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SOLUBLE FATTY ACID CONDENSATION
PRODUCTSIan C. Somerville, Fox Chase, Pa., assignor to
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DelawareNo Drawing. Application May 9, 1930
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15 Claims. (Cl. 260—4)

This invention relates to sulphonated condensation products of fatty acids with phenol-aldehydic condensed compounds, which new compounds have valuable tanning properties. One such product has been fully described in co-pending application #367,633 filed May 31, 1929, of which this application is a continuation in part.

The combination of phenols with aldehydes has long been known in the process of resin making. The type of product obtained is dependent on the conditions employed. With a low proportion of aldehyde to phenol, in presence of an alkaline catalyst, a less reactive product is obtained, which has not so much tendency to polymerization on further heating. A similar result is secured by use of an acid rather than an alkaline catalyst. By using less than 1.0 molecule of aldehyde to 1.0 molecule of phenol I can obtain an intermediate condensation product whose further reaction can be controlled readily. This is ordinarily in liquid form, but a solid resin may also be utilized.

While formaldehyde is the most reactive, any of the lower members of the aliphatic series of aldehydes may be used in this process, and also to some extent, benzaldehyde. Phenol is the most convenient starting material, though homologues of phenol are also effective.

This first condensation product can now be condensed by heating to a high temperature with preferably a long chain, unsaturated fatty acid, when a resinous material is formed. Condensation will take place with unsaturated fatty acids of short chain such as crotonic acid, but in general superior products are obtained when long chain unsaturated acids such as oleic are employed. Provided that the proportions of material used and conditions chosen have been suitably adjusted, the resin obtained can be sulphonated to give a water soluble product by means of concentrated sulphuric acid, oleum, chlorosulphonic acid or other strong sulphonating agent, such as sulphuric acid in presence of glacial acetic acid.

In this way a new class of compounds is produced, which compounds have valuable tanning properties in aqueous solution. They may also be used as mordants for basic dyes, and, alternatively assisting the penetration of acid or direct dyes on leather. They find application as wetting, cleansing, and emulsifying agents, in the leather

and textile industries. They act as dispersing agents for dyestuffs.

The invention is illustrated by the following examples but is in no way confined to these examples.

Example 1

(a) 470 g. phenol, 225 g. formaldehyde 37% are mixed in cold, 2½ cc. of 50% sulphuric acid added, and the mixture warmed up on water bath till reaction sets in, when the temperature rises of itself to 100° C. and vigorous refluxing occurs. Two layers form and after cooling these are separated, the upper aqueous layer being rejected.

(b) 400 g. of clear liquid obtained as above, 160 g. of ricinoleic acid are mixed and warmed up together with mechanical stirring to 100° C. in 12 minutes and then to 300° C. in 43 minutes. The resin obtained is clear when solidified after cooling.

(c) To 490 g. of resin obtained as above, 490 cc. of 20% oleum is slowly added while cooling the vessel in ice water and stirring the oleum above the solid resin. By stirring while maintaining the low temperature for 8 hours slow sulphonation occurs. The temperature of the bath outside is then raised to 60° C. for 8 hours, when sulphonation is completed.

(d) The reaction mixture is now diluted and the excess of sulphuric acid neutralized by adding 364 g. caustic soda.

The solution obtained can be used directly in tanning.

Example 2

To a mixture of 470 g. of phenol, 2.5 cc. of 50% sulphuric acid heated to 95–100° C. is slowly added with stirring, 235 g. of 40% formaldehyde solution. The mixture is stirred and heated at 90–105° C. for one hour. The unused starting materials are removed by steam distillation and decantation. The product is a soft viscous resin. This is condensed with oleic acid by mixing the resin with 198 g. of oleic acid and heating at 250° C. for 5 hours with stirring. The temperature is finally raised momentarily to 300° C. When cold the product is a clear, transparent, hard, brittle resin. It is sulphonated in the following manner:

The resin is dissolved in twice its weight of glacial acetic acid. The temperature of the solution is kept below 20° C. while 750 g. of concen-

trated sulphuric acid is slowly added with stirring. The temperature is raised to 100° C. and held at this point for 3 hours. The mixture is diluted with an equal volume of water and steam distilled to remove the acetic acid. The excess sulphuric acid is removed with calcium hydroxide.

The solution obtained can be used directly in tanning.

Example 3

The hard resin prepared as in Example 2 from the soft resin and oleic acid is sulphonated in the following manner:

The resin is dissolved in twice its weight of glacial acetic acid. To the cold solution is slowly added with stirring 840 g. of chlorosulphonic acid. The solution is heated for 3 hours at 100° C. Hydrogen chloride liberated during the reaction is absorbed in sodium hydroxide solution. The sulphonation mixture is diluted, steam distilled, and treated with calcium hydroxide as in Example 2.

Example 4

The soft resin prepared as in Example 2 is condensed with crotonic acid by mixing it with 60 g. of crotonic acid and heating at 150° C. for 5 hours. The temperature is finally raised momentarily to 300° C. When cold the product is a clear, transparent, hard, brittle resin. It is sulphonated by the method of Example 2 or 3.

Example 5

A mixture of 470 g. of phenol 132 g. of acet-aldehyde 120 cc. of water 37 cc. of concentrated sulphuric acid is heated cautiously during the first stages of the reaction and is then refluxed for 5 hours. The unused materials are removed by steam distillation and decantation. The soft resin is condensed with oleic acid by mixing the resin with 170 g. of oleic acid and heating at 250° C. for 5 hours. The product is dissolved in twice its weight of glacial acetic acid and sulphonated as in Example 2.

It is understood that deviations in the above examples are possible without departing from the spirit of this invention. Anyone versed in the art will recognize that temperatures, pressures, proportions of ingredients, sequence of operation, etc., can be varied. Condensing with an unsaturated fatty acid, the condensation product of a phenol and an aldehyde, temperatures over 200° C. are preferable though not absolutely necessary. The temperature at which the phenol aldehyde condensation takes place can also be varied within rather wide limitations, the preferred temperature range being between 70° to 110° C. It is understood that the invention is in no way to be confined except as limited by the following claims.

I claim

1. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde, then condensing this product with an unsaturated fatty acid to form a resinous material, finally sulphonating this resin.

2. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde, then condensing this product at over 200° C. with an unsaturated fatty acid to form a resinous material, finally sulphonating this resin.

3. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde in presence of a relatively small

amount of mineral acid, then condensing this product at over 200° C. with an unsaturated fatty acid containing more than ten carbon atoms to form a resinous material, finally sulphonating this resin.

4. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde in presence of a relatively small amount of mineral acid, then condensing this product at over 200° C. with oleic acid to form a resinous material, finally sulphonating this resin.

5. As new compositions of matter, the water soluble products formed by condensing phenol with an aldehyde in presence of a relatively small amount of mineral acid, then condensing this product at over 200° C. with an unsaturated fatty acid containing more than ten carbon atoms to form a resinous material, finally sulphonating this resin.

6. As new compositions of matter, the water soluble products formed by condensing phenol with an aldehyde in presence of a relatively small amount of mineral acid, then condensing this product at over 200° C. with oleic acid to form a resinous material, finally sulphonating this resin.

7. As new compositions of matter, the water soluble products formed by condensing phenol with formaldehyde in presence of a relatively small amount of mineral acid, then condensing this product at over 200° C. with an unsaturated fatty acid containing more than ten carbon atoms to form a resinous material, finally sulphonating this resin.

8. As a new product the compound formed by condensing phenol with formaldehyde in presence of a relatively small amount of mineral acid, then condensing this product at over 200° C. with oleic acid to form a resinous material, finally sulphonating this resin to give a water soluble product.

9. As a new product the compound formed by condensing phenol with formaldehyde in presence of a small amount of mineral acid at temperatures in the range 70° to 110° C., then condensing this product at temperatures over 200° C. with oleic acid to form a resinous material, finally sulphonating this resin to give a water soluble product.

10. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde then condensing this product at temperatures of substantially 200° C. to 300° C. with an unsaturated fatty acid to form a resinous material and finally sulphonating this product.

11. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde in the presence of a relatively small amount of mineral acid then condensing this product at temperatures of substantially 200° C. to 300° C. with an unsaturated fatty acid to form a resinous material and finally sulphonating the product.

12. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde then condensing this product at over 200° C. with an unsaturated fatty acid containing 18 carbon atoms to form a resinous material and finally sulphonating this resin.

13. As new compositions of matter, the water soluble products formed by condensing a phenol with an aldehyde in the presence of a relatively small amount of mineral acid then condensing this product at over 200° C. with an unsaturated fatty acid containing 18 carbon atoms to form

a resinous material and finally sulphonating this resin.

14. As new compositions of matter, water soluble products as described in claim 13 in which the unsaturated fatty acid is ricinoleic acid.

15. As a new composition of matter, the water

soluble product formed by condensing phenol with formaldehyde in the presence of a small amount of acid then condensing this product at over 200° C. with ricinoleic acid to form a resinous material and finally sulphonating this resin.

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