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CONDENSATION PRODUCTS AND PROCESS OF MAKING SAME

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This invention relates to the manufacture of condensation products having capillary activity wherein an aromatic amine, which contains at least one sulfonic acid-hydroxyalkyl-amide group or sulfonic acid-hydroxyalkylamide group, if desired esterified with sulfuric acid, is acylated with an aliphatic carboxylic acid containing more than 3 carbon atoms and, if desired, is esterified at the free hydroxyl group with sulfuric acid.

The aromatic amine containing at least one sulfonic acid-hydroxyalkyl- or sulfonic acid-hydroxyalkyl-arylamide group may be made by known methods, for example by causing a nitro-compound of the benzene series which is substituted in another position than in ortho-position to the nitro-group by a radical of the general formula

\[
\begin{align*}
\text{H} & \\
\text{S} & \\
\text{O} & \\
\text{N} & \\
\text{R} & 
\end{align*}
\]

in which \( R \) stands for hydrogen, alkyl, aralkyl or aryl radicals, to react with an alkanoyl halogen hydrin, or by causing a nitro compound of the benzene series to react with an hydroxyalkylamine or an arylohydroxyalkylamine and subsequent reduction of the nitro-group to the amino-group.

As nitro-compounds of the benzene series which are substituted in another position than in ortho-position to the nitro-group by a radical of the general formula

\[
\begin{align*}
\text{H} & \\
\text{S} & \\
\text{O} & \\
\text{N} & \\
\text{R} & 
\end{align*}
\]

in which \( R \) has the meaning explained above, there may be cited inter alia 1-nitrobenzene-3-sulffamide, 1-nitrobenzene-3-sulfanilide, 1-nitro-2-methylbenzene-3-sulfamide, 1-nitro-2-chlorobenzene-3-sulfamide, 1-nitro-4-chlorobenzene-3-sulfamide, 1-nitro-2:5-dimethylbenzene-3-sulfamide, 1-nitrobenzenes-sulfomethylamide, 1-nitrobenzenesulfamide, 1-nitrobenzenesulfanilide, 1-nitrobenzene-4-sulfoiodide and the like.

As aliphatic halogenhydrins there may be mentioned ethylene chlorohydrin, ethylene bromohydrin, ethylene iodine-hydrin, the propylene chlorohydrins, the trimethylene chlorohydrin, a-monochlorohydrin, a-h monochromohydrin, a-monochlorohydrin, dichlorohydrin and the like.

As nitrated arylsulfonic acid chlorides of the benzene series there come into consideration those products which correspond to the just cited nitrated arylsultamides and the equivalents thereof.

Among the hydroxyalkylamines there may be named ethanolamine and diethanolamine, and among the arylohydroxyalkyl-aminos N-mono-hydroxyethyl-aniline, N-monohydroxy-ethyl-meta- or N-monohydroxy-ethyl-para-toluidine and the like.

Esterification of the free hydroxyl-group may be carried out by means of sulfuric acid, chlorosulfonic acid or agents containing one or other of these acids. The esterification may precede or follow the conversion of the nitro-compounds into the amino-compounds or acylamino-compounds.

For the acylation are suitable aliphatic saturated or unsaturated carboxylic acids containing more than 3 carbon atoms, which acids may be unsubstituted or may contain hydroxy-groups or halogen atoms. Among others, the following come into question: butyric acids, such as n-butyric acid and isobutyric acid, crotonic acids and chlorocrotonic acids, valerianic acids, such as n-valeric acid and isopropyl acetic acid, caproic acid, caprylic acid, capric acid, lauric acid, palmitic acid, stearic acid, hydroxy-stearic acids, chlorostearic acids and bromo-stearic acids, oleic acid, ricinoleic acid and the like, further their natural or artificial mixtures. There come also into question such acids whose chain is interrupted by an organogenic element (cf. "Lehrbuch der organischen Chemie" by Paul Karrer, Leipzig, 1928, page 4: "Zusammensetzung und Analyse organischer Verbindungen" line 4), which in respect to hydrogen is not higher than trivalent. These elements are oxygen, sulfur and nitrogen.

As acids whose chain is interrupted by an organogenic element are, for example, stearoyl-glutine (cf. "Biochemische Zeitschrift", vol. 40, 1912, page 245), further ethers from higher alcohols and halogen acetic acids, such as the ether from cetyl alcohol and mono-chloroacetic acid, the thoether from cetyl mercaptan and mono-chloroacetic acid, or the ester from stearic acid and glycolic acid. The same products are obtained, whether one uses the...
free acid, its esters, such as its glyceride which is found, for instance in nature as beef tallow, coconut oil, olive oil, fish oil and hardened fish oil, and its anhydride. The acylation may follow the esterification of the hydroxy group, preferably in aqueous solution by means of a halide of the acid in presence of an alkali or another agent that binds acid. However, it is also possible to acylate before esterifying and in this case the procedure may be by way of fusing the amino-compound with the free acid or an ester thereof, for example a glyceride.

The condensation products obtainable by this invention are bright powders, easily soluble in water. They correspond to the general formula

\[
\text{HN-OR}_1-\text{R}_2-\text{SO}_2\text{H}
\]

in which \( R_1 \) represents an aliphatic radical containing at least 3 carbon atoms, \( R_2 \) an alkylene radical containing not more than 3 carbon atoms, and \( R_3 \) hydrogen, alkyl, aralkyl or aryl, and in which the group

\[
\text{SO}_2\text{O-OR}_4
\]

does not stand in ortho-position to the group.

The solutions are suitable, according to the aliphatic acid used, for use as wetting agents, penetrating agents, washing agents and emulsifiers. Among these products those claim quite generally the greater interest which derive from acidity to acids with straight chains consisting of at least 10 carbon atoms. Those products which are obtained, for example by use of lauric acid or oleic acid are characterized by a good washing action, as well as a good wetting action. Moreover, they lend to the treated textiles, for example to artificial silk, a soft, fleecy grip. This is for example the case with products derived from stearic acid. The products are generally fully stable towards the constituents imparting hardness to water, acids and alcalies. They may be used in neutral, acid or alkaline baths, as well as in baths containing much salt. They are suitable not only as washing and wetting agents but also as paste-forming agents for dyestuffs insoluble in water and, therefore, find use in dyes with vat-dyestuffs, or in dyeing cellulose acetate silk. Furthermore, they are suitable for use in acid baths for dyeing wool, since they promote uniform exhaustion and a levelling effect.

The following examples illustrate the invention, the parts being by weight:

**Example 1**

333 parts of 1-nitrobenzene-3-sulfonic acid-N-hydroxy-ethylanilide are stirred with 1800 parts of sulfuric acid at 10–20 °C. to produce the sulfuric acid ester. The solution thus made is added, while cooling, to 6000 parts of a concentrated solution of sodium chloride, whereby the sodium salt of the ester is precipitated. It is filtered and neutralized. By reduction with iron in an aqueous solution by usual methods, there is obtained the amino-compound of the probable formula

\[
\text{NH}_2-\text{SO}_2\text{NHCH}-\text{CH}_2-\text{O-OR}_4\text{Na}
\]

The 1-nitro-3-benzenesulfonic acid-N-hydroxyethylanilide used in this example can be made as follows:

278 parts of 1-nitrobenzene-3-sulfonic acid-anilide, 267 parts of a sodium hydroxide solution of 30 per cent. strength, 178 parts of ethylene-chloro-hydrin and 1000 parts of water are heated together in an autoclave at 120–130 °C. After cooling, the solid matter is washed with water. The 1-nitro-3-benzenesulfonic acid-N-hydroxyethylanilide is thus obtained in good yield.

(a) 440 parts of the amino-compound obtained as described above are dissolved in 1000 parts of water, 82 parts of anhydrous sodium acetate are added and then, at 5–15 °C, while stirring well, 300 parts of oleic acid chloride are gradually dropped in. The whole is then neutralized and stirred at about 15 °C for 2–3 hours. The pasty product thus formed may, if desired, be used directly in this form. It dissolves clearly in water and the solution has good wetting and washing properties. The new product corresponds very probably to the formula

\[
\text{HN-CH-CH-CH-C_3H_7-CH_2-CH_3-CH}_2-\text{SO}_2\text{HNa}
\]

The isomeric product deriving from the 1-amino-benzene-4-sulfonic acid possesses similar properties.

(b) 440 parts of the amino-compound described above are dissolved in 1000 parts of water and 82 parts of anhydrous sodium acetate are added. The mixture is stirred at 5–10 °C with 218 parts of lauric acid chloride and then further treated as described under a. The product shows properties similar to those of the product made from oleic acid chloride.

(c) By substituting for the oleic acid chloride 302 parts of stearic acid chloride and operating as described under a, there is obtained a similar product which is particularly suitable as a softening agent.

**Example 2**

By introducing 221 parts of 1-nitrobenzene-3-sulfonic acid chloride into an aqueous solution of 122 parts of ethanolamine, there is obtained in the usual way the 1-nitro-3-benzenesulfonic acid-hydroxyethylanilide. 246 parts of this substance are introduced, at 10–20 °C, into 1000 parts of sulfuric acid of 100 per cent. strength. The solution obtained is poured into about 3000 parts of concentrated solution of sodium chloride, whereby, after some stirring in the cold, the sodium salt of the sulfuric acid ester of 1-nitro-
3-benzene-sulfonic acid-hydroxyethylamide is obtained. This is reduced, as described in Example 1, to the amino-derivative of the probable formula

\[
\text{HN}_2\text{SO-N-CH=CH-O-SOH}
\]

Into a solution of 380 parts of this amino-body and 82 parts of anhydrous sodium acetate in 800 parts of water there are dropped, at 5-15°C, 300 parts of oleic acid chloride. The whole is then neutralized with sodium hydroxide and stirred for 2-3 hours at room temperature. The product, which may be used in the form of a paste or of a dry powder, has good wetting, washing and levelling properties. It corresponds very probably to the formula

\[
\text{HN-O-(CH)}_n\text{-CH=CH}-(\text{CH})_m\text{-CH}_2\text{-CH}=-\text{CH}_2
\]

If, instead of the oleic acid chloride 218 parts of lauric acid chloride are used, without otherwise altering the operation there is obtained a product in the form of a paste which is very effective as a washing and wetting agent. This product can also be used as an addition to dye-baths. It corresponds very probably to the formula

\[
\text{HN-O-(CH)}_n\text{-CH}_2\text{-CH}=-\text{CH}_2
\]

The corresponding product from the stearic acid corresponds very probably to the formula

\[
\text{HN-O-(CH)}_n\text{-CH}_2\text{-CH}=-\text{CH}_2
\]

The products from lower acids such as, for example,

\[
\text{HN-O-(CH)}_n\text{-CH}_2\text{-CH}=-\text{CH}_2
\]

are intended to be used as wetting and dispersing agents.

Products having a similar effect are also obtained when treating the 1-nitro-3-benzenesulfonic acid-hydroxyethylamide, prior to the reduction and acylation with the aliphatic acid, with an aralkylating agent, such as benzyl chloride, ortho- or para-chlorobenzyl chloride, or 2-chloro-1-methylnaphthalene and the like. The same products are also obtained when treating the reduced and acylated products with the aralkylating agents.

Example 3

If, instead of the hydroxyethylamide used in Example 2 that of 1-chloro-4-nitro-2-benzenesulfonic acid is used, there is obtained, by treatment with sulfuric acid and subsequent reduction, an amino-body which probably has the following formula

\[
\text{Cl SO-N-CH=CH-O-SOH}
\]

To a solution of 440 parts of this body and 82 parts of anhydrous sodium acetate in 800 parts of water, there are dropped at 5-15°C, 300 parts of oleic acid chloride. The whole is then neutralized and further stirred for 2-3 hours. The product obtained has properties similar to those of the products obtained in Example 1 or Example 3.

What we claim is:

1. As textile assistants, the condensation products of the general formula

\[
\text{HN-O-(CH)}_n\text{-CH=CH}-(\text{CH})_m\text{-CH}_2\text{-CH}=-\text{CH}_2
\]

in which \( R_1 \) represents an aliphatic radical having at least 10 carbon atoms in a straight chain, \( R_2 \) an alkyene radical having not more than 3 carbon atoms, and \( R_3 \) is a member of the group consisting of hydrogen, alkyl, aralkyl and aryl, and in which the group

\[
\text{SO-NH-CH}_{2}\text{CH}=\text{CH}_{2}\text{CH}=-\text{CH}_{2}
\]

do not stand in ortho-position to the

\[
\text{HN-O-(CH)}_n\text{-CH=CH}-(\text{CH})_m\text{-CH}_2\text{-CH}=-\text{CH}_2
\]

group, which products are light colored powders, easily soluble in water and suitable as wetting agents, penetrating agents, washing agents and emulsifiers in the textile industry.

2. As textile assistants, the condensation products of the general formula

\[
\text{HN-O-(CH)}_n\text{-CH=CH}-(\text{CH})_m\text{-CH}_2\text{-CH}=-\text{CH}_2
\]

in which \( R_1 \) represents an aliphatic radical having at least 10 carbon atoms in a straight chain, and \( R_2 \) an alkyene radical having not more than 3 carbon atoms, and in which the group

\[
\text{SO-NH-CH}_{2}\text{CH}=\text{CH}_{2}\text{CH}=-\text{CH}_{2}
\]

does not stand in ortho-position to the

\[
\text{HN-O-(CH)}_n\text{-CH=CH}-(\text{CH})_m\text{-CH}_2\text{-CH}=-\text{CH}_2
\]
group, which products are light colored powders, easily soluble in water and suitable as wetting agents, penetrating agents, washing agents and emulsifiers in the textile industry.

3. As textile assistants, the condensation products of the general formula

\[
\text{H-N-C-} \quad \text{R}_1 \quad \text{O-SO}_3\text{H}
\]

in which \( \text{R}_1 \) represents an aliphatic radical having at least 10 carbon atoms in a straight chain, and \( \text{R}_2 \) an alkylene radical having not more than 3 carbon atoms, and in which the group

\[
\text{SO}_3\text{N-} \quad \text{aryl}
\]
does not stand in ortho-position to the

40 in which \( \text{R} \) represents an aliphatic radical having at least 10 carbon atoms in a straight chain, which products are light colored powders, easily soluble in water and suitable as wetting agents, penetrating agents, washing agents and emulsifiers in the textile industry.

5. As textile assistants, the condensation products of the general formula

\[
\text{H-N-C-} \quad \text{R}_1 \quad \text{O-SO}_3\text{H}
\]

which product is a light colored powder, easily soluble in water and suitable as wetting agent, penetrating agent, washing agent and emulsifier in the textile industry.

50 which product is a light colored powder, easily soluble in water and suitable as wetting agent, penetrating agent, washing agent and emulsifier in the textile industry.

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