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PRODUCTION OF ASSISTANTS IN THE TEXTILE AND RELATED INDUSTRIES

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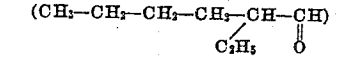
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20 Claims. (Cl. 260—130)

The present invention relates to the production of assistants in the textile and related industries.

We have found that products which may be employed with great advantage as assistants in the textile and related industries, i. e. as wetting, washing, foaming, dispersing and like agents, for example in the textile and leather industries can be obtained by causing a monomeric aliphatic carbonyl compound, i. e. an aliphatic aldehyde or ketone, containing more than 6 carbon atoms, to react with such organic substances that products are formed which are either directly soluble in water or which permit the introduction of groups which render them water-soluble, the said groups being introduced when necessary.

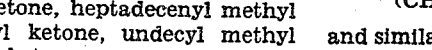
As initial materials the single aldehydes and ketones corresponding to the higher saturated and unsaturated fatty acids may be employed. Examples for aldehydes are lauric aldehyde, stearic aldehyde, oleic aldehyde or ricinoleic aldehyde, caprylic aldehyde, caprinic aldehyde, myristic aldehyde, palmitic aldehyde, 2-ethyl capronic aldehyde



undecylenic aldehyde, or nonylic aldehyde, which may be obtained for example by a catalytic dehydrogenation of the corresponding alcohols. Examples of suitable ketones are heptadecyl methyl ketone, heptadecyl ethyl ketone, heptadecyl n-propyl ketone, di-heptadecyl ketone, heptadecenyl ethyl ketone, heptadecenyl methyl ketone, nonyl methyl ketone, undecyl methyl ketone, decenyl ethyl ketone, pentadecyl methyl ketone, or laurone, which may be obtained from the corresponding fatty acids by splitting off water and carbon dioxide. Instead of single aldehydes or ketones, mixtures of aldehydes and ketones or mixtures of different aldehydes or ketones, as for example the readily accessible mixtures of aldehydes or ketones which correspond to the mixtures of fatty acids occurring in nature may be employed, such as coconut oil fatty acids, soya bean oil fatty acids, rape seed, cotton seed or linseed oil fatty acids, train oil fatty acids or montanic acids. For example, the mixture of ketones obtainable from coconut oil fatty acids and acetic acid may be employed with advantage.

The conversion of the initial materials into products which are directly soluble in water or which permit of the introduction of groups rendering them soluble in water may be carried out for example by condensing the aldehydes or ketones with polyhydric alcohols containing at least 3 hydroxyl groups, such as glycerine, sorbitol, or other hexitols, or by reaction with "Grignard's reagents" obtained from methyl, ethyl, n-propyl, or isopropyl bromide or monobromobenzene, and subsequent decomposition of the reaction products with water. The initial materials may also be condensed with hydrocyanic acid by the usual methods to form the corresponding hydroxy-nitriles, or they may be converted with any aldehydes or ketones containing preferably up to 9 carbon atoms, for example formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl-ethyl ketone, benzaldehyde, or benzophenone, into the corresponding adols or ketone-alcohols. Hydroxy amines, as for example mono-, di- and tri-alkylolamines, are also suitable for condensation with the aldehydes or ketones.

By converting the products thus obtainable which contain hydrogen atoms fixed to oxygen and/or nitrogen atoms, for example those containing hydroxy and/or amino groups with ethylene oxide, products are obtained which are soluble in water. Products which are directly soluble in water may also be obtained by causing the aldehydes or ketones to react with alcohol sulphonic acids, such as alpha-beta-dihydroxypropane sulphonic acid, with para-phenylhydrazine sulphonic acid, or with trimethyldihydroxypropane ammonium salts



and similar compounds.

It will be understood that the main subject matter of the present invention exists in a condensation (without the splitting off of water), such as occurs in the addition of hydrocyanic acid or of an aldehyde, such as formaldehyde, or in a condensation with the splitting off of water, such as occurs in the formation of acetals, hydrazones or oxazolidines.

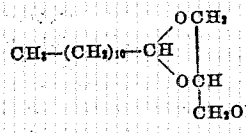
The products obtainable by the said methods are usually viscous liquids or solid wax-like bodies. The introduction of groups rendering the products soluble in water may be effected in all cases, for example by treatment with a sulphonating agent, such as sulphuric acid of from 80 to 100 per cent strength, fuming sulphuric acid, chlorsulphonic acid, phosphoric acid, or ethylene oxide. Products are always obtained which foam very strongly in aqueous solution, which have a high wetting, washing and dispersing power and which are capable of employment in an advantageous manner for example as assist-

ants for the textile and related industries.

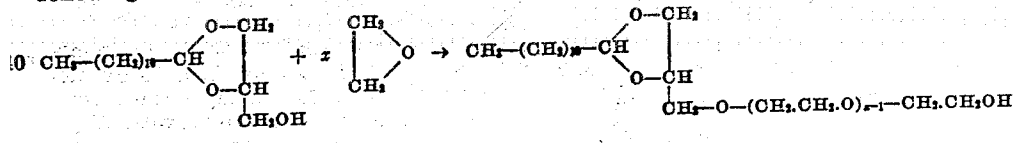
The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples. The parts are by weight.

Example 1

184 parts of lauric aldehyde, obtainable by the catalytic dehydrogenation of dodecyl alcohol, and 92 parts of glycerine are intimately stirred with 1 part of concentrated hydrochloric acid for 2 hours at 130° C. The homogeneous liquid formed is cooled, diluted with a little ethyl ether and washed about 4 times with an aqueous solution of sodium carbonate. After drying the clear, slightly yellow liquid with dry potash, it is subjected to distillation in vacuo, whereby the main part distils at about 190° C. at a pressure of 15 millimetres (mercury gauge). The main fraction has a hydroxyl value of 215 and consists presumably of the glycerine acetal of lauric aldehyde corresponding to the formula



By treating the product thus obtained with chlorsulphonic acid, an acid sulphuric ester is obtained the sodium salt of which foams very strongly in aqueous solution and has excellent wetting and washing action. Phosphoric acid or ethylene oxide may be employed instead of chlorsulphonic acid and in this case products having similar properties are obtained. The reaction with ethylene oxide proceeds according to the following scheme



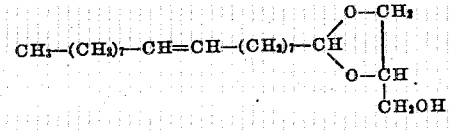
it is to be noted that the whole number x may vary so that the different molecules of the cyclic acetal may react with different numbers of molecules of ethylene oxide.

Example 2

184 parts of lauric aldehyde obtainable by the catalytic dehydrogenation of dodecyl alcohol and still containing about 20 per cent of dodecyl alcohol, and 880 parts of ethylene oxide are heated with 10 parts of nickel sulphate as a catalyst in a stirring autoclave at from 150° to 170° C. for 12 hours. A pale colored liquid is obtained which dissolves in water giving a clear solution which has a good foaming power and which has excellent wetting power.

Example 3

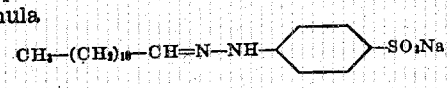
300 parts of oleic aldehyde, 150 parts of glycerine and 1 part of concentrated hydrochloric acid are intimately stirred for 7 hours at from 150° to 200° C. After cooling, the mass is diluted with an equal volume of ethyl ether and the remainders of glycerine separating out are drawn off; the solution is then washed out with an aqueous solution of common salt, dried with potash and freed from the ethyl ether by distillation. In a subsequent distillation at 2 millimetres of mercury 250 parts are distilled off at from 200° to 220° C.; the hydroxyl value of this main fraction is 164, the body contained therein corresponding presumably to the formula:



The yellowish oil thus obtained is sulphonated in the usual manner and yields an excellent wetting and washing agent. The product is subjected to sulphonation with a quantity of chlorsulphonic acid corresponding to the hydroxyl value. The aqueous solution of the sodium salt of the resulting product shows good foaming and wetting effects.

Example 4

22 parts of lauric aldehyde are added to a solution of 22 parts of para-phenylhydrazine sulphonic acid in 50 parts of an aqueous caustic soda solution containing such a quantity of caustic soda that the sulphonic acid is dissolved. While stirring, an aqueous normal hydrochloric acid solution is added until the alkaline reaction to litmus disappears. By heating for 2 hours to about 95° C., a tough, ropy oil is obtained which is easily soluble in water, in dilute aqueous solutions of alkalies and even in strongly alkaline aqueous solutions, such as mercerizing liquors. The product which corresponds presumably to the formula



is not precipitated from its aqueous solutions by calcium or magnesium salts.

In wetting out cotton, aqueous solutions of the following concentrations effect complete wetting.

	Grains of hydrazone per litre	
	At room temperature	At 70° C.
Neutral aqueous solution	0.5	0.3
Aqueous 0.75 per cent solution of caustic soda	0.9	0.8
Aqueous 0.5 per cent solution of sodium carbonate	0.8	0.95

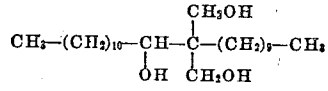
Example 5

A "Grignard" compound is prepared from 40 parts of magnesium shavings, 1000 parts of ethyl ether and 164 parts of ethyl bromide. 148 parts of lauric aldehyde dispersed in 500 parts of ethyl ether are introduced into the said mixture, the magnesium compound then being decomposed therein with the aid of cold, aqueous sulphuric acid. The resulting ethereal solution is washed with water and dried with potassium carbonate. After removal of the ether by distillation, from 96 to 97 per cent by weight of the product is obtained in a subsequent distillation at 16 millimetres of mercury at from 150° to 156° C. 105 parts of the undecyl ethyl carbinol obtained are mixed at about room temperature with 60 parts of 98 per cent chlorsulphonic acid dissolved in 90

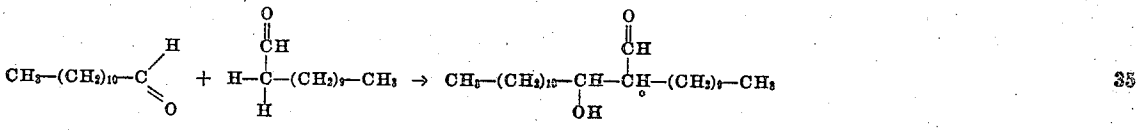
parts of diethyl ether. The product obtained, after neutralization with aqueous caustic soda solution, is an efficient wetting agent.

Example 6

560 parts of caustic potash are dissolved in 5000 parts of methyl alcohol. While intimately stirring, an intimate mixture of 920 parts of lauric aldehyde and 2000 parts of an aqueous 40 per cent solution of formaldehyde are slowly introduced, the mixture becoming warm by the reaction. The clear reaction mixture is then warmed for 1 hour to about 95° C. While passing through carbon dioxide, the methyl alcohol and the main portion of water are distilled off, a lower layer of salt, a supernatant aqueous layer and a supernatant oily layer thus being formed. The oily layer is dissolved in a little ethyl ether, separated from the other layers and washed four times with an equal volume of water, and then dried with potassium carbonate and the ether is removed by distillation in vacuo at 100° C. The resulting slightly colored oil has a hydroxyl value of 423 from which the body obtained may be assumed to correspond to the formula



This product is probably formed in the following manner



The latter aldol-like compound reacts with formaldehyde, the aldehyde group of the aldol-like compound being reduced to the grouping —CH_2OH and one molecule of CH_2O being added on to the carbon atom which bears the said aldehyde group so that the H-atom marked * is replaced by CH_2OH. 132 parts of the oil are dissolved in 175 parts of ethyl ether and, while stirring at from 10° to 20° C., a solution of 120 parts of chlorsulphonic acid in 175 parts of ethyl ether is added. After the reaction the whole is neutralized while cooling with about 225 parts of an aqueous 30 per cent caustic soda solution and the ether and water are distilled off in vacuo. The yield is about 390 parts. The aqueous solution of the resulting sodium salt of the acid sulphuric ester has a very high wetting power.

Example 7

270 parts of 79 per cent commercial ethylene diamine are slowly added to 610 parts of lauric aldehyde. The mixture is incorporated with 5 per cent of its weight of cobalt prepared from basic cobalt carbonate by heating in a current of hydrogen to 325° C. The whole is then heated in a stirring autoclave for 5 hours to 230° C. at a pressure of hydrogen of 180 atmospheres. The reaction product is then freed from the cobalt by filtration at from 50° to 100° C. and distilled at 15 millimetres of mercury. The main quantity of the resulting product boils between 130° and 200° C. Aqueous solutions of said fraction may find useful application for fixing substantive dyestuffs on cotton or artificial silk such as viscose. The hydrochloric salt of the product is rather difficultly soluble in water but its solution has a high foaming and wetting power. The wetting power of the product may still be increased by heating at 180° C. for 12 hours in a stirring autoclave, 220 parts of the fraction boiling between 130° and 200° C. with 350 parts of ethylene oxide and 1 part of potassium hydroxide.

What we claim is:—

1. The process of producing assistants in the textile and related industries which comprises reacting lauric aldehyde with ethylene diamine, and acting on the resulting product with ethylene oxide.

2. A water-soluble product obtainable by the interaction of lauric aldehyde and ethylene diamine.

3. A water-soluble product obtainable by the interaction of lauric aldehyde and ethylene diamine, said product being condensed with ethylene oxide.

4. The process of producing assistants in the textile and related industries which comprises reacting a monomeric, aliphatic carbonyl compound containing directly attached to the carbonyl group at least one aliphatic hydrocarbon radicle with at least 6 carbon atoms, with an organic substance containing at least one basic nitrogen atom and at least two reactive hydrogen atoms attached to nitrogen not directly attached to a nucleus, the said organic substance containing up to 6 carbon atoms and a grouping adapted for applying water-solubility to the final product, and introducing a water-solubilizing group by way of the radicle of the later substance.

5. The process of producing assistants in the textile and related industries which comprises reacting a monomeric, aliphatic carbonyl compound containing directly attached to the carbonyl group at least one aliphatic hydrocarbon radicle with at least 6 carbon atoms, with a primary aliphatic amine containing besides the amino group a further amino group, and introducing a water-solubilizing group by way of the radicle of the latter substance.

6. The process of producing assistants in the textile and related industries which comprises reacting a monomeric, aliphatic carbonyl compound containing directly attached to the carbonyl group at least one aliphatic hydrocarbon radicle with at least 6 carbon atoms, with an aliphatic, primary diamine, and introducing a water-solubilizing group by way of the radicle of the said diamine.

7. The process of producing assistants in the textile and related industries which comprises reacting a monomeric, aliphatic carbonyl compound containing directly attached to the carbonyl group at least one aliphatic hydrocarbon radicle with at least 6 carbon atoms, with ethylene diamine, and introducing a water-solubilizing group by way of the radicle of the ethylene diamine

8. The process of producing assistants in the textile and related industries which comprises causing a monomeric aliphatic compound corresponding to the formula



(wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydro-

carbon radicle and wherein the sum of the carbon atoms contained in X and Y is at least 6) to react with a compound



(wherein Z is an organic radicle containing up to 6 carbon atoms, a grouping adapted for applying water-solubility to the final product and at least the two hydrogen atoms shown in amino groups not directly attached to a nucleus) to form a compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z) and introducing a water-solubilizing group into Z at any time.

9. The process of producing assistants in the textile and related industries which comprises causing a monomeric aliphatic compound corresponding to the formula



(wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydrocarbon radicle and wherein the sum of the carbon atoms contained in X and Y is at least 6) to react with a compound



(wherein Z is an organic radicle with up to 6 carbon atoms containing a water-solubilizing group and containing at least the two hydrogen atoms shown in amino groups not directly attached to a nucleus) to form a compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z).

10. The process of producing assistants in the textile and related industries which comprises causing a monomeric aliphatic compound corresponding to the formula



(wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydrocarbon radicle and wherein the sum of the carbon atoms contained in X and Y is at least 6) to react with a compound



(wherein Z is an organic radicle with up to 6 carbon atoms containing at least the two hydrogen atoms shown in amino groups not directly attached to a nucleus) to form a compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z) and introducing a water-solubilizing group into a hydroxyl or amino group contained in Z.

11. The process of producing assistants in the textile and related industries which comprises causing a monomeric aliphatic compound corresponding to the formula



(wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydrocarbon radicle and wherein the sum of the carbon atoms contained in X and Y is at least 6) to react with a compound



(wherein Z is an aliphatic radicle containing at least the two hydrogen atoms shown in amino groups) to form a compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z), and introducing a water-solubilizing group into Z at any time.

12. The process of producing assistants in the textile and related industries which comprises causing a monomeric aliphatic compound corresponding to the formula



(wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydrocarbon radicle and wherein the sum of the carbon atoms contained in X and Y is at least 6) to react with a compound

(wherein Z is an aliphatic radicle containing a water-solubilizing group and containing at least the two hydrogen atoms shown in amino groups) to form a compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z).

13. The process of producing assistants in the textile and related industries which comprises causing a monomeric aliphatic compound corresponding to the formula

(wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydrocarbon radicle and wherein the sum of the carbon

atoms contained in X and Y is at least 6) to react with a compound



(wherein Z is an aliphatic radicle containing at least the two hydrogen atoms shown in amino groups) to form a compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z) and introducing a water-solubilizing group into a hydroxyl or amino group contained in Z.

14. A water-soluble conversion product of a monomeric aliphatic carbonyl compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z) wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydrocarbon radicle, wherein the sum of the carbon atoms contained in X and Y is at least 6, wherein Z is an organic radicle up to 6 carbon atoms attached to the C-atom shown by means of two linkages each of which originates from a nitrogen atom not directly attached to a nucleus and wherein A stands for a water-solubilizing group.

15. A water-soluble conversion product of a monomeric aliphatic aldehyde corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z), wherein X stands for an aliphatic hydrocarbon radicle containing at least 6 carbon atoms, wherein Z is an organic radicle up to 6 carbon atoms attached to the C-atom shown by means of two linkages each of which originates from a nitrogen atom not directly attached to a nucleus and wherein A stands for a water-solubilizing group.

16. A water-soluble conversion product of lauric aldehyde corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z), wherein X is the hydrocarbon radicle of lauric aldehyde, wherein Z is an organic radicle up to 6 carbon atoms attached to the C-atom shown by means of two linkages each of which originates from a nitrogen atom not directly attached to a nucleus, and wherein A stands for a water-solubilizing group.

17. A water-soluble conversion product of a monomeric aliphatic carbonyl compound corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z), wherein X stands for an aliphatic hydrocarbon radicle, Y stands for a member of the group consisting of hydrogen and an aliphatic hydrocarbon radicle, wherein the sum of the carbon atoms contained in X and Y is at least 6, wherein Z is an aliphatic radicle attached to the C-atom shown by means of two linkages each of which originates from a nitrogen atom and wherein A stands for a water-solubilizing group.

18. A water-soluble conversion product of a monomeric aliphatic aldehyde corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z) wherein X stands for an aliphatic hydrocarbon radicle containing at least 6 carbon atoms, wherein Z is an aliphatic radicle attached to the C-atom shown by means of two linkages each of which originates from a nitrogen atom and wherein A stands for a water-solubilizing group.

19. A water-soluble conversion product of lauric aldehyde corresponding to the formula



(wherein the two linkages between C and Z shown do not necessarily originate from the same atom of Z) wherein X is the hydrocarbon radicle of lauric aldehyde, wherein Z is an aliphatic radicle attached to the C-atom shown by means of two linkages each of which originates from a nitrogen atom and wherein A stands for a water-solubilizing group.

20. The process of producing assistants in the textile and related industries which comprises reacting a monomeric aliphatic carbonyl compound containing directly attached to the carbonyl group at least one aliphatic hydrocarbon radicle with at least 6 carbon atoms, with an aliphatic substance containing up to 6 carbon atoms, a grouping adapted for applying water-solubility to the final product, at least one basic nitrogen atom and at least two reactive hydrogen atoms attached to nitrogen which is not directly attached to a nucleus, and introducing a water-solubilizing group by way of the radicle of the latter substance.

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