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FATTY ACID CONDENSATION PRODUCTS AND PROCESS OF PREPARATION

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This invention relates to novel condensation products, more particularly to condensation products obtained by the treatment of fatty acids which are useful in industrial compositions. When the starting materials are unsaturated the resulting products are particularly useful as drying compositions in paints, varnishes, core oils, linoleum and similar products for partly or wholly replacing drying oils. When the starting materials are saturated the resulting products are useful, for example, as quenching oils or plasticizers.

It has now been found that novel fatty condensation products are obtained by heating non-hydroxylated fatty acids or mixtures containing a substantial amount of non-hydroxylated fatty acids, in the presence of a small amount of a catalyst, to a temperature between 220° and 330° C., with removal of the water formed in the reaction until the product contains a substantial amount of unsaponifiable matter having a mean molecular weight in accordance with that calculated for a condensation product of at least three molecules of fatty acid. Temperatures of between 250° and 300° C. are preferred.

Heating should be carried out under vacuum.

If the reaction is effected under high vacuum the reaction temperature may not at once attain the range 220°–330° C. since the mixture in the first stage of the reaction may boil at a lower temperature than 220° C., fatty acids passing into the vapour phase together with volatile reaction products. As the reaction proceeds the concentration of fatty acids in the mixture is reduced and the boiling point of the mixture increases, so that the temperature can gradually be raised.

In view of the evaporation of the fatty acids which takes place during the reaction, heating is preferably carried out while refluxing the fatty acids and higher boiling compounds. In this way a greater part of the starting material may be converted into the final condensation product.

The starting material may contain other constituents such as, for example, mono-, di- or tri-glycerides, or resin acids. In this case the mixture should contain a substantial or, preferably, a major amount of fatty acids. Such other constituents have a tendency to slow down the desired reaction and too great a proportion should be avoided. Even when they possess sufficient drying properties by themselves or develop them on heating, the amount of additional constituents should not exceed the amount of fatty acids by weight.

Fatty acids for use according to the invention should preferably have the formula

$$R.CO.OH$$

where R is a hydrocarbon group, preferably a long saturated hydrocarbon chain, which is preferably unsubstituted. The fatty acids must not contain hydroxyl groups in the hydrocarbon chain. It is preferred that R is an unsaturated alkyl group, preferably of a chain length of from 9 to 25 carbon atoms, most preferably of a chain length of from 17 to 21 carbon atoms.

Fatty acids which contain only one double bond, such as oleic acid, may be used but to obtain a drying product with good properties it is preferred to have present in the starting material at least a proportion of fatty acids which contain two or more double bonds in the molecule. Examples of such unsaturated acids are linoleic acid, linolenic acid or the highly unsaturated acids occurring in marine oils, such as herring oil.

The temperature and time of heating employed and the proportion of unsaponifiable matter that can be obtained depend to some degree on the type of fatty acids which are used as a starting material. Thus, with fatty acids which have a relatively low iodine value heating can be carried out at high temperatures for a long time, and high proportions of unsaponifiable matter, e.g. 70% to nearly 100%, can be obtained. With fatty acids of high iodine value, for example over 150, however, heating may have to be discontinued earlier, since gelation may take place and the proportion of unsaponifiable matter may then be lower, e.g. 40–60%. For the same reason in some cases it is preferred to mix fatty acids of different types before they are reacted to enable highly unsaturated acids to be more completely condensed in one operation.

With mixtures of fatty acids containing individual acids of different types, it may be advisable to fractionate the original mixture, e.g. by distillation, or to distill off the most volatile and less unsaturated acids during the condensation reaction (the reflux column being maintained at an appropriate high temperature for the purpose) so as to obtain a better drying product.

The fatty acids used as starting materials may in some cases with advantage be purified according to the usual methods.

The catalyst used in the processes of the invention may be an oxygen-containing boron compound. Preferred inorganic boron compounds are boric acid and boric oxide. Boron salts, such as, for example, the alkali pentaborates, preferably ammonium pentaborate, may also be used with advantage. Borax, however, has only a slight activity as a catalyst. Boron compounds with oxidizing properties are not preferred.

Preferred organic boron compounds are the esters of boric acid, such as boric acid trimethyl ester, boric acid triethyl ester, boric acid mannitol ester, the mixed anhydride of boric acid and acetic acid or the mixed anhydride of boric acid and higher fatty acids as obtained, for example, from a fatty oil such as groundnut oil.

The amount of catalyst may vary widely, for example, between 0.1 and 10% by weight of the starting material. An amount of catalyst of from 2–6%, by weight is in general preferred.

The process is preferably carried out in a stainless steel reaction vessel provided with a reflux column. The latter may be either heated or cooled, so as to reflux the fatty acids and other higher boiling products and to distil off reaction water and other volatile products and gases. The water and other volatile products may be condensed in a cooled trap together with any entrained higher boiling products.

The mixture in the vessel is heated to temperatures between 220° and 330° C. It is desirable to keep the reaction mixture at temperatures between 250° and 300° C. for at least the latter part of the reaction.

The catalyst may be mixed with the starting material or added during the heating in the reaction vessel, or it can be placed in the column.

The reflux column may be packed, for example, with helices, Raschig rings or the like. The reflux column may also be regulated in such a way that part of the fatty acids is alowed to distill off.

After heating, any unchanged fatty acid in the reaction

mixture may be extracted with a suitable solvent, for example alcohol. Alternatively, the reaction mixture may be distilled under vacuum to remove unchanged fatty acid. The residue after solvent treatment or distillation is the desired product. Preferably the reaction mixture is filtered, washed with hot water to remove the catalyst and dried under vacuum before or after solvent treatment or distillation.

The distillate or the alcohol extract obtained according to the processes of the invention may be re-used for a further reaction since it consists substantially of unchanged starting material. If the reaction is allowed to proceed to a stage where only a small proportion of unchanged starting material is contained in the reaction mixture there may be no need to remove these starting materials.

The residue obtained under the reaction conditions described forms the main product. When the starting material contains unsaturated fatty acids the product shows better drying properties than the corresponding triglycerides, decreased volatility and increased viscosity when compared with the fatty acids forming the starting material. The changes in these properties become more evident with increased time or temperature of heating. The analytical figures show the formation of a substantial proportion of unsaponifiable matter which is different from known fatty ketones. It has been found that this unsaponifiable matter is mainly responsible for the good drying properties and, when isolated, shows outstanding film forming properties.

The invention also includes the novel condensation products obtained by these processes as such or mixed with unchanged fatty acids.

The condensation products of the invention are characterised by a substantial amount, preferably at least 40%, of unsaponifiable matter, a low acid and saponification value, an increased iodine value according to Wijs as compared to the starting material, and a high mean molecular weight. The mean molecular weight of the unsaponifiable portion is roughly in accordance with, or higher than, the calculated molecular weight of a theoretical condensation product of three molecules of fatty acid. The condensation products have drying properties when the iodine value (determined according to Wijs' method) is 100 or higher. The condensation products have a molecular structure which contains at least three alkyl chains. Preferred products are those in which the alkyl chains are those of unsaturated acids derived from fatty oils.

The invention also includes the use of the above mentioned products having an iodine value (determined by Wijs' method) of 100 or higher, to replace drying materials, such as drying oils, oleo resinous varnishes or alkyd resins in the paint, varnish, linoleum and allied industries.

The new products may be mixed with the usual siccatives based on cobalt, lead or manganese and may be diluted with turpentine, mineral spirits and/or other volatile solvents to the desired viscosity.

As an example of the use of the condensation products according to the invention, a product obtained from soya bean oil fatty acids according to the process described above, in a yield of 75.4%, had an acid value of 8.6, a saponification value of 44.2, an iodine value of 175.3 (determined according to Wijs' method) and contained 82.5% unsaponifiable matter. It behaved as follows when tested as a paint vehicle or clear varnish. The viscosity was 37 poises/20° C. as in the case of a thin stand oil. A product to replace linseed oil was obtained by mixing 57 grams of the new condensation product with 33 grams of a 1:1 mixture of turpentine and mineral spirits. To replace on oleo resinous varnish a mixture of 90 grams of the condensation product with 10 grams of the 1:1 mixture of turpentine and mineral spirits was prepared. Small proportions of siccatives were sufficient to obtain shorter drying times than those of a good quality boiled linseed oil. With 0.1% cobalt calculated on the condensation products, for example, 240 minutes were required for a film to be dry to the touch and 300 minutes for it to dry hard. The increase in weight upon drying in air for the undiluted condensation product was higher than that for linseed stand oil of the same viscosity, showing high affinity for oxygen, though the product was obtained from soya bean oil fatty acids having an iodine value much below that of linseed oil. The hardness of the film was tested according to Sward's method and was found to be substantially higher than that of boiled linseed oil and as high as that of a maleic resin varnish of 30 gallon oil length. The film was more resistant to water and dilute sulphuric acid than films of linseed oil and many oleo resinous varnishes.

Zinc white enamels prepared from the condensation products showed no signs of livering.

In the case of poor drying oils such as herring oil, cotton oil, groundnut oil or rapeseed oil, even if the more saturated component acids were removed and the remaining unsaturated acids reconverted into triglycerides, the resulting products would have weaker drying properties than the products of the invention made from corresponding acids. The film formed by the product obtained from linoleic acid as in Example 4 below is harder than the film from any linoleic acid glyceride and its hardness approaches that of a linolenic acid glyceride.

The invention will now be illustrated by the following examples. In the examples the temperatures quoted are those of the metal bath surrounding the reaction vessel. The temperature within the reaction mixture was lower, by about 20° and 30° C. during the initial stages and by about 10° C. during the final stages of the reaction.

Example 1

110 grams fatty acids obtained from Norwegian herring oil by the Twitchell process (acid number of the herring oil acids: 182.7; iodine value: 132.7) and 2.75 grams crystalline boric acid were introduced into a 250 ccs. flask above which a fractionating column was vertically mounted. The column was connected to a vacuum pump through an air-cooled condenser mounted parallel to the fractionating column and a reception flask was provided at the bottom of the condenser. The fractionating column was provided with a packing consisting of stainless steel helices or glass Raschig rings.

After evacuation of the apparatus to about 2–3 mm. Hg the flask was slowly heated in a metal bath until the bath temperature was 290° C. The heating was carried out for 60 minutes until the bath temperature was 210° C. Heating was further continued for a further 150 minutes to raise the bath temperature from 210° to 290° C. The bath was maintained at 290° C. for 3 hours. The fractionating column was heated to about 175° C. by electrical resistance heating. At bath temperatures of from about 210° C. upwards some material commenced to distill off into the receiving flask. Condensation of material passing into the fractionating column commenced at a lower bath temperature. After the heating had been continued for 3 hours at 290° C. the reaction mixture was allowed to cool. 31.3 grams of fatty acids and some water and low boiling decomposition products were distilled off while 64.4 grams remained in the reaction vessel. The solid boric acid contained therein was filtered while the residue was still warm. Some material adhered to the packing of the reflux column and was recovered by extraction with petroleum spirit. The viscous residue which had an acid number of 10 and contained 81.3% unsaponifiable matter was thinned with petroleum spirit. 0.3% Pb and 0.066% Mn were added in the form of naphthenate driers to act as siccatives. When exposed to the air in a thin layer the varnish so prepared dried to a non-tacky film in less than one day. In a similar test but with only 0.3% by weight of boric acid a larger fraction was distilled off so that only about 38% of

residue remained in the reaction vessel. This residue had an acid number of 16.5 and dried after siccativation in 6 hours to a non-tacky and hard film.

The fatty acids of pilchard oil, sardine oil and whale oil when treated according to the procedure of this example gave varying quantities (50 to 80%) of residue in the form of oily liquids with good drying properties.

Example 2

110 grams herring oil fatty acids (acid number: 182, iodine value: 142.7) and 6.6 grams of ammonium pentaborate were heated in the apparatus of Example 1 for 60 minutes to a bath temperature of 210° C., then in 150 minutes to a bath temperature of 290° C. and finally for 60 minutes at a bath temperature of 290° C. After cooling 55.5 grams of residue which had the consistency of a highly viscous stand-oil was present in the reaction vessel.

The residue after dilution with petroleum spirit was filtered to remove the solid catalyst and washed with hot water to remove dissolved boric acid compounds. When the resultant product was treated as described in Example 1 a composition with good drying properties was obtained. A thin film of this composition under normal conditions of temperature and light was dry to the touch in 3½ hours and almost non-tacky after 24 hours.

Example 3

Commercial distilled linseed fatty acids (iodine number: 165) were slowly heated in the apparatus of Example 1 together with 6% by weight of boric acid until the bath temperature was up to 290° C. The heating was continued until about 25% of the original material distilled off as water (about 7%) and fatty acids (about 18%). The residue after the addition of siccatives and thinning dried in 3½ hours to a practically non-tacky and colourless film and was suitable for replacing boiled linseed oil in the preparation of paints or for use as a clear varnish.

In a similar experiment samples were taken during the heating of the batch at bath temperatures of 215, 245, 260, 275 and 290° C. The iodine numbers of these samples were 167.2; 177.8; 179.9; 179.7 and 190.5 and the refractive indices were 1.4674; 1.4700; 1.4730; 1.4793 and 1.4905 respectively. The last sample had a viscosity of 3.4 poise while the previous one had only 0.9 poise. Most of the distillate of lower iodine number was given off during the early part of the heating and this accounted for the rise of iodine value of the residue up to about 180. After further heating at a bath temperature of 290° C. for about 1 hour the residue had gelled. Such gels can find useful application in the varnish and related industries, e.g. in the preparation of linoleum and certain paints.

Example 4

When a linoleic acid concentrate from safflower fatty acids was treated according to Example 1 the yield of residue was about 65% of a fairly viscous oil which after the addition of driers gave a non-tacky film in about 7 hours. The oil had an acid number of 30.7, a saponification number 46.1, 20% carbonyl oxygen determined according to Knight and Swern, J.A.O.C.S. 26, 366–370 (1949), a hydroxyl number of 0 and contained 73.4% of unsaponifiable matter with a molecular weight of about 900 determined according to Mattiello, Protective and Decorative Coatings, part V, pp. 194–195 (1947). It was largely insoluble in ethyl alcohol, acetone and acetic acid but was soluble in aliphatic and aromatic hydrocarbons such as petroleum spirits or benzene.

The product showed a remarkable increase in iodine number. The concentrate before heating had an iodine number of 180 according to both the Wijs method and the Woburn method, while the product after heating had an iodine number of 211 according to the Wijs method and of 234 according to the Woburn method. The unsaponifiable part of the product (73.4%) showed a still higher iodine number, viz. 224 according to the Wijs method and 250 according to the Woburn method and a diene number according to the Ellis-Jones method of 10.3.

The unsaponifiable portion of the residue obtained by solvent extraction after saponification had still better drying properties than the product as a whole, drying after addition of siccatives and on thinning to a very hard film equalling china wood oil in hardness and with good water and alkali resistance.

The fatty distillate which had collected in the receiver and amounted to about 22% by weight of the material consisted largely of unchanged although contaminated linoleic acid and could be used again. It had an acid number of 143.0, a saponification number of 190.6 and an iodine number of 170.8. About 6% of water had collected in a chilled trap in the vacuum line.

Example 5

110 grams of cottonseed fatty acids obtained by the commercial distillation of the cotton-soapstock fatty acids were treated in a round-bottom flask. The fractionation column was mounted thereon and provided with the packing as described in Example 1. It also contained 6.6 grams of boric acid in the form of pieces obtained by applying a high pressure to a slurry of finely pulverized crystalline boric acid and a small amount of water in a tablet press and afterwards drying at about 70° C. in an oven. After evacuation of the apparatus the reaction vessel was heated as in Example 2. A residue of 47 grams remained, which after the addition of thinner and driers dried in 3½ hours and yielded a hard, elastic and non-tacky film of good surface coating properties.

Example 6

110 grams of oleic acid of 97% purity containing 2 to 3% of saturated fatty acids were treated with 6.6 grams of boric acid, which had been distributed in the reflux column as in Example 5. The times and temperatures were as described in Example 2. In addition to 6.4 grams of a fatty acid-distillate with an iodine number of 52, consisting mainly of a mixture of oleic and palmitic acids, 7.7 grams of an aqueous distillate were collected. The bulk of the material which remained in the flask was washed with hot water to remove dissolved boron compounds. After being thus purified, the residue had a refractive index of 1.4776, an acid number of 58.1, a saponification number of 85.6, an iodine value of 132.9, and a mean molecular weight of 661 as opposed to the values for the oleic acid which were refractive index: 1.4580, acid number: 198.5, saponification number: 199.3 and iodine number 88.0. Although the oleic acid had been free of unsaponifiable matter, the residue contained 44.7% unsaponifiable matter. The residue was soluble in ether and petroleum spirit but insoluble in alcohol and acetic acid. There was an overall weight loss of about 2½% of the starting material due to gaseous decomposition products.

Example 7

110 grams of groundnut oil fatty acids (acid number: 197.6; iodine number 98.7) were heated under vacuum in a flask fitted with a column containing Raschig rings along with pieces obtained by pressing and drying moistened pulverized boric acid. An air-cooled reflux condenser was mounted on top of this column. The fractionating column was electrically heated to 200° C. and from time to time the vacuum was released for an instant to allow any distillate which had accumulated in the upper part of the heated column to run back into the flask. The flask was slowly heated in a bath the temperature of which was raised to 290° C. and held at this temperature for 1 hour. Owing to the use of the reflux condenser, there was no distillate other than an aqueous fraction of about 8 grams which was condensed in a chilled trap in the vacuum line. The yield of residue was about 90%

including the samples which had been taken from time to time to follow the rise in iodine number and the drop in acid value caused by the increase in unsaponifiable content. The iodine value of the residue at the end of the experiment was 123.8, its acid value 70.6. It contained 20.6% of a fatty acid fraction (iodine number 9.4, acid number 175.5) which could be removed by heating under vacuum at 290° C. for one hour, the remainder, which possessed good drying properties, being polymeric and non-volatile under these conditions. A similar result was obtained when pieces of fused boric oxide about the size of peas were distributed among the packing of the fractionating column.

Example 8

A mixture of neutral oil and free fatty acids obtained during alkali-refining of rapeseed oil with an acid number of 112 and iodine number of 126.8 was treated with 6% of boric acid in the apparatus and manner described in Example 2. The residue, 77% by weight of the original fatty compound, was a viscous oil with an iodine value of 146.1. After addition of thinner and metal driers a film after drying for 19 hours exhibited only a slight tackiness.

Example 9

20 kilograms of refined sunflower soapstock fatty acids having an acid value of 160, a saponification value of 196, and an iodine value of 127, together with 0.5 kilogram of technically pure boric acid were heated under a vacuum of 15 to 25 mms. mercury in a stainless steel apparatus such as is used in manufacturing stand oil and alkyd resins. This apparatus consisted of a gas-heated 50 litre boiler including a stirring device and a vacuum sample taker and a reflux cooler mounted on the boiler and connected to a tubular cooler slanting towards the receiver. The heating was carried out over 3 hours until the temperature was raised to 260° C., continued for a further 4½ hours to raise the temperature to 290° C., and then for a further 4 hours at 290° C. During this time 5.5 kilograms of fatty acid and 0.8 kilogram of water collected in the receiver.

The remaining residue weighing 13.7 kilograms was repeatedly washed with boiling water and subsequently dried under vacuum at 100° C. and filtered on a filter press. The residue then showed the following characteristics:

Acid value	7.5.
Saponification value	86.
Iodine value (Wijs)	143.
Unsaponifiable matter	32%.
Viscosity	165 poises at 20° C.

After the addition of 0.3% lead and 0.02% manganese as naphthenates the residue dried to the touch in 90 minutes and to completion in 150 minutes to give a good water-resisting varnish-like film.

Example 10

In the apparatus described in Example 9, 20 kilograms of a fraction obtained from soya bean oil fatty acids (acid value 203.5, saponification value 206.3, iodine value according to Wijs 140.2, unsaponifiable matter 2.8%) and 0.4 kilogram technical boric acid were heated under a vacuum of 13–20 mm. to 260° C. within 10 hours and to 290° C. in 2 further hours. The fatty acids distilled off during this heating were continuously fed back to the reaction kettle. Then the heating was continued for 4 hours at a temperature between 260° and 290° C., during which time, however, the distillate obtained was collected in the receiver. In this way 0.6 kilogram of a fatty acid distillate and 17.4 kilograms of a residue having the character of a stand oil were obtained. After the residue had cooled down to about 100° C. the boric acid still contained in the residue was removed by repeated boiling with a few kilograms of water and removal of the washing-water. The residue had a viscosity of 194 poises at 120° C., an acid value of 7.3, a saponification value of 17.9, an iodine value according to Wijs of 154.1, and contained 86% of unsaponifiable matter.

After the addition of a lead/manganese naphthenate siccative (0.3% lead and 0.02% manganese) and diluting with a mixture of turpentine and mineral spirits (1:1) to the consistency of a varnish, a product with good drying properties and useful for the preparation of paints was obtained. A film of this product was dry to the touch in about 5 hours and completely dry in 7½ hours.

Example 11

20 kilograms distilled tall oil fatty acids with acid value 194.3, saponification value 196.9, iodine value according to Wijs 131.5, resin content 2%, and 0.4 kilogram technical grade boric acid are heated, with mechanical stirring, over two hours to 230° C. in the apparatus described in Example 10 under a vacuum of 4–12 mm. mercury. Heating was then carried out for a further 10 hours to 260° C. and then carried out for 14 hours in the range 260° to 290° C. The fatty acids distilling off were reintroduced into the kettle. Towards the end of the reaction only slight amounts of fatty acids were distilling off. After completion of the heating 17.5 kilograms of residue were obtained and washed five times, with 20 kilograms hot water each time, until the boric acid had been removed. The residue was then dried in vacuum and filtered in a filter press. The product thus obtained showed the following characteristics:

Acid value	6.0.
Saponification value	13.2.
Iodine value (Wijs)	155.9.
Unsaponifiable matter	92.1%.
Viscosity	91.5 poises at 20° C.

After addition of 0.3% lead and 0.02% manganese in the form of naphthenates as driers and thinning with mineral spirit to a viscosity of 1.5 poises at 20° C. a film of this product was dry to the touch in 6 hours and completely dry in 8 hours.

It should be noted that the temperatures given in Examples 9–11 inclusive, are the temperatures of the reaction mixtures, but not bath temperatures.

I claim:

1. A process for preparing condensation products which comprises heating an acid of the formula R.CO.OH where R is an unsubstituted long chain hydrocarbon radical, at a temperature of 220 to 330° C. in the presence of a catalyst selected from the group consisting of boric acid, boric oxide, ammonium pentaborate, trimethyl borate, triethyl borate, mannitol borate and the mixed anhydrides of boric acid and fatty acid, until the reaction mixture contains at least 32% by weight of unsaponifiable matter having a mean molecular weight at least three times that of said acid, the heating being carried out under such conditions that water liberated during the reaction is removed from the reaction zone as it is formed but the loss of the major part of the acid is avoided.

2. A process for preparing condensation products which comprises heating an acid of the formula R.CO.OH where R is an unsubstituted long chain hydrocarbon radical, at a temperature of 220 to 330° C. in the presence of a catalyst selected from the group consisting of boric acid, boric oxide, ammonium pentaborate, trimethyl borate, triethyl borate, mannitol borate and the mixed anhydrides of boric acid and fatty acid, until the reaction mixture contains at least 32% by weight of unsaponifiable matter having a mean molecular weight at least three times that of said acid, the heating being carried out under such conditions that water liberated during the reaction is removed from the reaction zone as it is formed but the loss of the major part of the acid is avoided,

and the reaction mixture being kept at 250 to 300° C. at least during the latter part of the reaction.

3. A process according to claim 2 wherein any substantial amounts of residual carboxylic acid are ultimately removed.

4. A process according to claim 1 wherein the treated carboxylic acid contains from 10 to 26 carbon atoms in the molecule.

5. A process according to claim 2 wherein the treated carboxylic acid contains 18 to 22 carbon atoms in the molecule.

6. A process according to claim 2 wherein the treated carboxylic acid is unsaturated and contains 18 to 22 carbon atoms in the molecule.

7. A process for preparing condensation products which comprises heating an acid of the formula R.CO.OH where R is an unsubstituted long chain hydrocarbon radical, at a temperature of 220 to 330° C. in the presence of a boric acid catalyst, until the reaction mixture contains at least 32% by weight of unsaponifiable matter having a mean molecular weight at least three times that of said acid, the heating being carried out under such conditions that water liberated during the reaction is removed from the reaction zone as it is formed but the loss of the major part of the acid is avoided.

8. A process for preparing condensation products which comprises heating an acid of the formula R.CO.OH where

R is an unsubstituted long chain hydrocarbon radical, at a temperature of 220 to 330° C. in the presence of a boric oxide catalyst, until the reaction mixture contains at least 32% by weight of unsaponifiable matter having a mean molecular weight at least three times that of said acid, the heating being carried out under such conditions that water liberated during the reaction is removed from the reaction zone as it is formed but the loss of the major part of the acid is avoided.

9. The product prepared by the process of claim 1.

10. The product prepared by the process of claim 6.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,923,718 February 2, 1960

Johannes Donatus Von Mikusch-Buchberg

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 67, before "hydrocarbon chain" insert -- or unsaturated --.

Signed and sealed this 9th day of August 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents