Patented Dec. 19, 1944 2,365,300

UNITED STATES PATENT OFFICE

2,365,300

MIXED ESTERS

Ernest Segessemann, Newark, N. J., assignor to National Oil Products Company, Harrison, N. J., a corporation of New Jersey

No Drawing. Application July 6, 1940, Serial No. 344,235

4 Claims. (Cl. 260—97.5)

The invention relates in general to the production of valuable products from tall oil and more particularly to the manufacture of so-called mixed esters of polyhydric alcohols of the aliphatic series.

"Tall oil" or "talloel," which literally means "pine oil" is the resinous and fatty by-product obtained in the production of paper pulp from resin-bearing wood by the so-called "sulphate process." In this process wood is digested with an alkaline liquor containing sodium sulphate during which operation tall oil in the form of its sodium soap accumulates on the surface of the waste liquor. Tall oil, which essentially comprises a mixture of fatty and resinic acids, is obtainable on the market in large quantities at exceedingly low prices. While some uses for tall oil have been found, the supply thereof greatly exceeds its present demand.

The general object of the present invention is to produce new and valuable products from tall oil.

Another object of the invention is to produce low cost oils and fats which may be used as substitutes for many of the higher priced natural oils and fats now used in various industries.

A specific object of the invention is to manufacture low cost drying oils for the paint, lacquer, varnish and other industries.

A further object of the invention is to produce a low cost substitute for tallow and like fats.

An additional object of the invention is to produce an improved low cost substitute for sulphonated tallow and like fats.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The foregoing and other objects are accomplished according to the present invention by the production of so-called mixed esters of aliphatic polyhydric alcohols wherein at least one of the hydroxy groups is esterified with a tall oil acid. The remaining hydroxy groups of the polyhydric alcohol are esterified by a saturated or unsaturated higher fatty acid depending upon the type of product desired.

The present invention is particularly directed to the production of low cost drying oils or substitutes therefor. In the preparation of such products at least one of the hydroxy groups of the polyhydric alcohol is esterified with a tall oil acid and the remaining hydroxy groups are esterified with an unsaturated fatty acid, particularly those derived from drying oils. The degree of unsaturation in the mixed ester of the invention may be varied to suit the conditions at hand by selecting the fatty acids of the desired degree of unsaturation.

Products resembling tallow and like fats may also be produced according to the invention by employing in the esterification process fatty acids of a higher degree of saturation than those used in the preparation of drying oils or substitutes therefor. These tallow substitutes are preferably produced so as to contain at least one double bond to permit sulfonation or phosphation of the same by the usual procedures.

The foregoing mixed esters of the invention may be produced according to various specific procedures, all of which fall within the general generic process of the invention. While any suitable aliphatic polyhydric alcohol may be used in the preparation of the esters of the invention, the use of glycerol is highly preferred. In the first esterification step glycerol may be reacted with either tall oil acids or the higher fatty acids to produce a partial ester of glycerol which is subsequently completely esterified with acids of the type not used in the first step. Likewise, all three components may be simultaneously reacted in the properly calculated quantities to produce a glycerol ester wherein at least one hydroxy group is esterified with a tall oil acid and at least one esterified with a fatty acid. The esters of the invention may also be produced by reacting a triglyceride with glycerol to produce a partial ester and then reacting said ester with tall oil acids to produce the mixed ester. Likewise, the tall oil acids and the triglycerides may be reacted together, whereby some of the tall oil acids replace some of the fatty acids in the triglyceride molecule, thus producing a mass composed of mixed esters, free fatty acids and tall oil acids. This mass may then be reacted with glycerol to yield a substantially uniform composition comprising essentially the mixed esters of the invention.

In carrying out the foregoing esterification steps, heat is generally used. It is also preferred to use an esterification catalyst such as a powdered metal or oxide thereof, an alkaline carbonate or the like.

The invention accordingly comprises the several steps and relation of one or more of such steps with respect to each of the others, and the products possessing the features, properties and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

According to the broader aspects of the invention, mixed esters of polyhydric alcohols are produced in which the acyl groups constitute the

residues of tall oil acids and higher fatty acids. The degree of unsaturation in the mixed ester of the invention may be varied according to the type of product desired. In the manufacture of drying oils or substitutes therefor the degree of unsaturation is preferably high, whereas in the production of tallow or other fat substitutes, the degree of unsaturation should be relatively lower.

In the preparation of the mixed esters of the invention, any suitable aliphatic polyhydric alcohol may be used including, inter alia, glycerol, glycol, glycol derivatives such as ethylene glycol, diethylene glycol, propylene glycol, etc., sorbitol, mannitol and the like. While any of the foregoing and other aliphatic polyhydric alcohols may be employed to meet the ends of the invention, it is highly preferred to use glycerol. This polyhydric alcohol is more abundant than the others, and most important of all, it yields mixed esters of greater value in that these esters possess far superior properties, particularly as far as oils and fats are concerned.

The expression "tall oil acids" is employed herein to connote ordinary crude or refined tall oil which essentially comprises a mixture of higher fatty acids and resin acids. It is to be understood that the foregoing expression is also to include the higher fatty acids recovered from tall oil. In the production of the mixed esters of the invention, it is highly preferred to use tall oil which has been refined according to known processes, as by distillation of crude tall oil under reduced pressure with or without the aid of steam distillation.

In the manufacture of highly unsaturated mixed esters of the invention suitable for use as drying or semi-drying oils, the higher fatty acids employed must be highly unsaturated. It is preferred to employ the mixed fatty acids obtained by hydrolysis of natural drying oils and of semi-drying oils, such as the fatty acids produced by saponification or catalytic splitting of linseed, tung, perilla, soya-bean, menhaden, cod or like oils. Likewise, the unsaturated fatty acids of the drying oils may be used in their more purified form whenever they are commercially available, including, among others, linoleic, telfairic, elaeomargaric, linolenic, jecoric, isanic, clupanadonic, arachidonic, tariric and like acids. The expression "drying oil fatty acids" is used herein to connote the foregoing and like acids as well as those directly produced from drying or semi-drying oils as aforementioned. According to the invention, the drying or semi-drying oil substitutes are produced by mixing with tall oil acids a suitable quantity of the drying oil fatty acids and an amount of the polyhydric alcohol (preferably glycerol) equivalent to or slightly in excess of that required for complete esterification of the acids, the mixture then being heated, preferably with agitation, at temperatures ranging generally from about 180° C. to just below the boiling point of the polyhydric alcohol, for about 3 to 8 hours or until esterification is substantially completed. Likewise, the polyhydric alcohol may be first partially esterified by heating at about 180° C. to 200° C. with either the tall oil acids or the drying oil fatty acids until the greater part of the acids has reacted, after which the other component acids are added with a slight increase in temperature, and the reaction carried on until esterification of all the component acids is substantially completed.

The esterification steps may be carried out at atmospheric or under reduced pressure, the temperature to be varied accordingly. Moreover, the esterification steps may be carried out in an inert atmosphere as by passing a stream of a non-oxidizing gas, such as carbon dioxide, nitrogen, or the like, through the reacting mass to prevent discoloration of the product, as well as to aid in the removal of the moisture in the mass. While the reaction will proceed without the use of catalysts, it is preferred to accelerate the esterification by the use of suitable catalyzing agents, such as zinc oxide, zinc carbonate, magnesium oxide, calcium oxide, finely powdered zinc, tin or the like.

In the preparation of the more saturated esters suitable as substitutes for tallow and like fats, the foregoing procedure is applicable, except that more highly saturated fatty acids will be used in lieu of the drying oil fatty acids. Such acids would include, inter alia, stearic, palmitic, oleic and like acids, preferably those having no points of unsaturation and in no case having more than one double bond. These more saturated mixed esters may be sulfonated according to well known methods to produce agents for use in the paper, textile, leather and other industries where sulfonated fats are employed.

The mixed esters of the invention may also be produced by heating in a closed vessel provided with a vent for escaping water vapors and an agitator, a mixture of glycerol and a triglyceride containing oil of the drying type or of the saturated variety depending upon the degree of saturation required in the end product. The proportions of the glycerol and triglyceride should be such that mono and/or diglycerides are produced. This reaction is preferably carried out within a temperature range of about 150° C. to 250° C., depending upon the nature of the fatty materials used and the type of partial glyceride desired. The presence of a catalyst during the reaction is desirable, examples of which include powdered tin, zinc or aluminum, sodium or potassium alcoholates, sodium or potassium carbonates or the like. The partial glycerides thus obtained are then completely esterified by heating with an equivalent quantity of tall oil acids at a temperature ranging generally from about 180° C. to 290° C. in the presence or not of a suitable catalyst. An inert gas may be passed through the mass during each of the reactions with advantageous results. The foregoing procedure may be slightly modified by heating the triglyceride with the tall oil acids at about 200° C. to 300° C., thus effecting a re-esterification of the triglyceride and liberating a portion of the fatty acids originally combined with the triglyceride. The liberated fatty acids and remaining tall oil acids are then esterified with glycerol.

Any suitable triglyceride may be employed depending upon the type of mixed ester desired. In the production of drying or semi-drying oils, the triglyceride or oil containing the same may be selected from the drying oil class which includes linseed oil, tung oil, perilla oil, soyabean oil, menhaden oil, cod oil, etc. When a fat or a non-drying oil substituted or the like is desired, then a more saturated oil should be used, such as cottonseed, olive, castor and like oils, or hydrogenated fish oils, or other animal or vegetable oil, as well as polymerized oils.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following examples which are given merely to further illustrate the invention and are not to

be construed in a limiting sense, all parts given being by weight.

Example I

100 parts of distilled tall oil (having a resinic acid content of 32%) were heated with 26 parts of glycerol of 88% strength and 0.5 gm. of zinc oxide at 180–190° C. with rapid stirring. After five hours of heating the acid number of the mixture dropped to below 10.0, the tall oil having been converted substantially into mono and diglycerides. At this stage 100 gms. of linseed oil fatty acids, which had been preheated to 190° C. were added and the heating continued in such a manner that the temperature rose gradually and reached 250° at the end of the third hour. The water evolved during the reaction was allowed to escape, the fatty acids and glycerol being returned to the reaction chamber by suitable reflux condensation. During the process of reaction a stream of carbon dioxide was allowed to pass through the reaction mass introduced by means of an inlet tube reaching to the bottom of the vessel. The product thus obtained was a light amber-colored oil having an acid number below 5.0, generally around 3.0.

When applied to a surface, the product will dry to a flexible non-tacky film and it will dry in a shorter time than the films produced by straight tall oil-glycerol esters.

Example II

65 parts of cod oil fatty acids were mixed with 22 parts of anhydrous glycerol and 0.2 part of finely powdered tin. The mixture was then heated in an atmosphere of nitrogen at a temperature of 180° to 200° C. for four hours. 135 parts of distilled tall oil (having a resinic acid content of 38.5%) were then added slowly and at such a rate that the cooling effect of the addition did not reduce the temperature in the reaction chamber at any time to below 180° C. Heating was then continued for six additional hours, or until the acid number of the mixed ester had dropped to below 5.0.

Example III

25 parts of glycerol of 88% strength, 70 parts of distilled tall oil and 130 parts of commercial clupanadonic acid (as obtained from Armour & Co., Chicago) were mixed and then heated with rapid agitation in an atmosphere of hydrogen at such rate that after the first hour a temperature of 120° C. was reached, and that at the end of the seventh hour the temperature had risen to 260° C. The product thus obtained was a clear oil having an acid number of less than 5.0 and exhibiting excellent film-forming properties.

Example IV

100 parts of distilled tall oil, 100 parts of perilla oil fatty acids, 38 parts of diethyleneglycol and 0.5 part of zinc oxide were heated with rapid agitation in an atmosphere of carbon dioxide for six hours, the temperature being regulated at such a rate that after the first hour 200° C. was reached and that at the end of the sixth hour it had risen to 240° C. The product thus obtained was a clear, brown-colored oil having an acid number of around 10.0 and possessing good film-forming properties.

Example V

100 parts of hydrogenated sardine oil (having an iodine value of 6.0 and a titre of 52.0° C.), 6 parts of anhydrous glycerol and 1 part of potassium carbonate were heated in a closed vessel provided with rapid agitation for two hours, the temperature being allowed to rise gradually and at a rate that after the second hour 210° C. was reached. The product of reaction which consisted substantially of the diglyceride of hydrogenated sardine oil was cooled to 190° C. and 38 parts of tall oil having an acid value of 185 were added. This mixture was then heated at such a rate that the temperature rose gradually and after five hours it had reached 245° C. The product thus obtained, consisting mainly of hydrogenated sardine oil in which one of the fatty acid chains had been replaced with a tall oil acid chain, was a cream-colored fat of paste-like consistency having an acid value below 5.0. It resembled beef tallow in many respects and could be used as a substitute for the latter in the various industries.

The following is an example for sulfonating this product: To 150 parts of the product obtained as described above, 27 parts of sulfuric acid of 98% strength were added slowly, and at such a rate that the temperature did not exceed 50° C. The mass was agitated for a total period of two hours while the temperature was maintained at 50° C. It was then poured into a wash solution consisting of 300 parts of water, 15 parts of common salt and 70 parts of caustic soda of 23.5% strength. After thorough agitation the mixture was allowed to stand at 50° C. for 15 to 20 hours. The water which had separated to the bottom of the vessel was then drawn off and the sulfonated product neutralized with caustic soda. The product thus obtained was a light, cream-colored paste of the general appearance of sulfonated tallow. It was readily emulsifiable in hot water and would find application in the industries wherever sulfonated tallow is used, as for instance in the textile, tanning, paper and other industries.

Example VI

200 parts of linseed oil were heated with 28.5 parts of glycerol of 88% strength and 0.75 part of potassium carbonate for 3 hours at temperatures ranging from 200° C. to 240° C. The operation was carried out in a closed vessel provided with a rapid stirring device and with a vent to allow the escape of gases. A current of carbon dioxide was passed through the reacting masses by means of an inlet tube reaching to the bottom of the reaction chamber. After three hours the temperature was lowered to 170° C., and 200 parts of distilled tall oil were added, and the mixture heated for 6.5 hours with agitation and under a carbon dioxide atmosphere at such a rate that the temperature rose gradually from 170° C. to 280° C. The product thus obtained was a light, brown-colored oil having an acid value of less than 5.0. It had excellent film-forming properties, making it of value in the paint and varnish industries and other industries wherever drying oils are employed.

Example VII

100 parts of hydrogenated sardine oil (having an iodine value of 6.0 and a titre of 52.0° C.) were mixed with 100 parts of distilled tall oil and 2 parts of powdered tin. The mixture was then heated for 4 hours at 250° C. to 260° C. and then cooled to 195° C., whereupon 12 parts of anhydrous glycerol were added. Heating was then continued for 5 hours during which time the temperature was allowed to rise gradually until it reached 255° C. at the end of the fifth

hour. The product thus obtained was a cream-colored paste having an acid value of 6 to 8.

Example VIII

200 parts of cod oil were heated with 70 parts of tall oil in a carbon dioxide atmosphere at 200° C. to 260° C. for 5 hours. The mass was then cooled to 160° C. and 9 parts of glycerol of 88% strength were added. Heating was then continued, allowing the temperature to rise until it had reached 250° C. after the fourth hour. The product was a brown-colored, clear oil useful as a substitute for drying oils.

The expression "residue" of fatty or tall oil acids is used herein to connote that portion of the original acid that forms the acyl group in the final product. While the products of the invention have been found to be good fat and drying oil substitutes, it is evident that they may find a wide variety of uses in many industries. Partial mixed esters may also be produced in accordance with the invention, such, for example, as the diglycerides wherein the acyl groups constitute a tall oil acid residue and a fatty acid residue, one of the hydroxy groups remaining free.

Since certain changes in carrying out the above process and certain modifications in the products which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described and all statements of the scope of the invention, which, as a matter of language might be said to fall therebetween; and that they are intended to be inclusive in scope and not exclusive, in that if desired, other materials may be added to my novel composition of matter herein claimed without departing from the spirit of the invention. Particularly it is to be understood that in said claims, ingredients or components recited in the singular are intended to include compatible mixtures of said ingredients wherever the sense permits.

Having described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. A mixed glycerol ester in which at least one of the acyl groups constitutes a residue of the acids in tall oil and at least one of the acyl groups constitutes a residue of the fatty acids in an oil selected from the group consisting of animal, vegetable and fish oils.

2. As a new composition of matter, a drying oil substitute comprising mixed glycerol esters in which at least one of the acyl groups in each ester molecule constitutes a residue of the acids in tall oil and at least one of the acyl groups constitutes a residue of a highly unsaturated fatty acid derived from an oil selected from the group consisting of animal, vegetable and fish oils.

3. As a new composition of matter, a fat substitute comprising mixed glycerol esters in which at least one of the acyl groups in each ester molecule constitutes a residue of the acids in tall oil and at least one of the acyl groups constitutes a residue of a fatty acid containing no more than one double bond and derived from an oil selected from the group consisting of animal, vegetable and fish oils.

4. A new composition of matter, comprising a neutralized sulfated mixed glycerol ester in which at least one of the acyl groups constitutes a residue of the acids in tall oil and at least one of acyl groups constitutes a residue of the fatty acids in an oil selected from the group consisting of animal, vegetable and fish oils.

ERNEST SEGESSEMANN.