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COMPOUNDS FOR IMPREGNATING FIBROUS MATERIALS AND METHOD FOR THEIR PRODUCTION

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16 Claims. (Cl. 260—286)

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This is a continuation of our application Serial No. 520,824, filed February 2, 1944, now abandoned.

This invention relates to new compounds valuable for different purposes, particularly as textile treating agents.

It is an object of this invention to prepare new water-soluble chemical compounds useful for treating textile fibres in aqueous media. A further object is to prepare novel compounds which impart soft feel and water repellency to textile cloths and textile fibres. Furthermore, the so obtained water repellency is absolutely fast to dry cleaning and laundering. Other and further objects of this invention will appear as the description proceeds.

We have found that by using certain novel intermediary compositions compounds, having the properties mentioned above, can be produced. Said intermediary novel compounds will be obtained according to our invention by subjecting amides of fatty acids containing from 12 to 30 carbon atoms to prolonged heating to high temperatures.

In order to produce the intermediaries in accordance with this invention, stearamide, for instance, is heated first to a high temperature (300–350° C.) whereby a far-going decomposition occurs. Until now it was assumed that a reaction occurred here whereby the amide is split into the corresponding acid and nitrile under evolution of ammonia. This reaction takes place according to the following equation:

$$2C_{17}H_{35}CONH_2 \rightarrow C_{17}H_{35}CN + C_{17}H_{35} - COOH + NH_3$$

This reaction is indeed observed; a fact which can be substantiated by measuring the amount of ammonia evolved and by checking the acid number of the reaction mixture.

However, if the heating is continued long enough and a sufficiently high temperature maintained, the reaction products from the above mentioned reaction react further, which may also be followed by checking the acid number intermittently of the reaction mixture.

If the heating is continued long enough the acid number increases initially, reaches a maximum and declines.

The product which is obtained by prolonged heating of stearamide to high temperatures (300–350° C.) and which shows the low acid number of only five to fifteen, is of deep brown, dark color and almost liquid at room temperature. This crude mixture is distilled under reduced pressure whereby about 80 percent distill within the range of 150–200° C. at five millimeters as a colorless

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oil. The bulk of the distillate boils between 180–190° C. at five mm. This distillate has a nitrogen content of 2.5 per cent, molecular weight (Rast) found 488.

The product is subsequently chloromethylated in well known fashion and the so-obtained compound is reacted, for instance, with pyridine to form the pyridinium compound.

Instead of the above mentioned stearamide, amides of fatty acids may be used containing from 12–30 carbon atoms, such as lauramide, myristic acid amide, palmitic acid amide, montanic acid amide, etc., in general, amides of fatty acids as obtained from naturally occurring fats. In the case of amides of unsaturated fatty acids the sequence of reactions should be undertaken with the exclusion of air, which may be accomplished by bubbling through some inert gas such as nitrogen, since otherwise extensive resinification will take place. As starting material may further be used amides of acids which are obtained by catalytic oxidation of hydrocarbons, as, for instance, paraffin.

Other tertiary bases may be used in place of pyridine, such as the picolines, quinoline, etc.

Instead of using pure amides, like stearamide as starting material, mixtures of amides, like stearamide and palmitic acid amide may just as well be used, or others, such as are generally found in commercial fatty acid amides.

Also, we heated an equivalent mixture of stearic acid and stearonitrile to 300–350° C. for a longer period. In this case we also observed a marked decrease in the acid number of the mixture. The obtained reaction product resembles the one obtained from stearamide and distills under identical conditions under reduced pressure. The following chloro-methyl compound and the corresponding pyridinium compound too, showed the same properties as the compounds obtained from stearamide. In the course of this reaction we further noted that a small amount of stearamide added to the reaction mixture catalyzes the reaction.

A very similar product as the two mentioned before was obtained when an equivalent mixture of stearic acid and stearamide was heated to 300° C. We noticed in this case the splitting off of water. This reaction may be accelerated by adding zinc chloride or other agents which further the removal of water as catalysts.

Without limiting our invention to any special procedure, the following examples are given to illustrate our preferred methods of operating (parts by weight):

EXAMPLE I

566 parts of commercial stearamide containing about 5 per cent free fatty acid are heated to 320° C. for 17½ hours in a nitrogen atmosphere. The reaction is performed in a three-neck flask fitted with a gas inlet tube, thermometer, and a short outlet tube bent at an angle. This outlet tube is connected with a large test tube with side-arms which in turn is connected to a separatory funnel. The connection and delivery tube reaches below the level of a known amount of sulfuric acid placed in the separatory funnel. From there the gases are led into a vessel containing a saturated solution of barium hydroxide. The nitrogen is used as a carrier gas for the ammonia and other gases evolved in the reaction mixture. The ammonia is absorbed in the sulfuric acid which is titrated in aliquot parts taken from the lower end of the separatory funnel; the evolution of carbon dioxide is checked in the barium hydroxide solution. The side-arm test tube directly attached to the reaction vessel serves as a receptacle for distillate and other impurities carried from the reaction mixture by the nitrogen stream. By determining the acid number of the mixture at certain time intervals and checking the amount of ammonia delivered, a fairly accurate picture of the course of the reaction may be obtained. The following table will illustrate this point:

Table I

Time of Hrs.	Acid No. of Mixture	Ammonia Evolved (Percent of Theory)
0	10.2	0
2½		28.6
3½		38.3
4½	65.7	54.9
6		61.3
7½	62.9	62.3
9½	40.0	65.2
13½	31.3	65.7
17½	15.2	65.6

The reaction is interrupted at an acid number of 15.2. The dark, almost liquid mass is distilled under reduced pressure. No appreciable precipitate is formed in the barium hydroxide solution. The distillate is a colorless half-solid melting completely at 32° C. The yield is 428 parts or 75.5 per cent of the original amount. The distillate has a nitrogen content of 2.50 per cent. Molecular weight found 488.

Two hundred parts of this distillate are treated with 16.4 parts of paraformaldehyde in a solution of 200 parts per volume of benzene. The reaction mixture is treated with a strong stream of hydrochloric gas for several hours. The reaction is somewhat exothermic yielding a viscous mass as the end product. The mass is subjected to distillation under reduced pressure in order to free it from the solvent present, and 350 parts are treated with 60 parts of pyridine under agitation whereby care has to be taken that the temperature does not exceed 60° C. The so-obtained buff-colored viscous mass shows excellent water solubility or dispersibility. A solution of 8 per cent of the mass in water containing about one per cent sodium acetate is used for padding. The padded swatches are squeezed, dried, and cured for two to five minutes at about 150° C.

EXAMPLE II

284 parts of stearic acid are melted together with 265 parts commercial stearonitrile and subsequently heated to temperatures of about 325° C.

During a period of 24 hours, the acid number of the mixture decreased to 70.9 from the original value of 101.2. After adding 5.5 grams of stearamide (one per cent by weight), the acid number drops to 22.5 within 12 hours, or a total of 36 hours reaction time. Upon distillation under reduced pressure, 393 grams (71.5 per cent) of a colorless distillate are obtained from the dark brown, almost liquid crude. This distillate solidifies on standing and melts at 34° C.; it has an acid number of 12.3 and shows a nitrogen content of 2.6 per cent. The subsequent treatment is substantially the same as in Example I and produces comparable results.

EXAMPLE III

The analogous reaction as constituted in Example I is carried out with commercial lauric acid amide instead of stearic acid amide. The amide is heated to 270° C. for about one hour, whereafter the original acid number of 12.8 increases to 113.3 and the evolution of ammonia ceases. Subsequently, the reaction vessel is closed and the reaction temperature raised to 310° C. The heating is continued for another 15 hours, whereafter the acid number has decreased to 8.4. Upon distillation of the reaction mass at reduced pressure, a yield of 82 per cent of colorless liquid is obtained, boiling at 135–180° C. at 4 mm. The distillate shows a nitrogen content of 3.45 per cent. Molecular weight found 360.

This product is subsequently chloromethylated and by conversion of the chloromethylated product into a pyridinium compound as described in Example I, an easily water soluble final product is obtained.

EXAMPLE IV

284 parts of stearic acid are mixed with 283 parts of stearamide. After melting, the temperature of the mixture is raised to 330–340° C. and is kept there for a total of 36 hours. The acid number of the mixture is checked frequently and shows a maximum increase to 114.5 from 99.3 after which it falls gradually to 14.2. A dark, almost liquid material results which is subjected to vacuum distillation. At 150–200° C. at 5 mm. a clear, colorless distillate is collected weighing 444 parts (81 per cent) of input. It melts at 33° C. and has a nitrogen content of 2.49 per cent, acid number after distillation 16.1. The material is subsequently treated as indicated in Example I, yielding a final product with properties very similar to the final product obtained from stearamide only.

The water solutions or dispersions obtained according to our invention may be used for treating textiles, for instance, as described in a copending application Serial No. 710,218, filed November 15, 1946, now Patent No. 2,489,473.

It will be understood that many variations and modifications may be made in the details of procedure above set forth without departing from the spirit of this invention.

We claim:

1. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating, at a temperature above approximately 300° C. and below approximately 350° C., a material selected from the group consisting of amides of fatty acids containing 12–30 carbon atoms, mixtures of fatty acids containing 12–30 carbon atoms with nitriles of fatty acids containing the same number of carbon atoms as said fatty acids,

and mixtures of fatty acids containing 12–30 carbon atoms with amides of fatty acids containing the same number of carbon atoms as said fatty acids, said heating being continued until the acid number of said heated material is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

2. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating an amide of a fatty acid containing 12–30 carbon atoms, at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

3. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating a mixture of fatty acids containing 12–30 carbon atoms and nitriles of fatty acids containing the same number of carbon atoms as said fatty acids at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

4. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating a mixture of fatty acids containing 12–30 carbon atoms and an amide of fatty acids containing the same number of carbon atoms as said fatty acids at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

5. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the heating of stearamide at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 15.2, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

6. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating a mixture of stearic acid and stearonitrile at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 12.3, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

7. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product

resulting from the sequential steps of heating a mixture of stearic acid and stearamide at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

8. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties, thereto which comprises the product resulting from the sequential steps of heating mixtures of fatty acids containing 12–30 carbon atoms and nitriles of fatty acids containing the same number of carbon atoms as said fatty acids, said fatty acids and said nitriles being present in equivalent molecular proportions, at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

9. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating a mixture of fatty acids containing 12–30 carbon atoms and amides of fatty acids containing the same number of carbon atoms as said fatty acids, said fatty acids and said amides being present in equivalent molecular proportion, at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

10. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating a mixture of stearic acid and stearonitrile, an equivalent molecular proportions, at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 12.3, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

11. A composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating a mixture of stearic acid and stearamide in equivalent molecular proportions, at a temperature above approximately 300° C. and below approximately 350° C., until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

12. The process of preparing a composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto, which comprises the sequential steps of heating, at a temperature above approximately 300° C. and below approximately 350° C., a material selected from the group consisting of amides of fatty acids containing 12–30 carbon atoms, mixtures of fatty acids containing 12–30 carbon atoms

with nitriles of fatty acids containing the same number of carbon atoms as said fatty acids and mixtures of fatty acids containing 12–30 carbon atoms with amides of fatty acids containing the same number of carbon atoms as said fatty acids, until the acid number of the product of the heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

13. The process of preparing a composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto, which comprises the sequential steps of heating an amide of a fatty acid containing 12–30 carbon atoms at a temperature above approximately 300° C. and below approximately 350° C. until the acid number of the product of said heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

14. The process of preparing a composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto, which comprises the sequential steps of heating a mixture of fatty acids containing 12–30 carbon atoms and nitriles of fatty acids containing the same number of carbon atoms as said fatty acids, at a temperature above approximately 300° C. and below approximately 350° C. until the acid number of the product of said heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

15. The process of preparing a composition satisfactory for impregnating fibrous materials to impart water-repellent properties thereto, which comprises the sequential steps of heating a mixture of fatty acids containing 12–30 carbon atoms and amides of fatty acids containing the same number of carbon atoms as said fatty acids at a temperature above approximately 300° C. and below approximately 350° C. until the acid number of the product of said heating is below approximately 16.1, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

16. A composition satisfactory for impregnating fibrous material to impart water-repellent properties thereto which comprises the product resulting from the sequential steps of heating lauramide at a temperature above approximately 300° C. and below 350° C., until the acid number of the product is below approximately 8.4, thereafter chloromethylating said product of said heating, and thereafter reacting the resulting chloromethylated product with a tertiary amine.

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REFERENCES CITED

The following references are of record in the file of this patent:

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