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FATTY AMIDE POLYMERS

Willard L. Morgan, Columbus, Ohio, and Earle D. McLeod, Rumford, R. I., assignors to Arnold, Hoffman & Co. Incorporated, Providence, R. I., a corporation of Rhode Island

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16 Claims. (Cl. 260—22)

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This application is a continuation in part of our copending application Serial #357,443, filed September 19, 1940.

This invention relates to new condensation products which are suitable as assistants for the modification of the properties of textile fibers.

Many materials have been used as textile assistants for altering the softness, the easy wetting or the repellency of textile fibers, or for increasing the stiffness or apparent weight, but each has been subject to some fault; thus, tallows, oils, and sulphonated oils or tallows have long been used in the finishing of textiles for softening effects, but these effects are not permanent and are lost the first time the goods are washed. These materials also suffer from rancidity or objectionable odor development in the goods. Fatty alcohols and fatty alkyd resins have also been used as textile softeners, but these also wash out. Fatty amides and the quarternary salts of these, as well as fatty quaternaries produced from pyridine or the betaines, and fatty imidazoles, have been suggested as textile modifying agents and in particular as textile softeners. While these materials are mostly fairly expensive and dark in color, these substances have shown the advantage of being somewhat resistant to washing. The quaternary salts of fatty acid condensations with aliphatic polyamines have also been used, particularly as these have shown a maximum resistance to washing up to this time. However, each of these types of materials has left considerable to be desired as with regards to resistance to washing and as each of these materials has been unstable with respect to heat and oxidation, their use has been attended with the serious difficulty of the cloth being yellowed either by reason of the initially dark color of the product, or by its decomposition due to the heat used in drying the fabric. Furthermore, goods which have been finished with these materials have frequently during a few months' storage become seriously yellow due to the softener being sensitive to oxidation.

Many resinous materials have also been applied to textiles for various types of modification of their properties. Among these we find the alkyds, fatty alkyds, methacrylates, and vinyls which, due to their general water insolubility and sticky nature, cause considerable difficulty as they must be applied in the form of dispersions which are

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generally unstable. These materials leave much to be desired in their permanency on cloth due to alteration on ageing and poor resistance to washing particularly in the case of the alkyds. Urea-formaldehyde resins have also been widely applied but these frequently impart odors to the cloth or tender it and the special high temperatures necessary for its baking call for expensive equipment.

It is an object of this invention to provide a new class of textile assistants such as wetting, softening, lubricating, waterproofing, and stiffening agents having improved properties. It is a further object to produce textile assistants which are resistant to heat and to oxidation which permit the finishing and storage of the finished goods for long periods without any yellowing, odor development, or tendering.

As further objects of our invention, we describe condensation products which may be easily applied from aqueous solutions or dispersions to give finishes on cloth of a maximum softness, which effects are completely permanent to washing and to dry cleaning.

A further object of our invention is to provide condensation products of resinous nature which give permanent bodying or stiffness effects coupled with desirable soft feel. These materials, because of high effectiveness, can be economically used to replace sulphonated tallows in textile finishing.

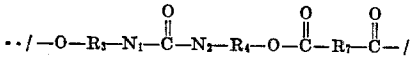
A still further object of our invention is to describe new condensation products and resinous materials which may be applied permanently to textile materials from aqueous solution without any special heating or baking of the treated cloth.

The condensation products proposed by this invention are resinous or semi-resinous materials in which dialkylol substituted carbamido compounds carrying side chains containing polyamino acid amide radicals are linked together by reaction with polybasic acids.

These compounds are readily prepared by reacting the carbamyl derivatives such as urea, thiourea, guanidine salts, biuret, diguanidine, or guanyl urea with the acid amide condensation products secured from aliphatic polyamines carrying hydroxyl groups and acids or acid esters or acid chlorides and thereafter reacting the products thus secured with polycarboxylic acids.

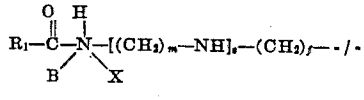
As suitable acids for forming the polyamino acid amides with the polyamines, we prefer those containing six or more carbons and preferably saturated aliphatic acids such as lauric, stearic, palm oil acids, although we may use the lower molecular weight aliphatic acids including acetic and we may use the unsaturated or substituted fatty acids, such as ricinoleic, oleic, sebacic or chlorostearic, or the cycloaliphatic, aromatic, or resin acids may also be used, such as naphthenic, phthalic, benzoic, creostinic, and abietic, or the resin acid secured from rosin and maleic anhydride. These acids may be condensed with any hydroxyl substituted polyamines such as hydroxyethyl ethylene diamine, hydroxylethyl diethylene triamine, diamino propanols, such as 1-3 diamino propanols, N-3 amino 2 propanol ethylene diamine, or the alkylol substituted polyamines which are readily secured from ethylene or propylene oxide by reaction with polyamines. The polyamino acid amide products thus secured are reacted with the carbamyl derivatives already indicated and thereafter the free hydroxyl groups are then reacted with polybasic acids such as succinic, maleic, sebacic, phthalic, and adipic.

The condensation products of this invention are materials of high molecular weight in which units of the following general formula are linked together at the dotted line in large numbers:



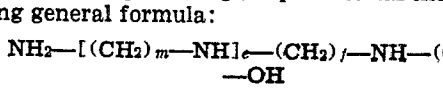
In this formula R_7 is a hydrocarbon residue resulting from the dicarboxylic acid which has been used.

R_3 and R_4 represent simple alkylene groups of from two to three carbon atoms. These groups and the adjacent nitrogen originate from the amine used in the condensation and attached to the nitrogens N_1 and N_2 is the remaining part of the fatty amino acid amide as a side chain. The fatty acid precondensed with the amine forms the terminal part of the side chain. The amino acid amide side chains residues are of the following type in which the radicals may depend for their nature on the amine and the acid reacted therewith.



In this formula just given for the side chains of the polyamino acid amide type, R_1 corresponds preferably to a saturated aliphatic chain such as would result from the use of a saturated fatty acid or any of the other various types of acids already enumerated; thus, R_1 may also represent other hydrocarbon radicals such as a cyclo alkyl, an unsaturated hydrocarbon, an aryl radical, or a residue from a terpene acid. In each case the corresponding acid, acid chloride, or ester may be used as a source to introduce this radical into our condensation products as will be shown later.

The letters *f*, *e*, and *m* represent small integers, *f* varying from 2 to 6, *e* from 0 to 3 and *m* from 2 to 3, and any of the hydrogens in the CH_2 groups may be substituted by a simple alkyl or hydroxy group. It is evident from the two general formulas above that the alkylol polyamine employed in producing the product has the following general formula:



wherein *e* varies from 0 to 3, *f* from 2 to 6, and *m* from 2 to 3.

The condensation products of this invention are in some cases directly water soluble or water dispersible. In most cases the condensations are readily dissolved after treatment with acids, such as acetic, lactic, boric, oxalic, benzoic, salicylic, furoic, citric, tartaric, formic, phthalic, succinic, or alkyl naphthalene sulphonic acids or after reaction with an alkylating agent, such as, ethyl chloride, benzyl chloride, ethylene oxide, ethylene chlorohydrin, diethyl sulphate, or dimethyl sulphate. The salts or alkylated products of our substituted new condensates are indicated in the general formula given where B represents the acid hydrogen or alkyl groups and X the acid radical or halogene group, while for our primary condensations B and X disappear from the formula.

The condensation products of this invention are readily prepared by heating equimolal quantities of the acid and hydroxylated amine at temperatures from 130 to 200° C. until the reaction is complete as shown by the loss of one molecule of water. The mix is then cooled back to 180° and one half mol or more of the urea or other carbamyl derivative added. Ammonia is rapidly liberated as the urea becomes substituted, the temperature being held between 170 and 200° C. After holding the product for a short period up to one-half hour during which time the ammonia is driven off, preferably one mol of the polycarboxylic acid is added at temperatures above 150° C. and the temperature is rapidly raised to 200° C. as the polybasic acid reacts and water is liberated. Depending upon the number of hydroxyl groups present in the primary condensation, we may increase the molal proportions of the polybasic acid used in order that all or part of these may be reacted with the polybasic acid. The product may be cooled and used directly or at temperatures of 80 to 140° C. the various solubilizing acid or alkylating agents may be added in quantities of .2 to .5 mol or more.

The linking by urea or other carbamyl compounds of two or more acid polyamine amide groups which are thereafter linked into long continuous resin-like chains results in products of very large molecular weight which are found to show high substantivity to the various textile fibers, such as, cotton, viscose, cellulose acetate, linen, jute, wool, nylon, and protein fibers and to give textile treatments which are permanent to washing and dry cleaning. This marked substantivity is found to arise from the presence of the urea or other similar carbamyl groups and particularly to the very high molecular weight of the products secured by the polymeric chains formed by the polybasic acid linkages. The urea group also increases the solubility in water which is very important since such large molecules which are desirable for substantivity are poorly soluble. Water solubility is also brought about by the formation of salts at the nitrogen groups. We have found that the sensitiveness to oxidation and to heat or light of the acid polyamine amide condensations and other proposed nitrogen containing textile assistants which results in yellowing either in processing, drying, storage, or use of the treated fabrics is mainly caused by the presence of primary amino or $-NH_2$ groups in the compounds and to a much lesser extent by secondary amino —(NH— groups. It is the primary amino group left in the acid polyamine amide condensations which is reacted upon by the urea

or other carbamyl compound and removed during the formation of our new reaction products, and we are thus able to secure compounds free of these difficulties. Likewise, the urea and other carbamyl compounds will react with and eliminate secondary amino groups and the yellowing arising from such groups and it is an alternative under this invention to use sufficient urea or other carbamyl compound to combine with all the primary and secondary amino groups in the acid polyamine amide, as well as merely the single groups as shown in the general formula already given. The resistance to scorching under heat is also found to be lowered to some degree by the use of unsaturated acids as the source of R_1 and while we may use them in many types of application, for products of maximum resistance we prefer the use of the saturated fatty acids.

Inasmuch as urea, thiourea, and guanidine are each decomposed readily at temperatures below 180° C. or the reaction temperatures employed, it was impossible to foresee that the large molecule substituted urea condensations would be stable at these temperatures or could be formed. Thus, the heating of urea and fatty acids at 160° does not lead to substituted ureas, but decompositions occur yielding only fatty amides as shown in U. S. 1,989,968 and U. S. 2,109,941. In a similar way we have been unable to react urea with simple fatty amides or fatty ethanol amides and we find that it is only when we use the amide of an acid and a polyamine containing either or both a primary or secondary amino group that reaction to our substituted ureas can be secured. The condensations go readily and are free of side reactions, thus, leading to full yields of products which do not need to be purified.

In view of the fact that polyamino acid amides change rapidly at elevated temperatures and that urea compounds are relatively unstable, it could not be foreseen that the polyamino acid amide substituted carbamyl compounds could be heated to the high temperature necessary for reaction or that in view of their large molecular size they would react further with polybasic acids. However, we have found that these reactions can be carried out smoothly with theoretical yields giving products which need no further purification.

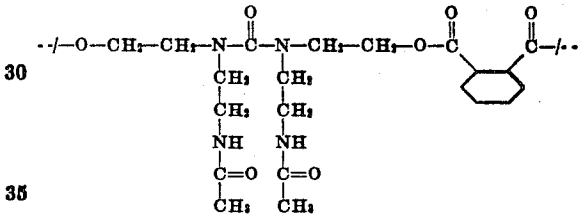
The production of resinous like materials indicates the formation of long polymeric chains which due to equimolar quantities of polybasic acids used have one hydroxyl and one carboxyl end group between which lie one of more repeating units as set forth in the aforementioned general formula. By reason of the resinous nature of the products, many of these when applied to cloth show definite stiffening effects and the effects become permanently attached to the various textile fibers. As we have already indicated, despite the large molecular weight of these compounds, the solubilizing groups present permit us to apply these in aqueous solutions or dispersions

and the materials become permanently fixed to the textile fibers by their substantivity on the same, thus not requiring any special curing or baking beyond the normal drying to develop stiffening and other effects. Where the side chains contain large fatty groups, various degrees of soft feel are permanently secured along with the stiffness or bodying effects.

The invention will be further illustrated, but is not limited by the following examples in which the quantities are stated in parts by weight:

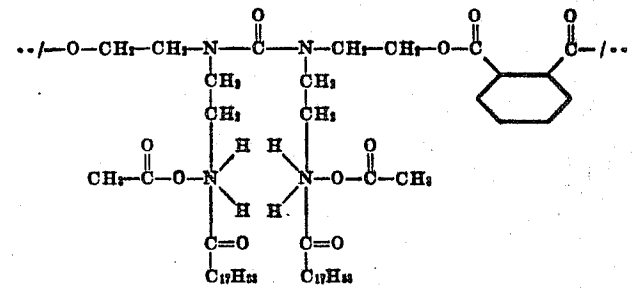
Example 1

60 parts (1 mol) of acetic acid and 104 parts (1 mol) of hydroxyethyl ethylene diamine were slowly heated until one mol of water was removed. The product was an amber liquid to which 30 parts of urea (½ mol) was slowly added at 180°–185° C. and the temperature raised to 190° during which time ammonia was evolved. At 190° C. 74 parts (1 mol equivalent) of phthalic anhydride was added and the temperature raised to 200° C. The product was an amber liquid soluble in water after treating with acetic acid, was not heat sensitive, and had the following unit formula:



Example 2

282 parts (1 mol) of oleic acid and 104 parts (1 mol) of hydroxy ethyl ethylene diamine were slowly heated until one mol of water was eliminated. 30 parts (½ mol) of urea was then added at 180°–185° C. and the temperature raised to 190° C. during which time ammonia was evolved. At 190° C. 74 parts of phthalic anhydride (1 mol equivalent) were added and the temperature raised to 200° C. The product was soluble in water after treating with acetic acid and imparted a firm body to cloth. It had the following unit formula for its acetate salt:

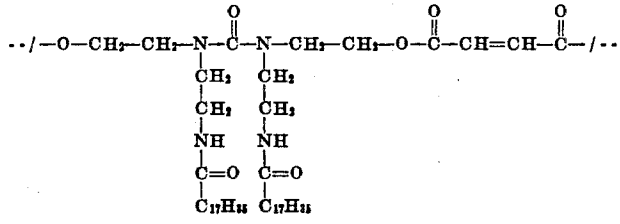


Equimolal quantities of lauric, linoleic, ricinoleic, or soya bean fatty acids may be substituted for the oleic acid illustrated above. The oleic acid compound applied in a quetch to cotton cloth in a ratio of 6 pounds to 50 gallons gave a full bodied fabric finish which was resistant to washing. The cloth was dried in the normal way with no special curing or baking process being necessary to render the resin permanent.

Example 3

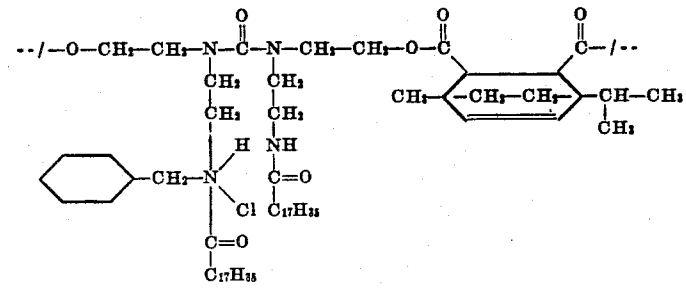
N,N' ethanol ethyl stearylamide urea was pre-

pared by condensing equimolal proportions of stearic acid and hydroxyethyl ethylene diamine at 130–170° until one mol of water was split off followed by cross condensation with urea which was slowly added at 180–185° C. (and the temperature raised to 190° C.). To 766 parts (1 mol) of this material 98 parts (1 mol) of maleic anhydrid were added at 190° C. and the temperature raised to 200° C. during which time water was removed. The product was a dark waxy compound soluble in water after treatment with acid and had the following unit formula:



Example 4

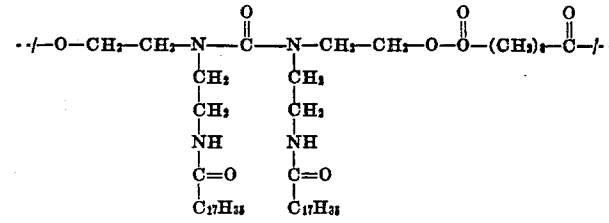
To 766 parts (1 mol) of N,N' ethanol ethyl stearylamide urea prepared as in example 3 were added 215 parts (1 mol) of petrex acid, a polybasic acid which is defined by its producer Hercules Powder Co., as 3-isopropyl-6-methyl-3,6-endo-ethylene Δ^4 tetra hydro phthalic anhydride, and the temperature was raised to 200° C. during which water was removed. The product was a tacky resin melting at 60–65° C. and was soluble in water after treating with acids. It showed little tendency to scorch on cloth. After alkylating with benzyl chloride to secure solubility in water, it had the following formula:



Cotton cloth was impregnated with a bath containing 6 pounds to 50 gallons of the above compound, and was mangled followed by regular drying on a tenter frame. A leathery finish was obtained which was resistant to washing and dry cleaning.

Example 5

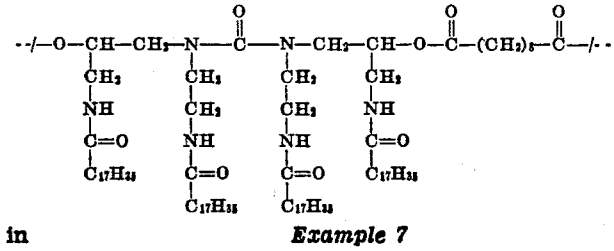
To 766 parts (1 mol) of N,N' ethanol ethyl-stearyl amide urea prepared as in Example 3, were added 202 parts (1 mol) of sebacic acid at 180° C. and the temperature was raised to 200° C. during which time water was distilled off. The product was soluble in water after treatment with acetic or lactic acid, light in color, and was slightly tacky in nature. It had the following unit formula:



Applied to cloth from a 2 pound in 50 gallon solution this gave a permanent finish which was similar to the handle of cloth treated with ten to fifteen times as much sulphonated tallow.

Example 6

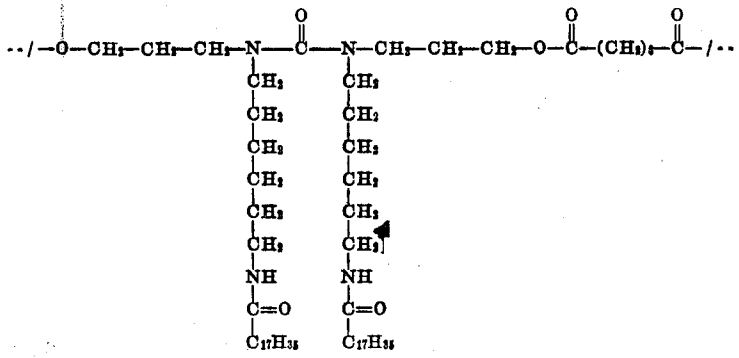
568 parts (2 mols) of stearic acid were heated with 133 parts of N-3 amino-2 propanol ethylene diamine until 1 mol of water was collected after which 30 parts (½ mol) of urea was slowly added at 180–185° C. and the temperature raised to 190° C. during which time ammonia was evolved. At 190° C. 101 parts (1 mol equivalent) of sebacic acid were slowly added and the temperature raised to 200° C. while water was distilled off. The product had the following unit formula:



Example 7

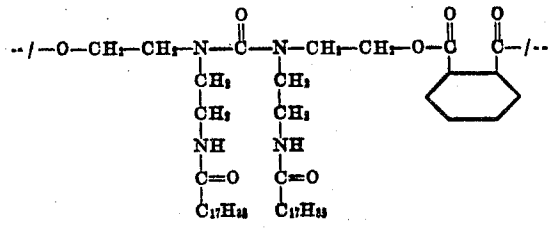
284 parts (1 mol) stearic acid were heated with 116 parts (1 mol) hexamethylene diamine until 1 mol of water was driven off. At 60–100° C. propylene oxide was bubbled through the condensate until 1 mol (58 parts) had been absorbed. The temperature was raised to 180° C., 30 parts (½ mol) urea was slowly added and the tem-

perature gradually raised to 190° C., during which time ammonia was evolved. At 190° C. 101 parts (1 mol equivalent) sebacic acid were added slowly and the temperature raised to 200° C. The product was soluble in water after treatment with acids and had the following unit formula:



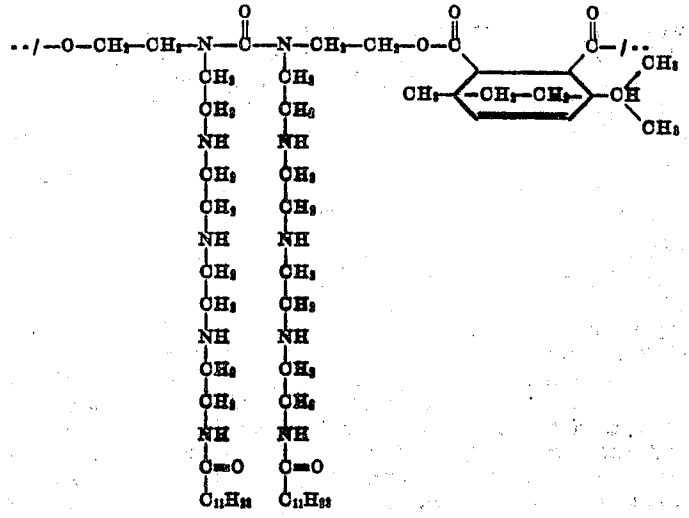
Example 8

284 parts (1 mol) stearic acid was heated with 60 parts (1 mol) ethylene diamine until 1 mol of water was driven off. At 60–80° C. ethylene oxide was bubbled through the condensate until 1 mol (44 parts) had been absorbed. The temperature was raised to 180° C., 30 parts (½ mol) urea was slowly added and the temperature gradually raised to 190° C., during which time ammonia was evolved. At 190° C. 74 parts phthalic anhydride (1 mol equivalent) was added and the temperature raised to 200° C. The product was soluble in water after treatment with acid and had the following unit formula:



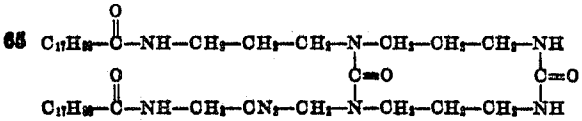
Example 9

200 parts (1 mol) lauric acid was heated with 192 parts (1 mol) tetraethylene pentamine until 1 mol of water was split off. Ethylene oxide was bubbled through the condensate at 80° C. until 1 mol (44 parts) had been absorbed. After raising the temperature to 180° C., 30 parts (½ mol) urea was slowly added and the temperature gradually increased to 190° C. during which time ammonia was evolved. To 1 mol of the above condensate, 215 parts (1 mol) of "Petrex" acid, which is defined by its producer, Hercules Powder Co., as 3 isopropyl-6-methyl 3,6-endoethyleneΔ^4 tetrahydro phthalic anhydride, was added and the temperature raised to 200° C., during which time water was drawn off. The product was soluble in water after treating with acetic or lactic acid. It had the following unit formula:



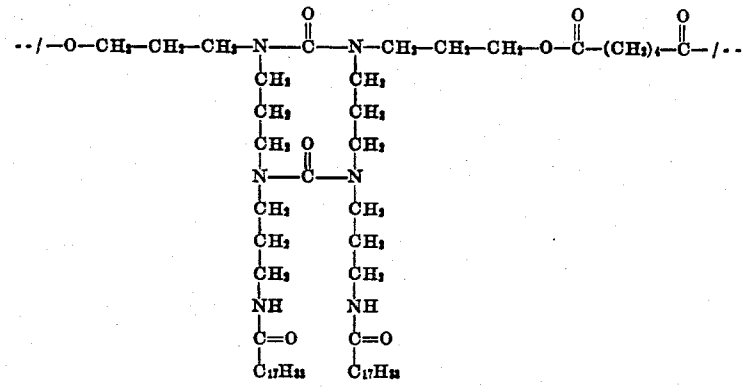
Example 10

282 parts (1 mol) of oleic acid was heated with 131 parts (1 mol) of dipropylene triamine until one mol of water was evolved. 60 parts (1 mol) of urea was added at 180° C. and the temperature raised to 190° C. during which time ammonia was liberated. 816 parts (1 mol) of the condensate obtained above having the formula



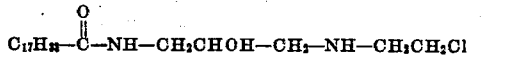
was treated with propylene oxide at temperatures between 60–100° C. until 2 mols of oxide was absorbed. This addition product was then heated to 190° C. at which point 146 parts (1 mol) of hexanedioic acid (adipic acid) was slowly added and the temperature raised to 200° C. during which time water was split out. The product was water

soluble after treatment with acids and consisted of repeating units of the following formula:

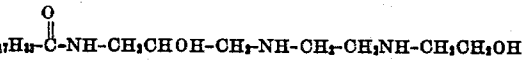


Example 11

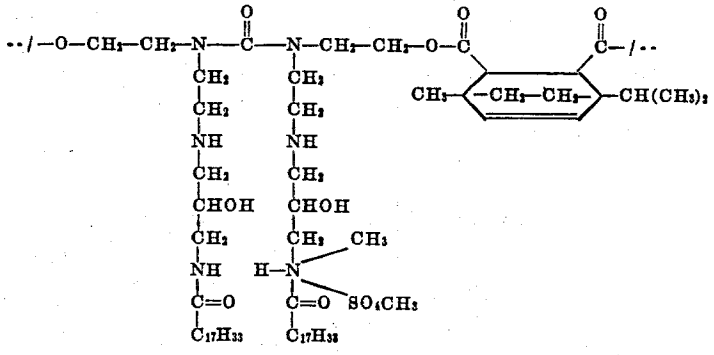
90 parts (1 mol) of 1-3 diamino isopropanol was heated with 282 parts (1 mol) of oleic acid until one mol of water was liberated. This condensate was further reacted with ethylene dichloride, one mol of hydrochloric acid being split off. This fatty amide having a formula as follows:



was treated with ammonia after which the addition product with ethylene oxide was formed by bubbling ethylene oxide through the liquid amide at temperatures between 60–80° C. Its addition product had the following formula:



938 parts (2 mols) of this ethylene oxide addition product was condensed with 60 parts (1 mol) of urea at temperatures between 180–190° C. during which time ammonia was evolved. At 190° C. 215 parts (1 mol) of "Petrex" acid, a polybasic acid defined by Hercules Powder Co. its producer as 3-isopropyl-6-methyl 3,6-endoethyleneΔ⁴ tetra hydro phthalic anhydride, was added and the temperature raised to 200° C. during which time water was driven off. The product was a tacky, resinous material, melting between 65–70° C. and was water soluble when treated with equimolar quantities of acids or alkylating agents. Its formula after alkylating with dimethyl sulphate was as follows:

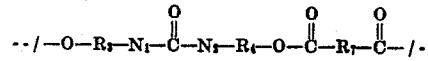


Cotton cloth impregnated with a solution containing 5 pounds per 50 gallons of water possessed a leathery feel which was resistant to washing and dry cleaning processes.

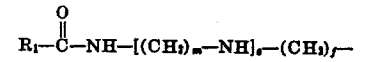
As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A condensation product having one hydroxyl and one carboxyl end group and consisting of repeating units of the following general formula:



wherein R_7 is a hydrocarbon residue resulting from a polycarboxylic acid and in which R_3 and R_4 represents simple alkylene groups of from 2 to 3 carbons and in which there is attached to the nitrogens N_1 and N_2 acid amide side chains of the following general formula:



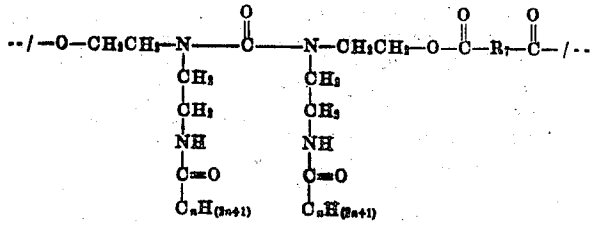
in which R_1 represents a hydrocarbon radical resulting from an organic acid and in which the integers f varies from 2 to 6 and e from 0 to 3 and m from 2 to 3.

2. The salt of an acid with a condensation compound described by the general formula in claim 1.

3. The alkylated product of the condensate described in claim 1 obtained by alkylating with a compound selected from the group consisting of ethyl chloride, ethylene oxide, benzyl chloride, diethyl sulfate and dimethyl sulfate.

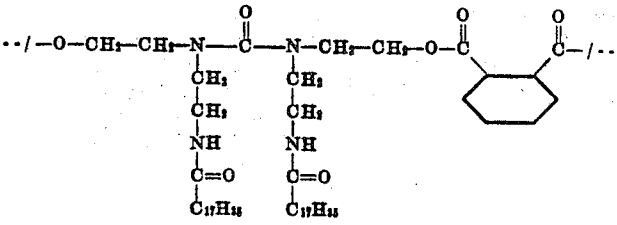
4. The condensation products having one hydroxyl and one carboxyl end group and consisting

of repeating units of the following general formula:

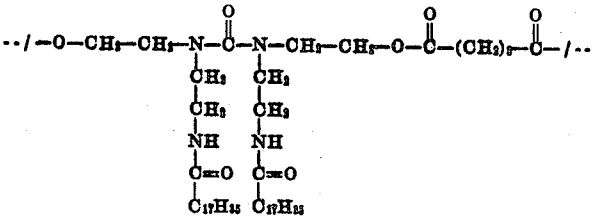


wherein n ranges from 1 to 17 and R_7 is the hydrocarbon residue from a dicarboxylic acid.

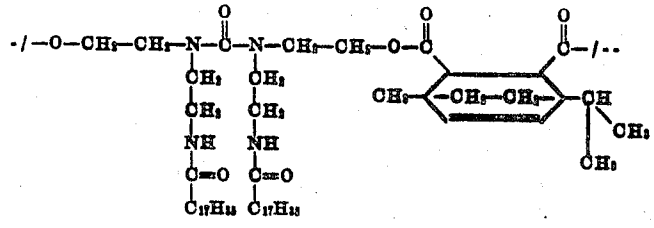
5. A new chemical compound having one hydroxyl and one carboxyl end group and consisting of repeating units of the following formula:



6. A new chemical compound having one hydroxyl and one carboxyl end group and consisting of repeating units of the following formula:



7. A new chemical compound having one hydroxyl and one carboxyl end group and consisting of repeating units of the following formula:



8. A process of forming a condensation product as defined in claim 1 in which equimolar quantities of an organic monocarboxylic acid and an alkylol polyamine of the following general formula

$$NH_2—[(CH_2)_m—NH]_e—(CH_2)_f—NH—(CH_2)_m—OH$$

wherein e varies from 0 to 3, f from 2 to 6, and m from 2 to 3 are condensed at temperatures between 130–170° C. and thereafter reacted with one-half mol of urea at 170–200° C. and thereafter reacted with equimolar quantities of a polycarboxylic acid at temperatures from 150–200° C.

9. A process of forming a condensation product as defined in claim 1 in which equimolar quantities of an organic monocarboxylic acid and an alkylol polyamine of the following general formula

$$NH_2—[(CH_2)_m—NH]_e—(CH_2)_f—NH—(CH_2)_m—OH$$

wherein e varies from 0 to 3, f from 2 to 6, and m from 2 to 3 are condensed at temperatures between 130–170° C. and thereafter reacted with one-half mol of urea at temperatures between 170–200° C. and thereafter further reacted with sufficient polycarboxylic acid to react with all of the hydroxyl groups present.

10. A process of forming a condensation product as defined in claim 1 in which equimolar quantities of an organic monocarboxylic acid and an alkylol polyamine of the following general formula

$$NH_2—[(CH_2)_m—NH]_e—(CH_2)_f—NH—(CH_2)_m—OH$$

wherein e varies from 0 to 3, f from 2 to 6, and m from 2 to 3 are condensed at temperatures between 130–170° C. and thereafter reacted with one-half mol of urea at temperatures between 170–200° C. and thereafter further reacted with an equimolar quantity of a polycarboxylic acid at temperatures from 150–200° C. and thereafter solubilized by adding one mol of acid.

11. A process of forming a condensation product as defined in claim 1 in which equimolar quantities of an organic monocarboxylic acid and an alkylol polyamine of the following general formula

$$NH_2—[(CH_2)_m—NH]_e—(CH_2)_f—NH—(CH_2)_m—OH$$

wherein e varies from 0 to 3, f from 2 to 6, and m from 2 to 3 are condensed at temperatures between 130–170° C. and thereafter reacted with one-half mol of urea at 170–200° C. and thereafter reacted with an equimolar quantity of

polycarboxylic acid at 150–200° C. and solubilized by the addition of one mol of a water soluble acid.

12. A process of forming a condensation product as defined in claim 1 in which equimolar quantities of an organic monocarboxylic acid and an alkylol polyamine of the following general formula

$$NH_2—[(CH_2)_m—NH]_e—(CH_2)_f—NH—(CH_2)_m—OH$$

wherein e varies from 0 to 3, f from 2 to 6, and m from 2 to 3 are condensed at temperatures between 130–170° C., said condensate containing free secondary amino groups which is then reacted with one-half mol of urea for each secondary amino group at temperatures between 170–200° C. and thereafter further reacted with an equimolar quantity of a polycarboxylic acid at temperatures between 150–200° C.

13. A process of forming a condensation product as defined in claim 1 in which equimolar quantities of an organic monocarboxylic acid and an alkylol polyamine of the following general formula

$$NH_2—[(CH_2)_m—NH]_e—(CH_2)_f—NH—(CH_2)_m—OH$$

wherein e varies from 0 to 3, f from 2 to 6, and m from 2 to 3 are condensed at temperatures between 130—170° C. and thereafter reacted with one-half mol of urea at 170–200° C. and thereafter reacted with an equimolar quantity of polycarboxylic acid at 150–200° C. and solubilized by reacting with one mol of an alkylating agent selected from the group consisting of ethyl chloride ethylene oxide, benzyl chloride, dimethyl sulfate and diethyl sulfate.

14. A textile material impregnated with a condensation product as described in claim 1.

15. A textile material impregnated with an alkylated condensation product obtained by alkylating a condensation product as described in claim 1 with a compound selected from the group consisting of ethyl chloride, ethylene oxide, benzyl chloride, diethyl sulfate and dimethyl sulfate.

16. A textile material impregnated with the salt which is the addition product of an acid to a condensation product as described in claim 1.

WILLARD L. MORGAN.
EARLE D. McLEOD.