

1

3,116,263

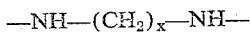
TEXTILE FINISHING COMPOSITION

Heinz Werner Enders, Stadtbergen, near Augsburg, and
Hans Deiner and Eugen Walter Kurz, Augsburg, Ger-
many, assignors to Chemische Fabrik Pforsee G.m.b.H.,
Augsburg, Germany, a firm
No Drawing. Filed July 31, 1961, Ser. No. 127,903
Claims priority, application Germany Apr. 22, 1961
9 Claims. (Cl. 260-21)

This invention relates to the finishing of textile materials, and is more particularly concerned with textile finishing agents and auxiliary materials for improving known textile finishing agents.

A class of known finishing agents consists essentially of compounds each molecule of which has at least two urea radicals connected by alkylene chains of two to four carbon members, a plurality of methylol radicals replacing hydrogen atoms in the amino groups of the urea radicals, and at least one alkyl radical of more than ten, and preferably eleven to twenty-two carbon atoms bound to a nitrogen atom of a urea radical. Such textile finishing agents impart a soft hand and water repellency to the treated material. The amine derivatives are commercially available in the form of more or less viscous aqueous emulsions.

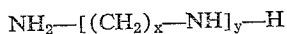
The afore-described amine derivatives may be prepared by heating one mol of an amine containing the group



wherein x is an integer between 2 and 4, with at least one mol, and preferably with two to three mols urea to a temperature of approximately 130° C. until 1.0 to 1.3 mols ammonia per mol of urea are liberated. The reaction product is dissolved in water, and is reacted at an elevated temperature above 40° C. with at least one mole, and preferably with one to two mols of an alkyl isocyanate the alkyl radical of which has more than ten, and preferably fifteen to nineteen carbon atoms. At least two mols formaldehyde are then added in the form of a neutral aqueous solution.

Suitable amines for preparing textile treating agents according to the afore-described method include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, dipropylene triamine, tripropylene tetramine, butylene diamine, dibutylene triamine, tributylene tetramine. Diethylene triamine is the preferred starting material.

The aforementioned amines are represented by the formula



wherein x is an integer between 2 and 4, and y is an integer between 1 and 3.

The reaction product is obtained in the form of an aqueous emulsion which may be diluted to the desired concentration in the presence of lower alkanolic acids such as acetic acid to form textile treating baths. The stability of the diluted emulsions is variable and depends, among other factors, on minor variations in the composition of the amine starting material which is not usually employed as a pure compound, but as a technical mixture in which one amine or the other may predominate. Dilution of the less stable emulsions causes a substantial increase in the particle size of the dispersed phase, and a concomitant deterioration of the finish obtained from the solution. Such an undesirable particle size growth is also frequently observed during storage.

It has now been found that the inadequate stability of emulsions of the aforescribed amine derivatives can be remedied, and that textile treating solutions having additional valuable properties can be obtained by adding

2

to the emulsions certain water insoluble precondensates of aminotriazines which are soluble in dilute aqueous solutions of monocarboxylic lower alkanolic acids. The aminotriazine precondensates of the invention are derived from aminotriazines which have at least two amino radicals, but no hydroxyl radical directly attached to the triazine ring, from formaldehyde, and monohydric lower alkanols having one to five carbon atoms. The precondensates have for each triazine ring at least one aliphatic radical of more than ten carbon atoms, and preferably of eleven to twenty-two carbon atoms, and at least 0.2 equivalent of the basic amino groups of an alkanolamine of the formula



wherein R is hydrogen, a lower alkyl radical having one to four carbon atoms, a hydroxyalkyl radical having two to four carbon atoms, or one of the radicals



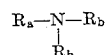
or $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NR}_1\text{R}_2$; R_1 is a hydroxyalkyl radical having two to four carbon atoms; and R_2 is hydrogen or a hydroxyalkyl radical having two to four carbon atoms.

The precondensates are added to the amine derivative emulsions in the form of 25 percent to 75 percent solutions in water insoluble organic solvents free from hydroxyl radicals.

The dilute aqueous solutions of monocarboxylic lower alkanolic acids may consist of 5 to 30 percent, and preferably of 5 to 10 percent aqueous solutions of formic acid or acetic acid, the latter being preferred.

Several methods are available for preparing the aforementioned water insoluble precondensates which are soluble in dilute aqueous solutions of monocarboxylic lower alkanolic acids.

According to a first method, one mol of an aminotriazine such as melamine is heated with one to two mols of an aliphatic monocarboxylic acid having more than ten carbon atoms, and preferably 15 to 19 carbon atoms; with 6 to 18 mols, and preferably with 9 to 15 mols paraformaldehyde; 0.2 to 1.2, and preferably 0.5 to 1.0 mols of an alkanolamine preferably of the formula



wherein R_a is hydrogen or a hydroxyalkyl radical having two to three carbon atoms, and R_b is a hydroxyalkyl radical having two to three carbon atoms; and a lower monohydric alkanol having one to five carbon atoms to a temperature of 110 to 140° C. while permitting volatile constituents to distil from the solution. Heating is continued until a sample of the product is soluble in a dilute aqueous monocarboxylic acid solution, such as hot 5 to 10 percent acetic acid.

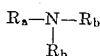
The aliphatic monocarboxylic acid having more than ten carbon atoms may be replaced in the above condensation reaction by an equivalent amount of the corresponding anhydride, that is, by one half to one mol of anhydride.

Precondensates of the same type are obtained by jointly replacing the aminotriazine and the aliphatic monocarboxylic acid or anhydride by one mol of a melamine derivative in which one to three hydrogen atoms of the amino groups of the melamine molecule are replaced by aliphatic acyl radicals having more than ten carbon atoms, and preferably fifteen to nineteen carbon atoms.

Another method of preparing the precondensates of the invention starts from methylolaminotriazines, and more particularly from methylol melamines, the methylol radicals of which are etherified with lower monohydric alkanols having one to four carbon atoms. One mol of an etherified methylol melamine is reacted with one to two

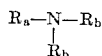
3

mols of an aliphatic monocarboxylic acid having more than ten carbon atoms, and preferably fifteen to nineteen carbon atoms, at a temperature of 130° to 200° C. Heating is preferably continued until substantially all the fatty acid is present in the combined form. The reaction may be performed at atmospheric pressure or in a vacuum. The intermediate product obtained is heated to 100 to 130° C. at ambient pressure or in a vacuum with 0.2 to 1.2, and preferably with 0.5 to 1.0 mols of an alkanolamine, which is preferably of the formula



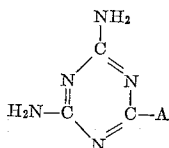
wherein R_a and R_b represent the afore-mentioned radicals. Heating is continued until a sample of the product is soluble in a dilute aqueous solution of a monocarboxylic acid such as formic or acetic acid.

According to an additional method of preparing the precondensates of the invention, one mol of a 2,4-diamino-6-alkyl-1,3,5-triazine¹ is heated to 130 to 160° C. with paraformaldehyde preferably in amounts of 5 to 8 mols, with 0.2 to 1.2 mols, and preferably with 0.4 to 1.0 mols of an alkanolamine which is preferably of the formula



wherein R_a and R_b have the same meaning, and with a lower monohydric alkanol having one to five carbon atoms. The volatile constituents are permitted to distil from the reaction mixture, and heating is continued until the product is soluble in a dilute monocarboxylic acid, and particularly in hot five to ten percent aqueous acetic acid.

A further method of synthesizing the pre-condensates of the invention starts with an aminotriazine derivative which is obtained by reacting one mol of a compound of the formula

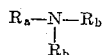


wherein A is hydrogen, amino radical, alkyl radical with 1 to 22 carbon atoms; with at least 1 mol of an alkyl isocyanate per mol of said aminotriazine derivative and at most one mol of said alkyl isocyanate per equivalent amino radicals. Especially used are derivatives obtained by heating one mol of melamine with 1.2 to 2 mols of said alkylisocyanate.

The alkyl radical of said alkyl isocyanate has more than ten, and preferably fifteen to nineteen carbon atoms.

The reaction is performed at 200 to 260° C. until a clear liquid is obtained.

One mol of this intermediate aminotriazine derivative obtained is heated to 130 to 160° C. with six to eighteen (preferably nine to fifteen) mols paraformaldehyde, 0.2 to 2.0 (preferably 0.7 to 1.5) mols of an alkanolamine, preferably of the formula



wherein R_a and R_b have the same meaning, and a lower monohydric alkanol having at most five carbon atoms and preferably four carbon atoms. The volatile constituents are permitted to evaporate from the solution, and heating is continued until the product is soluble in dilute monocarboxylic acids, such as hot five to ten percent aqueous acetic acid.

The test for completion of the precondensation reaction may be performed most conveniently with 5 to 30 per-

¹ The alkyl radical has more than 10, particularly 11-22 carbon atoms.

4

cent aqueous solutions of formic or acetic acid. The test is carried out by adding the precondensation product to the hot aqueous solution of the carboxylic acid, or by adding the precondensate to the acid solution in the cold, and by heating the mixture.

The precondensates prepared by the afore-described methods are added to the emulsions of amine derivative textile treating agents in amounts of 0.1 to 30 percent, based on the weight of the amine derivative in the emulsion. The precondensates are preferably dissolved in approximately equal amounts of solvents prior to addition to the emulsions.

Suitable substantially water insoluble liquid organic solvents which may be mixed with the precondensates of the invention include chlorinated hydrocarbons such as carbon tetrachloride or trichloroethylene, but also unsubstituted hydrocarbons of which gasoline, benzene, and tetrahydronaphthalene are typical examples. The solvents may also be employed as mixtures having a density near one. The amount of solvent added is preferably equal to the weight of the precondensate.

Addition of the mixture of precondensate and solvent greatly improves the storage ability of shelf life of the initially described class of known finishing agents. Even when cooled for three days to temperatures as low as -15° C., the mixtures of precondensates and amine derivative emulsions may be diluted to form perfectly operative textile treating bath if the mixtures are carefully thawed.

The stability of diluted treating solutions prepared according to the invention from the first-mentioned amine derivatives with the addition of the precondensates is substantially improved. A diluted emulsion of an amine derivative which could normally not be used after more than three or four days has a useful life of about three weeks if it contains the precondensates.

The addition of the precondensates also improves the stability of the diluted amino derivative emulsions at relatively high temperatures of about 40° C., and permits the textile treating temperature to be raised to such temperatures without flocculation or other precipitation of the amine derivative.

Textile treating solutions according to the invention may be prepared by adding to the mixture of the concentrated amine derivative emulsion and of the solvent solution of the precondensate approximately ten to thirty percent acetic acid based on the weight of the amino derivative and of the precondensate. The acetic acid is preferably admixed in the form of a strong aqueous solution containing 50 percent acetic acid or more. The acid containing mixture is then vigorously stirred with about three to six weights of hot water of 60 to 80° C., whereupon cold water may be added to dilute to the desired treating bath concentration.

The textile treating solution contains the amine derivative initially described together with the precondensate of the invention which is capable of being cured by acid. Yet the useful life of the treating solution, which is slightly acid, is extended by the addition of the precondensate, and its stability is improved. This is quite surprising and contrary to the expected effect of the addition.

The amine derivative emulsion containing the solvent solution of the precondensate in the dispersed phase is added to the textile treating solution in amounts which will usually vary between one and 20 grams, and preferably between two and fifteen grams, depending on the nature of the material treated, on the processing method to be employed, and on the finish to be produced.

The textile material is treated with the solution on conventional padding equipment or the like on which the material is impregnated with the solution, the excess solution is removed by squeezing between rolls, and the water is driven off by drying. The finishing agents thereby deposited on the material are cured to make them insoluble in water and water repellent. Curing is

performed at 120 to 160° C. for periods of approximately 20 minute to one minute, as is conventional.

The treatment with the textile treating agents of the invention may be combined with other finishing operations. Other water repellent agents such as emulsions of paraffine, which may additionally contain metal salts and acids, may be applied simultaneously, and the treating agents of the invention may be combined to particular advantage in the same bath with other formaldehyde precondensates such as methylol derivatives of urea, melamine, or ethylene urea, or with the ethers of these methylol derivatives with lower monohydric alkanols in the presence of acid or acid generating catalysts. The products of the invention may also be combined with other textile finishing agents such as polyvinyl acetate dispersions.

When native or regenerated cellulose fibers are treated with the finishing agents of the invention, their water resistance is improved. They not only repel water, but their tendency to absorb water and to swell is reduced, and they obtain a softer hand.

According to an additional feature of the invention, the emulsions of amino derivatives containing the precondensates of the invention may further be mixed with N-alkyl-N',N'-alkylene ureas wherein the alkyl radical has at least ten and preferably 11 to 22 carbon atoms, and the alkylene radical has two or three carbon atoms, the former number being preferred.

The N-alkyl-N',N'-alkylene urea is added to the aqueous dispersion of the amine derivative in amounts of 2 to 80 percent, and preferably 15 to 40 percent of the weight of the first mentioned amine derivative in respect of the water-free amine derivative. The N-alkyl-N',N'-alkylene urea is added in the form of its aqueous dispersion.

The dispersion of N-alkyl-N',N'-alkylene urea is prepared by reacting an alkylene imine having an alkylene radical of two or three carbon atoms with an alkyl isocyanate the alkyl group of which has more than ten, and preferably 15 to 19 carbon atoms, in the aqueous solution of an emulsifying agent, and preferably of a nonionic emulsifying agent. The resulting dispersion is stabilized and protected against atmospheric carbon dioxide by means of volatile or non-volatile alkaline compounds. When volatile alkaline stabilizing agents are employed, the dispersions are preferably further mixed with solutions of compounds of the formula



wherein R_c is an alkyl radical having more than ten, and preferably 11 to 22 carbon atoms; R_d is a pyridine or hydroxyethyl morpholine radical; and Z is the monobasic radical of an acid. The amount of the last mentioned addition agent is about 15 to 40 percent, and preferably 20 to 30 percent of the weight of the N-alkyl-N',N'-alkylene urea.

Quite surprisingly, the N-alkyl-N',N'-alkylene urea when mixed with the first mentioned amine derivative and the acid soluble precondensate forms a perfectly stable liquid capable of extended storage.

The mixture described in the preceding paragraphs permits a textile treating solution to be prepared in a single step from a single product which is diluted to the desired concentration. Only one type of concentrate needs to be stocked, and only one measurement is necessary for the dilution.

The hand of textile materials treated by the last described mixture is particularly pleasant, and its water resistance is greatly improved. The mixtures may be combined with conventional textile finishing agents in the manner described hereinabove, and the method of preparing dilute treating solutions follows by analogy from what has been said before.

Textiles treated with the first mentioned amine derivatives and the acid soluble precondensates whether or not these treating agents are further mixed with N-alkyl-

N',N'-alkylene urea, are particularly resistant to laundering. These products may therefore be applied to textiles in combination with reactant-type resins such as methylol ethylene urea employing as catalysts salts of multivalent metals such as magnesium, with strong inorganic acids to produce a so-called "wash-and-wear" finish.

The term "textile material" as employed in this specification and the appended claims will be understood to relate to woven and knit fabrics, as well as to felts and other non-woven textiles, to yarns, threads, loose fibers, and to the various intermediate products obtained during conversion of fibers into fabrics. The textile material may consist of natural or synthetic fibrous matter such as polyesters, polyamides, polyacrylonitrile and its copolymers, native and regenerated cellulose, and cellulose derivatives. The products and methods of the invention are applied with best success to fibrous material of native or regenerated cellulose.

The following examples are illustrative of methods of producing and using the acid soluble, water insoluble precondensates of the invention, and their mixtures with other finishing agents, but it will be understood that the invention is not limited to the examples. All parts are parts by weight unless otherwise stated.

Example I

In a three neck flask fitted with a condenser, a stirrer, and a thermometer, 90 parts of stearic acid are heated to the melting point just above 60° C. 148 parts of methanol, 75 parts of paraformaldehyde, and 25 parts of melamine are added while the contents of the flask are vigorously stirred, and a temperature of about 60° is maintained. As soon as the addition of the ingredients is completed, the temperature is gradually raised to 120° C. within two hours while the methanol is permitted to distil off. Within an additional hour, the temperature is further raised to 130°, and 25 parts of triethanolamine are added at that temperature, whereby the temperature drops to about 115° C. Stirring is continued at 115° C. until a sample taken from the flask is clearly soluble in hot aqueous 6 percent acetic acid. 190 parts of trichloroethylene are added with agitation. A clear brownish solution is obtained. It is poured into a container and cooled to room temperature. Upon addition of 10 to 15 percent acetic acid in the form of a strong aqueous solution, an emulsion having very small dispersed particles is formed which may be readily diluted with water. A stirrer is preferably used, when moderately large or large amounts of emulsion are to be diluted.

Example II

370 parts of methanol, 69 parts of triethanolamine, 187 parts of paraformaldehyde, and 63 parts of melamine are mixed in a three neck flask equipped with a condenser, a stirrer and a thermometer. The temperature is slowly raised while the contents of the flask are stirred. When the temperature in the flask reaches 40° C., 225 parts of technical stearic anhydride (acid value 3-7) are added, and the temperature is further increased to 120° C. within 2 to 3 hours while the alcohol is permitted to distil off. The temperature of 120° is maintained until the product of the reaction is clearly soluble in hot 6 percent acetic acid. 475 parts of trichloroethylene are then added. A brownish solution is formed. 10 to 15 percent of acetic acid are added in the form of a strong aqueous solution, and the mixture is capable of dilution with water to form an emulsion having very small dispersed particles.

Example III

324 parts of hexamethylol melamine are finely pulverized and stirred into 2000 parts methanol containing 100 parts concentrated hydrochloric acid. After about ten minutes stirring, the methylol compound dissolves. The solution is mixed with 160 parts of anhydrous so-

dium carbonate which is sufficient to make it neutral against litmus paper. Sodium chloride is precipitated and is filtered off. The filtrate is evaporated in a vacuum until a sirupy residue containing about 99 percent methylated methylol melamine is obtained. The residue is filtered hot to remove additional sodium chloride. The filtrate consists essentially of the methyl ether of hexamethylol melamine.

One part of the ether is heated to 180 to 200° C. with about 1.3 parts of stearic acid in a vacuum of 10 to 20 millimeters Hg, until the product has an acid value of 5 to 8. 90 parts of the resulting fused ester of methylated methylol melamine and of stearic acid and 15 parts of triethanolamine are mixed and heated to a temperature of 115 to 120° C. in a vacuum of 10 to 20 mm. Hg for one hour. A sample taken from the reaction mixture is soluble in hot dilute acetic acid.

The product which forms a yellowish brown wax-like mass when cooled, is mixed still hot and liquid with 110 parts tetrachloroethylene, whereby a clear solution is obtained. When mixed with 20 to 30 percent acetic acid, the solution is readily emulsifiable in water.

Example IV

182 parts methanol, 35 parts triethanolamine, 90 parts paraformaldehyde, and 190 parts technical 1,3-diamino-5-hexadecyl-2,4,6-triazine containing 80 percent of the pure compound, the balance being a mixture of fatty acids having an average molecular weight of about 255, are jointly heated with stirring in a three neck flask equipped with stirrer, thermometer, and condenser. The temperature is gradually raised to 140 to 145° C. within about two to three hours and the alcohol is permitted to distill off. The maximum temperature is maintained for a period sufficient to make a sample of the product soluble in hot 6 percent acetic acid. The contents of the flask are then cooled to 90° C., and 260 parts of trichloroethylene are added, whereby a light yellow solution is obtained. When 15 to 30 percent of acetic acid and water are added, a stable emulsion is obtained from this solution.

Example V

100 parts of dipalmitoyl melamine are mixed with 55 parts paraformaldehyde, 200 parts propanol, and 20 parts triisopropanolamine, and the mixture is heated to 140 to 145° C. When a sample of the product is found to be soluble in hot 10 percent acetic acid, 150 parts monochlorobenzene are added. When mixed with 20 to 30 percent acetic acid and water, the resulting solution forms a stable emulsion having exceedingly small dispersed particles.

Example VI

525 parts of isobutanol are mixed with 35 parts diethanolamine, 90 parts paraformaldehyde, and 150 parts of the condensation product obtained by jointly heating one mol of melamine with two mols of heptadecyl isocyanate to about 240° C. The mixture is refluxed for three hours, and the residual alcohol is permitted to distill off while the mixture is gradually heated to 150 to 155° C. over a period of two to three hours. This temperature is maintained until the reaction product is soluble in hot 6 percent acetic acid. The product is then cooled to about 110° C., and mixed with 240 parts toluene. A nearly clear light brown solution is obtained which is readily emulsifiable with water when first mixed with 12 to 30 percent acetic acid in the form of a strong aqueous solution. The emulsion is very stable.

Example VII

170 parts of a technical grade of stearo-guanamine containing 88 percent of the pure compound, whereas the remainder is essentially stearyl nitrile, and 90 parts paraformaldehyde are mixed with 180 parts methanol, and the mixture is refluxed until a clear solution is formed.

The solution is cooled to 50° C., and 30 parts of a 15 percent solution of hydrochloric acid in methanol are added. The mixture is refluxed for five minutes, and neutralized with anhydrous sodium carbonate against litmus paper. The methanol is evaporated in a vacuum, the residue is taken up in hot benzene, and the resulting solution is filtered while still hot. The filtrate is evaporated to dryness in a vacuum.

150 parts of the methylated methylol stearguanamine obtained (about 60 percent stearguanamine) are reacted with 21 parts triethanolamine at 140 to 145° C. with stirring until the product is clearly soluble in hot 6 percent acetic acid. It is cooled to about 80° C. and mixed with an equal quantity of a mixture composed of one part of tetrachloroethylene and three parts of benzene.

Example VIII

103 parts of diethylene triamine are mixed with 120 parts of urea while the mixture is heated. At about 95 to 100° C. ammonia gas starts developing and the mixture becomes a clear liquid whose temperature is raised to 130° C. The ammonia developing is absorbed in an amount of 5 N sulfuric acid equivalent to 40 parts of ammonia. Heating of the mixture is stopped when the acid is neutralized by the ammonia. The liquid reaction product is poured on a plate and permitted to solidify. 50 parts of the reaction product are dissolved in 505 parts at about 40° C. 135 parts of octadecyl isocyanate are added gradually during 15 minutes with vigorous stirring. A dispersion is formed, and stirring is continued at 40° for 15 minutes, then for an hour at 70° C. 160 parts of an aqueous, neutral, 37 percent formaldehyde solution are added while stirring continuously, and the temperature is held at 70° C. for fifteen minutes longer.

The temperature is reduced to 50° C., and 10 parts of the clear brownish solution obtained in Example I are added with stirring. An emulsion is formed which may be further homogenized on a colloid mill for more uniform particle size. When it is cooled to room temperature, a white substance having the consistence of a paste is obtained. It is almost neutral.

One part of the paste is dissolved in four to five parts of water of 60° C. with the addition of 0.1 part of 60 percent acetic acid, and this solution is further diluted with cold water as desired to form a textile finishing bath.

Example IX

The initial steps of the procedure of Example VIII are repeated, but the amount of octadecyl isocyanate added is increased to 190 parts. The emulsion obtained thereby is mixed by means of a high speed stirrer with 30 parts of the solution obtained in Example II while the emulsion is still at a temperature of about 50 to 60° C.

A very viscous emulsion forms after cooling. To 100 parts of the viscous mass six parts of acetic acid are added and then four to five times the quantity of water of about 60° C. A homogeneous emulsion is readily formed and may be further diluted with cold water as needed.

Example X

131 parts dipropylenetriamine and 120 parts urea are reacted at 125 to 130° C. in a flask equipped with a stirrer, a thermometer, a gas inlet tube, and a gas outlet tube, until 40 parts of ammonia are released. The resulting fused mass is cooled and dissolved in 700 parts water. 270 parts octadecyl isocyanate are added and the mixture is stirred at 40 to 50° C. for about two hours. 240 parts of a 30 percent aqueous formaldehyde solution are added and the mixture is kept for two additional hours at 60° C. while it is being stirred. Its pH is 8.5 to 9.

If the resulting emulsion is cooled to room temperature, a paste-like product is obtained which cannot readily be diluted with water after a period of storage, and which forms a precipitate if an attempt is made to dilute it with warm water to form a textile treating bath.

If the emulsion is mixed prior to cooling with 300 parts of the solution obtained in Example III, there is also obtained a pasty product on cooling. This product, however, is readily soluble in hot water even after prolonged storage when the paste is mixed with 8 percent acetic acid. Hot textile finishing baths may be readily made up therefrom, and do not show any precipitate.

Example XI

146 parts of triethylene tetramine are reacted with 180 parts of urea in a manner analogous to the method of Example X, until 60 parts of ammonia are evolved. The reaction product is dissolved in 2660 parts of water at 40°. To the solution are added 560 parts heptadecyl isocyanate by vigorous stirring within fifteen minutes. The temperature is increased to 70° C. and held at 70° C. for an hour. 650 parts of aqueous 37 percent formaldehyde solution are added, and stirring is continued for twenty minutes. An emulsion is formed.

If the emulsion is cooled to room temperature, it forms a paste. When stored at -10° C. for a few days, this paste can no longer be diluted with water.

If the emulsion, while still hot, is mixed by means of a high speed stirrer with 100 parts of the solution prepared in Example IV, a similar paste is obtained at room temperature. After storage for several days at temperatures between -10 and -15° C., the latter paste is readily dispersed with 5 percent of its weight of acetic acid in 4 to 6 times its weight of water, and the concentrate formed may further be diluted at will to form a textile finishing bath which is stable both at low and high temperatures.

Example XII

Following a procedure analogous to that of Example XI, 60 parts of ethylenediamine are reacted with 120 parts of urea until 34 parts of ammonia gas are developed. 50 parts of the reaction product dissolved in 500 parts of water are reacted first with 135 parts octadecyl isocyanate, than with 110 parts of aqueous 37 percent formaldehyde solution. The emulsion obtained is stabilized by the addition of 130 parts of the solution obtained in Example V, and may be employed for making textile finishing baths.

Example XIII

An emulsion capable of extended storage and insensitive to relatively high and low temperatures can also be prepared according to the method of Example VIII when 2 parts of the solution prepared according to Example VI are substituted for ten parts of the solution of Example I.

Example XIV

An emulsion of an N-alkyl-N',N'-alkylene urea is prepared as follows:

28.5 parts ethylenimine are diluted with 125 parts distilled water. 45 parts of a glycerin triricinoleate etherified with 30 mols ethylene oxide are dissolved in 126.5 parts distilled water and 15 parts aqueous ammonium hydroxide ($d=0.90$). The two aqueous solutions are mixed at 20° C., and 200 parts octadecyl isocyanate are added drop by drop to the resulting mixture with stirring and intensive cooling. When the reaction is completed, 450 parts distilled water and 10 parts ammonium hydroxide solution are added, and the mixture is homogenized mechanically by means of a high speed agitator. The total weight of the resulting emulsion is adjusted to 1,000 parts by means of a solution prepared from 66 parts of octadecyl-oxyethylene-hydroxyethylmorpholinium chloride in 134 parts of distilled water.

Thirty parts of the above emulsion are combined with 100 parts of one of the emulsions prepared according to Examples VIII or IX, and with 15 parts of a precondensate prepared according to Example I or Example IV, and the mixture is emulsified by mechanical stirring. This emulsified mixture is readily diluted with five times its weight of hot water in the presence of 7 percent of its

weight of 60 percent acetic acid, and may then further be diluted as desired to form a stable textile finishing bath.

Example XV

30 gr. of the emulsion prepared according to Example VIII are diluted as mentioned there to make one liter of a treating bath. A cotton poplin is saturated with this bath, squeezed between rollers to a pick-up of about 80 percent, dried at 100° C. and cured two minutes at about 150° C.

The finished poplin is water repellent. Its water absorption is decreased and its crease retention is improved. It has a very pleasant soft hand. The finish has excellent resistance to laundering and dry cleaning.

If the treating bath additionally contains 110 gr. of an aqueous 50 percent solution of dimethylol ethylene urea and 10 gr. magnesium chloride hexahydrate per liter, the textile material has a good wash-and-wear finish.

Example XVI

45 gr. of the emulsion prepared according to Example XIV are diluted as mentioned there to one liter with water. Rayon gabardine is saturated with the solution so obtained, extracted to a pick-up of about 100 percent, dried at 110° C., and cured for five minutes at 140° C. The treated fabric is water repellent, its ability to absorb water is reduced, and it has an excellent soft hand.

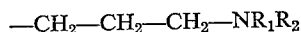
Various modifications are contemplated and may be obviously resorted to by those skilled in the art without departing from the spirit and scope of the invention as hereinafter defined by the appended claims, as only preferred embodiments thereof have been disclosed.

What we claim is:

1. An aqueous textile finishing composition comprising a combination with a dispersed phase of an amine derivative having at least two urea radicals, respective nitrogen atoms of said radicals being connected by alkylene groups having two to four carbon atoms, a plurality of methylol radicals and at least one alkyl radical having at least ten carbon atoms being attached to a nitrogen atom of said urea radicals; a water insoluble precondensate of an aminotriazine, said precondensate being soluble in dilute aqueous solutions of monocarboxylic lower alkanolic acids, said aminotriazine having at least two amino radicals and no hydroxyl radicals attached to the triazine ring thereof, said aminotriazine being condensed with formaldehyde and a monohydric lower alkanol, said precondensate having for each triazine ring at least one aliphatic radical of at least ten carbon atoms and at least 0.2 amino radical equivalent of an alkanolamine of the formula



wherein R is selected from the group consisting of hydrogen, a hydroxyalkyl radical having two to four carbon atoms, an alkyl radical having one to four carbon atoms, the radical $-\text{CH}_2-\text{CH}_2-\text{NR}_1\text{R}_2$, and the radical



R_1 is a hydroxyalkyl radical having two to four carbon atoms; and R_2 is selected from the group consisting of hydrogen, and a hydroxyalkyl radical having two to four carbon atoms; and a substantially water insoluble organic solvent free of hydroxyl radicals, the amount of said precondensate being 0.1 percent to 30 percent of said amine derivative, and the amount of said solvent being between substantially one third and three times the amount of said precondensate.

2. A composition according to claim 1, wherein said aminotriazine is melamine, and said aliphatic radical of at least ten carbon atoms is an aliphatic radical of fifteen to nineteen carbon atoms.

3. A composition according to claim 1, wherein said precondensate being dissolved in said solvent.

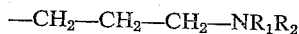
4. A composition according to claim 1, wherein the

nitrogen atoms of the urea radicals are connected by alkylene groups having two to three carbon atoms, and the amount of said precondensate is 0.5 percent to 5 percent of said amine derivative.

5. A composition according to claim 1, wherein said precondensate is obtained by reacting an aminotriazine having at least two amino radicals and no hydroxyl radicals directly bound to the triazine ring thereof, with formaldehyde, a lower monohydric alkanol, a fatty acid compound selected from the group consisting of fatty acids having an alkyl radical of 15 to 19 carbon atoms and anhydrides of said fatty acids, and an alkanolamine of the formula



wherein R is selected from the group consisting of hydrogen, a hydroxyalkyl radical having two to four carbon atoms, an alkyl radical having one to four carbon atoms, the radical $-\text{CH}_2-\text{CH}_2-\text{NR}_1\text{R}_2$, and the radical

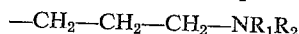


R_1 is a hydroxyalkyl radical having two to four carbon atoms; and R_2 is selected from the group consisting of hydrogen, and a hydroxyalkyl radical having two to four carbon atoms; at a temperature substantially between 110°C . and 140°C . until the reaction product is soluble in a hot dilute aqueous solution of a lower monocarboxylic alkanolic acid.

6. A composition according to claim 1 wherein said precondensate is obtained by reacting a 2,4-diamino-6-alkyltriazine having an alkyl radical of 15 to 19 carbon atoms with formaldehyde, a lower monohydric alkanol, and an alkanolamine of the formula

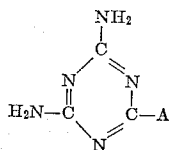


wherein R is a radical selected from the group consisting of hydrogen, hydroxyalkyl radicals having two to four carbon atoms, alkyl radicals having one to four carbon atoms, and the radicals $-\text{CH}_2-\text{CH}_2-\text{NR}_1\text{R}_2$, and



R_1 is a hydroxyalkyl radical having two to four carbon atoms; and R_2 is selected from the group consisting of hydrogen and hydroxyalkyl radicals having two to four carbon atoms, at a temperature substantially between 130°C . and 160°C . until the reaction product is soluble in a hot dilute aqueous solution of a lower monocarboxylic alkanolic acid.

7. A product according to claim 1 wherein said precondensate is obtained by reacting an aminotriazine derivative which results by heating one mol of a compound of the formula

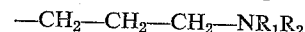


wherein A is hydrogen, amino radical, alkyl radical with 1 to 22 carbon atoms; with at least 1 mol of an alkyl isocyanate, the alkyl radical has 15 to 19 carbon atoms per mol of said compound and at most 1 mol of said alkyl isocyanate per equivalent of amino radicals at temperatures between 200°C . and 260°C .; with formaldehyde,

a lower monohydric alkanol, and an alkanolamine of the formula



wherein R is a radical selected from the group consisting of hydrogen, hydroxyalkyl radical having two to four carbon atoms, alkyl radicals having one to four carbon atoms, and the radicals $-\text{CH}_2-\text{CH}_2-\text{NR}_1\text{R}_2$, and



R_1 is a hydroxyalkyl radical having two to four carbon atoms; and R_2 is selected from the group consisting of hydrogen and hydroxyalkyl radicals having two to four carbon atoms, at a temperature substantially between 130°C . and 160°C . until the reaction product is soluble in a hot dilute aqueous solution of a lower monocarboxylic alkanolic acid.

8. An aqueous textile finishing composition comprising in combination with a dispersed phase of an amine derivative having at least two urea radicals, respective nitrogen atoms of said radicals being connected by alkylene groups having two to four carbon atoms, a plurality of methylol radicals and at least one alkyl radical having at least ten carbon atoms being attached to a nitrogen atom of said urea radicals; a water insoluble precondensate of an aminotriazine, said precondensate being soluble in dilute aqueous solutions of monocarboxylic lower alkanolic acids, said aminotriazine having at least two amino radicals and no hydroxyl radicals attached to the triazine ring thereof, said aminotriazine being condensed with formaldehyde and a monohydric lower alkanol, said precondensate having for each triazine ring at least one aliphatic radical of at least ten carbon atoms and at least 0.2 amino radical equivalent of an alkanolamine of the formula



wherein R is selected from the group consisting of hydrogen, a hydroxyalkyl radical having two to four carbon atoms, an alkyl radical having one to four carbon atoms, the radical $-\text{CH}_2-\text{CH}_2-\text{NR}_1\text{R}_2$, and the radical $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NR}_1\text{R}_2$; R_1 is a hydroxyalkyl radical having two to four carbon atoms; and R_2 is selected from the group consisting of hydrogen, and a hydroxyalkyl radical having two to four carbon atoms; a substantially water insoluble organic solvent free of hydroxyl radicals; and an N-alkyl-N',N'-alkylene-urea, the alkyl radical has at least 10 carbon atoms, the alkylene radical has two to three carbon atoms, the amount of said precondensate being 0.1% to 30% of said amine derivative, the amount of said solvent being between substantially one third and three times the amount of said precondensate and the amount of said N-alkyl-N',N'-alkylene-urea being 2% to 80% of said amine derivative.

9. A product according to claim 8, wherein said precondensate is added in form of a solution in said organic solvent and said N-alkyl-N',N'-alkylene-urea is added in form of an aqueous dispersion to the aqueous dispersion of said amine derivative.

References Cited in the file of this patent

UNITED STATES PATENTS

2,049,217	Meunier	July 28, 1936
2,314,968	Bestian et al.	Mar. 30, 1943
2,864,781	Albrecht et al.	Dec. 16, 1958
3,006,896	Horst et al.	Oct. 31, 1961