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ESTERS

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12 Claims. (Cl. 260—333)

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The present invention relates to higher fatty acid esters of hydroxy compounds resulting from the condensation of formaldehyde with ketones. These condensation products may contain a single hydroxymethyl group or a plurality of hydroxymethyl groups depending upon the conditions of the condensation. In addition, the ketone group may or may not be reduced to a hydroxyl group. In accordance with the present invention part or all of these hydroxyl groups may be esterified with higher fatty acids containing in excess of seven carbon atoms. The resulting products may be drying oils, plasticizers, waxes, emulsifying agents, surface active agents, intermediates and the like depending upon the number of hydroxyl groups present in the condensation product, the extent to which these hydroxyls have been esterified, and the nature of the acids used for esterification.

It is, therefore, a primary object of the present invention to prepare higher fatty acid esters of hydroxy condensation products of formaldehyde with a ketone.

It is another object of the present invention to prepare higher fatty acid esters of mono or polyhydric condensation products of formaldehyde with a ketone, partially or completely esterified with higher fatty acids, the products possessing characteristics making them useful as drying oils, plasticizers, waxes, emulsifying agents, surface active agents, intermediates and the like.

These and other objects of the invention will be apparent from the following description with particular reference to specific examples which are to be considered as illustrative only and not as limiting the invention.

In general, the invention involves the preparation of esters of fatty acids of more than seven carbon atoms, of hydroxy condensation products of formaldehyde with a ketone. These esters include a wide variety of compounds in view of the variation which is possible in the ketone used in the condensation, the extent of the condensation and accordingly the number of hydroxyl groups present in the condensation product, the extent to which the hydroxyl groups are esterified, and the nature of the fatty acids employed for esterification. Thus the ketones may be aliphatic or alicyclic such as cyclohexanone, cyclopentanone, acetone, methyl ethyl ketone, diethyl ketone, mesityl oxide, diacetyl, acetonylacetone, diacetone alcohol, levulinic acid and the like.

Likewise, the fatty acids employed may be selected from a large group. In the preparation of drying oils the acids may be isolated or mixed acids derived from drying or semi-drying oils such as cottonseed oil, soybean oil, linseed oil, perilla oil, tung oil, oiticica oil, sardine oil, menhaden oil, and other drying and semi-drying

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oils in general. These acids may be in the unchanged condition in which they exist in the natural oil or may be artificially conjugated, in accordance with known methods. In the preparation of plasticizers, waxes, emulsifying agents, surface active agents, intermediates, and the like the acids may be saturated or unsaturated and may be composed of any suitable isolated acid or mixture of acids. For preparing waxes it is usually desirable to employ a high molecular weight saturated acid as this contributes to the hardness of the resultant wax.

The products of the present invention are characterized by superior properties as compared with known products. Thus, for example, drying oils produced according to the present invention generally possess better drying properties and produce films of greater hardness and resistance to abrasion, water, and mild chemicals than do the corresponding naturally occurring oils. Waxes, described herein, are characterized by extreme hardness, high melting point, and light color.

The preparation of some of the condensation products of ketones referred to herein have been recorded in the literature. Apel et al., Ann., 289, 46 (1896), and Apel and Tollens, Ber., 27, 1087 (1894). Improved methods of preparing these condensation products will be found in the examples of the present application and in the co-pending application of the present inventor Serial No. 599,947 filed of even date herewith and entitled Condensation of ketones with formaldehyde, now Patent No. 2,462,031, issued February 15, 1949. The condensation reaction results in a mixture of products which may be of varying degrees of hydroxylation and in some cases may be in the form of a sirupy liquid. It will be apparent that this mixture of condensation products may be used in that condition for esterification if it is not desired to produce the ester as a pure compound.

If the sirup is not readily crystallizable, and if a pure crystalline condensation product is desired, it may be obtained in some instances by forming an aectal or ester or other derivative which may subsequently be hydrolyzed to the free hydroxy compound. The formation of an acetal often takes place readily when the crude sirup is stirred with acetone. Usually there is sufficient acid present as a result of the method of preparation to catalyze acetal formation. If necessary, a small amount of acid catalyst, such as sulfuric acid, may be added. As an alternative, an acetal derivative may be obtained by heating the sirup in aqueous methanol with an alydehyde such as benzaldehyde and a small amount of mineral acid for a suitable period of time. The acetal may be isolated from the solution by filtration after which it may be purified

by crystallization from a suitable solvent such as alcohol. The isolated aectal derivative may be converted to the hydroxy compound by treatment with a strong acid, such as hydrochloric acid. The volatile ketone or aldehyde may then be distilled off, leaving the pure hydroxy compound as a light-colored oil which crystallizes readily on cooling. Where the aldehyde liberated is as high boiling as benzaldehyde, the application of vacuum or the use of steam distillation is desirable.

The esterification with the fatty acid may be accomplished with either the crude sirup or with the isolated pure hydroxy compound. Likewise, it is possible to esterify the acetal directly. This may be accomplished under the influence of an acid catalyst, preferably oxalic acid as it effects the least amount of discoloration. Other strong acidic catalysts, such as p-toluenesulfonic acid and sulfuric acid, may likewise be used to catalyze this reaction.

Where the free hydroxy compound is employed in the esterification, any of the well known processes of the prior art may be employed. Several advantageous procedures, however, have been evolved. In one case it has been found possible to obtain excellent products by heating and stirring at around 200° C., equivalent quantities of the acid and the polyfunctional alcohol for a period of three to four hours. The polyfunctional alcohol, if it is used in a sirupy condition, may advantageously be brought into contact with the other reagents by dissolving it in water. During the reaction the water is rapidly driven off. The color of the product is improved by the use of an inert atmosphere such as that provided by carbon dioxide or nitrogen whereas the rate of esterification is accelerated by the employment of a small amount of catalyst such as the stearates, naphthenates, abietates, or other fat soluble salts of metals such as calicum, cadmium, cerium, strontium, zinc, and the like. Catalysts such as litharge, and those of an acidic nature such as sulfuric acid and hydrogen chloride, may be valuable in some cases. Near the end of the reaction the application of a vacuum is valuable in order to remove the last trace of volatile or unreacted material. Following this general procedure then, it is easily possible to obtain a product with an acid number and hydroxyl number lower than 30. If still lower values are desired, heating may be continued for a longer period of time. In cases where an oil is desired which is completely free of any fatty acid, the material may be dissolved in petroleum ether or naphtha and titrated to neutrality with alcohol caustic. The precipitated soaps may then either be filtered off or extracted with aqueous ethanol. The product is then recovered from the hydrocarbon solution by desolvation. Another process of purification which may be employed when an extremely pure oil is desired is that in which unreacted acid and highly hydroxylated or partially esterified alcohol is extracted by the use of ethanol.

Still another method of esterification which has been found particularly advantageous is that in which a small amount of a hydrocarbon solvent, such as xylene, is used for the purpose of removing the water of esterification azeotropically. By controlling the amount of solvent employed, the temperature of the reaction mixture may be raised to any desired degree. The advantage of this derives from the fact that any water produced is readily removed thus driving the reaction in the desired direction.

The esterification may likewise be accomplished azeotropically by the use of high boiling hydrocarbon solvent such as the isomeric triisopropylbenzenes in sufficient quantity to keep the soluble reactants and products in solution. Here again an azeotrope is formed with the water of esterification. This, however, is not as satisfactory as the use of a small amount of solvent such as xylene since it requires the use of a large amount of solvent which because of its low volatility is more difficult to remove at the end of a reaction. In either case the apparatus may be arranged so that the azeotropes distill in such a manner that the water is separated in the distillate and the hydrocarbon is returned to the reaction vessel.

The esters may be obtained also by a transesterification reaction between the polyhydric alcohol and a glyceride such as soybean or linseed oil or other esters of saturated or unsaturated higher fatty acids. Here again, an elevated temperature and stirring are advisable together with the use of catalysts such as oil soluble salts of calcium, strontium, barium, zinc, lithium, and the like.

The esters which are intended for waxes, emulsifying agents, plasticizers, etc. may be prepared by any of the previously mentioned esterification procedures or by any of the other methods of esterification commonly used in the art.

Example 1.—The soybean acid ester of the condensation product of acetone and formaldehyde

In a vessel equipped with an agitator and a reflux condenser was placed 116 parts of acetone, 480 parts of formaldehyde in the form of paraformaldehyde and 1700 parts of water. Thereafter 56 parts of calcium oxide was added with stirring. The reaction mixture thereupon was heated to 50° C. whereupon external heating was discontinued. The exothermic nature of the reaction caused the temperature to rise to 90° C. whereupon the reaction mixture was cooled to room temperature. If desired, the same effect may be attained by maintaining the reaction mixture at a temperature of 50°–55° C. for one to three hours. The solution thereupon was treated with dilute sulfuric acid until it was barely acid to Congo red indicator. Oxalic acid solution was added to make the reaction mixture strongly acid to Congo red indicator and to precipitate the last traces of calcium ion. The easily filtrable precipitate of calcium sulfate and calcium oxalate was removed whereupon the aqueous solution was evaporated in vacuo. The almost water-white sirup which resulted was treated with an organic solvent such as benzene and again evaporated in vacuo, the benzene serving to remove occluded water azeotropically. The sirup which resulted had a hydroxyl content of 28–30% and contained a substantial amount of an anhydroenneaheptitol which may be more accurately described as tetrahydro-3,3,5,5-tetrakis - (hydroxymethyl) -4-pyranol.

In a reaction vessel which was equipped with an agitator and a water trap with condenser was placed 125 parts of the above described sirupy condensation product as an 80% aqueous solution together with 520 parts of soybean fatty acids, 7 parts of calcium stearate, and 120 parts of xylene or similar hydrocarbon solvent. The calcium stearate is useful as it serves to accelerate the reaction at first; it does not, however, appear to decrease the time required for heat-

ing. The reaction mixture was stirred and heated under nitrogen for 4.5 hours at a temperature which started at 140° C. and which was gradually raised to 225° C. There resulted on removal of the xylene a product of low acid number whose physical constants follow:

Specific gravity 25/25, 0.9493
Color (Gardner), 14–15
Viscosity (Gardner), N
Iodine number, 122.8
Saponification equivalent, 331.4
Hydroxyl number, 28.5
Acid number, less than 20

The drying times as compared with ordinary soybean oil are indicated in the following table.

Compound	Tack, hours	Set, hours	Drying, hours
Soybean oil	6	12	----------
Soybean ester of the condensation product of acetone and formaldehyde	3.5	6.0	8.5

Twenty-four hours prior to the casting of 0.0015" thick films the oils were treated with siccatives consisting of 0.01% manganese and 0.01% cobalt as the soluble naphthenates. The films were cast on smooth glass plates and drying times according to the finger-tip method were noted under standardized conditions of 74° F. and a humidity of 57%. In addition to the above marked distinction, the synthetic oil yielded a more tack-free film which exhibited a greater hardness, better "through dry" and a greater resistance to abrasion.

Example 2.—Linseed acid ester of the condensation product of acetone and formaldehyde

In an appropriate vessel equipped with agitator was placed 130 parts of the condensation product of acetone and formaldehyde of Example 1, 400 parts of linseed fatty acids, and 5 parts of calcium stearate. The polyhydric alcohol was in the form of an aqueous solution. The reaction mixture was stirred vigorously and heated gradually under nitrogen, a temperature of 160° C. being maintained for two hours. Thereafter, the temperature was raised to 180° C. and gradually to 200° C. until there resulted a product with low acid number. The reconstituted oil had the following physical properties.

Specific gravity 25/25, 0.9715
Color (Gardner), 12–13
Viscosity (Gardner), I–J
Iodine number, 157.5
Saponification equivalent, 344.8
Hydroxyl number, 29.8
Acid number, less than 20
Brown heat time, 64 minutes

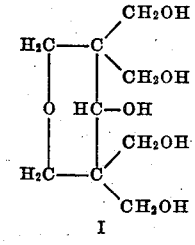
The drying times as compared with ordinary linseed oil are indicated in the following table.

Compound	Tack, hours	Set, hours	Drying, hours
Linseed oil	3	6	8.5
Linseed acid ester of the condensation product of acetone and formaldehyde	2	5	8.5

The drying tests were conducted under the conditions described in Example 1. The film which resulted from the reconstituted oil was definitely superior to the film from ordinary linseed oil from the point of view of resistance to abrasion and mild chemicals, and toughness. Of special significance is the constant known as the Brown heat time. This constant is a measure of the time necessary for gelation to occur under a given set of conditions. Whereas for the reconstituted oil sixty-four minutes were required, linseed oil required more than seven hours.

Example 3.—The soybean acid ester of the crystalline anhydroenneaheptitol resulting from the condensation of acetone and formaldehyde

A crystalline diacetone derivative was obtained from the sirupy condensation product of acetone and formaldehyde of Example 1 by allowing a mixture of equal volumes of the sirup and acetone to remain overnight. There resulted a crystalline precipitate of a diacetone derivative of the anhydroenneaheptitol which was filtered and crystallized several times from alcohol to yield a product melting at 229° C. The formation of this material was catalyzed by the residual acid in the sirupy condensation product. This diacetone derivative was dissolved in a dilute solution of hydrochloric acid in order to effect hydrolysis after which the aqueous phase and the acetone which resulted from the cleavage was evaporated to yield a theoretical amount of crystalline anhydroenneaheptitol which on crystallization from alcohol yielded a product melting at 156° C. This product was shown by various analytical techniques to possess structure I.



I

The soybean acid ester of this material was prepared by reacting 70 parts of it with 484 parts of soybean fatty acids in the presence of 10 parts of calcium stearate. The reaction mixture was stirred and heated under nitrogen at 200°–210° C. for four hours. In order to obtain a product which was entirely free of acid, the reaction mixture was dissolved in a hydrocarbon solvent and neutralized with alcoholic caustic. The resulting soaps were extracted with 70% ethanol whereupon the solution was desolvated to yield a light colored reconstituted drying oil whose desirable properties were similar to those of the oil described in Example 1.

Example 4.—The linseed acid ester of the crystalline anhydroenneaheptitol resulting from the condensation product of acetone and formaldehyde

The linseed oil fatty acid ester of the crystalline anhydroenneaheptitol was prepared exactly like the soybean ester described in the preceding example to obtain a completely esterified material. Here again, the film from the synthetic oil indicated the desirable characteristics of greater "through dry," better "spring," greater resistance to abrasion, and greater hardness.

Example 5.—The direct esterification with soybean acids of diacetone anhydroenneaheptitol

The diacetone derivative of the anhydroenneaheptitol resulting from the condensation of acetone and formaldehyde was prepared as indicated

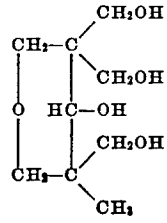
in Example 3. In the presence of an acidic catalyst this can be esterified directly since the acidic catalyst serves to effect the hydrolysis of the acetone groups. Thus a mixture of 40 parts of the diacetone derivative with 190 parts of soybean fatty acids and 2.5 parts of oxalic acid was stirred and heated at 200–210° C. under nitrogen. After one hour an additional 2.5 parts of oxalic acid was added. The reaction mixture was heated for four hours to obtain a light colored, completely esterified reconstituted drying oil.

Example 6.—The partial ester of the condensation product of acetone and formaldehyde and stearic acid

A mixture of 100 parts of the sirupy condensation product described in Example 1 as an 80% solution, together with 290 parts of stearic acid and 10 parts of calcium stearate was heated at 210° C. under nitrogen for 2.5 hours. An ethanolic solution of the product was treated with charcoal, filtered and allowed to precipitate to yield a white solid melting at 57° C. The hydroxyl content of the product (3.2%) indicated two free hydroxyl groups. The acid content of the product was negligible. The product readily emulsified oleaginous material such as vegetable oils and water when heated and shaken especially in the presence of a small amount of dilute alkali. The products of this nature are valuable as emulsifying agents in various food and pharmaceutical preparations.

Example 7.—The linseed acid ester of the reaction product of methyl ethyl ketone and formaldehyde

In an appropriate vessel was placed 288 parts of methyl ethyl ketone, 780 parts of formaldehyde as paraformaldehyde and 3000 parts of water. There was added slowly with stirring 112 parts of calcium oxide whereupon the temperature rose spontaneously to 50° C. Thereafter cooling was employed so that the temperature would not rise higher and once the initial exothermic reaction had subsided, the reaction mixture was heated and stirred at 50°–55° C. for two hours. The product was worked up as described in Example 1 for the condensation product of acetone and formaldehyde to yield an almost colorless sirup whose hydroxyl content was of the order of 30%. Because of the procedure used to remove the calcium ion the product was acidic in nature. This acidity could in large part be removed by the use of a basic ion exchange resin such as Amberlite IR–4. The sirupy product was used in the form of an aqueous solution for esterification purposes. The high hydroxyl content of the product together with certain other analytical investigations leads to the conclusion that the product is analogous to the one obtained from acetone whereupon the structure of the chief constituent may be postulated as desoxyanhydroenneaheptitol II.



I

In an appropriate vessel equipped with stirrer and water trap was placed 48.4 parts of this sirupy condensation product as an 80% solution, 200 parts of linseed fatty acids, 3 parts of calcium stearate, and 100 parts of xylene. The reaction mixture was heated for five hours at maximum temperature of 190°. A higher temperature could have been employed if desired. Heating was stopped when practically the theoretical amount of water had collected and the acid number was sufficiently low. The reconstituted oil obtained after removal of the xylene possessed the following physical properties:

Specific gravity 25/25, 0.9153
Color (Gardner), 13–14
Viscosity (Gardner), A
Hydroxyl number, 42.4
Acid number, 5.6

The reconstituted oil not only dried more rapidly than linseed oil but also yielded a film exhibiting greater "through dry," toughness, and resistance to abrasion and mild chemicals.

Example 8.—The partial lauryl ester of the sirupy condensation product of methyl ethyl ketone and formaldehyde

A solution of 40 parts of the sirupy condensation product described in the preceding example in 300 parts of pyridine and 200 parts of chloroform was treated with 95 parts of lauroyl chloride with external cooling. After 20 hours the reaction mixture was poured over ice whereupon the product was extracted with ether. The ether solution after having been washed with dilute acid and with water was dried and desolvated to yield a product which was an oil at room temperature but which solidified readily on cooling. Analytical data (2.1% OH) indicated that the product was approximately two-thirds esterified. This material served as an emulsifying agent for vegetable oils in water, especially in the presence of a small amount of dilute alkali, and is valuable for use as an emulsifying agent in various food and pharmaceutical preparations.

Example 9.—The soy bean acid ester of the condensation product of cyclopentanone and formaldehyde

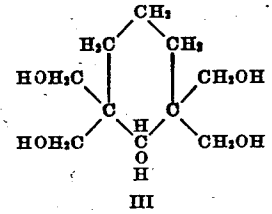
A reaction mixture consisting of 84 parts of cyclopentanone, 165 parts of paraformaldehyde, and 1200 parts of water was treated with 28 parts of calcium oxide after which the reaction mixture was heated and stirred at 60° C. for 30 minutes. The filtered solution was acidified to Congo red paper with dilute sulfuric acid solution whereupon the precipitated calcium sulfate was removed by filtration and the filtrate was desolvated to yield an oil whose hydroxyl content was 27.4%. The hydroxyl content of 2,2,5,5-tetramethylolcyclopentanone is 33.3%.

Fifty parts of this condensation product was reacted for 4 hours at 200–210° C. with stirring under nitrogen with 230 parts of soy bean acids in the presence of 6 parts of calcium stearate. There resulted a synthetic drying oil with low acid number and a hydroxyl content which indicated essentially complete esterification. The resulting film from this material was vastly superior to the film of soybean oil indicating greater toughness and greater resistance to abrasion.

Example 10.—The soybean acid ester of 2,2,6,6-tetramethylolcyclohexanol

In an appropriate vessel equipped with agitator and reflux condenser was placed 392 parts of

cyclohexanone, 660 parts of formaldehyde in the form of paraformaldehyde, 3500 parts of water, and 112 parts of calcium oxide. With stirring the temperature of the solution rose spontaneously to 55° C. whereupon the exothermic nature of the reaction was checked by external cooling. Thereafter the reaction mixture was heated and stirred at 50–55° C. for two hours. The reaction mixture after having been acidified to Congo red paper with dilute sulfuric acid was filtered and desolvated to yield a sirup which crystallized readily on trituration with alcohol. Crystallization from absolute ethanol yielded a product melting at 130–131° C. whose structure is indicated by III.



III

The soybean acid ester of 2,2,6,6-tetramethylolcyclohexanol was prepared by reacting 96 parts of the polyhydric alcohol with 500 parts of soybean fatty acids in the presence of 104 parts of xylene in a vessel equipped with agitator and a water trap. The reaction mixture was heated and stirred for four hours at a maximum temperature of 225° C. At the end of this time the xylene had removed azeotropically practically the theoretical amount of water and the reaction mixture indicated a low acid number. After removal of the xylene there resulted a product with the following properties:

Specific gravity 25/25, 0.9474
Color (Gardner), 4
Viscosity (Gardner), E–F
Iodine number, 121.2
Saponification equivalent, 339.2
Hydroxyl number, 33.5
Acid number, less than 10

The drying times of this oil as compared with soybean oil and linseed oil are indicated in the following table:

Compound	Tack, hours	Set, hours	Drying, hours
Soybean Oil	6	12	
Soybean acid ester of 2,2,6,6-tetramethylolcyclohexanol	4	7	8.5
Linseed Oil	3	6	8.5

The conditions used for this drying test were those indicated in Example 1. The film which resulted was tack-free and extremely resistant to abrasion, being superior not only to the film from soybean oil but also to the film from linseed oil.

Example 11.—The linseed acid ester of 2,2,6,6-tetramethylolcyclohexanol

The linseed acid ester of 2,2,6,6-tetramethylolcyclohexanol was prepared similarly to the soybean ester described in the preceding example using 85 parts of the alcohol, 454 parts of linseed fatty acid ester, 6 parts of calcium stearate, and 90 parts of xylene. Heating and stirring under nitrogen was effected for four hours at a temperature which was gradually raised from 165° C. to 230° C. The light colored product had the following physical properties:

Specific gravity 25/25, 0.9545
Color (Gardner), 5
Viscosity (Gardner), D–E
Iodine number, 154.2
Saponification equivalent, 334.4
Hydroxyl number, 16.3
Acid number, 5
Brown heat time, 157 minutes

The Brown heat time of ordinary linseed oil was greater than seven hours. The drying times of this reconstituted oil compared with linseed oil under the conditions outlined in Example 1 are indicated in the following table.

Compound	Tack, hours	Set, hours	Drying, hours
Linseed Oil	3	6	8.5
Linseed acid ester of 2,2,6,6-tetramethylolcyclohexanol	2	5	8.5

Here again the film was more tack-free and indicated better "through dry" and better resistance to abrasion than did the corresponding film from linseed oil.

Example 12.—The stearic acid ester of 2,2,6,6-tetramethylolcyclohexanol

A mixture of 50 parts of the polyhydric alcohol and 324 parts of stearic acid was heated at 210° C. with stirring. As soon as water was evolved the temperature was raised to 215° C. whereupon a homogeneous reaction mixture resulted. Thereafter the mixture was heated and stirred at this temperature for one hour, vacuum having been applied at the end of the reaction. The product was allowed to precipitate from 95% alcohol to yield a hard, white wax which melted at 59° C. The saponification equivalent of 311 (calculated 310.5) and the low hydroxyl number of 6 indicated that the product was the pentastearate of 2,2,6,6-tetramethylolcyclohexanol. This material passessed very desirable wax-like properties particularly because of its extreme hardness and pleasing light color.

Example 13.—Varnish prepared from soybean acid ester of the condensation product of acetone and formaldehyde

A mixture of 200 parts of the reconstituted oil described in Example 1 and 73 parts of a resin mixture consisting of approximately 12% phenolic type resin and 88% ester gum available commercially as Cook's HG–42 resin was heated at 280° C. for 795 minutes at the end of which time it was possible to obtain a 24-inch string. The reaction mixture was then diluted with 400 parts of mineral spirits.

The resulting varnish was treated with siccatives consisting of .02% cobalt and .02% manganese as the soluble naphthenates. The hardness of the resulting film was tested by the Rocker hardness procedure. The hardness of this film compared to the hardness of films of varnishes prepared from soybean oil, linseed oil, and tung oil is indicated in the following table.

Varnish From—	Hardness
Soybean oil	31.0
Linseed oil	41.3
Tung oil	56.4
Soybean acid ester of the condensation product of acetone and formaldehyde	60.1

Thus, it is seen that there resulted a varnish

whose film compared favorably in hardness with the film from tung oil. The film also exhibited a marked resistance to hot and cold water and mild chemicals such as 1% sodium hydroxide solution.

Example 14.—Varnish from the linseed acid ester of the condensation product of acetone and formaldehyde

The varnish was prepared according to the same formula indicated in the preceding example using the reconstituted oil described in Example 2. It was necessary to cook the varnish only 375 minutes in order to obtain a 24-inch string. A similar varnish using dehydrated castor oil required 525 minutes whereas a varnish of the same nature with linseed oil required 585 minutes. The resulting varnish yielded a film which was harder than the film from tung oil when tested by the Rocker procedure and which indicated greater resistance to the action of hot and cold water and 1% sodium hydroxide solution than did varnish from materials such as linseed oil.

Example 15.—Varnish prepared from the linseed acid ester of 2,2,6,6-tetramethylolcyclohexanol

In this case the oil prepared in Example 11 was subjected to the same varnish formulation indicated in Example 13. In this case 495 minutes were required in order to obtain a 24-inch string. This, as reference to the preceding example will indicate, was faster than the time required for dehydrated castor oil or linseed oil. The resulting film from this varnish indicated a hardness on the Rocker scale of 80.5 as compared to 56.4 for tung oil. The film likewise was quite resistant to hot and cold water and 1% sodium hydroxide solution.

In addition to the resins indicated in these examples, other resins may be used in preparing varnishes with the new synthetic drying oils described herein, as for example, ester gums, alkyds, polyindene, coumarone, phenolic type resins, or any of the resins customarily employed in making varnishes. It is particularly desirable to employ in varnishes, ester gums prepared according to my co-pending application Serial No. 599,949, filed of even date herewith, entitled Rosin acid esters, now Patent No. 2,470,964, issued May 24, 1949, and/or alkyds prepared according to my co-pending and now abandoned application Serial No. 599,950, filed of even date herewith entitled Alkyd resins.

In some cases in the preparation of varnish and similar coating materials it is advisable to heat a reaction mixture consisting of a glyceride such as soybean oil, linseed oil, dehydrated castor oil, etc. with rosin acid and one of the polyhydric alcohols described in the co-pending application entitled Condensation of ketones with formaldehyde. Instead of ordinary gum or wood rosin or abietic acid such materials as polymerized rosin, disproportionated rosin, hydrogenated rosin, or the rosin portions of tall oil may be used. In such a reaction mixture, although the reaction is by nature complex, the glyceride is alcoholyzed yielding a partial fatty acid ester of glycerol and of the above-mentioned polyhydric alcohol. The rosin acid serves to complete the esterification of these partial esters, yielding a very desirable coating composition. If desired, a catalyst may be added to aid in the alcoholysis. This may consist of the abietate, naphthenate, stearate, or other fat soluble salt of calcium, cadmium, cerium, strontium, zinc, and the like. The temperatures employed vary from 200–300° C. and the time of reaction may vary from 4 to 16 hours depending on the glyceride employed and the temperature used.

While numerous examples of the invention have been given it will be apparent that other modifications are possible. It is to be understood, therefore, that the invention is limited only by the appended claims.

I claim as my invention:

1. An ester comprising a polyhydroxy condensation product having at least four hydroxyl groups, said polyhydroxy condensation product resulting from the condensation of formaldehyde and a ketone having at least four replaceable hydrogen atoms adjacent the carbonyl group, in which the molal ratio of formaldehyde to ketone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the ketone, said condensation product being substantially completely esterified with a higher fatty acid.

2. An ester comprising a polyhydroxy condensation product having at least four hydroxyl groups, said polyhydroxy condensation product resulting from the condensation of formaldehyde and an aliphatic ketone having at least four replaceable hydrogen atoms adjacent the carbonyl group, in which the molal ratio of formaldehyde to ketone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the ketone, said condensation product being substantially completely esterified with a higher fatty acid.

3. An ester comprising a polyhydroxy condensation product having at least four hydroxyl groups, said polyhydroxy condensation product resulting from the condensation of formaldehyde and an alicyclic ketone having at least four replaceable hydrogen atoms adjacent the carbonyl group, in which the molal ratio of formaldehyde to ketone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the ketone, said condensation product being substantially completely esterified with a higher fatty acid.

4. An ester comprising a polyhydroxy condensation product having at least four hydroxyl groups, said polyhydroxy condensation product resulting from the condensation of formaldehyde and a ketone having at least four replaceable hydrogen atoms adjacent the carbonyl group, in which the molal ratio of formaldehyde to ketone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the ketone, said condensation product being substantially completely esterified with the mixed fatty acids of a fatty oil.

5. An ester comprising a polyhydroxy condensation product having at least four hydroxyl groups, said polyhydroxy condensation product resulting from the condensation of formaldehyde and a ketone having at least four replaceable hydrogen atoms adjacent the carbonyl group, in which the molal ratio of formaldehyde to ketone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the ketone, said condensation product being substantially completely esterified with the mixed fatty acids of a drying oil.

6. An ester comprising a polyhydroxy condensation product having at least four hydroxyl groups, said polyhydroxy condensation product resulting from the condensation of formalde-

hyde and a ketone having at least four replaceable hydrogen atoms adjacent the carbonyl group, in which the molal ratio of formaldehyde to ketone is not substantially less than one mole of mormaldehyde per mole of active hydrogen in the ketone, said condensation product being substantially completely esterified with predominantly unsaturated higher fatty acids.

7. An ester comprising a polyhydroxy condensation product resulting from the condensation of formaldehyde and cyclohexanone, in which the molal ratio of formaldehyde to cyclohexanone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the cyclohexanone, said condensation product being substantially completely esterified with a higher fatty acid.

8. An ester comprising a polyhydroxy condensation product resulting from the condensation of formaldehyde and acetone, in which the molal ratio of formaldehyde to acetone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the acetone, said condensation product being substantially completely esterified with a higher fatty acid.

9. An ester comprising a polyhydroxy condensation product resulting from the condensation of formaldehyde and methyl ethyl ketone, in which the molal ratio of formaldehyde to methyl ethyl ketone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the methyl ethyl ketone, said condensation product being substantially completely esterified with a higher fatty acid.

10. An ester comprising a polyhydroxy condensation product resulting from the condensation of formaldehyde and cyclohexanone, in which the molal ratio of formaldehyde to cyclohexanone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the cyclohexanone, said condensation product being substantially completely esterified with an unsaturated higher fatty acid.

11. An ester comprising a polyhydroxy condensation product resulting from the condensation of formaldehyde and acetone, in which the molal ratio of formaldehyde to acetone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the acetone, said condensation product being substantially completely esterified with an unsaturated higher fatty acid.

12. An ester comprising a polyhydroxy condensation product resulting from the condensation of formaldehyde and methyl ethyl ketone, in which the molal ratio of formaldehyde to methyl ethyl ketone is not substantially less than one mole of formaldehyde per mole of active hydrogen in the methyl ethyl ketone, said condensation product being substantially completely esterified with an unsaturated higher fatty acid.

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