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UPGRADED OIL COMPRISING AT LEAST ONE UNSATURATED OIL WHICH IS AN ESTER OF A C_{10} TO C_{22} FATTY ACID AND AN AT LEAST TRIHYDRIC ALCOHOL

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This invention relates to a chemical composition and more particularly to upgraded natural and synthetic oils.

Natural and synthetic oils find wide use, for example, as film-forming materials and modifying agents in coating compositions, in linoleum and other sheet materials and as coatings for fabrics, for example, in rain coats, tarpaulins and the like. In these applications, such oils have been subject to several disadvantages. Non-drying oils such as castor oil and olive oil and their synthetic counterparts do not air dry to hard tack-free films. Even the most widely used of the drying oils such as linseed oil and dehydrated castor oil dry slowly and do not achieve the hardness and freedom from tack desirable in many applications. Films and coatings of such natural oils and their synthetic counterparts, especially the non-drying oils, remain soft and sticky even after prolonged exposure to air.

I have found a method for upgrading natural and synthetic oils, that is, I have found a method for greatly improving the drying properties of natural and synthetic oils. Particularly, I have found a method for making such oils dry more rapidly without heating to form films, coatings and the like with greatly improved hardness and freedom from tack.

In accordance with this invention, natural and synthetic oils are upgraded by mixing therewith at least about 5% and preferably about from 10 to 65% by weight based on the weight of oil of at least one compound containing a plurality of vinyl cyclic acetal radicals.

As is conventional in the art, the terms "drying oil," "semi-drying oil" and "non-drying oil" as used herein refer to oils which react, react slowly or do not react with oxygen on exposure to air.

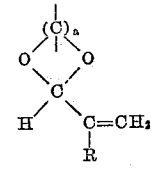
The term "natural oils" refers to naturally occurring fixed oils, particularly vegetable and animal oils, which consist primarily of C_{10} to C_{22} saturated and unsaturated fatty acids mainly in the form of triglycerides. Examples of drying natural oils are tung oil, oiticica oil, linseed oil, perilla oil and dehydrated castor oil. Examples of semi-drying natural oils are safflower oil, soya bean oil, peanut oil, corn oil, sunflower oil, cottonseed oil, menhaden oil, cod-liver oil, tuna oil, sesame oil and whale oil. Examples of non-drying natural oils are castor oil, olive oil and animal oils such as lard oil and neat's-foot oil.

The term "synthetic oils" refers to oils analogous to the aforementioned natural oils prepared, for example, by esterifying polyols containing three or more hydroxyl groups per molecule, such as glycerol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane, pentaerythritol, sorbitol, mannitol and hexane-1,2,5,6-tetrol, with fatty acids such as linoleic acid, linolenic acid, oleic acid, tall oil acids, eleostearic acid, arachidonic acid and other fatty acids such as those derivable from the aforementioned natural oils. The esterification reaction can be carried out by mixing one or more of the aforementioned fatty acids with at least an equivalent amount, and preferably a small excess of one or more of the aforementioned polyols and heating the mixture at about from 200 to 300° C. in an inert atmosphere until the acid number of the mixture is less than about 10. Optionally, lower

temperatures in combination with basic catalysts such as litharge can be used. Acid number refers to the number of milligrams of potassium hydroxide necessary to neutralize the free fatty acids in one gram of the synthetic oil.

Although any of the natural oils or their synthetic counterparts containing a substantial portion of unsaturated fatty acid can be upgraded in accordance with this invention, marked improvement in the natural and synthetic oils is usually only obtained with oils having an acid component consisting of at least about 50% of unsaturated acid. Drying and semi-drying natural and synthetic oils are particularly preferred constituents of the compositions of this invention.

The compounds containing a plurality of vinyl cyclic acetal radicals which are used in the compositions of this invention are not part of this invention and are disclosed and claimed in copending application Serial Nos. 737,506 and 737,507, filed on May 26, 1958, by Carol K. Ikeda, now U.S. Patents Nos. 3,010,923 and 3,010,918, issued November 28, 1961. These compounds contain a plurality of vinyl cyclic acetal radicals having the structural formula:



wherein



represents carbon atoms in the ring, "a" is an integer having a value of at least 2, all but one (that is, $2a-1$) of the valences of the carbon atoms in the ring being satisfied by the monovalent radicals selected from the class consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl, chloroalkyl, fluoroalkyl, alkoxyalkyl, cyano, chloroalkoxyalkyl, fluoroalkoxyalkyl, cyanoalkoxyalkyl, cyanoalkyl, alkenyl, chloroaryl and fluoroaryl radicals when the value of "a" is 2 and, when the value of "a" is greater than 2, the class consisting additionally of fluoro, chloro, acylamido and phenylsulfonyl radicals; and wherein R is a monovalent radical selected from the class consisting of hydrogen, alkyl, alkenyl, aryl, chloro, fluoro, bromo, cyano, acyloxy, chloroalkyl, fluoroalkyl, cyanoalkyl, alkoxy, aryloxy and carbalkoxy radicals. The unsatisfied valence of one of the carbon atoms in the chain represented by



is the valence through which the vinyl cyclic acetal radicals are connected to the remainder of the compound. For reasons of economy, ease of operation and availability of suitable starting materials, the preferred number of vinyl cyclic acetal radicals in a given compound is 2 to 4, although higher numbers can be made. For example, six such radicals can be attached to a hexavalent radical derived from mellitic acid.

The polyvalent radical which joins the plurality of vinyl cyclic acetal radicals in the compounds used in the compositions of this invention is not critical; however, substituents known to have an inhibiting effect on vinyl polymerization should be avoided or placed in a shielded or sterically hindered position so that the inhibiting effect is minimized. Likewise, strongly acidic radicals which form insoluble complexes with metallic driers are prefer-

ably avoided. Examples of suitable connecting radicals are adipate, diglycolate, thiodipropionate, imidodiacetate, oxysuccinate, maleate, itaconate, phthalate, pyromellitate, orthoformate, 2-methyl-3-nitrobutane-1, 2-dicarboxylate, 2,2'-di(oxyethyl)ether, 2,2'-di(oxyphenyl)propane, 1,1,1-tri(oxymethyl)propane, ethylene and hexamethylene radicals.

One preferred method for preparing the compounds containing a plurality of vinyl cyclic acetal radicals is to first prepare a hydroxy-substituted vinyl cyclic acetal, then react the hydroxy-substituted vinyl cyclic acetal with a polycarboxylic acid ester under ester interchange conditions. For example, first acrolein or an alpha-substituted acrolein can be reacted with a polyol in the presence of a catalytic amount of a mildly acidic compound such as ammonium chloride or oxalic acid at a temperature of about from 50 to 110° C. to yield, for example, hydroxy-substituted 2-vinyl-1,3-dioxolanes, -dioxanes and -dioxepanes or -dioxocanes. Examples of alpha-substituted acroleins are acroleins in which the alpha substituent is a methyl, ethyl, propyl, butyl, vinyl, phenyl, chloro, fluoro, bromo, cyano, acetoxy, butyroxy, benzoyl, chloromethyl, fluoroethyl, cyanoethyl, methoxy, butoxy, phenoxy, carbomethoxy or carboethoxy group. Examples of polyols are glycerol, hexane-1,2,6-triol, heptane-1,4,7-triol, pentane-1,3,5-triol and butane-1,2,4-triol. The hydroxy-substituted vinyl cyclic acetal can then be reacted with a lower alkyl ester, that is, a 1 to 4 carbon atom alkyl ester, particularly methyl and ethyl esters, of a polycarboxylic acid such as isophthalic acid, terephthalic acid, sebacic acid, itaconic acid, maleic acid, pyromellitic acid, or octahydronaphthalene dicarboxylic acid at a temperature of about from 50 to 250° C. in the presence of basic catalyst such as an oxide, hydroxide, carbonate or alkoxide of an alkali or alkaline earth metal. Both of the aforementioned reactions are preferably carried out in a solvent which forms a binary with the water or alcohol by-products, respectively, in which case the binary is continuously distilled, separated and the solvent is refluxed.

The compounds having a plurality of vinyl cyclic acetal radicals connected by hydrocarbon or ether linkages can be prepared, for example, by reacting compounds such as decane-1,2,9,10-tetrol or diglycerol, respectively, with acrolein or with an alpha-substituted acrolein under the conditions described above used for preparing hydroxy-substituted vinyl cyclic acetals.

The compositions of this invention are prepared by physically mixing at least about 5%, and preferably about 10 to 65% based on the weight of oil of one or more of the aforementioned compounds containing a plurality of vinyl cyclic acetal radicals with one or more of the aforementioned natural or synthetic oils. Where necessary, the compatibility of the compositions of this invention often can be improved by heating the mixtures at a temperature of about from 50 to 250° C. for about from 15 minutes to 2 hours, oils such as tung oil and dehydrated castor oil being preferably used at the lower temperatures. In addition to improving the compatibility, in some cases the heat treatment also improves the hardness, freedom from tack and other film-forming properties of the upgraded oils, particularly compositions containing drying or semi-drying oils together with compounds containing a plurality of vinyl cyclic acetal radicals which also contain unsaturation other than that in the vinyl cyclic acetal radical, for example, the maleic and itaconic acid diesters of hydroxy-substituted vinyl cyclic acetals. In various applications, for example, in coating compositions, conventional solvents, pigments, fillers, flow control agents and other film-forming materials such as alkyd resins and amino-aldehyde resins can be added to the compositions. It is particularly preferred to add pigments and fillers in conventional amounts to compositions containing non-drying oils such as castor oil, lard oil, olive oil and neat's-foot oil in order to accentuate the improved drying properties of these oils. Examples of pigments are metal oxides, sulfides, sulfates, silicates, chromates, iron blues, organic colors and metal flake pigments. The drying time of the upgraded natural and synthetic oils of this invention can be further accelerated by adding thereto small portions of conventional siccative metal driers such as, for example, lead, manganese, zinc, iron, nickel, calcium, copper, tin, zirconium and cobalt acetate, naphthenate, linoleate, resinate, tallate or octoate and butyl phthalate, for example, 0.0005 to 3% of metal (in the drier) based on the total weight of upgraded natural or synthetic oil.

The upgraded natural or synthetic oils of this invention dry rapidly at room temperature to form tough, durable films, coatings and the like having greatly improved hardness and freedom from tack. The upgraded oils are useful, for example, in coating compositions, in linoleum, as potting compounds, as coatings for fabrics and in a wide variety of other applications in which natural and synthetic oils are now used.

The following examples are intended to illustrate the invention and not to limit it in any way. Parts and percentages are by weight unless otherwise specified.

Examples 1 to 6

One part of the following compounds containing a plurality of vinyl cyclic acetal radicals was mixed with 5 parts of safflower oil and heated for 30 minutes at 225 to 250° C. in a nitrogen atmosphere, then 0.1% of Co^{+2} in the form of cobalt butyl phthalate was added thereto. A film of each of the resulting mixtures was cast on a glass panel using a doctor blade with a clearance of 2.4 mils. The films were then allowed to stand for 8 days at room temperature, after which time their tack and hardness were measured. The following results were obtained:

Example	Diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane	Tack Time, Seconds	Pfund Hardness Numbers
1	1 Part of 2,3 - dicarboxybicyclo-(2.2.1)-5-heptene diester.	16.0	0.321
2	1 Part of 1,2 - dicarboxycyclo - hexene-4 acid diester.	15.3	0.366
3	1 Part of itaconic acid diester	3.0	0.354
4	1 Part of maleic acid diester	2.3	0.321
5	0.5 Part of 2,3-dicarboxybicyclo-(2.2.1)-5-heptene acid diester and 0.5 part of itaconic acid diester.	5.9	0.354
6	0.5 Part of 1,2-dicarboxycyclo-hexene-4 acid diester and 0.5 part of itaconic acid diester.	6.0	0.421
Control	None	23.0	0.147

The tack of the films was measured with a Zapon tack tester which consisted essentially of a strip of 1 inch wide iron bar bent in the form of a V, one leg of which was about 1 inch long and the other leg of which was about 3 inches long. The angle between the legs was about 135°. The 1-inch leg was wrapped in aluminum foil, then a 100 gram weight was placed on the 1-inch leg which in turn was placed on the film to be tested. After 15 seconds, the weight was removed and the tack time, in seconds, necessary for tester to fall over on the 3-inch leg was measured. The tack time increases with the tack of the film. Hardness was measured on a modified Pfund hardness tester. The hardness of the film being tested was determined from the impression made in the film by the loaded hemispherical indenter of the tester and was expressed in Pfund hardness numbers. The Pfund hardness numbers increase with the hardness of the film being tested and are directly proportional to Knoop hardness values determined on a standard Tukon tester.

The liquid solvent-free compositions of Examples 1 through 6 above can be used as clear coating compositions for protecting and decorating metal, wood, ceramics, fabrics and the like.

Similar results can be obtained by substituting equal weights of, for example, the terephthalate acid diester of 5 - hydroxymethyl - 5-methyl-2-vinyl-1,3-dioxane, the sebacic acid diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxepane or the maleic acid diester of 4(4'-hydroxybutyl)-2-isopropenyl-1,3-dioxolane for the diesters described above.

Examples 7 to 11

One part of the following compounds containing a plurality of vinyl cyclic acetal radicals was mixed with five parts of linseed oil and heated for 30 minutes at 225 to 250° C. in a nitrogen atmosphere, then 0.1% of Co^{+2} was added thereto. A 2.4-mil film of each of the resulting mixtures was doctor-knife coated onto a glass panel and allowed to dry at room temperature for 8 days. The following results were obtained:

Example	Diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane	Tack Time, Seconds	Pfund Hardness Numbers
7	1 Part of 2,3 - dicarboxybicyclo-(2.2.1)-5-heptene acid diester.	21.9	0.471
8	1 Part of 1,2-dicarboxycyclo-hexene-4 acid diester.	25.0	0.421
9	1 Part of itaconic acid diester	10.0	0.553
10	1 Part of maleic acid diester	30.7	0.510
11	0.5 Part of 2,3-dicarboxybicyclo-(2.2.1)-5-heptene acid diester and 0.5 part of itaconic acid diester.	33.0	0.454
Control	None	40.6	0.275

A 200-gram load was used on the Zapon tack tester.

If 1 part of the diether of 4(4'-hydroxymethyl)-2-vinyl-1,3-dioxolane formed by reacting diglycerol with acrolein as described hereinbefore or 1 part of bis(2-vinyl-1,3-dioxan-4-yl) ethane formed from octane-1,3,6,8-tetrol and acrolein are substituted for the diesters used in this example substantially similar results are obtained.

Examples 12 to 15

One part of the following compounds containing a plurality of vinyl cyclic acetal radicals were mixed with five parts of castor oil and heated at 225 to 250° C. for 30 minutes in a nitrogen atmosphere, then 0.1% of Co^{+2} was added thereto. A 2.4-mil film of each of the resulting mixtures was coated onto a glass panel and allowed to stand for 4 days at room temperature. The resulting films had the following properties:

Example	Diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane	Tack Time, Seconds	Pfund Hardness Numbers
12	1 Part of 2,3 - dicarboxybicyclo-(2.2.1)-5-heptene acid diester.	21.0	0.075
13	1 Part of itaconic acid diester	4.2	0.075
14	1 Part of maleic acid diester	10.0	0.075
15	0.5 Part of 2,3-dicarboxybicyclo-(2.2.1)-5-heptene acid diester and 0.5 part of itaconic acid diester.	20.3	0.130
Control	None	(1)	(2)

[1] Too high to measure.
[2] Too low to measure.

The tack times were determined using a 20-gram weight on the Zapon tack tester.

Examples 16 to 20

Various portions of the maleic diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane were mixed with 25 parts of soya bean oil and heated at 225 to 250° C. for 30 minutes, then 0.1% of Co^{+2} was added thereto. A 2.4-mil film of each of the resulting mixtures was cast on a glass panel and allowed to dry for 4 days at room temperature. The resulting films had the following properties:

Example	Parts of maleic diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane	Tack Time, Seconds	Pfund Hardness Numbers
16	1.25	21	0.105
17	2.5	10	0.138
18	5.0	10	0.295
19	7.5	8	0.331
20	10.0	12	0.275
Control	None	34	0.105

A 500-gram load was used on the Zapon tack tester.

Examples 21 to 23

Coating compositions having the following formulation were prepared by milling the following materials on a paint mill until a smooth uniform dispersion was obtained:

	Parts
Oil	706
Maleic acid diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane	140
Soya lecithin	7
Zinc oxide	529
Titanium dioxide	357
Magnesium silicate	765
Mineral spirits (boiling point 145 to 215° C.)	388

A control for each of the aforementioned compositions was prepared by similar procedure except that an equal weight of the particular oil used in the composition was substituted for the compound containing a plurality of vinyl cyclic acetal radicals. Also, each composition including the control contained 0.1% of Co^{+2} based on the combined weight of oil and compound containing a plurality of vinyl cyclic acetal groups.

A 2.4-mil film of each of the paints described above was coated onto a glass panel and allowed to stand for 3 days at room temperature. The resulting films had the following hardness:

Example	Oil	Pfund Hardness Number
20	Linseed oil	1.66
Control	do	1.14
21	Soya bean oil	0.85
Control	do	0.57
22	Safflower oil	2.27
Control	do	1.22
23	Castor oil	0.180
Control	do	0.075

Examples 24 to 27

Raw linseed oil and bis(2-vinyl-1,3-dioxolane-4-butyl) phthalate were mixed in the following weight ratios:

Example	Parts Raw Linseed Oil	Parts bis(2-vinyl-1,3-dioxolane 4-butyl) phthalate
24	80	20
25	60	40
26	40	60
27	20	80

To each mixture was added 0.04% Co^{+2} based on the total weight of mixture. Each of the resulting compositions was coated onto steel panels and air dried at room temperature overnight. The resulting films had properties similar to those shown in Examples 7 to 10.

The compositions described above can be made into linoleum by milling therewith pulverized cork, wood flour and pigments and spreading the resulting composition onto a layer of canvas or burlap backing.

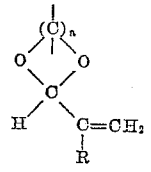
Example 28

About 292 parts of refined tall oil fatty acids consisting primarily of about equal weights of linoleic acid and oleic acid and about 2% of unsaturated fatty acids was heated with 38 parts of pentaerythritol at a temperature of 200 to 250° C. for about 8 hours in a nitrogen atmosphere. About 283 parts of the resulting synthetic oil, primarily the tetraester of pentaerythritol, having an acid number of 5.5 were obtained.

One part of the maleic acid diester of 4(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane together with 0.1% based on the total weight of composition of Co^{+2} in the form of cobalt butyl phthalate were mixed with 5 parts of the synthetic oil just described. A 2.4-mil film of the resulting upgraded synthetic oil was coated onto a glass panel and allowed to stand for 42 hours at room temperature. The dried film had a tack time measured with a 500 gram load of 5 seconds and a Pfund hardness number of 0.388. A control film of the synthetic oil without any compound containing a plurality of vinyl cyclic acetal radicals had a tack time of 13 seconds and a Pfund hardness number of 0.194.

I claim:

1. An upgraded oil which comprises (1) at least one unsaturated oil which is an ester of a C_{10} to C_{22} fatty acid and an at least trihydric alcohol and (2) at least about 5% based on the weight of oil of at least one compound containing two to six, inclusive, vinyl cyclic acetal radicals having the structural formula:



wherein



represents carbon atoms in the ring, "*a*" is an integer having a value of 2 to 3, all but one of the valences of said carbon atoms in the ring being satisfied by monovalent radicals selected from the class consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl, chloroalkyl, fluoroalkyl, alkoxyalkyl, cyano, chloroalkoxyalkyl, fluoroalkoxyalkyl, cyanoalkoxyalkyl, cyanoalkyl, alkenyl, chloroaryl and fluoroaryl radicals when the value of "*a*" is 2 and, when the value of "*a*" is 3, said class consisting additionally of fluoro, chloro, acylamido and phenylsulfonyl radicals, and the one remaining valence connects the vinyl cyclic acetal radical to at least one other such radical through an interposed polyvalent radical; and wherein R is a monovalent radical selected from the class consisting of hydrogen, alkyl, alkenyl, aryl, chloro, fluoro, bromo, cyano, acyloxy, chloroalkyl, fluoroalkyl, cyanoalkyl, alkoxy, aryloxy and carbalkoxy radicals.

2. An upgraded oil of claim 1 wherein said oil is a drying oil.

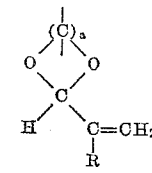
3. An upgraded oil of claim 1 wherein said oil is a semi-drying oil.

4. An upgraded oil of claim 1 wherein said compound containing a plurality of vinyl cyclic acetal radicals is present in an amount of about from 10 to 65% based on the total weight of oil.

5. A composition of claim 1 containing pigment.

6. A composition of claim 1 containing metallic drier.

7. A process for upgrading oils which comprises mixing at least one unsaturated oil which is an ester of a C_{10} to C_{22} fatty acid and an at least trihydric alcohol with at least about 5% based on the weight of said oil of at least one compound containing two to six, inclusive, vinyl cyclic acetal radicals and heating the resulting mixture at a temperature of about from 50 to 250° C. for about from 15 to 120 minutes, said plurality of vinyl cyclic acetal radicals having the structural formula:



wherein



represents carbon atoms in the ring, "*a*" is an integer having a value of 2 to 3, all but one of the valences of said carbon atoms in the ring being satisfied by monovalent radicals selected from the class consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl, chloroalkyl, fluoroalkyl, alkoxyalkyl, cyano, chloroalkoxyalkyl, fluoroalkoxyalkyl, cyanoalkoxyalkyl, cyanoalkyl, alkenyl, chloroaryl and fluoroaryl radicals when the value of "*a*" is 2 and, when the value of "*a*" is 3, said class consisting additionally of fluoro, chloro, acylamido and phenylsulfonyl radicals, and the one remaining valence connects the vinyl cyclic acetal radical to at least one other such radical through an interposed polyvalent radical; and wherein R is a monovalent radical selected from the class consisting of hydrogen, alkyl, alkenyl, aryl, chloro, fluoro, bromo, cyano, acyloxy, chloroalkyl, fluoroalkyl, cyanoalkyl, alkoxy, aryloxy and carbalkoxy radicals.

8. A process of claim 7 wherein said compound containing a plurality of vinyl cyclic acetal radicals contains ethylenic unsaturation in addition to that in said vinyl cyclic acetal radicals.

9. A process of claim 8 wherein said oil is a semi-drying oil.

10. A process of claim 8 wherein said oil is a drying oil.

11. An upgraded oil of claim 1 wherein said compound having a plurality of vinyl cyclic acetal radicals is a diester, said interposed polyvalent radical which connects said vinyl cyclic acetal radicals comprising a dicarboxylate radical.

12. An upgraded oil comprising linseed oil and about from 10 to 65%, based on the weight of said linseed oil, of the itaconic acid diester of 4-(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane.

13. An upgraded oil comprising the tall oil tetraester of pentaerythritol and about from 10 to 65%, based on the weight of said tall oil tetraester, of the maleic acid diester of 4-(4'-hydroxybutyl)-2-vinyl-1,3-dioxolane.

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