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STABILIZATION OF NONDRYING AND SEMIDRYING OILS

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13 Claims. (Cl. 87—9)

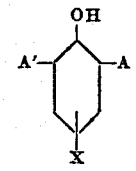
This invention relates to agents for inhibiting rancidity development in certain non-drying and semi-drying oils comprising fatty acid glycerides and particularly to such oils as are employed in compositions for manufacturing artificial leather.

It has been proposed heretofore to inhibit the development of rancidity in oxidizable oils and compositions containing the same through the use of various compounds such as, for example, aromatic non-hydroxy nitro compounds, such as dinitrotoluene, nitronaphthalene, and the like; organic substances containing negative constituents, e. g., nitronaphthols, nitrophenols, and the like; other aromatic nitrogen compounds, alkaloids, and the like; phenols having a nuclear hydrogen substituted by an aryl group, e. g., ortho- and para-hydroxydiphenyl, disclosed in U. S. Patent 1,784,360; diarylamines, e. g., diphenylamine, disclosed in U. S. Patent 1,675,631; hydroquinones, disclosed in U. S. Patent 1,720,992; and also through the use of phenols broadly disclosed in U. S. Patent 1,745,604.

The above compounds have met with some measure of success but are not suitable for use in non-drying and semi-drying oils comprising fatty acid glycerides which have a tendency to become rancid and have, in the raw state, a normal iodine number below 135, particularly, when such oils are employed in coating compositions or "dopes", such as are used in the manufacture of white and light colored artificial leather. Such compounds are either unsatisfactory as regards the inhibition of rancidity, seriously affect the initial color, discolor the oils on exposure to the sunlight, particularly when employed in oils used in making artificial leather, render artificial leather compositions sensitive to water, causing spotting or fading of the color, or else have an objectionable odor.

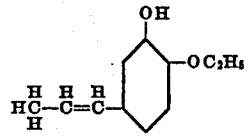
An object of the present invention is to provide compounds for inhibiting the development of rancidity in non-drying and semi-drying oils comprising fatty acid glycerides which have a tendency to become rancid and have, in the raw state, a normal iodine number below 135. A further object is to provide agents for inhibiting the development of rancidity in such oils which are particularly adapted for use in compositions employed in the manufacture of artificial leather. Still further objects are to provide new compositions of matter and to advance the art. Other objects will appear hereinafter.

These objects may be accomplished in accordance with our invention which comprises incorporating, in non-drying and semi-drying oils comprising fatty acid glycerides which have a tendency to become rancid and have, in the raw state, a normal iodine number below 135 and preferably below 120, creosole and certain of its related compounds. The compounds which we contemplate employing comprise a class having the type formula:

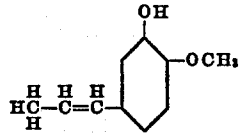


wherein A represents an alkoxy group, A' represents H or an alkoxy group which may be the same as or different from A, and X represents a member of the group consisting of CH=CH—CH$_3$, and CHO. Among the compounds of this class which we have found to be particularly adapted for our purpose are the following:

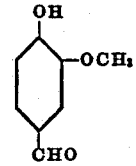
5-propenyl guaethol



5-propenyl guaiacol



Vanillin



We have found that these compounds are effective for inhibiting rancidity in compositions containing non-drying and semi-drying oils comprising fatty acid glycerides which have a tendency to become rancid and have, in the raw state, a normal iodine number below 135 and particularly in such oils having an iodine number below 120; do not give an objectionable odor to the compositions, do not give rise to objectionable discoloration of the compositions,

and do not render the composition sensitive to water.

In order to test the effect of our compounds in coating compositions or "dopes" employed in the manufacture of artificial leather a representative "dope" was prepared as follows:

	Parts by weight
Pyroxylin	11.5
Castor oil	18.0
Pigment	11.0
Ethyl alcohol	36.0
Ethyl acetate	23.5
Inhibitor (2% based on castor oil content)	0.36

The pyroxylin was dispersed in a mixture of the ethyl alcohol and ethyl acetate, and the pigment ground in a portion of the castor oil. The remaining castor oil was mixed with the pyroxylin dispersion, following which the pigment in oil was added and the whole thoroughly mixed. The inhibitor was added as an alcoholic solution along with the pigment in oil.

In order to determine the effect of the inhibitors on the color of a dope of this type, the pigment composed a mixture of 98.5% lithopone and 1.5% ultramarine blue. The composition containing this pigment, because of its pale blue color, is highly susceptible to discoloration by inhibitors of the wrong type, and also lends itself well to observations for "water spotting".

By the term "water spotting" is meant a color change, such as fading, which takes place when the artificial leather is brought into contact with water.

A suitable procedure for testing rancidity inhibitors in compositions of the above type follows: Various dopes are applied to pieces of fabric in the usual manner for making artificial leather, which treated pieces of fabric are then subjected to the following tests. A sample of treated fabric of standard size (e. g., 2" x 5") is placed in a small glass-stoppered flask and stored at a temperature of about 65° C. The various bottles are opened once a week and, from the odor emitted, a determination as to when rancidity develops is made.

The various pieces of treated fabric are subjected to exposure to the light from a glass-enclosed carbon arc for 16 hours and the change in color is compared with that of a sample of cloth treated with the same dope containing no inhibitor, in order to determine the effect of the inhibitors on the color change caused by exposure to sunlight.

A small strip of each sample of the treated fabric is immersed in water for 2 days and then dried. A comparison of the samples will disclose the effect of the inhibitors on water spotting or color change caused by the water.

The following table discloses the result obtained by the use of certain of our preferred inhibitors when incorporated in an artificial leather prepared as above described. In each case, 2% of the inhibitor, based on the castor oil, was employed:

Inhibitor	Days for rancidity development*	Color change	Water spotting
None	7		
5-propenyl guaiacol	100+	Noticeable	None.
5-propenyl guaethol	100+	do	Do.
Vanillin	100+	Slight	Slight.

*"+" sign indicates no rancidity after number of days shown.

None of these compounds or inhibitors had any effect on the initial color of the artificial leather or gave the artificial leather an obectionable odor.

Ethyl and benzyl cellulose and similar cellulose ethers may be employed instead of nitrocellulose in cellulose derivative compositions comprising a non-drying or a semi-drying oil together with an inhibitor as above described.

By reason of its cheapness and ready availability creosole comprises the preferred inhibitor of our invention at the present time. In the above tests, we have employed about 2% of the inhibitor, based on the oil. However, it is not necessary to employ this specific amount as larger or smaller proportions of the inhibitor may be employed, as desired. The proportion of inhibitor will depend upon the particular type of composition and particularly the kind of oil used. However, it will be found to be unnecessary to employ more than about 5% in most cases. In some cases as little as 0.25% is useful.

We have disclosed our compounds as employed in coating compositions or dopes such as are generally used in the manufacture of artificial leather, which coating compositions contained castor oil. However, our inhibitors are adapted to be employed in other types of compositions containing non-drying and semi-drying oils comprising fatty acid glycerides which have a tendency to become rancid and have, in the raw state, a normal iodine number below 135 or in such oils, when employed for other purposes. For example, our inhibitors may be employed in—

(1) Compositions, containing olive oil, which are employed for lubricating textile fibers,

(2) edible and medicinal oils and compositions based thereon,

(3) certain lubricants comprising non-drying and semi-drying oils, and

(4) compositions comprising resins and softeners derived from the various fatty acid glycerides.

In the case of edible and medicinal oils and compositions based thereon, only the non-toxic compounds such as vanillin should be employed.

Among non-drying and semi-drying oils which may be treated satisfactorily with our inhibitors are olive oil, rapeseed oil, cod liver oil, corn oil, peanut oil, coconut oil, cottonseed oil, palm oil, lard oil, neat's-foot oil, butterfat, lard, beef tallow, wool fat and the like. These oils, fats and tallows may be raw or they may have been previously subjected to various treatments, such as blowing with air at more or less elevated temperatures, simple heat treatments, or the oils may be employed in making resins and softeners for use in artificial leather and like compositions. Accordingly, when we refer to fatty acid glycerides having an iodine number below 135 in the claims, we intend to include such resins and softeners as well as the other fatty substances above mentioned.

While we have disclosed certain compounds of a class and certain oils employed in particular compositions, it is to be understood that other compounds of the same class may be employed for treating other oils of the kind described and the proportions and constituents of the compositions in which they are employed may be widely varied without departing from the spirit of our invention. Accordingly, the scope of our invention is to be limited solely by the appended claims construed as broadly as is permissible in view of the prior art.

I claim:

1. A composition of matter comprising a fatty substance of the group consisting of non-drying and semi-drying oils having a tendency to become rancid to which has been added an ortho-alkoxy phenol in which at least one of the positions 4 and 5 is substituted by a CHO group in an amount sufficient to inhibit rancidification of the fatty substance.

2. A composition of matter comprising a fatty substance of the group consisting of non-drying and semi-drying oils having a tendency to become rancid to which has been added vanillin in an amount sufficient to inhibit rancidification of the fatty substance.

3. A composition of matter comprising a fatty substance of the group consisting of fatty acid glycerides having a tendency to become rancid and having, in the raw state, a normal iodine number below 135 to which has been added an ortho-alkoxy phenol in which at least one of the positions 4 and 5 is substituted by CHO in an amount sufficient to inhibit rancidification of the fatty substance.

4. A composition of matter comprising a fatty substance having a tendency to become rancid to which has been added an ortho-alkoxy phenol in which at least one of the positions 4 and 5 is substituted by CHO in an amount sufficient to inhibit the rancidification of the fatty substance.

5. A composition of matter comprising a fatty substance of the group consisting of fatty acid glycerides having a tendency to become rancid and having, in the raw state, a normal iodine number below 135 to which has been added vanillin in an amount sufficient to inhibit rancidification of the fatty substance.

6. A composition of matter comprising a fatty substance having a tendency to become rancid to which has been added vanillin in an amount sufficient to inhibit rancidification of the fatty substance.

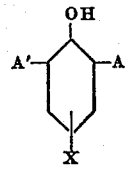
7. A composition of matter comprising castor oil to which has been added an ortho-alkoxy phenol in which at least one of the two positions 4 and 5 is substituted by a CHO group in an amount sufficient to inhibit rancidification of the castor oil.

8. A composition of matter comprising castor oil to which has been added vanillin in an amount sufficient to inhibit rancidification of the castor oil.

9. A composition of matter comprising pyroxylin and a fatty substance of the group consisting of non-drying and semi-drying oils comprising fatty acid glycerides, having a tendency to become rancid and having, in the raw state, a normal iodine number below 135 to which has been added an ortho-alkoxy phenol in which at least one of the two positions 4 and 5 is substituted by CHO in an amount sufficient to inhibit rancidification of the fatty substance.

10. A composition of matter comprising pyroxylin and a fatty substance of the group consisting of non-drying and semi-drying oils comprising fatty acid glycerides having a tendency to become rancid and having, in the raw state, a normal iodine number below 135 to which has been added vanillin in an amount sufficient to inhibit rancidification of the fatty substance.

11. The method of stabilizing fatty acid glycerides having an iodine number below 135 which comprises incorporating therein a compound of the type:



wherein A represents an alkoxy group, A' represents H or an alkoxy group and X represents CHO.

12. A composition of matter comprising an organic compound having a tendency to deteriorate in the presence of oxygen to which has been added an ortho-alkoxy phenol in which at least one of the positions 4 and 5 is substituted by a CHO in an amount sufficient to inhibit such deterioration.

13. A composition of matter comprising an organic compound having a tendency to deteriorate in the presence of oxygen to which has been added vanillin in an amount sufficient to inhibit such deterioration.

JAMES K. HUNT.

CERTIFICATE OF CORRECTION.

Patent No. 2,064,610. December 15, 1936.

JAMES K. HUNT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 3-4, for "obectionable" read objectionable; page 3, second column, line 41, claim 12, after "CHO" insert the word group; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of March, A. D. 1937.

(Seal) Henry Van Arsdale
Acting Commissioner of Patents.

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