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LICANIC ACID RESIN AND PROCESS OF MAKING

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This invention relates to resinous licanic acid compositions and more particularly to the resin obtained by decomposition of licanic acid, and modified products of such resin. This application is a continuation in part of our application Serial No. 70,612 filed March 24, 1936, and contains subject matter derived from our application Serial No. 63,862 filed February 14, 1936.

The resin composition of this invention may be prepared from licanic acid itself or from a mixture of licanic acid with the other fatty acids that occur in oiticica oil and poyoak oil. The production of the resin is obtained by decomposing the licanic acid by proper heat treatment of that acid or fatty acid mixtures containing licanic acid under conditions that facilitate the splitting-off the elements of water from the licanic acid molecule with progressive decomposition of the acid into a resin. This resin is useful in coating compositions and serves especially as a substitute for shellac. This resin may be modified by treatment with maleic anhydride and the resulting product may be esterified to produce valuable modified products of the licanic acid resin; which is evidence that the conjugated double bond structure has been retained although the acid has been decomposed.

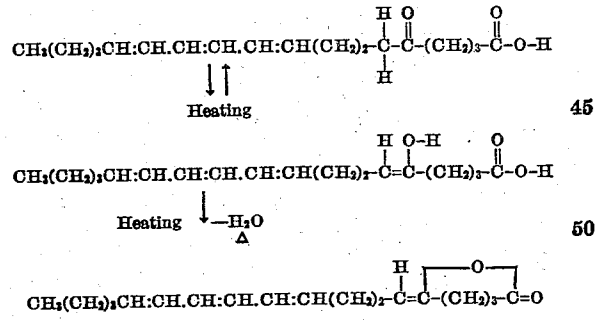
Prior workers in the fatty acids field have proposed thickening, bodying or gelling of the fatty acids of various drying and semi-drying oils, the sole purpose being to produce an improved stand oil. The product is a viscous liquid oil having substantial body but definitely is not a resin and does not possess the solidity, hardness, and fracture characteristics that distinguish the resins from the bodied oils.

In the prior processes the oils or fatty acids thereof are subjected to treating conditions conducive to increasing the body or viscosity of the oil but in all cases the treating conditions are controlled to prevent decomposition of the oil. Therefore, the fatty acids do not decompose but simply polymerize and thereby effect an increase in viscosity. In a typical process the oil or fatty acids are distilled to remove the unpolymerizable constituents and the distillation is carried out in the presence of a non-oxidizing gas such as for example under an atmosphere of carbon dioxide. The still residue is a thickened liquid known as stand oil. It has no fracture characteristic, it is not a solid at room temperatures and does not possess any of the other physical or chemical characteristics of the resins.

Our present invention is based upon the discovery that licanic acid when treated under proper decomposing conditions will decompose into a resinous product that is a solid at normal, atmospheric temperatures and has a fracture and hardness characteristic that definitely identifies it as a resin. Among the numerous fatty acids of drying and semi-drying oils, we have found by our exhaustive tests that the fatty acids of only two of these oils are suitable as starting materials for the production of our new resin, and they are the fatty acids of oiticica oil and poyoak oil. It appears that both of these oils contain licanic acid or a like acid having a ketone group in the fatty acid molecule. This licanic or ketone group acid may be isolated from the other fatty acids in the oiticica or poyoak oil before being decomposed into the desired resin product; or a mixture of this acid with the other associated acids in oiticica or poyoak oil may be used in our process, but it is only the ketone type acid that decomposes and resinifies.

The resin obtained by decomposition of the licanic acid alone is harder and accordingly more desirable for a number of uses than the resin obtained by decomposition of the mixture of icanic acid with the other fatty acids in oiticica and poyoak oils. The resinified product derived from the mixed acids is somewhat softer and more wax-like because of the presence of non-resinifying components.

Our numerous tests show that with the exception of the oiticica and poyoak oil acids, the fatty acids of the drying and semi-drying oils do not resinify upon heating and therefore do not form the resin products of our invention. The characterizing constituent of the oiticica and poyoak oils, namely the licanic acid with a ketone group, is an essential to our decomposition and resinifying process in which water is produced by combination of certain of the hydrogen and oxygen atoms in the acid molecule. When the water is split-off a rearrangement of the molecule takes place which is totally different from the ordinary dehydration of a fatty acid. This decomposition reaction, which forms a resin, may be illustrated empirically as follows:



The resinification involved in our process as illustrated by the above formulas is the result of an actual decomposition with evolution of water from the licanic acid molecule. We believe it likely that the ketone group undergoes a condensation with the carboxyl group of the acid as

indicated in the above formula, but we do not wish to limit the explanation to this reaction.

To effect the decomposition of the licanic acid with resulting resinification, the licanic acid must be heated under conditions to cause decomposition to take place as evidenced by the evolution of water. Thus, if licanic acid is heated in an open vessel, it begins to lose water at about 200° C. and eventually decreases in acid value and becomes very viscous, approaching a solid state or substantially resinifying. The speed with which this decomposition takes place is dependent upon the temperature. Thus while the effect begins at about 200° C. it is much more apparent at temperatures somewhat higher than this and, for direct heating, temperatures of between 240° C. and 300° C. and preferably between about 240° C. and 270° C. can be used. The top limit given is merely a practical one and is not critical to the reaction, the actual limit being a temperature at which the acid is materially darkened or otherwise injured.

The direct heating may take place either in vacuum (such as a vacuum of between about 1 mm. and 4 mm. of mercury) or in an open kettle and preferably is accompanied by gentle agitation to facilitate removal of the water.

A preferred method of accomplishing the decomposition reaction is by dissolving the licanic acid in a solvent having a boiling point somewhat above 200° C. and then boiling the mixture under such conditions that the solvent is refluxed back to the boiling mass after separation of the evolved water. Under these solvent conditions, decomposition of the resin is facilitated. In such case a somewhat lower temperature is sufficient, as for example, temperatures in the order of about 225° C. to 275° C., though higher temperatures may also be used in this connection. Various organic solvents of types now on the market are available—about the only requirement being that the solvent shall be substantially inert to the acid and so have a boiling range between about 200° C. and 300° C. A product which has been found excellent for this purpose is a product now on the market and widely known under the name of "Hydrosolvent #4"—a hydrocarbon which has a boiling range of between about 215° C. and 238° C.

When licanic acid is thus heated under decomposing conditions until the evolution of water has ceased, it will be found that the acid has changed in many respects. Its acid number is greatly reduced (e. g. in one case from 175 to about 101) and on cooling it will set to a solid mass with a characteristic fracture and pleasant odor. This resinous mass is thermoplastic, being readily softened with heat, is soluble at normal temperatures in the usual ketone, ester, aromatic hydrocarbon solvents and in blown oils, such as blown linseed oil, but is substantially insoluble in cold aliphatic hydrocarbons and raw oils. Thus it is clearly distinguishable from the viscous products which result from heating the usual drying oil and semi-drying oil fatty acids. The latter are usually soluble in mineral spirits or other petroleum hydrocarbons.

The invention may be readily understood from the following example:

Oiticica oil fatty acids were separated from the oiticica oil by one of the methods commonly known in the art. The separated fatty acids were dissolved in a 50% solution in an aliphatic hydrocarbon solvent having a boiling range between 50° C. and 100° C. (e. g. hexane). The solution was then chilled down to a temperature of about 0° C. which caused the material which is here called licanic acid to separate out as a wax-like white solid. It was found that this acid was very susceptible to atmospheric oxidation so that either the separated acid or even the mixed raw acids were difficult to store. The acids prepared by saponification of the oil with alkali are usually light in color and when used promptly after preparation yield a light colored product, whereas the acids which are available commercially are quite dark in color and additional manipulation is required to produce light colored licanic acid.

A quantity of licanic acid prepared as above set forth was dissolved, using equal parts by weight, in Hydrosolvent #4. The solution was heated in a closed vessel equipped with a special form of reflux adapted to condense the water and solvent and return the solvent to the vessel without the water. The solution was kept boiling vigorously at about 225° C. until water no longer was being condensed in the reflux apparatus. This usually requires about three hours. It was found that about 100 parts of acid having an acid number of 176 evolved about 5.4 parts of water. This is simply an observation made and is not intended in any way as a limitation, as experience may show that this figure is subject to substantial modification.

After the evolution of water was completed, the solution was allowed to cool down and the resin was more completely precipitated by adding an excess of methanol. After removal of the solvent this resin product had an acid number of 93, was a hard solid at room temperatures and had a fracture characteristic of the resins.

Further modification of the licanic acid or licanic acid resin may be obtained by treating with maleic anhydride and the reaction product esterified. These treatments may be carried out in open vessels or in a closed system with solvents or combinations thereof. The maleic anhydride reaction may be effected by treatment of the licanic acid either before or after its decomposition into a resin. Whichever procedure is used the resulting product may then be esterified with glycerine or glycerides. If the treatment is carried out before decomposition, that is, upon the normal licanic acid, the resulting product is then subjected to decomposition and resinification in a manner similar to that described hereinabove. In accordance with one illustrative embodiment the licanic acid may be dissolved in an aliphatic hydrocarbon, then the maleic anhydride added and the solution heated until considerable frothing takes place which indicates the reaction between the licanic acid and the maleic anhydride. The resulting product may then be heated, substantially as above described, under vacuum to effect resinification. The product so prepared is a solid at room temperature and in one instance possessed an acid value of about 204 as compared with an acid value of 272 of the addition product of licanic acid and maleic anhydride prior to resinification.

The product resulting from esterifying with glycerol the resinified licanic acid-maleic anhydride reaction product (whether the reaction with the maleic anhydride is conducted before or after resinification of the licanic acid) is a resinous body which is definitely a solid at normal room temperature so that it has a characteristic fracture, and in this regard it definitely distinguishes from the usual product obtained by the reaction of maleic anhydride and a drying oil which is

characteristically soft or balsam-like. It should be noted that the resinification of the licanic acid is a distinct step from the esterification, and this resinification can take place only prior to esterification, though such resinification may take place either before or after the maleic anhydride addition. In other words, the resinified glyceride of this invention cannot be produced by any steps aimed to accomplish resinification after esterification.

It is to be understood that the foregoing examples are given only by way of illustration and may be modified and changed in many particulars without departing from the spirit of our invention.

What we claim is:

1. A resinous body consisting essentially of the product resulting from decomposing licanic acid by heating said acid to between about 200° C. and 300° C. until the evolution of water substantially ceases and the acid is decomposed into a resin.

2. A resin product normally solid at atmospheric temperatures and having a definite resin fracture characteristic, comprising a residue of heat treated fatty acids containing decomposed and resinified licanic acid, said fatty acids being those acids which occur in drying oils of the group consisting of oiticica and poyoak oils.

3. A process of preparing resinous licanic acid comprising decomposing licanic acid by heating said acid under decomposing conditions and with the evolution of water until a resinous product, which is solid at atmospheric temperatures and which has a definite fracture characteristic of resins, is produced.

4. A process for preparing a resin product as defined in claim 3 in which the licanic acid is mixed with the other fatty acids normally occurring in a drying oil selected from the group consisting of oiticica oil and poyoak oil.

5. A process of preparing licanic acid resin comprising decomposing licanic acid by dissolving said acid in an organic solvent having a boiling point of at least about 200° C. and heating the licanic acid solution so as to continuously distill off the solvent and water until further evolution of water has ceased and the licanic acid has been decomposed and resinified.

6. In a process of preparing modified resinous products of licanic acid, the preliminary step of resinifying the licanic acid by heating said acid until evolution of water substantially ceases and the acid is decomposed into a resin.

7. A resin product normally solid at atmospheric temperatures and having a definite resin fracture characteristic comprising decomposed resinified licanic acid.

8. A resin product normally solid at atmospheric temperatures and having a definite resin fracture characteristic comprising decomposed resinified ketone group fatty acid of oiticica oil.

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