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AMINO-METHYLENE DERIVATIVES OF SALICYLAMIDE AND PROCESS THEREFOR

Donald Price, New York, N. Y., and Rolston Lyman Bond, Cranford, N. J., assignors to National Oil Products Company, Harrison, N. J., a corporation of New Jersey

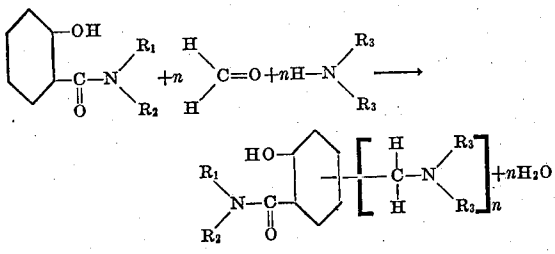
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9 Claims. (Cl. 260—559)

This invention relates to novel higher fatty salicylic derivatives and to a method for preparing the same.

Various derivatives of parahydroxy benzoic acid have been condensed with formaldehyde and primary and secondary amines, amino methylene derivatives apparently being formed during the reaction. This reaction has not, however, hitherto been found applicable to any corresponding salicylic acid derivatives.

It has been discovered by this invention that specifically the N-alkylated salicylamides, such as N-octadecyl salicylamide, are capable of reacting with formaldehyde and secondary amines to form compounds which appear to be amino methylene derivatives. The resultant products are useful for many purposes and particularly, when converted to their salts, for imparting water repellency to textiles. The reactions whereby salicylic derivatives are prepared according to this invention probably take the following course:



wherein:

R_1 represents an aliphatic radicle, which may be interrupted by ester, imido, imino and like linking groups; and which, in those cases where the final product is to be employed as a textile water repellent agent, preferably contains from 12 to 22 carbon atoms.

R_2 represents hydrogen or an aliphatic radicle which may be interrupted by ester, amido, ether, imino and like linking groups.

R_3 in each occurrence, and independently of its other occurrence, represents an alkyl radicle containing up to 22 carbon atoms, which alkyl radicles, in those cases where the final product is to be employed as a textile water repellent agent, preferably containing from 1 to 4 carbon atoms.

n represents a whole number from 1 to 2.

Salicylamides operative as starting materials in the process of this invention are in general those amides of salicylic acid containing an aliphatic radicle substituted in the amido nitrogen thereof. Examples of salicylamides which are suitable as starting materials in the practice of this invention are the N-methyl, -ethyl, -butyl, -capryl, -decyl, -lauryl, -myristyl, -palmityl, -margaryl, -stearyl, -oleyl, -arachidyl, -erucyl, and like salicylamides. Likewise, the di-N alkyl salicylamides may be employed, such as N-stearyl, N-methyl salicylamide, di-N propyl salicylamide, di-N stearyl salicylamide, and the like. The aliphatic radicle substituted in the amido nitrogen need not be a simple alkyl chain, but may be branched or interrupted by ester, amido, ether, imino, etc., groups; for instance, the N-salicylamido, N-stearamido ethylene diamide would be suitable as a starting material in the process of this invention. Particularly where an aliphatic radicle substituted in the amido nitrogen of the salicylamide includes or consists of a higher fatty alkyl group containing from 12 to 22 carbon atoms, the acid salts and alkali phenates of the condensation products obtained therefrom in accordance with this invention are highly efficient agents for imparting permanent water repellency to textile fabrics. Instead of the pure salicylamides, there may, of course, be employed mixtures of salicylamides coming within the requirements above set forth, for instance, amides formed by interaction of salicylic acid with amines derived from the mixed fatty radicles contained in the natural oils, fats and waxes, or with amines derived from petroleum fractions.

Amines which may be condensed with salicylamides and formaldehyde in accordance with this invention include any secondary alkyl amines, such as dimethylamine, diethylamine, dipropyl amine, dibutyl amine, methyl decyl amine, methyl stearylamine distearylamine and the like. Preferably, in those cases where the ultimate condensation products are to be employed in textile treatment, these should be short chain secondary amines, containing alkyl radicles of not over 4 carbon atoms.

The condensation of this invention may be carried out by mixing the selected N-aliphatic substituted salicylamide, formaldehyde and the selected amine, and heating the mixture at temperatures upwards of 40° C. and preferably upwards of 60° C. for from 3 to 8 hours. The molecular proportions of the reactants supplied may be varied in accordance with the final products desired. If the reactants are supplied in substantially equal molecular proportions, only one amino methylene group will be introduced into the salicylyl residue by the reaction set forth hereinabove, and n will equal 1. If excess form-

aldehyde and amine are furnished, two amino methylene groups will be introduced, and *n* will equal 2. At the conclusion of the reaction, the excess amine and formaldehyde may be removed by washing, and the impurities, by-products, etc., may be separated by distillation. The reaction may advantageously be carried out in the presence of an inert solvent such as methanol, ethanol, methyl ethyl ketone, dioxane, ethylene dichloride, trichlorethylene and the like.

The condensation products produced as above outlined are readily converted to salts and solubilized by dilute mineral and organic acids to give foamy, saponaceous solutions. Examples of suitable organic acids are formic, acetic, lactic, oxalic and like acids. Suitable mineral acids are hydrochloric, sulfuric, phosphoric, nitric and like acids. These acid salt compositions, preferably the salts produced by the action of organic acids, are capable of combining with reactive textile fibers such as cellulosic fibers, silk and wool to impart water-repellency thereto, such treatments being carried out by impregnating the fibers with the condensation products of this invention and thereafter baking at temperatures between 100° and 200° C., either wet or dry. This last feature whereby baking may be carried out in the wet is highly unique and useful, since in general the reactive water-repellent agents heretofore developed cannot be baked wet without deteriorating the fabric. Likewise, by virtue of the phenolic OH groups attached to the benzene nucleus in the compounds of this invention, these compounds are capable of reacting with strong alkalis, such as sodium, potassium, tetraethylammonium and like hydroxides, to form phenates which are soluble and/or dispersible in aqueous media. Such aqueous preparations are highly effective agents for imparting water repellency to textiles, having no tendency to yellow textile fabrics as has been the experience with many water repellents of this general type heretofore employed. In addition to their usefulness for water proofing of textiles, the products of this invention are likewise useful by reason of their surface active properties, being suitable as wetting, dispersing, penetrating, flotation, etc., agents.

Following are examples for the preparation of condensation products according to this invention, all parts given being by weight.

Example I

Diethylamino methylene N-octadecyl salicylamide

An octadecyl salicylamide was prepared by mixing 54 parts (1 mol) of octadecylamine, 28 parts (1 mol) of salicylic acid and 40 parts of pyridine and heating to 60° C. until a homogeneous solution resulted. 20 parts of phosphorus trichloride were slowly added to the solution which was then stirred and maintained at 60° C., for one hour, followed by one hour of stirring and heating at 120° C. The resultant mass was dropped into a mixture of 400 parts of concentrated sulfuric acid and 800 parts of ice. The resultant solid product was separated from the liquid by filtration, washed on the filter with water, removed from the filter and stirred with 600 parts of a solution containing 40 parts of sodium carbonate and 40 parts of sodium chloride. The resultant purified amide was separated from the salt solution by filtration, washed and pressed dry.

213 parts (1 mol) of the octadecyl salicylamide produced as just described were dissolved in 40 parts (1 mol) of diethylamine and to this solution were added 46 parts (1 mol) of 37% of formaldehyde. The mixture was then refluxed at 60° C. for 5 hours. The resultant condensation product was insoluble in water but formed a soapy solution in dilute acetic acid. The solubilized product was found to be suitable for impregating textiles to impart water repellency thereto.

Example II

Di (diethylamino methylene) N-octadecyl salicylamide

N-octadecyl salicylamide was prepared by the reaction of salicylic acid chloride with octadecylamine. 20 parts (1 mol) of this N-octadecyl salicylamide were condensed with 11 parts (2 mols) of diethylamine and 8.3 parts (2 mols) of 37% formaldehyde at 60° C. for 6 hours. The product was a reddish viscous oil readily soluble in dilute organic and mineral acids such as acetic acid, sulfuric acid and the like to give foamy, soapy solutions. This product, solubilized with 3% acetic acid, likewise was found capable of reaction with textile fibers to impart water repellency thereto.

Example III

Di (dimethylamino methylene) N-octadecyl salicylamide

The diethylamine of Example II was replaced with 14 parts (2 mols) of 33% aqueous dimethylamine solution, the procedure of that example being carried out identically in all other respects. The resultant product was a solid, which upon recrystallization from benzene exhibited a melting range 62–64° C. Analysis showed carbon 73.2%, hydrogen 11.0% (theory 73.9% and 11.4% respectively). The product was readily soluble in dilute acids.

Example IV

Diethylamino methylene N-tetradecyl salicylamide

To a solution of 33.5 parts (1 mol) of N-tetradecyl salicylamide in 100 parts of 95% ethanol there were added 8.5 parts (1 mol) of 37% formaldehyde. 7.7 parts (1 mol) of diethylamine were then added with cooling and stirring. The resultant mixture was then refluxed at 80° C. for 6 hours. The resultant product was a waxy, brown solid soluble in dilute acids.

Example V

Diallylamino methylene N-tetradecyl salicylamide

To a solution of 33.5 parts (1 mol) of N-tetradecyl salicylamide in 100 parts of 95% ethanol, there were added 8.5 parts (1 mol) of 37% formaldehyde and 9.8 parts (1 mol) of diallyl amine. The mixture was refluxed with stirring at 80° C. for 6 hours and then subjected to evaporation on a steam bath to remove the impurities. The resultant product obtained was a waxy solid which dissolved readily in 10% phosphoric acid to give a foamy, soapy solution.

Example VI

Diethylamino methylene N-octadecyl salicylamide

39 parts (1 mol) of N-octadecyl salicylamide were dissolved in 100 parts of trichloroethylene and then 8 parts (1 mol) of 37% formaldehyde, and 7 parts (1 mol) of diethylamine were added to the solution. The solution was refluxed 6 hours at 80° C. The resultant condensation prod-

uct was readily soluble in dilute acids to give a foamy, soapy solution.

EXAMPLE VII

Dibutylaminomethylene N-octadecyl salicylamide

To a solution of 100 parts (1 mol) of N-octadecyl salicylamine in 200 parts of 95% ethyl alcohol were added 32 parts (1 mol) of di-n-butyl amine and 20 parts (1 mol) of 37% formalin. After refluxing for five hours, the solvent was removed, leaving 109 parts of the product as a dark viscous liquid which emulsified in dilute acetic acid solution to produce a thick smooth cream.

EXAMPLE VIII

Di (dimethylaminomethylene) N-di-octadecyl salicylamide

100 parts of di-n-octadecyl amine were dissolved in 200 parts of methyl ethyl ketone, and to the solution were added 27 parts of salicylic acid and 15.5 parts of pyridine. The solution was raised to reflux temperature and 29 parts of phosphorus trichloride added dropwise and with stirring. The reaction was refluxed thereafter 2½ hours, then stirred into a hot (70–80°) 25% solution of sulfuric acid. This was followed by washes with water, 20% sodium carbonate and water. The solvent was then removed and the intermediate, N-di-octadecyl salicylamide dissolved in 200 parts of 95% ethyl alcohol. To this were added 64 parts of 33% dimethylamine solution and 38 parts of 37% formalin, and the resulting solution refluxed 18 hours. When the solvent was evaporated 154 parts of the product were obtained as a viscous paste which dispersed in dilute acetic acid solution to give a thick cream.

EXAMPLE IX

Imparting water repellence to fabric by salts

All of the products above described were found to be capable of reacting with textile fibers to impart water repellency thereto. As a specific example carried out upon the purified product of Example I, a 10% solution in 10% acetic acid was prepared from this product. Cotton cloth was immersed in this solution, wrung out to an uptake of 100% of solution, based on the dry weight of the cloth, and immediately baked without preliminary drying at 150° C. for 6 minutes. The resultant cloth product was substantially unimpaired in strength and exhibited a very high degree of water repellency, which persisted after a number of washings.

EXAMPLE X

Imparting water repellence to fabric by phenates

	Parts
Diethylaminomethylene N-octadecyl salicylamide (prepared as in Example I)	10
Ethanol (95%)	10
Caustic soda solution (5% aqueous)	100

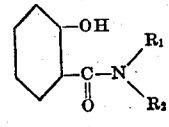
An emulsion was prepared from the ingredients above listed by mixing the salicylamide and alcohol to form a paste, and thereafter slowly adding the caustic soda with high speed stirring. There resulted a creamy emulsion.

Cotton fabric was immersed in this emulsion, removed, wrung out to an uptake of 100% of emulsion, based on the dry weight of the fabric, and air dried. The dried fabric was baked at 180° C. for 3 minutes, and then rinsed in an aqueous bath containing 0.1% of di-dodecyl naphthalene sodium sulfonate. The fabric was then dried, and was found to be highly water repellent which property persisted after numerous launderings. No yellowing or other adverse effect upon the color of the fabric was observed.

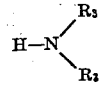
From the foregoing general discussion and detailed examples it will be seen that this invention provides novel salicylic derivatives having, inter alia, the properties of reacting with textile fibers to impart water repellency thereto. The products furthermore exhibit a high degree of surface activity, rendering them suitable as welting, penetrating, flotation, etc., agents. The raw materials employed in the production of these products in accordance with this invention are the readily and cheaply procurable amines, formaldehyde and salicylic acid.

We therefore claim:

1. Process which comprises heating to condense an amide having the general formula:



with formaldehyde and an amine having the formula:



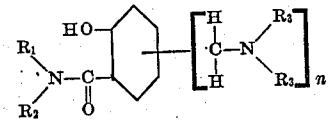
in which formulae R_1 represents an aliphatic radicle containing up to 22 carbon atoms; R_2 represents a substituent chosen from the group consisting of hydrogen and aliphatic radicles containing up to 22 carbon atoms; and R_3 in each occurrence, and independently of its other occurrence, represents an alkyl radicle containing up to 22 carbon atoms said reactants being present in the ratio of 1 mol of the amide to from 1–2 mols of formaldehyde and amine.

2. Process which comprises heating to condense N-octadecyl salicylamide with formaldehyde and with dimethylamine said reactants being present in the ratio of 1 mol of the amide to from 1–2 mols of formaldehyde and amine.

3. Process which comprises heating to condense N-tetradecyl salicylamide with formaldehyde and with diethylamine said reactants being present in the ratio of 1 mol of the amide to from 1–2 mols of formaldehyde and amine.

4. Process which comprises heating to condense di-N-octadecyl salicylamide with formaldehyde and with diethylamine said reactants being present in the ratio of 1 mol of the amide to from 1–2 mols of formaldehyde and amine.

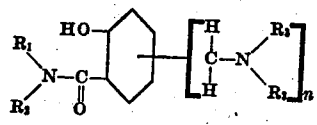
5. A substance chosen from the group consisting of compounds having the general formula:



wherein R_1 represents an aliphatic radicle containing up to 22 carbon atoms; R_2 represents a substituent chosen from the group consisting of hydrogen and aliphatic radicles containing up to 22 carbon atoms; R_3 in each occurrence, and independently of its other occurrence, represents an alkyl radicle containing up to 22 carbon atoms; n represents a whole number from 1 to 2; and salts and phenates thereof.

6. A water-repellency imparting agent for textiles comprising substance chosen from the group

consisting of salts and phenates of compounds having the general formula:



wherein R_1 represents an alkyl radicle containing from 12 to 22 carbon atoms; R_2 represents a substituent chosen from the group consisting of hydrogen and alkyl radicles containing from 12 to 22 carbon atoms; R_3 in each occurrence, and independently of any other occurrence, represents an alkyl radicle containing up to 4 carbon atoms; and n represents a whole number from 1 to 2.

7. A substance chosen from the group consisting of salts and phenates of dimethylamino methylene N-octadecyl salicylamide.

8. A substance chosen from the group consisting of salts and phenates of diethylamino methylene N-tetradecyl salicylamide.

9. A substance chosen from the group consisting of salts and phenates of diethylamino methylene di N-octadecyl salicylamide.

DONALD PRICE.
ROLSTON LYMAN BOND.