Patented Dec. 9, 1941

2,265,161

UNITED STATES PATENT OFFICE

2,265,161

PROCESS OF MODIFYING DERIVATIVES OF NATURAL ROSINS AND PRODUCTS THEREOF

Torsten Hasselstrom and Edward A. Brennan, Savannah, Ga.

No Drawing. Application August 9, 1937, Serial No. 158,258

5 Claims. (Cl. 260—103)

The present invention relates to novel derivatives of natural rosin and compounds thereof, and to a process of treating derivatives of natural rosin.

It is well known in the art that the instability of esters of natural gum and wood rosin, such as, for instance, methyl esters, ethyl esters, ester gum, etc., greatly reduces the commercial applications for such substances. Various processes have been suggested for overcoming these disadvantages of esters of gum and wood rosin, among which processes may be mentioned hydrogenation of the initial rosin and hydrogenation of the esters of natural gum and wood rosin. These prior processes are found in practice to suffer from the disadvantage of high costs of manufacture, so that the employment thereof has been greatly limited. It is well known that the normal esters of natural rosin, such as the esters of Steele's abietic acid (alpha-abietic acid) are not readily susceptible to monosulfonation: and hence sulfonates thereof are not manufactured or commercially available, as the degree of sulfonation is very small—seldom amounting to 1 percent, and the product is apparently a disulfonate. In distinction therefrom, the procedure according to the present invention permits obtaining esters by modification of natural rosin substances, such as Steele's abietic acid, which are capable of undergoing a considerable monosulfonation.

This invention relates primarily to a process which effects a change in the relative position of the double bonds in the esters, and like derivatives of abietic types of resin acids and in like derivatives of natural rosin, and to products thereof which are not formed through intermediate addition-, subtraction-, or substitution-products but are produced through reactions known to those skilled in the art as intramolecular re-arrangements for effecting a change in the position of the double bonds of the natural rosin derivatives and/or to effect Waldens' conversion and/or to effect stereo-isomerism and/or geometric isomerism; and according to this invention, this type of reaction has been applied in a normal and useful manner for producing valuable modified rosin derivatives, such as modified rosin esters.

The modified-rosin derivatives of natural rosin, such as for instance, modified methyl esters of rosin, modified ethyl esters thereof, etc., have the advantage of displaying greater stability to atmospheric conditions, so that they provide better bases for the manufacture of varnishes, lacquers, solvent plasticizers, etc. As set hereinafter, they are capable of sulfonation, with the formation of a stable sulfonate and may be characterized through such a capability and product.

The process effects an intramolecular rearrangement of the double bonds initially present in the molecule of the rosin derivative, so that the product may be regarded and established as an isomerized natural rosin derivative.

The starting material in practicing the present process and in the manufacture of the product may be any ester or like acid derivative of natural rosin in the initial state or following segregations or purifications thereof, which derivatives are not originally capable of yielding a stable sulfonate on sulfonation; thus, it will be understood that the invention may be practiced upon derivatives such as esters of such resin acids as sapinic, sapietic, abietic, pimaric, etc., or mixtures thereof, as set out in the co-pending Hasselstrom and Brennan application, Serial No. 108,308, filed October 29, 1936.

It is a characteristic of this invention that an intramolecular rearrangement proceeds without substantially reducing the unsaturation of the original molecule of the resin acid derivative (which may be regarded empirically as $C_{20}H_{29}O_2.R$ of the original oleo-resin gum and/or wood rosin; and where "R" represents an alcohol of aromatic or aliphatic type). Thus, for example, a stabilized rosin ester can be produced without essential change of the original saturation of the ester.

It is also a characteristic of this invention that the product can be prepared from pseudo-pimaric acid (Brennan et al., United States Patent No. 2,072,628) and/or from modified rosin as set forth in the co-pending application (Hasselstrom et al., Serial Number 108,308, filed October 29, 1936), and can be produced from any unmodified natural rosin material which is capable of producing a sulfonate, by appropriate esterification.

It has been found that high yields can be obtained at a relatively low temperature of treatment, by employing catalysts which are effective for provoking and/or promoting intramolecular rearrangements.

By way of illustration, examples of practicing the invention are set below to facilitate the understanding of the invention by those skilled in the art; it is obvious that these examples are illustrative and not restrictive.

Example I

1000 g. of commercial rosin methyl ester were poured over 10 g. of iodine. The mixture was heated at atmospheric pressure to 175–180° C. for about two hours. The original straw color of the rosin methyl ester was changed to very light straw color. The yield is about quantitative.

50 g. of the isomerized rosin methyl ester was sulfonated with 100 cc. of concentrated sulfuric acid (sp. g. 1.84), brought to about minus 5° to plus 15° C. and stirred for about 20 minutes, then poured into cracked ice. The brownish precipitate was filtered out, and washed with cold water until the wash liquor clouded when mixed with the original liquid: the washed precipitate was extracted three times with boiling water, leaving a brownish insoluble, semi-solid resinous material. The hot aqueous extracts, on cooling, deposited a crystalline sulfonic acid in a yield of about 50 to 60% by weight of the original material. After re-crystallization from water and from glacial acetic acid, the isomerized rosin ester sulfonate melted at about 145–146° C.

In order to obtain further proof that an intramolecular re-arrangement had taken place within the molecule of the original rosin derivative and that this rearrangement was similar to that described in the said co-pending application (Hasselstrom et al. Serial Number 108,308), the isomerized rosin methyl ester sulfonate was converted into the corresponding dimethyl ester, which had about the same melting point (about 174.5° C.) and appears to be identical with the dimethyl ester of pseudopimaric acid sulfonate prepared from pseudopimaric acid sulfonate on esterification with dimethyl sulfate.

Example II

1000 g. of isomerized rosin (obtained according to Hasselstrom et al. Serial Number 108,308) was dissolved in 1500 cc. methanol and saponified with 200 g. of sodium hydroxide dissolved in 250 cc. of water. Then 450 g. of dimethyl sulfate were added gradually; the mixture was heated for about three hours, at a temperature of about 100° C. and with refluxing; the excess of methanol was removed by distillation. Finally the methyl ester was obtained by means of a vacuum distillation at about 1 mm. pressure and was a viscous light-straw-colored oil having a boiling range of about 185 to 210° C. at about 1 mm. pressure. 50 g. of this methyl ester was sulfonated according to Example I. The resulting sulfonic acid of the methyl ester melted at about 145–146° C. and was apparently identical with the methyl ester sulfonate obtained in the previous example since the melting point was not lowered in a melting point test of a mixture therewith.

It has been found that the isomerized methyl ester of a rosin, which has been produced through such an intra-molecular rearrangement, is substantially stable to oxidation and superior in this respect to the methyl ester of common rosin. When exposed for one week to an atmosphere of oxygen, the methyl ester of rosin shows an increase of about 3.08% by weight of the initial material whereas the isomerized rosin methyl ester increases about 0.4% by weight of the initial product.

Thus it is noted that the novel rosin methyl ester can be obtained from isomerized rosin by means of esterification or by heating the methyl ester of rosin with a suitable catalyst to provoke an intra-molecular rearrangement, which product is capable of producing a novel type of methyl ester sulfonate on sulfonation.

It has been found that various substances may be employed as catalysts. Thus, the halogens, either per se or as the hydrides, may be employed, including chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen iodide. Other halogen products may be employed, with due care in operation, such as organic acid chlorides, phosphorus pentachlorides, etc. Further organic sulfonic acid compounds may be employed, including alkyl and aralkyl sulfonates and sulfonic acids, such as benzylsulfonic acid: in particular, the sulfonate obtained by sulfonation of the pseudopimaric acid of our prior patent and the sulfonate obtained as described in Example I above have been found effective for provoking the reaction. Apparently, some advantage is attained by employing mixtures of catalysts.

It is pointed out that the action is one of producing molecular rearrangements, and generally non-metallic catalysts are employable which are capable of producing molecular rearrangements in the terpene series: and the group may be referred to as comprising such catalysts and more particularly the non-metallic catalysts of the group consisting of the alkyl and aralkyl sulfonates (thus including the corresponding sulfonic acids) and the halogen-containing substances of the above natures. The quantity to be employed varies with the particular agent and condition of treatment, and it is found that quantities from one-tenth of a percent to 5 percent give the desired effects. The upper limit of proportion of iodine, for example, is around 5 percent, as a greater proportion leads to a definite halogenation as distinguished from the intramolecular rearrangement.

The temperature to be employed likewise varies according to the initial product being treated, the catalyst, and the purpose of employment of the final resin. The higher temperatures produce a more rapid reaction, but decomposition with the formation of carbon monoxide and carbon dioxide may occur, these decompositions being particularly rapid at 240° C. and above. It has been found that the catalysts are not effective for provoking an operation of commercial rapidity at temperatures below 130° C. The reaction being an exothermic one, care should be exerted in controlling the temperature within the range of 130° to 240° C. The resulting conversion takes place either instantaneously or over a period of time: thus, the time may extend up to four hours, or even more, according to the material being treated, the proportion and constitution of the catalyst, and the temperature treatment. If performed without a catalyst, the conversion is very slow: and hence its is commercially preferable to catalyze the reaction.

When commercial colophony rosin, or the ester derivative thereof, is subjected to the foregoing treatment in the presence of about 1 percent of iodine, the resulting product, directly or upon esterification is susceptible to the sulfonation for yielding from 30 to 40 percent of monosulfonate. The residue is a neutral oil which is apparently a hydroxy acid material arising by hydration of the resin acids at the double bonds therein, this hydration being provoked also by the action of

sulfonation. This neutral oil may be employed as a blending agent or plasticizer, etc.: as it has improved characteristics with respect to resistance to light, air and heat.

It has been found that when the hydroxyl or carboxyl group of the rosin molecule is substituted by an ester or like group of aliphatic or aromatic type, and this rosin derivative is subjected to the treatment described hereinabove, the resulting isomerized rosin derivative is characterized by increased resistance to light, air and heat. The isomerized rosin derivative is further characterized by its ability to form a monosulfonic acid on sulfonation.

It his also been found that when a rosin or resinous material containing pseudo-pimaric acid and/or a resinous material obtained according to the invention described in the co-pending application of Hasselstrom et al., Serial Number 108,308, is subjected to esterification by methods known to the art, the resultant esters are characterized by increased resistance to light, air and heat; and further characterized by their ability to form monosulfonic acids on sulfonation. It is believed that the corresponding esters of the isomerized rosins described hereinafter and also the monosulfonic acid derivatives obtained from these corresponding esters on sulfonation are substantially identical in composition.

The refined esters are of straw to water-white color, and show great stability to atmospheric condition.

Even in the crude and relatively unrefined condition, they are of great value in the manufacture of certain lubricants. They can be employed directly because of their superior stability in grinding pigments, thus taking advantage of the penetrating and wetting propetries of these compounds: as an extender in phenolic varnishes; as printing inks; as anti-sludging agents, co-solvents, etc.; as a heat-interchange medium; as a vehicle for waxes in polishes, emulsions, etc.; in aluminum and other metallic paints to prevent skinning and to increase gloss; in leather and linoleum lacquers; to prolong the plastic nature of linseed oil putties and caulking compounds; as perfume fixatives for scented paper, polishes, and lacquers; as solvent plasticizers for use in the plastic industry with ethyl cellulose, vinyl acetate-chloride, etc.; as fixatives for poisons in insecticides.

It is obvious that the invention is not limited to the examples specifically set out, nor to the modifications indicated therein: but that it may be employed in many ways within the scope of the appended method claims: and that the produce therefrom is comprised within the following article claims.

What we claim is:

1. The process of preparing modified resin substances which are substantially stable to light, air and heat and capable of monosulfonation, which comprises the step of heating a material containing an ester of a natural rosin acid of abietic type in the presence of $\frac{1}{10}$ to 5% of iodine and under a temperature of 130 to 240° C. until intramolecular rearrangement has occurred in the resin acid radicals substantially without change of the unsaturation of the material.

2. The process of preparing modified resin substances which are substantially stable to light, air and heat and capable of monosulfonation, which comprises the step of heating a material containing an ester of a natural rosin acid of abietic type, in the presence of substantially 1% of iodine, and under a temperature of 130 to 240° C. until intramolecular rearrangement has occurred in the resin acid radicals substantially without change of the unsaturation of the material.

3. The process of increasing the resistance to light, air and heat of an ester of natural rosin, which comprises the step of heating the said ester of natural rosin at a temperature of 130 to 240° C. in the presence of $\frac{1}{10}$ to 5% of iodine until intramolecular rearrangement has occurred in the resin acid radicals thereof substantially without change of the unsaturation of the ester.

4. The process of increasing the resistance to light, air and heat of an ester of natural rosin, which comprises the step of heating the said ester of natural rosin at a temperature of 130 to 240° C. in the presence of substantially 1% of iodine until intramolecular rearrangement has occurred in the resin acid radicals thereof substantially without change of the unsaturation of the ester.

5. The process of preparing a resin ester material which is substantially stable to light, air and heat from a natural rosin containing Steele's abietic acid, which comprises esterifying the Steele's abietic acid of the rosin, and then heating said ester in the presence of substantially 1% of iodine to a temperature of 130 to 240° C., and for a time sufficient to provoke a major conversion of the Steele's abietic acid radicals into pseudo-pimaric acid radicals substantially without change in the unsaturation of said rosin.

TORSTEN HASSELSTROM.
EDWARD A. BRENNAN.