operation the toluol is distilled off and the batch cooled and treated to effect a separation of the unoxidized and non-hardening oil constituents. This is accomplished by treating the batch with 3 to 4 volumes of petroleum naphtha (boiling range 60° to 160° C.).

The unoxidized and non-hardening oil constituents, together with any remaining uncombined fatty acids dissolve in the extracting solvent to form an upper layer. The highly oxidized oil constituents, viz., the oxidized glycerides of linoleic and linolenic acids, combined with the free fatty acids form a lower layer. The upper layer is removed by decantation. The extraction process is preferably repeated two or three times to insure an adequate separation. The remaining portion comprising the reaction products of the fatty acids and the oxidized glycerides of linoleic and linolenic acids is then subjected to low heat and preferably at reduced pressure to remove the last portions of the extracting solvent. The resin-like reaction product, either in solution or freed of solvent, constitutes another embodiment of our product invention and for convenience in subsequent handling may be dissolved in a suitable solvent such as toluol, xylene, ethyl alcohol, or other similar coating solvent.

Method III

The third method comprises the steps of admixing with a drying or semi-drying oil a substantial amount of fatty acids selected from the group specified, subjecting the mixture to oxidation limited to the formation of uncoagulated products of oxidation, and separating from the reaction products a substantial proportion of the unoxidized and non-hardening oil constituents thereof.

Example.—To 12 parts of linseed oil is added one part of the free fatty acids of linseed oil and the mixture is heated to about 80° C. A suitable drier, for example .04% cobalt linoleate, is added. The batch is then vigorously blown with air for a period of 10 to 25 hours. When a tested sample just fails to completely dissolve in ethyl ether, oxidation is discontinued. The batch is transferred from the oxidizer to a tank fitted with an agitator. It is then treated with 3 to 4 volumes of petroleum ether (boiling range 30° to 75° C.). The unoxidized and non-hardening oil constituents and any remaining uncombined fatty acids dissolve in the extracting solvent to form an upper layer. The oxidized glycerides of linoleic and linolenic acids combined with the linseed oil fatty acids form a lower layer. The upper layer is removed by decantation and the extraction process repeated two or three times to assure adequate separation, the balance of the extracting solvent being removed by low heat. The remaining portion comprises chiefly the reaction products of the highly oxidized glycerides of linoleic and linolenic acids with the linoleic and linolenic fatty acids. It may also comprise a small proportion of highly oxidized fatty acid complexes, that is, fatty acids (linoleic and linolenic) which have become oxidized and then reacted with additional free fatty acid to form a resin-like substance. These reaction products, with or without the presence of such fatty acid complexes, constitute an embodiment of our product invention. For convenience in handling they may be dissolved in toluol, ethyl alcohol, butyl alcohol, or similar coating solvent.

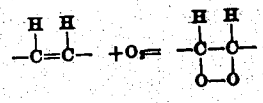
It is to be noted that in each method the oxidation of the drying or semi-drying oil is discontinued at or just before the point where the constituents of the oxidized oil or the reaction products thereof with the fatty acids commence to coagulate to the gel or linoxyn phase. This point may be determined by the ethyl ether test. As long as no linoxyn is formed the constituents of the oil undergoing oxidation will dissolve completely in ethyl ether, but upon the formation of linoxyn a jelly-like precipitate will appear in the sample tested. Following the described methods the yield of resin-like products resulting from the reaction of the fatty acids with those oxidized oil constituents soluble in ethyl ether but insoluble in petroleum ether, varies from 60% to 85% based on the combined weight of the oil and fatty acids employed. In practicing our process invention according to Method I or II, the percentage yield of those desired oxidized constituents of the oil may be somewhat increased by adding to the oil, prior to oxidation, a small amount—.1% to 2.0%—of maleic acid (or maleic acid anhydride) or equivalent acidic substance difficultly volatile at a processing temperature.

The desired oxidized oil constituents which constitute the oil base in the preparation of the resin-like product of our invention are constituents which are soluble in ethyl ether, but insoluble in petroleum ether, and comprise chiefly the oxidized glycerides of linoleic and linolenic acids in fluid and uncoagulated phase. The unoxidized oil constituents which are not oxidized in the oxidizing treatment and are removed in the separation process are either constituents of the oil which are capable of being converted by the oxidizing treatment into a substance having the property of hardening, but were not so converted, such as the glycerides of linoleic and linolenic acids, or they are constituents of the oil which are unoxidizable by such treatment or by contact with air and do not possess the property of hardening such as the glycerides of saturated fatty acids of which stearic or palmitic are examples. The non-hardening oil constituents include, in addition to the above-mentioned unoxidized glycerides of the saturated fatty acids, those oxidized oil constituents which do not possess the property of hardening even though oxidized, such as the oxidized glycerides of oleic acid. It is these unoxidized and non-hardening constituents of the oil normally present after completion of the oxidizing treatment which are removed to a substantial extent by the separation treatment above described. Furthermore, as noted in the particular description of Methods II and III, the separation treatment when conducted subsequent to the interaction of the fatty acids and the oxidized oil constituents, removes any uncombined fatty acids remaining after completion of the refluxing operation.

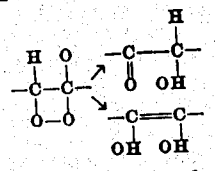
The products of our invention are substances of a resin-like nature and of high molecular weight. Although the invention is not predicated upon any particular theories we believe that the following chemical reactions may occur.

The oxidation of the long chain unsaturated fatty acid glycerides such as the glycerides of linoleic and linolenic acids present in drying and semi-drying oils produces keto and hydroxy groups at the points of unsaturation, i. e., where the double bonds occur in the carbon chain.

As a result of the oxidation a peroxide group is first formed, thus:—



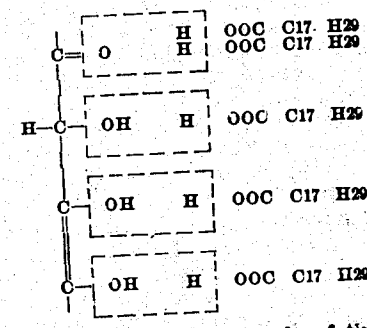
These peroxide groups then rearrange themselves into one or both of the following forms "A" and "B":—



(A)

(B)

It is with these keto and hydroxy groups "A" and "B" that the long chain fatty acids of 14 to 22 carbon atoms are caused to react. The attachment of the fatty acid with the splitting off of water may occur as follows, taking linoleic acid as an illustrative example:—



(A)

(B)

Considering that each molecule of the glyceride of either linoleic or linolenic acid contains three fatty acid radicals and therefore six or nine unsaturated groups or double bonds respectively and that after oxidation producing keto and hydroxy groups at these points of unsaturation, one to three molecules of the selected fatty acid may become attached at each original point of unsaturation or double bond. It will readily be seen that reaction products of very high molecular weight will be formed. It is these products, comprising the fluid oxidized glycerides of linoleic or linolenic acids resulting from the oxidation of a drying or semi-drying oil and with which are united one or more fatty acid chains of 14 to 22 carbon atoms and from which reaction products a substantial proportion of the petroleum ether soluble constituents have been separated, which constitute the embodiment of our product invention.

Although it is desirable that the amount of unoxidized and non-hardening oil constituents remaining admixed with the ultimate reaction products should be at a minimum, nevertheless, the difficulty of securing, in commercial operation a quantitative elimination of these constituents, makes it inexpedient to attempt to obtain this end. As above pointed out, our invention contemplates the elimination from the oxidized oil products, or from the reaction products resulting from the interaction of the fatty acids with such oxidized oil products, of a substantial proportion of the unoxidized and non-hardening oil constituents. The properties and advantages characterizing the products of our invention may be realized and enjoyed if the separation of the undesirable constituents of the oxidized oil from the desired oxidized oil constituents or from the reaction products of the oxidized oil and fatty acids is carried to such an extent that the ultimate reaction products contain but approximately 10% or less of such undesirable oil constituents, i. e., constituents soluble in petroleum ether.

Prepared in accordance with the above disclosure, the novel products of our invention exhibit highly desirable properties particularly adapted for use as or in vehicles for enamels, paints, varnishes, lacquers, or other protective coating compositions, or as or in binders for moldable composition such as linoleum. The reaction products obtained by interaction of the oxidized glycerides of linoleic or linolenic acids of oxidized drying or semi-drying oil with fatty acids of the unsaturated series of 14 to 22 carbon atoms and separated from a substantial proportion of the unoxidized and non-hardening oil constituents, impart to protective coating compositions improved gloss, improved adhesion and increased toughness. Such reaction products also possess the property of fast drying or setting upon evaporation of the coating solvent, and do not require further oxidation to harden as is usual with drying or semi-drying oil products. The reaction products obtained by interaction of the oxidized glycerides of linoleic or linolenic acids of oxidized drying or semi-drying oil with fatty acids of the saturated series of 14 to 22 carbon atoms and separated from a substantial proportion of the unoxidized and non-hardening oil constituents, impart to protective coating compositions both improved gloss and improved adhesion and are particularly adapted for use in conjunction with cellulose ester vehicles. When so used they retard the otherwise too rapid setting of the vehicle and impart to the protective coating a markedly improved and permanent flexibility.

It should be clear from the foregoing description that the advantages of our invention reside in the discovery and development of certain new resin-like substances prepared from drying or semi-drying oils and fatty acids by limited oxidation of the drying or semi-drying oil, reaction of selected long chain fatty acids with certain oxidized constituents of such oil, and the separation of specified undesirable non-hardening constituents of the oxidized oil either before or after the interaction of the desired oxidized oil constituents and fatty acids, whereby the ultimate resinous reaction products contain less than about 10% of constituents soluble in petroleum ether. It is apparent that the teachings of this invention may be applied in many ways and that the novel products will find wide and varied use.

We claim:

1. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, effecting interaction of a fatty acid characterized by 14 to 22 carbon atoms, in an amount in excess of the amount normally present in the oil, with oxidized glyceride constituents of the products of oxidation, and separating and removing unoxidized oil constituents and non-hardening oil constituents.

2. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment, discontinuing the oxidizing treatment prior to coagulation of the oxidized oil, treating the oxidized oil to remove therefrom unoxidized oil constituents and non-hardening oil constituents, and effecting

interaction of the remaining oxidized glyceride constituents of the oxidized oil with a fatty acid characterized by 14 to 22 carbon atoms.

3. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, effecting interaction of oxidized glyceride constituents of the products of oxidation with a fatty acid characterized by 14 to 22 carbon atoms and present in an amount in excess of that normally present in the oil, and extracting with a low boiling hydro-carbon.

4. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, extracting the resulting products with a low boiling hydro-carbon to remove therefrom unoxidized and non-hardening oil constituents, and effecting interaction of oxidized glyceride constituents with a fatty acid characterized by 14 to 22 carbon atoms.

5. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, and effecting interaction of a fatty acid characterized by 14 to 22 carbon atoms, in an amount in excess of the amount normally present in the oil, with oxidized glyceride constituents of the products of oxidation.

6. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, refluxing with oxidized glyceride constituents of such products of oxidation 5% to 25% of a fatty acid characterized by 14 to 22 carbon atoms, and, by fractional extraction, removing unoxidized oil constituents and non-hardening oil constituents.

7. The process which comprises the steps of subjecting a substance comprising linseed oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, effecting interaction of a fatty acid characterized by 14 to 22 carbon atoms, in an amount in excess of the amount normally present in the oil, with oxidized glyceride constituents of the products of oxidation, and separating and removing unoxidized oil constituents and non-hardening oil constituents.

8. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation in the presence of a fatty acid characterized by 14 to 22 carbon atoms, in an amount in excess of the amount normally present in the oil and thereby effecting interaction of said fatty acid with oxidized constituents of said products of oxidation, and separating and removing unoxidized oil constituents and non-hardening oil constituents.

9. A composition comprising the reaction product of a fatty acid characterized by 14 to 22 carbon atoms and oxidized glyceride constituents resulting from oxidation of a drying or semi-drying oil, the amount of said fatty acid being in excess of the amount thereof normally present in said oil and said reaction product having associated with it less than 10% of unoxidized and non-hardening oil constituents soluble in petroleum ether.

10. A composition comprising the reaction product of a fatty acid characterized by 14 to 22 carbon atoms and that component of oxidized drying or semi-drying oil which after oxidation of the oil is in fluid phase, is separated from a substantial proportion of unoxidized and non-hardening oil constituents of the oxidized oil, and is capable of hardening without further substantial oxidation.

11. A composition comprising the reaction product of a fatty acid characterized by 14 to 22 carbon atoms and that component of oxidized drying or semi-drying oil which after oxidation of the oil is in fluid phase, is separated from a substantial proportion of unoxidized and non-hardening oil constituents of the oxidized oil, and is capable of hardening without further substantial oxidation, said composition having associated with it less than 10% of constituents soluble in petroleum ether and being substantially identical with the product of the process of claim 1.

12. A composition comprising the reaction product of a fatty acid characterized by 14 to 22 carbon atoms and that component of oxidized linseed oil which after oxidation of the oil is in fluid phase, is separated from a substantial proportion of the unoxidized and non-hardening oil constituents, and is capable of hardening without further substantial oxidation.

13. A composition of matter comprising the reaction product of a fatty acid of 14 to 22 carbon atoms and an oxidized drying or semi-drying oil, the amount of said fatty acid being in excess of the amount thereof normally present in said oil and said reaction product having associated therewith less than 10% of constituents soluble in petroleum ether.

14. A composition of matter comprising the reaction product of a fatty acid of 14 to 22 carbon atoms and oxidized glycerides of linoleic and/or linolenic acids obtained by oxidation of a drying or semi-drying oil and separation therefrom of a substantial proportion of unoxidized and non-hardening constituents of the oxidized oil.

15. A composition comprising the reaction product of a fatty acid characterized by 14 to 22 carbon atoms and liquid oxidized glyceride constituents resulting from oxidation of a drying or semi-drying oil.

16. A composition of matter comprising the reaction product of a fatty acid of 14 to 22 carbon atoms and liquid oxidized glycerides of linoleic and/or linolenic acids.

17. A composition comprising the reaction product of a drying oil fatty acid characterized by 14 to 22 carbon atoms and oxidized glycerides of linoleic and/or linolenic acids obtained by oxidation of a drying or semi-drying oil and separation therefrom of a substantial proportion of unoxidized and non-hardening constituents of the oxidized oil.

18. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation in the presence of a fatty acid characterized by 14 to 22 carbon atoms and present, in an amount in excess of the amount normally present in the oil and thereby effecting interaction of the fatty acid with oxidized glyceride constituents of said product of oxidation, and separating and removing unoxidized oil constituents and non-hardening oil constituents and uncombined fatty acid.

19. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, treating the product of said oxidation with fatty acid characterized by 14 to 22 carbon atoms and thereby effecting interaction of the fatty acid with oxidized glyceride constituents of said products of oxidation, and separating and removing from the product of said last-named treatment unoxidized oil constituents and non-hardening oil constituents.

20. The process which comprises the steps of subjecting a substance comprising a drying or semi-drying oil to oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, treating the product of said oxidation with fatty acid characterized by 14 to 22 carbon atoms and thereby effecting interaction of the fatty acid with oxidized glyceride constituents of said products of oxidation, and extracting the products of said last-named treatment with a low-boiling hydrocarbon.

21. A composition comprising the reaction product of that component of oxidized drying or semi-drying oil which after oxidation of the oil is in fluid phase, is separated from a substantial proportion of unoxidized and non-hardening oil constituents of the oxidized oil, and is capable of hardening without further substantial oxidation, and an excess, over the amount thereof normally present in said oil, of fatty acid characterized by 14 to 22 carbon atoms.

22. A composition comprising the reaction product of liquid oxidized glyceride constituents resulting from oxidation of drying or semi-drying oil limited to the formation of liquid oxidized constituents and an excess of fatty acid, over the amount thereof normally present in said oil, characterized by 14 to 22 carbon atoms.

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