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ESTERS OF POLYALLYL ALCOHOL

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1

This invention relates to esters of polymeric allyl-type alcohols and more particularly to polymeric allyl-type esters of unsaturated monobasic aliphatic acids.

Natural fatty oils consist principally of mixtures of glycerides of fatty acids. In drying oils, unsaturated fatty acid radicals are present. The oils which dry the fastest have, in general, the highest degree of unsaturation, although speed of drying is dependent also upon the position of the unsaturated linkages in the molecule.

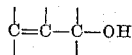
It is known that when unsaturated fatty acids are freed from their compounds with glycerol and re-esterified with alcohols containing more than three hydroxyl groups in the molecule, the resulting esters dry more rapidly than the corresponding glycerides. Alcohols which have been mentioned for this use are erythritol, pentaerythritol, adonitol, xylitol, arabitol, mannitol, dulcitol and sorbitol.

It has now been found that esters of unsaturated fatty acids with aliphatic alcohols having three or more hydroxyl groups separated from one another by at least four, preferably five, carbon atoms, have improved drying properties and are capable of forming films of desirable characteristics. Valuable coating compositions of many kinds, such as paints, enamels and lacquers, are formed from the new esters.

Accordingly, it is an object of the present invention to provide new esters. Another object is to provide esters capable of forming the basis of improved coating compositions. Another object is to provide a method of preparing said esters. Another object is to provide new paints, enamels, lacquers and other coating compositions. Other objects will be apparent from the description of the invention given hereinafter.

The new compounds are esters of unsaturated fatty acids with aliphatic alcohols having three or more hydroxyl groups separated from one another by at least four carbon atoms. Preferred alcohols are those resulting from the polymerization of an allyl-type alcohol or formed from a polymer of a derivative of an allyl-type alcohol.

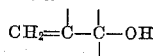
Allyl-type alcohols are unsaturated alcohols having an olefinic double bond of aliphatic character between two carbon atoms, one of which is directly joined to a saturated carbinol carbon atom. They have a structure which may be represented by the general structural formula



Preferred allyl-type alcohols have a terminal methylene group attached by an olefinic double

2

bond to a carbon atom which is directly attached to a saturated carbinol carbon atom, as represented by the formula



Allyl-type alcohols useful in the present invention preferably have not more than about eighteen carbon atoms and have at least one unsaturated carbon-to-carbon linkage for each six carbon atoms.

Examples of preferred allyl-type alcohols are allyl alcohol, methallyl alcohol, ethallyl alcohol, chloroallyl alcohol, 3-hydroxy-butene-1, 3-hydroxy-pentene-1, 3-hydroxy-hexene-1, 3-hydroxy-3-methyl-butene-1, 3-hydroxy-3-methyl-pentene-1, 3-hydroxy-3-ethyl-pentene-1, 3-hydroxy-2-methyl-butene-1, 3-hydroxy-2-methyl-pentene-1, 3-hydroxy-2,3-dimethyl-butene-1, 3-hydroxy-pentadiene-1,4, 3-hydroxy-hexene-1-yne-5, 3-hydroxy-2-methyl-pentene-1-yne-4, and 4-hydroxy-2,5-dimethyl-hexadiene-1,5. Other allyl-type alcohols are crotyl alcohol, tiglyl alcohol, 3-chlorobutene-2-ol-1, cinnamyl alcohol, 1-hydroxy-hexadiene-2,4, 1-hydroxy-hexadiene-2,5, 1-hydroxy-butadiene-2,3, 2-hydroxy-hexadiene-3,5, 1-hydroxy-2-methyl-hexene-2, 1-hydroxy-2-methyl-pentene-2, 1-hydroxy-3,7-dimethyl-octadiene-2,7, 2-cyclohexenol, 2-cyclopentenol, etc.

Polymers of allyl-type alcohols can be formed from polymers of derivatives of allyl-type alcohols. Preferred derivatives are halides and esters. Allyl-type halides can be polymerized by any of a plurality of methods, such as exposure to actinic light, or treatment with boron trifluoride at a low temperature under anhydrous conditions, as disclosed in the co-pending application of Adelson and Dannenberg, Serial Number 417,140, filed October 30, 1941, now Patent No. 2,331,869. The polymers consist of monomer units joined principally by carbon-to-carbon linkages. Polymers of allyl-type halides are hydrolyzed only with difficulty to polymers of allyl-type alcohols by conventional techniques, but hydrolysis proceeds readily under the catalytic action of a cuprous compound, as disclosed in the co-pending application of Van de Griendt and Peters, Serial Number 340,990, filed June 17, 1940.

Allyl-type esters are convenient starting materials in the preparation of polymers of allyl-type alcohols. Suitable allyl-type esters are those of carboxylic acids devoid of a polymerizable unsaturated group, i. e. saturated aliphatic, including alicyclic, aromatic, etc., carboxylic acids. Representative examples of suitable allyl-type esters are allyl formate, allyl acetate, allyl pro-

pionate, allyl butyrate, allyl isobutyrate, beta-methylallyl acetate, beta-chlorallyl acetate, beta-ethylallyl formate, beta-phenylallyl acetate, beta-methoxyallyl acetate, beta-chloromethylallyl acetate, allyl benzoate, beta-methylallyl acetate, allyl toluate, allyl salicylate, allyl glycolate, allyl methoxyacetate, beta-methylallyl chloracetate, allyl beta-chloropropionate, allyl lactate, allyl naphthenate, beta-methylallyl chlorobenzoate, allyl alpha-hydroxyisobutyrate, allyl acetylglycolate, allyl stearate, allyl levulinate, beta-methylallyl butyrate, alpha-methylallyl acetate, alpha-phenylallyl acetate, allyl ethoxyformate, beta-methylallyl phenoxyformate, allyl naphthoate, allyl esters of hydrogenated abietic acid, diallyl malonate, diallyl succinate, diallyl adipate, diallyl maleate, diallyl phthalate, and the like.

Others are allyl-type esters of ethereal oxygen-containing carboxylic acids, such as diallyl diglycolate, diallyl dilactate, diallyl dihydroacrylate, dimethylallyl diglycolate, dicrotyl dilactate, dipropargyl diglycolate, etc. Another group consists of the allyl-type esters of inorganic acids, notably of the ortho acids of boron and silicon.

Allyl-type esters can be polymerized by heating in the presence of a polymerization catalyst, such as oxygen or an oxygen-yielding catalyst, as disclosed in the co-pending abandoned application of Adelson and Dannenberg, Serial Number 417,278, filed October 31, 1941. A number of types of inorganic salts act as polymerization catalysts. The esters can be polymerized also with heat in the absence of added catalyst. The polymers consist of monomer units joined by carbon-to-carbon linkages. The alcohols can be formed by hydrolysis or alcoholysis of the ester polymers, the latter preferably in the presence of a basic metal alcoholate, as described and claimed in the co-pending application of Adelson and Evans, Serial Number 425,118, filed December 31, 1941, now Patent No. 2,473,124.

The polymers consisting of monomer units joined solely by carbon-to-carbon linkages are operable as components of the compounds of the invention. There are obvious methods, in addition to those already mentioned, of forming the polymeric allyl-type alcohols, and other alcohols which, while not polymeric allyl-type alcohols, are operable because they contain in the molecule three or more hydroxyl groups separated from one another by at least four, preferably five, carbon atoms.

Preferred alcohols are polymers of monohydric allyl-type alcohols of not over eighteen carbon atoms in the molecule, which polymers consist of from three to about ten monomer units and have a corresponding number of hydroxyl radicals. Instead of the raw polymers of the allyl-type alcohols, which usually contain residual unsaturation, there may be used air-blown or hydrogenated polymers, or polymers treated with sulfur dioxide or the like. This applies also to polymers of derivatives of allyl-type alcohols.

The acid radicals of the compounds of the invention may correspond to substantially any unsaturated fatty acid. Preferred acids have at least sixteen carbon atoms and have an iodine number (Wijs) of at least 120. Examples of preferred acids are palmitoleic, oleic, linoleic, linolenic, arachidonic, clupanodonic, eleostearic, and licanic acids.

Other preferred acids can be made by the treatment (isomerization) of acids containing isolated double bonds to bring about conjugation of the double bonds as disclosed by Scheiber in

U. S. Patent 1,896,467. Others are made by dehydrating acids containing one or more hydroxyl groups, as exemplified by the dehydration of ricinoleic acid, forming the acid known as 9,11-linoleic acid, octadecadienic acid and ricinic acid. Others result from dehydrogenation of fatty oil acids, the process usually involving in actual practice the introduction of halogen, followed by dehydrohalogenation. Obviously, isomerization, dehydration and dehydrogenation can be effected upon derivatives of the acids, such as the glycerides, rather than upon the acids themselves, followed by the production of the acids from the derivatives. There are many other suitable acids.

The acids can be synthesized by known chemical processes. Most of the acids, however, can be obtained more economically from naturally occurring drying oils, which are principally mixtures of glycerides of fatty acids, some of which latter are unsaturated. For example, chia, hempseed, linseed, perilla, safflower, soybean and walnut oils consist of glycerides of oleic, linoleic, linolenic and a small proportion of saturated acids. Fish oils commercially available for use in coating compositions contain glycerides of the above acids and, in addition, of palmitoleic, arachidonic and chipanodonic acids. The glycerides of oiticica oil are those of the valuable, triply conjugated keto acid called licanic acid, in addition to glycerides of oleic and saturated acids. The acid radicals of tung oil are those of saturated acids, oleic acid and the triply conjugated eleostearic acid. In poppyseed and sunflowerseed oils, glycerides of oleic, linoleic and saturated fatty acids are present. Many other oils containing these and other glycerides are known. Examples of other oils are oiticica oil, Japanese wood oil, walnut seed oil, rubber seed oil, dehydrated castor oil, etc. In most oils, at least a portion of the glycerides are mixed glycerides, in which the molecule contains more than one kind of acid radical.

Among the other natural sources of fatty acids are waxes, which in general are esters of higher fatty acids with monohydric alcohols. Tall oil contains a substantial proportion of unsaturated fatty acids.

The acids can be freed from their compounds with glycerol and other alcohols by any of several known methods, notably by hydrolysis or saponification. Hydrolysis is effected with water under superatmospheric pressures and temperatures. A Twitchell reagent, such as sulfostearic acid, catalyzes hydrolysis at atmospheric pressures. Acids can be used as hydrolyzing agents. Enzymes, such as the lipases, act hydrolytically upon glycerides in aqueous acidic emulsion. The usual method, however, is to saponify the glycerides with a metallic base, such as sodium hydroxide, potassium hydroxide, manganese oxide, zinc oxide, magnesium oxide, ammonia, sodium bisulfite, etc., followed by conversion of the metallic salts of the acids to the free acids themselves. Other catalysts and other processes are known for obtaining acids from esters. The acids are separated from the glycerol and other impurities by known methods. They can be purified by distillation, crystallization, solvent extraction, etc. They can be separated from one another, or used in admixture with one another and/or modified by the addition of other acids.

The compounds with which the invention is principally concerned are esters of unsaturated fatty acids with polymeric allyl-type alcohols, a

preferred subgroup consisting of esters of unsaturated fatty acids having at least sixteen carbon atoms and an iodine number (Wijs) of at least 120 with polymers of monohydric allyl-type alcohols of three to about eighteen carbon atoms, which polymers consist of from three to about ten monomer units and have a corresponding number of hydroxyl radicals.

One method of forming the compounds is the direct esterification of the alcohol with the acid. This can be brought about by heating a mixture of the reactants, preferably with the continuous removal of water. The presence of an inert homogenizing liquid, such as a substance in which both reactants are soluble, shortens the reaction time. The liquid can be selected also with regard to its boiling point, so as to form a suitable azeotrope with water, making possible the continuous removal of water by azeotropic distillation. Suggested homogenizing liquids are kerosene, high boiling ethers, high boiling naphthas and high boiling coal tar solvents. Acids have a catalytic effect on the esterification.

Another method of forming the esters is acid exchange between a polymer of an allyl-type ester and an unsaturated fatty acid. Conveniently the acid radical of the starting ester corresponds to an acid having a boiling point under the conditions of the reaction lower than that of any other products or reactants, thus permitting continuous removal of the acid product by continuous distillation. However, this provision is by no means essential. Suggested starting esters are compounds of polymers of allyl-type alcohols with lower fatty acids, e. g. formic, acetic, propionic, butyric, etc., acids, dicarboxylic acids, e. g. oxalic, malonic, succinic, phthalic, etc., acids, and inorganic acids, e. g. orthosilicic, orthoboric, phosphoric, etc., acids.

A modification is ester interchange, involving a polymer of an allyl-type ester and an unsaturated fatty acid ester. Suitable acid radicals for the former are given in the preceding paragraph. For the latter esters, convenient alcohol radicals are those of lower aliphatic alcohols, such as methyl, ethyl, propyl, etc., alcohols, and of glycerol.

Less desirable, but nevertheless feasible, is the preparation of the esters of the invention by the action of an acid halide or anhydride upon the alcohol. Other methods of preparation can be used. Regardless of the method, it is usually desirable to provide the reaction mixture with a blanket of an inert gas, such as carbon dioxide or nitrogen, where the temperatures of the reaction are likely to cause oxidation or premature "drying" or polymerization of the ester. Atmospheric, reduced or superatmospheric pressures can be used. Esterification can be carried out in a continuous or batch-wise manner.

In accordance with the usual method of operation, a mixture of unsaturated fatty acids is esterified with a mixture of polymers of allyl-type alcohols. The latter mixture is ordinarily the product resulting from subjecting a single allyl-type alcohol to polymerization conditions or the product formed by converting to the alcohols a mixture of polymers formed from a single allyl-type alcohol derivative, and consists of a mixture of polymeric molecules having substantially the same monomer unit structure but differing in length, i. e. in the number of units per polymeric molecule. Such a mixture may be collectively termed a "homopolymer."

The mixture of polymers of allyl-type alcohols

may, however, be formed by the polymerization of one allyl-type alcohol in the presence of one or more other allyl-type alcohols, or by converting to the alcohols a mixture of polymers formed by the polymerization of a derivative of one allyl-type alcohol in the presence of one or more other allyl-type alcohols. The product may consist of a mixture of polymeric molecules, some or all of which consist of two or more kinds of monomer units, the polymeric molecules usually differing also in length. Such a mixture may be collectively termed an "interpolymer." It is also, generically, a "co-polymer."

Where the polymerization of two different allyl-type compounds results in a mixture of polymeric molecules which differ in length and in the structure of the monomer units, but each of which is composed of only one kind of monomer unit, the mixture is merely a mixture of homopolymers, or, less specifically, a "co-polymer." A mixture of homopolymers can, of course, be formed also by admixing separately formed homopolymers. Likewise, there can be formed mixtures of one or more homopolymers with one or more interpolymers.

The compounds of the invention are thus, conveniently, mixtures of esters formed by direct or indirect esterification of a mixture of unsaturated fatty acids with an allyl-type alcohol homopolymer, interpolymer, mixture of homopolymers, mixture of interpolymers, or mixture of homopolymers and interpolymers. The acids need not be pure but may contain other compounds, notably saturated fatty acids, preferably in amount not over about 25% by weight of the total acids. Similarly, the allyl-type alcohol fraction may contain substances such as aliphatic monohydric, dihydric and trihydric alcohols. Also, a single unsaturated fatty acid can be esterified with a mixture of polymers of allyl-type alcohols, or a single polymer of an allyl-type alcohol can be esterified with a mixture of acids. Separately prepared compounds of the invention can be used in admixture with one another.

The compounds are normally liquid substances having many of the characteristics of naturally occurring drying oils. They differ in being faster in drying and in their greater sensitivity to driers. They can be purified and decolorized, where necessary, by treatment with acid or alkali, by bleaching with actinic light and by the use of adsorbents, such as activated carbon, silica gel and fuller's earth. They can be bodied by heating in the presence or absence of oxygen, temperatures of 100° F. to 500° F. being usual. They can be bodied also by blowing with molecular oxygen. Bodying, as well as subsequent drying, are promoted by the presence of driers, such as red lead, litharge, manganese oxide and, preferably, the more readily soluble cobalt, lead, manganese, etc., resinates, linoleates and naphthenates. From about 0.01% to 1.0% of drier by weight of synthetic drying oil is customary. Small amounts of oxygen-liberating substances have been found to hasten drying. Of these representative examples are ozone, hydrogen peroxide, sodium peroxide, calcium peroxide, barium peroxide, benzoyl peroxide, perborates, percarbonates, etc.

Bodging and drying of the compounds of the invention are presumed to be accompanied by cross-linking involving the unsaturated fatty acid radicals and finally resulting in a three-dimensional molecular structure. Cross-linking can occur by polymerization of the radicals, in

which the double-bonded carbon atoms of the radicals become directly linked to similar carbon atoms of other radicals with a corresponding reduction in unsaturation. Cross-linking can also be effected by so-called element conversion, in which the double-bonded carbon atoms of the unsaturated radicals become linked to similar carbon atoms of other unsaturated radicals through one or more atoms of oxygen, sulfur, or the like, with a corresponding reduction in unsaturation. It is probable that in bodying and drying both kinds of cross-linking occur.

Bodied and unbodied compounds of the invention can be used in the preparation of paints, enamels, and lacquers. They may sometimes be used alone, except that one or more driers should usually be present. Fused driers, such as metallic resins, linoleates and naphthenates, are preferred, although many other driers are effective. Litharge, lead acetate, lead carbonate, manganese dioxide, manganese borate and the corresponding calcium and zinc compounds can be used. More often, the coating compositions contain in addition one or more other film-formers, solvents, plasticizers, dyes, pigments and fillers. These and other modifying substances can be incorporated by any of the methods well known in the art.

Examples of other substances which can often be used to advantage in conjunction with the compounds of the invention are other synthetic drying oils, natural drying oils, gilsonite, rosin, colophony, shellac, copal, dammar gum, pitch, asphalt, protein plastics, cellulose derivatives, and synthetic plastics. Among the latter are phenol-aldehyde, urea-aldehyde, alkyd, superpolyamide and superpolyester-amide resins. Another group consists of polymers of compounds containing in the molecule a single polymerizable unsaturated carbon-to-carbon linkage, such as unsaturated esters of saturated monobasic acids, e. g. vinyl, allyl and methallyl esters of acetic, propionic, butyric, etc., acids; saturated esters of unsaturated monobasic acids, such as methyl, ethyl, propyl, etc., esters of acrylic and methacrylic acids; styrene; alpha-methyl styrene; ethylene halides; vinyl halides; vinylidene halides, allyl alcohol, allyl halides, etc. Related plastics are formed by a chemical after-treatment of one or more polymers. Typical examples of these are polyvinyl acetals, after-chlorinated polyvinyl chloride, etc. Another group consists of polymers and chemically modified polymers of compounds having two or more polymerizable unsaturated carbon-to-carbon linkages unconjugated with respect to one another. Examples are the unsaturated polyesters of saturated polycarboxylic acids such as vinyl, allyl and methallyl esters of oxalic, malonic, succinic, glutaric, citric, tartaric, phthalic, isophthalic and naphthalene dicarboxylic acids; unsaturated polyesters of polybasic inorganic acids such as vinyl, allyl, methallyl, cyclohexenyl esters of the ortho acids of silicon and boron and the corresponding esters of sulfuric and phosphoric acids; unsaturated carboxylic acid polyesters of unsaturated polyhydric alcohols such as acrylic and methacrylic polyesters of glycol, diethylene glycol, triethylene glycol, trimethylene glycol, glycerol, etc.; unsaturated polyethers of polyhydric alcohols such as vinyl, allyl and methallyl polyethers of glycol, diethylene glycol, triethylene glycol, trimethylene glycol, glycerol, etc.; ethers having two or more unsaturated aliphatic radicals such as vinyl, allyl, methallyl and crotyl diethers; unsaturated esters

of unsaturated acids such as vinyl, allyl and methallyl esters of acrylic and methacrylic acids. Other modifiers are substances formed by the polymerization and co-polymerization of compounds having two or more conjugated polymerizable unsaturated linkages, such as butadiene, the pentadienes, the hexadienes, etc., monovinyl acetylene and divinyl acetylene.

Besides their rapidity of drying, the compounds represent a distinct advance in the coating industry because they are generally color-stable at room temperature, thus permitting the production of light-colored paints and enamels which maintain their color over long periods of time. Further, films based on the compounds exhibit marked superiority to most of the films heretofore commercially available in toughness, flexibility, gloss and resistance to weathering.

Compositions based on the compounds can be used for many purposes. They provide protective coatings for a variety of surfaces including wood, steel, brass, copper, zinc, brick, cement, tile, cloth and paper. They can be used for sizing and impregnating fibrous material, such as woven cloth, felt and paper. Others can be so formulated that they are suitable as adhesives and interlayers in laminated articles, which may comprise paper, wood, woven textiles, felt, glass, metal and the like, an outstanding example being a structure consisting of layers of woven glass cloth laminated and impregnated with the compounds of the invention. Some of the compounds can be dried as tough, durable, self-sustaining films.

Some of the many ways in which the invention can be carried out are illustrated by the following examples in which parts are on a weight basis.

Example I

A mixture of 155 parts of allyl alcohol and 2 parts of hydrogen peroxide was heated at 100° C. under a reflux condenser. The hydrogen peroxide consumed was replenished at frequent intervals. After 116 hours the unreacted monomer was distilled from the reaction mixture under vacuum. The residue was 134 g. of viscous liquid having a refractive index of $n_D^{20} = 1.5143$ and consisted mainly of polyallyl alcohol. The molecular weight was about 300, indicating that the average polymer molecule contained 5 monomer units.

A mixture of 17.6 parts of the polyallyl alcohol and 63.2 parts of a mixture of fatty acids obtained from linseed oil was heated in an atmosphere of nitrogen under a reflux condenser for three hours during which period the temperature rose from about 200° C. to 302° C. 4.1 parts of water along with 0.4 part of oil were removed during the reaction. 80.5 parts of polyallyl esters of linseed fatty acids were obtained. The mixture of ethers was a pale greenish yellow viscous oil analyzing as follows:

	Found	Calcd. for (C ₂₁ H ₃₂ O ₂) _n
65 Per cent carbon.....	77.4	78.7
Per cent hydrogen.....	11.1	11.3
Per cent oxygen (by difference).....	11.5	10.0
Saponification value equiv./100 g.....	0.319	0.312
Acid value equiv./100 g.....	0.04(7)	0
Acid number mg. KOH/100 g.....	26.4	0
Ester value equiv./100 g.....	0.27(2)	0.312
70 Apparent mol. wt. (ebull. C ₆ H ₆ -2 points extrapolated).....	1450	(320)
d ₂₀ ⁴ (in air).....	0.965(9)	
n _D ²⁰ /D.....	1.4923	

A mixture of lead, manganese and cobalt naphthenate siccatives was added to a small amount

of the esters and the resulting composition was spread out in a thin layer which dried overnight to a tack-free film.

Example II

A mixture of 17 parts of polyallyl alcohol obtained by the polymerization of allyl alcohol in the presence of hydrogen peroxide and 54.1 parts of linseed fatty acids was heated under reflux conditions in an atmosphere of nitrogen for three and one-half hours during which period the temperature rose from 214° C. to 299° C. 3.6 parts of water and 1 part of oil were removed. 65.2 parts of polyallyl esters of linseed fatty acids were obtained. The esters resembled those obtained in Example I and analyzed as follows:

	Found	Calcd. for (C ₂₁ H ₃₈ O ₂) _n
Per cent carbon.....	77.2	78.7
Per cent hydrogen.....	11.0	11.3
Per cent oxygen (by difference).....	11.8	10.0
Saponification value equiv./100 g.....	0.308	0.312
Acid value equiv./100 g.....	0.022	0
Acid number mg. KOH/100 g.....	12.3	0
Ester value equiv./100 g.....	0.28(6)	0.312
Apparent mol. wt. (ebull. C ₆ H ₆ -2 points extrapolated).....	1050	(320) _n
n ₂₀ /D.....	1.4945	
d ₂₀ /4.....	0.975(2)	

Example III

0.9 part of a siccative mixture consisting of lead naphthenate 5 parts, manganese naphthenate 5 parts and cobalt naphthenate 5 parts, was added to 100 parts of the mixture of polyallyl esters of linseed fatty acids obtained in Example I. A glass plate was coated with a thin film of the composition which was allowed to dry at atmospheric pressure and temperature.

Another composition was prepared using the same amount of the mixture of siccatives and linseed oil in place of the polyallyl esters of linseed fatty acids. A film prepared from the composition was allowed to dry in like manner.

The film containing the polyallyl esters dried four times as fast as the film comprising the linseed oil and at the end of 168 hours was four times as hard, hardness being determined by the Sward rocker in accordance with the method described by Scofield in Circular 511 of the National Paint and Lacquer Association.

Example IV

A film of a mixture of polyallyl esters of linseed fatty acids in the absence of siccatives dried in 190 hours under atmospheric conditions and attained a hardness of 3.4. A similar film of linseed oil in the absence of siccatives had a hardness of only 2.1 at the end of 190 hours.

Example V

11.4 parts of polyallyl alcohol obtained by the hydrolysis of polyallyl acetate prepared by the polymerization of allyl acetate in the presence of 4% of benzoyl peroxide were mixed with 42.3 parts of oleic acid. The mixture was heated with stirring in an atmosphere of nitrogen for three

hours at 217° C. to 290° C. with the continuous removal of water. The residual polyallyl oleate was a viscous yellow substance having an acid number of 21. A mixture of polyallyl oleate, 100 parts, and 0.9 part of the siccative mixture used in Example III as a thin film dried quickly to a non-tacky condition with a gain in weight of 4.3%. So far as is known none of the naturally occurring esters (glycerides) of oleic acid exhibits drying properties either in the presence or absence of siccatives.

Example VI

9 parts of poly(ethyl alloxy formate) were heated with 14 parts of linseed fatty acids at 270° C. for 10 minutes, followed by heating at 300° C. for 30 minutes. A pale yellow oil having an acid number of 57 and exhibiting drying properties in the presence and absence of siccatives was obtained.

We claim as our invention:

1. An ester of dehydrated castor oil fatty acids and a polyallyl alcohol consisting of at least three allyl alcohol monomer units per molecule and having a corresponding number of hydroxyl radicals, the monomer units being joined together exclusively by carbon-to-carbon bonds.
2. An ester of oleic acid and a polyallyl alcohol consisting of at least three allyl alcohol monomer units per molecule and having a corresponding number of hydroxyl radicals, the monomer units being joined together exclusively by carbon-to-carbon bonds.
3. An ester of a diolefinic higher fatty acid and a polyallyl alcohol consisting of at least three allyl alcohol monomer units per molecule and having a corresponding number of hydroxyl radicals, the monomer units being joined together exclusively by carbon-to-carbon bonds.
4. An ester of an unsaturated higher fatty acid having an iodine value of at least 120 and a polyallyl alcohol consisting of at least three allyl alcohol monomer units per molecule and having a corresponding number of hydroxyl radicals, the monomer units being joined together exclusively by carbon-to-carbon bonds.

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