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CERTAIN N-METHYLOL-N-(3-METHYLOL IMIDAZOLIDON - 2 - YL)ETHYL ACYLAMIDES AND PROCESS

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The present invention relates to improvements in the treatment of cellulosic fibrous material. More particularly, the invention is especially concerned with the treatment of cellulosic textile materials such as fibers, yarn or fabrics prepared principally from cotton, viscose, cellulose acetate or other cellulosic compounds, said treatment involving the impregnation of the textile material with novel finishing compositions comprised in important part of thermosetting resin-forming compounds together with certain improved softening agents, the latter compounds independently constituting new compositions of matter. As herein employed the term "impregnation" is meant to include procedures by which the material being treated is coated with the finishing compositions. The invention is concerned further with novel processes for the production of the softening agents of this invention, as well as with cellulosic textile material possessing improved physical properties, said cellulosic textile material having been treated with the finishing compositions of this invention as herein described.

The modification of cellulosic textile material by chemical treatment has, over recent years, resulted in an increased interest in such material for uses which were heretofore restricted to synthetic textiles. By way of illustration, a prominent application lies in the production of so-called "wash and wear" fabrics wherein the cellulosic textile material is treated by initially impregnating the materal with a finishing composition consisting of an aqueous solution containing a thermosetting resin-forming compound, and ordinarily, an acid-producing catalyst. The impregnated cellulosic textile material is subsequently dried and cured, thereby at least partially polymerizing the resin-forming compound in situ and effecting a chemical bonding of the resin or resin-forming compound with the cellulosic textile material. The polymerization and bonding processes are accelerated by the presence of the acid-producing catalyst.

When treated in this manner, the impregnated cellulosic textile material has been found to evidence substantially improved crease-resistance and dimensional stability. Unfortunately, however, certain disadvantages ordinarily accompany the treatment of cellulosic textile material by impregnation with a thermosetting resin-forming compound as hereinabove described. Included among these disadvantages are a loss of tear-strength in the impregnated material, and the impartation thereto of a harsh hand or feeling. In order to overcome these disadvantages, softening agents have frequently been incorporated in, or utilized in conjunction with, the finishing composition with which the cellulosic textile material is treated.

Most softening agents are long-chain organic compounds which have the ability to lubricate the fibers of the material being treated, thus permitting the fibers more freedom of movement and improving the tear-strength of yarn or fabric containing the treated fibers. In addition, an enhanced hand is produced by the amount of softening agent located on the surface of the treated material.

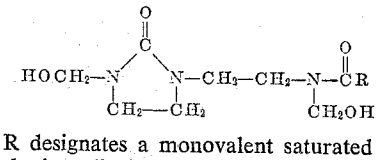
To qualify as an efficient softening agent for use in conjunction with the treatment of cellulosic fibrous material, and particularly cellulosic textile material, by impregnation with a thermosetting resin-forming compound as hereinbefore described, the softening agent should evidence or possess the following desirable characteristics.

Both the chlorine retention of the softening agent and its tendency to yellow or cause yellowing in the treated material should be at a minimum. The softening agent should also improve the tear-strength and hand of the treated material without adversely affecting the crease-resistance or other important physical properties of the treated material to any substantial extent. In addition, it is desirable that the softening agent be compatible with and stable in the finishing composition so as to permit incorporation therein, thus facilitating a simultaneous impregnation of the material to be treated with both the resin-forming compound and the softening agent.

The first softening agents employed for the treatment of cellulosic textile material were of the anionic type, such as sulfated tallows or tall oils. These compounds proved initially effective, but their effectiveness was dissipated rapidly during subsequent laundering. Cationic softening agents such as quaternarized fatty amines have also been considered attractive because of their substantive pick-up by the cellulosic textile material. Their use, however, frequently suffered the attendant disadvantage of an increased tendency toward yellowing in the treated material, while their effectiveness was often lost after relatively few launderings. These disadvantages of the prior art can now be overcome and still further improvements realized, through the practice of the present invention.

This invention is based upon the discovery that certain novel heterocyclic organic compounds, viz. methylolated imidazolidonyl ethyl acylamides wherein the acylamide radicals possess at least about 8 carbon atoms, serve as improved softening agents for cellulosic fibrous materials, and are particularly suited for use in conjunction with the treatment of cellulosic fibrous material with a thermosetting resin-forming compound. Illustratively, by treating, i.e. impregnating or coating a cellulosic textile material with a finishing composition comprised of an aqueous solution containing a thermosetting resin-forming compound, at least one of the novel softening agents of this invention and, preferably, an acid-producing catalyst, and by subsequently drying and curing the treated material, impregnated cellulosic textile material can be obtained possessing a high degree of tear-strength and evidencing a smooth hand. Moreover, the improved cellulosic textile products of this invention advantageously retain these desirable physical properties, as well as other properties accruable as a consequence of impregnation with a thermosetting resin-forming compound, to a substantial extent even after repeated launderings, with little or no concomitant yellowing. Further, in addition to the treatment of cellulosic textile material, the finishing compositions of this invention can be employed in similar manner and with like advantageous effect to treat other cellulosic fibrous material, such as paper products prepared principally from cellulosic fibers.

More particularly, the softening agents of this invention are the N-methylol-N[2-(3-methylol imidazolidon-2-yl-1) ethyl] acylamides represented by the general formula:



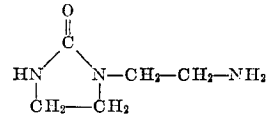
(I)

wherein R designates a monovalent saturated or unsaturated aliphatic radical possessing at least about 8 carbon atoms and preferably from about 12 to about 22 carbon atoms, as for instance an alkyl radical such as an octyl, decyl, dodecyl, tetradecyl, octadecyl or docosyl radical; an alkenyl radical such as an octenyl, decenyl, tetradecenyl, octadecenyl or docosenyl radical; and the like. Of the above aliphatic radicals, the designation R prefer-

ably represents an alkyl radical. In addition, mixtures of N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamides, wherein more than one monovalent aliphatic radical of the type hereinabove described is present, can also be employed as softening agents in accordance with this invention.

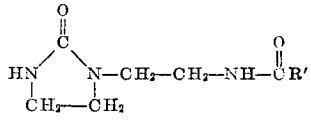
It has been found that the effectiveness of the softening agents of the invention increases in direct relationship with respect to the number of carbon atoms in the aliphatic radical designated above by R. Thus, by way of illustration, greater tear strength and a smoother hand is evidenced by cellulosic textile material treated with the finishing composition of the invention as herein described, wherein the softening agent is such that R designates an alkyl radical possessing 17 carbon atoms, as compared with identical textile material similarly treated, wherein however, the softening agent is such that R designates an alkyl radical containing only 11 carbon atoms. In this connection, the methylolated imidazolidonyl ethyl acylamides represented by formula I above, wherein R designates a monovalent aliphatic radical possessing less than about 8 carbon atoms have not been found suitable for use as softening agents in accordance with the invention.

The methylolated imidazolidonyl ethyl acylamides can be prepared by a two-step process involving the initial condensation of a fatty acid, or aliphatic fatty acid ester, with 2-(imidazolidon-2-yl-1)ethylamine, the latter compound being represented by the formula:



(II)

so as to form the corresponding N-[2-(imidazolidon-2-yl-1)ethyl] acylamide intermediate, represented by the general formula:



(III)

wherein R' designates a monovalent aliphatic radical containing from 1 to 22 carbon atoms. This intermediate product is then methylolated by reaction with either formaldehyde or paraformaldehyde so as to produce the desired N-methylol-N [2-(3-methylol imidazolidon-2-yl-1) ethyl] acylamide. It is to be observed that the softening agents of this invention are produced by selecting the fatty acid or aliphatic fatty acid ester reactant such that the acyl radical contained thereby possesses a monovalent aliphatic radical designated by R, wherein R is as defined above, i.e., contains at least about 8 carbon atoms.

The 2-(imidazolidon-2-yl-1)ethylamine reactant can itself be obtained from any convenient source. The compound can, for example, be produced by processes such as those described in U.S. Patent 2,613,212 by the reaction of diethylene triamine with urea at a temperature of between about 100° C. and about 300° C. The resulting product need not be purified, but can, if desired, be employed in crude form for subsequent reaction with either a fatty acid or an aliphatic fatty acid ester as herein described.

The condensation of the 2-(imidazolidon-2-yl-1)ethylamine with a fatty acid to produce the N-[2-(imidazolidon-2-yl-1)ethyl] acylamide intermediate is carried out by heating a mixture of the reactants at a temperature of between about 30° C. and about 200° C. or slightly higher, and preferably at a temperature of between about 100° C. and about 150° C., while removing the water formed during the course of the reaction. The concentration in which the reactants are employed is not critical to the process although the ethylamine derivative is preferably utilized in at least a stoichiometric proportion. Generally, a suitable solvent such as xylene or toluene is also incorporated in the reaction mixture. Such a solvent further serves as an entraining agent, thereby facilitating the removal of water as an azeotropic mixture with the solvent during the course of the reaction. Under such conditions, the condensation is performed by azeotropically refluxing the reaction mixture. However, the condensation can also be carried out in the absence of an azeotroping agent, as for example, by utilizing an elevated reaction temperature and ordinarily a reduced pressure sufficient to permit the removal of water formed during the reaction.

In a similar manner, the condensation of the 2-(imidazolidon-2-yl-1)ethylamine with an aliphatic fatty acid ester to produce the N-[2-imidazolidon-2-yl-1)ethyl] acylamide intermediate is carried out by heating a mixture of the reactants at a temperature of between about 30° C. and about 200° C. or slightly higher, and preferably with reflux and at a temperature of between about 100° C. and 150° C., while removing the alcohol formed during the course of the reaction. The aliphatic fatty acid ester employed as a reactant is preferably one represented by the general formula: RCOOR'', wherein R is as defined above, and R'' independently designates a monovalent saturated or unsaturated aliphatic radical and preferably an alkyl radical. More preferably, R'' designates a monovalent aliphatic radical such that the corresponding alcohol, R''OH is a lower boiling alcohol than ROH. Thus, the alcohol R''OH, formed during the condensation, can readily be removed by a suitable adjustment of the reaction temperature, in this manner precluding the possibility of producing substantial quantities of mixed products containing more than one type of monovalent aliphatic radical. The concentration in which the reactants are employed is not critical to the process, although the ethylamine derivative is preferably utilized in at least a stoichiometric proportion. It has also been found generally desirable to incorporate in the reaction mixture a catalytic amount of a conventional transesterification catalyst such as an alkali metal alkylate, e.g. sodium ethylate or potassium ethylate, and the like, said catalyst preferably being employed in a concentration of from about 0.1 to about 1 percent by weight and preferably from about 0.25 to about 0.5 percent by weight based upon total weight of the reactants, although higher or lower concentrations can also be employed. It is to be noted in this respect that the catalyst can also be produced in situ, as for example, by the incorporation of an alkali metal and an alkyl alcohol in the reaction mixture in amounts sufficient to provide therein a catalytic amount of alkali metal alkylate.

The completion of the condensation of the 2-(imidazolidon-2-yl-1)ethylamine with either the fatty acid or the aliphatic fatty acid ester as hereinabove described can be determined conveniently by a cessation in the formation of water or of alcohol respectively that is produced during the course of the reaction. Upon completion of the condensation, the resulting N-[2-imidazolidon-2-yl-1)-ethyl] acylamide intermediate can be recovered from the crude reaction product in any suitable manner. A satisfactory procedure, for example involves distilling off any remaining solvent, generally under reduced pressure, and thereafter cooling the residue to about room temperature or somewhat lower, whereby the desired intermediate is recoverable in solid form. The product can subsequently be purified by recrystallization from a suitable solvent such as methanol. Other suitable recovery procedures can also be employed. For example, the crude product obtained upon completion of the condensation can be cooled as indicated above, without the prior distillation of any remaining solvent. The desired intermediate can then be separated in solid form; any solvent that is present remaining in the liquid phase. Moreover, the crude reaction product itself can be employed for the subsequent methylolation, thus completely obviating the necessity for utilizing a recovery procedure.

The methylolation of the N-[2-(imidazolidon-2-yl-1)-ethyl] acylamide intermediate is carried out by heating

an aqueous mixture or solution containing the intermediate and either formaldehyde or paraformaldehyde at a temperature of between about 20° C. and about 100° C. or slightly higher and preferably at a temperature of between about 30° C. and 60° C. The proportion in which the reactants are introduced is not critical to the process although stoichiometric proportions are preferably used. Thus, for example, 2 moles of formaldehyde are required to methylolate the primary and secondary amino-nitrogen atoms contained in one mole of the N-[2-(imidazolidon-2-yl-1)ethyl] acylamide intermediate. It has been found particularly desirable to carry out the methylolation in the presence of a catalytic amount of an alkaline catalyst such as sodium hydroxide, potassium hydroxide, triethanol amine, sodium carbonate, or the like, the catalyst preferably being employed in a concentration sufficient to engender a pH value of from about 8 to about 10 in the reaction mixture. Higher or lower concentrations of catalyst can also be utilized, although increasing saponification of the resulting product may render the use of higher catalyst concentrations less desirable. In addition, a suitable solvent such as water, methanol, ethanol, etc. is generally incorporated in the reaction mixture.

Upon completion of the methylolation, the resulting N-methylol-N-[2 - (3 - methylol imidazolidon-2-yl-1)ethyl] acylamide can be recovered in any convenient manner. A suitable recovery procedure, for instance, involves neutralizing any remaining alkaline catalyst by the addition of dilute acid such as dilute sulfuric acid or dilute acetic acid, and thereafter distilling off the solvent, when present, preferably under reduced pressure. The N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamide product can subsequently be recovered in solid or semi-solid form, i.e. as a solid, paste, gel, etc., by cooling the residue to about room temperature or somewhat lower. The crude reaction product can then be purified, if desired, by recrystallization from a suitable solvent such as methanol, or employed directly for use as a softening agent as herein described. Generally the N-methylol-N-[2 - (3 - methylol imidazolidon-2-yl-1)ethyl] acylamide is dispersed in water and employed as an aqueous dispersion. Such dispersions are readily dissolved or emulsified in the finishing compositions of this invention.

In further accord with this invention, the N-methylol-N-[2-(3-methylol imidazalidon-2-yl-1)ethyl] acylamides prepared by the above reactions are employed as softening agents for cellulosic fibrous material by incorporating the product in a finishing composition consisting of an aqueous solution containing a thermosetting resin-forming compound, at least one of the softening agents of the invention, and preferably, an acid-producing catalyst such as thse commonly ulitized in conjunction with the production of thermosetting resins or with the impregnating of textile material by thermosetting resin-forming compounds. Suitable catalysts, for example, include 2-amino-2-methylpropanol-1 hydrochloride, magnesium fluoroborate, monoethanolamine hydrochloride, and the like. The use of such a catalyst, however, is not essential to the invention. Of the thermosetting resin-forming compounds suitable for use in the invention, particular good results can be realized using an aminoplastic resin-forming compound such as the 1,3-dimethylol-5-alkylperhydrotriazones, urea-formaldehyde, melamine-formaldehyde, tetramethylol acetylene diureine or cyclic ethylene urea-formaldeyhde (1,3-di-methylol imidazolidone-2), etc.

More particularly, the finishing compositions of this invention are generally comprised of from about 3 percent to about 15 percent by weight and preferably from about 5 percent to about 12 percent by weight of the thermosetting resin-forming compound, from about 0.1 percent to about 5 percent by weight and preferably from about 0.3 percent to about 2 percent by weight of at least one of the softening agents of this invention and, when the use of an acid-producing catalyst is desired, from about 0.5 percent to about 3 percent by weight and preferably from about 1 percent to about 2.5 percent by weight of said acid-producing catalyst, water constituting the principal remaining constituent of the finishing composition. It has also been found desirable to incorporate in the finishing composition small amounts of both a surface-active wetting agent, for example from about 0.1 percent to about 0.5 percent by weight of a compound such as an alkyl phenyl polyethylene glycol ether or the like, and a bodying agent, as for instance from about 1 percent to about 5 percent by weight of a compound such as polyvinyl alcohol, a cold water-soluble starch ether, or the like. Still other finishing agents, such as water-repelling agents, can also be incorporated in the finishing compositions in minor amounts. In addition the proportions of the individual components of the finishing compositions of the invention can, in light of this disclosure, be varied by those skilled in the art within somewhat broader ranges, depending upon the amounts desired to be picked-up by the material being treated. Moreover, satisfactory results can be obtained by incorporating the softening agents of the invention, preferably in amounts as hereinabove prescribed in any finishing composition conventionally employed to impregnate a cellulosic textile material with a thermosetting resin-forming compound, and particularly with an aminoplastic resin-forming compound.

In practice, the cellulosic fibrous material to be treated is immersed or otherwise subjected to contact with the finishing composition of the invention until impregnated or coated therewith to a desired extent in accordance with conventional padding operations. The treated material is then dried generally while substantially wrinkle-free and preferably by air at a temperature of up to about 110° C. Thereafter, the treated material, still desirably maintained substantially wrinkle-free, is cured by heating the material at a temperature of from about 130° C. to about 160° C., and preferably at a temperature of from about 145° C. to about 155° C., for a period of from about 1 to about 5 minutes. Other conventional drying and curing operations can also be employed. The cured material is subsequently generally neutralized and washed, especially when an acid-producing catalyst has been incorporated in the finishing composition. The neutralization can be effected, for example, by immersing the cured material in an aqueous solution containing small amounts, i.e. up to about 0.1 percent by weight of sodium carbonate. The cured material is then washed with water until all traces of alkali are removed, and again dried. Ordinarily, temperatures of up to about 60° C. have been found satisfactory for use in such operations.

It is to be observed that the amount of finishing composition that impregnates the material being treated can be controlled during the padding operation. Thus, for example, by decreasing the roll pressure of the padding mangle, when such apparatus is employed, the material being treated is impregnated with increasing amounts of the finishing composition. The amount impregnated can also be controlled by varying the proportions of the various components of the finishing composition. In accordance with the present invention, suitable techniques are employed to insure the impregnation of the material being treated with preferably from about 3 percent to about 15 percent and more preferably from about 5 percent to about 12 percent by weight of the thermosetting resin-forming compound, preferably from about 0.1 percent to about 5 percent and more preferably from about 0.3 percent to about 2 percent by weight of at least one of the softening agents of this invention, and, when the use of an acid-producing catalyst is desired, preferably from about 0.5 percent to about 3 percent and more preferably from about 1 percent to about 2.5 percent by weight of said acid-producing catalyst. Further, good results can

be achieved by impregnating any cellulosic fibrous material with a conventional amount of a thermosetting resin-forming compound and a softening agent of this invention in an amount as herein prescribed.

The invention and the advantages accruable in accordance therewith, can be illustrated further by the following specific examples of its practice.

EXAMPLE I

A reaction mixture consisting of 412 grams (4 moles) of diethylene triamine and 120 grams (2 moles) of urea was charged to a 1 liter three-neck flask and slowly heated to a maximum temperature of 190° C. until ammonia evolution had essentially ceased. The crude reaction product was then fractionally distilled, whereupon 207 grams of a substantially pure 2-(imidazolidon-2-yl-1)ethylamine product was obtained at a temperature of from 156° C. to 180° C. under a pressure of 0.5 mm. of mercury.

EXAMPLE II

To a 1 liter three-neck flask equipped with a reflux condenser and decanting head there were charged 142 grams (0.5 mole) of stearic acid, 65 grams (0.5 mole) of 2-(imidazolidon-2-yl-1)ethylamine obtained as described above in Example I and about 30 cubic centimeters of xylene. The charge was refluxed at a temperature maintained in the range of from 170° C. to 190° C. while the water formed during the ensuing reaction was collected in the decanter as an azeotropic mixture with xylene. Upon completion of the reaction, as indicated by a cessation in the formation of water, heating was discontinued. The reaction mixture was then cooled to room temperature, whereupon N-[2-(imidazolidon-2-yl-1)ethyl] stearamide was obtained as a wax-like solid product. The product was purified by recrystallization from methanol and dried. Analysis of the product indicated the following properties: melting point, 124° C. to 125° C.; elemental analysis for nitrogen, calculated for $C_{23}H_{45}O_3N_3$, 10.6 percent; found, 10.6 percent.

Ninety-nine grams (0.25 mole) of the N-[2-(imidazolidon-2-yl-1)ethyl] stearamide product obtained as described above, 16.5 grams (0.55 mole based upon formaldehyde) of paraformaldehyde and 600 ml. of water were charged to a 1 liter three-neck flask and heated to a temperature of 60° C., with stirring. To the heated reaction mixture, 0.25 gram of sodium hydroxide dissolved in a small amount of water was added, and heating then continued at a temperature maintained in the range of from 60° C. to 70° C. Heating was discontinued when the reaction mixture assumed a milky, jelly-like consistency. Upon cooling to room temperature, the resulting N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)-ethyl] stearamide product was recovered in essentially a quantitative yield as a white paste, calculated to contain about 18 to 19 percent solids, by weight. A portion of the paste was stirred well with methanol, filtered and dried. Analysis of the purified N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] stearamide product indicated the following: melting point, 89° C. to 90° C.; elemental analysis for nitrogen, calculated for $C_{25}H_{49}O_4N_3$, 9.2 percent; found, 9.4 percent. The product was found to be an effective softening agent in accordance with the invention.

EXAMPLE III

The procedures described above in Example II were repeated employing, however, as the 2-(imidazolidon-2-yl-1)ethylamine reactant, the crude product obtained by heating a reaction mixture consisting of 612 grams (6 moles) of diethylene triamine and 240 grams (4 moles) of urea to a temperature of 210° C., and subsequently distilling off the excess diethylene triamine under reduced pressure until a vapor temperature of 155° C. at 1 mm. of mercury pressure was reached. Upon completion of the methylolation, the N-methylol-N[2-(3-methylol imidazolidon-2-yl-1)ethyl] stearamide thus produced in essentially a quantitative yield was found to be an effective softening agent in accordance with the invention.

EXAMPLE IV

In a manner as described above in Example II, a mixture consisting of 108 grams (0.5 mole) of a commercial grade of palmitic acid (Emersol 621, acid number, 256.3, equivalent weight, 217), 65 grams (0.5 mole) of 2-(imidazolidon-2-yl-1)ethylamine, obtained as described in Example I, and 100 cc. of xylene were refluxed while removing the water formed during the course of the reaction as an azeotropic mixture with xylene. Upon completion of the reaction, the remaining xylene was distilled off under reduced pressure. The liquid residue was poured into a shallow pan and allowed to cool to room temperature, whereupon N-[2-imidazolidon-2-yl-1)ethyl] palmitamide was recovered as a waxy, light-tan solid product.

A mixture containing 41.5 grams (0.125 mole) of the N-[2-(imidazolidon-2-yl-1)ethyl] palmitamide product obtained as described above, 8 grams (0.27 mole based upon formaldehyde) of paraformaldehyde and 50 cc. of methanol was heated to a temperature of 50° C., with stirring. To the heated reaction mixture, 1 cubic centimeter of a 10 percent aqueous sodium hydroxide solution was added, and heating then continued at the same temperature until a clear, straw-colored solution was obtained. The methanol was thereafter distilled off under reduced pressure and the remaining residue cooled to room temperature whereupon N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] palmitamide was recovered in essentially a quantitative yield as a clear gelatinous product. The product was found to be an effective softening agent in accordance with the invention. For subsequent use as a softening agent, the N-methylol-N-[2-(3-methylol imidazolidon -2-yl-1)ethyl] palmitamide product was dissolved in 50 cc. of water, forming a clear aqueous solution containing 50 percent by weight of the softening agent.

EXAMPLE V

The procedures described above in Example IV were repeated employing, however, as the 2-(imidazolidon-2-yl-1)ethylamine reactant, the crude product obtained by heating a reaction mixture consisting of 612 grams (6 moles) of diethylene triamine and 240 grams (4 moles) of urea to a temperature of 240° C. and subsequently distilling off the excess diethylene triamine under reduced pressure until a vapor temperature of 155° C. at 1 mm. of mercury pressure was reached. Upon completion of the methylolation, the N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] palmitamide thus produced in essentially a quantitative yield was found to be an effective softening agent in accordance with the invention.

The above procedure utilizing a crude 2-(imidazolidon-2-yl-1)ethylamine reactant was also repeated employing, however, as the fatty acid reactant, lauric acid (Neo-Fat 12, equivalent weight 200.5). Upon completion of the methylolation the N-methylol-N[2-(3-methylol imidazolidon-2-yl-1)ethyl] lauramide thus produced in essentially a quantitative yield was found to be an effective softening agent in accordance with the invention.

EXAMPLE VI

To a 500 milliliter three-neck flask there were charged 244 grams (approximately 1 mole) of a commercially available methyl myristate (Uniphat A–50, described as consisting of 2 percent by weight methyl laurate, 4 percent by weight methyl palmitate and 94 percent by weight of methyl myristate), 109 grams (1 mole of 2-(imidazolidon-2-yl-1)ethylamine obtained as described in Example I and 1.7 grams of sodium as sodium ethylate. The mixture, which formed a two-layer system, was gradually heated under reduced pressure, whereupon the charge became homogeneous. Heating was continued, under a pressure of 1 to 2 millimeters of mercury, to a kettle temperature of 150° C., at which temperature a sample of distillate showed signs of crystallization upon being

cooled to room temperature. The entire reaction mixture was then cooled to room temperature, whereupon N-[2-imidazolidon-2-yl-1)ethyl] myristamide (also containing small amounts of the corresponding lauramide and palmitamide) was obtained as a white waxy solid product. The product was recrystallized from 95 percent ethanol in a 251 gram (78 percent of theoretical) yield.

A mixture containing 113 grams (0.33 mole) of the N-[2-(imidazolidon-2-yl-1)ethyl] myristamide product obtained as described above, 22 grams (0.67 mole based upon formaldehyde) of paraformaldehyde and 200 cubic centimeters of methanol were charged to a 500 milliliter three-neck flask and heated to a temperature of 50° C., with stirring. To the heated reaction mixture, 1 cubic centimeter of a 10 percent sodium hydroxide solution was added, and heating was then continued at the same temperature until a clear, straw-colored solution was obtained. The pH of the solution was adjusted to 7 by the addition of dilute sulfuric acid. The methanol was thereafter distilled off under reduced pressure, and the remaining residue cooled to room temperature whereupon approximately 50 grams of N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1-)ethyl] myristamide (also containing small amounts of the corresponding lauramide and palmitamide) was recovered in essentially a quantitative yield as a white waxy product. For subsequent use as a softening agent, the N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] myristamide product was dissolved in sufficient water to form a clear aqueous solution containing 50 percent by weight of the softening agent.

EXAMPLE VII

The procedures described above in Example VI were repeated employing, however, as the 2-(imidazolidon-2-yl-1)ethylamine reactant, the crude product obtained by heating a reaction mixture consisting of 612 grams (6 moles) of diethylene triamine and 240 grams (4 moles) of urea to a temperature of 240° C. and subsequently distilling off the excess diethylene triamine under reduced pressure until a vapor temperature of 155° C. at 1 mm. of mercury pressure was reached. Upon completion of the methylolation, the N-methylol-N[2-(3-methylol imidazolidon-2-yl-1)ethyl] myristamide (also containing small amounts of the corresponding lauramide and palmitamide) thus produced in essentially a quantitative yield was found to be an effective softening agent in accordance with the invention.

EXAMPLE VIII

Finishing compositions were prepared containing the following: 1,3-dimethylol imidazolidone-2, 7.5 percent by weight; 2-amino-2-methyl-propanol-1 hydrochloride, 0.5 percent by weight; various amounts of different softening agents as indicated below in Table A; 0.24 percent by weight of an alkyl phenyl polyethylene glycol ether (Tergitol NPX, Union Carbide Chemicals Co.), and 5 percent by weight of a cold water-soluble starch ether (Solvitose HDF, Paisley Products, Inc.), the remaining component being water. Samples of cellulosic textile material were then treated with the finishing compositions and tested by the procedures described below. The results obtained are tabulated below in Table A.

Treating Procedure

The fabric used was desized percale sheeting having a 96 x 90 (warp-fill) count. Numbered sheets, each measuring 10 inches x 24 inches, cut in the warp direction, were conditioned to constant weight at a temperature of 70° F. and 65 percent relative humidity. After immersion in the finishing composition at 50° C. for 2.5 minutes, the sheets were put through a hand wringer and then reimmersed in the finishing composition for another 2.5 minutes. A second pass was made through the wringer and the specimens were allowed to air-dry, ironed at a low heat to remove wrinkles, oven-dried at 110° C. for 10 minutes and cured at 150° C. for five minutes. After washing with a 0.5 percent sodium carbonate solution, the sheets were given three cold water rinses and a boiling water rinse. The sheets were then brought again to constant weight at a temperature of 70° F. and 65 percent relative humidity.

Test Methods

Tear strength.—The tear strength was determined according to Federal Specification CCC–T–191b test method 5132. Three specimens, each measuring 4 inches x 2.5 inches, with the long dimension parallel to the warp direction, were cut from each sheet. By means of a Elmendorf tear tester, the force in grams required to tear through 43 mm. of fabric was obtained in triplicate. The averages of the values are recorded below in Table A.

Chlorine retention.—Damage caused by retained chlorine was determined according to AATCC tentative test method 69–52. Six specimens, each measuring 4 inches x 6 inches, were cut from each sheet with the long dimension parallel to warp direction. The test specimens were held in boiling water for three minutes and then three of the specimens were immersed for 15 minutes in a weight of test solution (containing 0.25 percent available chlorine) equal to 50 times the weight of the specimen. The control specimens and treated specimens were given six fresh water rinses and then dried by ironing at a rayon heat for approximately 10 seconds. After conditioning at 65 percent humidity and 70° F. for 24 hours, the control and treated specimens were placed in a scorch tester (type SO–3, manufactured by the Atlas Electrical Devices Co., Chicago, Ill.), at 365° F. for 30 seconds. The actual damage was determined by recording the breaking strength in kilograms of each specimen with an Amthor tensile tester (manufactured by the Amthor Testing Instruments Co., Brooklyn, N.Y.). The average values of the breaking strengths of both the control and treated specimens are recorded below in Table A.

Crease resistance.—Crease-resistance was determined by measuring the angle of recovery according to Federal Specification CCC–T–191b test method 5212. Specimens, each measuring 4 cm. x 1.5 cm., cut parallel to both the warp and fill direction were placed into a specimen holder to produce a fold 1.8 cm. from the free end. The specimens were subjected to a 1.5-pound weight for five minutes and then allowed to recover for five minutes while held on a protractor. The percent angle recovery in the warp direction is recorded below in Table A.

Discoloration.—Specimens, each measuring 4 inches x 6 inches, were subjected to accelerated ageing conditions in an oven at a temperature of 100° C. for 96 hours. The amount of yellowing was determined by measuring the reflectances on a Photovolt reflectometer (model 610) before and after ageing. A deviation of −1.0 indicates a trace of discoloration, a deviation of −2.0 indicates noticeable yellowing while a deviation of −3.0, or more, indicates considerable yellowing.

In Table A below, softening agent No. 1 is N-methylol-N-[2-(3-methylol immidazolidon-2-yl-1)ethyl] stearamide, produced as described in Example II above; softening agent No. 2 is N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] palmitamide, produced as described in Example IV above; softening agent No. 3 is a conventional glyoxalidine softening agent, 1-(2-hydroxyethyl)-2-heptadecyl imidazoline. Also included in the table for comparison are data obtained from runs in one of which water was substituted for the finishing composition (untreated) and in another of which no softening agent was employed (control). As further tabulated, the concentration of softening agent in the finishing composition is indicated in percent by weight; the dry pick-up represents the amount of finishing composition retained by the treated material after drying and curing, and is indicated in percent by weight based upon the weight of the untreated fabric; the amount of softening agent on the fabric is similarly indicated.

TABLE A

Softening agent employed	Concentration of softening agent in finishing composition	Dry pick-up	Amount of softening agent on fabric	Tear strength	Chlorine retention (breaking strength)		Crease resistance (percent angle of recovery)	Discoloration (reflectance deviation)
					Control	Bleached		
Untreated				1,109	30.8	24.8	49.5	−1.0
Control		4.85		433	19.0	12.3	81.5	−0.5
No. 1	0.5	6.53	0.34	544	16.5	13.7	81.0	−1.0
No. 1	1.0	7.95	0.70	613	16.5	14.5	81.0	−1.0
No. 1	2.0	9.03	1.46	688	18.1	14.8	85.0	−1.0
No. 2	0.5	6.43	0.30	603	19.8	11.2	78.5	−1.0
No. 2	1.0	6.53	0.58	661	17.2	11.5	77.8	−1.0
No. 2	2.0	7.16	1.51	715	18.2	11.7	79.0	−0.5
No. 3	0.5	4.45	0.21	603	16.7	7.0	75.5	−3.0
No. 3	1.0	7.90	0.69	587	17.7	10.8	80.0	−4.5
No. 3	2.0	9.28	1.50	613	17.8	9.8	76.0	−6.0

Several of the advantages accurable in accordance with the invention, viz. improved tear strength accompanied by less chlorine retention and discoloration, can readily be seen from the above table.

EXAMPLE IX

In a manner similar to that described above in Example VIII, finishing compositions were prepared containing different softening agents of this invention in varying amounts. In Table B below, softening agent No. 1 is N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)-ethyl] stearamide, produced as described in Example III above; softening agent No. 2 is the corresponding palmitamide, produced as described in Example V above; softening agent No. 3 is the corresponding lauramide, produced as described in Example V above; and softening agent No. 4 is the corresponding myristamide, produced as described in Example VII above. These finishing compositions were employed to treat cellulosic textile material essentially as described above in Example VIII, and the treated material tested as further described therein.

TABLE B

Softening agent	Amount of softening agent in finishing composition	Dry pick-up	Amount of softening agent on fabric	Tear strength	Crease resistance (percent angle of recovery)	Discoloration (reflectance deviation)
Untreated				1,082	46.1	−0.5
Control		4.25		432	80.6	−1.0
No. 1	0.5	5.04	0.25	528	81.1	−1.0
No. 1	1.0	5.20	0.49	560	79.4	−1.0
No. 1	2.0	5.80	1.02	581	83.3	−1.0
No. 2	0.5	5.15	0.29	469	78.8	−1.0
No. 2	1.0	5.40	0.52	517	79.4	−1.0
No. 2	2.0	5.95	1.04	533	82.2	−1.0
No. 3	0.5	5.35	0.29	474	80.0	−0.5
No. 3	1.0	6.15	0.58	480	78.8	−1.0
No. 3	2.0	6.25	1.09	512	79.4	−0.5
No. 4	0.5	5.30	0.26	480	80.6	0
No. 4	1.0	5.35	0.50	512	81.1	−1.0
No. 4	2.0	5.90	1.03	549	83.8	0

EXAMPLE X

In a manner similar to that described above in Example VIII, finishing compositions were prepared containing different softening agents in varying amounts. In Table C below, softening agent No. 1 is N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] stearamide prepared as described above in Example III, softening agent No. 2 is a commercially available cationic softening agent. These finishing compositions were employed to treat cellulosic textile material essentially as described in Example VIII and the treated material tested as further described therein.

TABLE C

Softening agent	Amount of softening agent in finishing composition	Dry pick-up	Amount of softening agent on fabric	Tear strength	Crease resistance (percent angle of recovery)	Discoloration (reflectance deviation)
Untreated				1,056	47.7	−1.0
Control		5.85		416	82.2	−1.0
No. 1	0.5	5.95	0.30	469	83.3	−1.0
No. 1	1.0	6.20	0.59	523	83.9	−1.0
No. 1	2.0	6.62	1.15	549	84.4	−1.0
No. 2	0.5	6.14	0.31	469	82.2	−3.0
No. 2	1.0	6.33	0.60	485	81.7	−3.0
No. 2	2.0	7.02	1.24	491	81.7	−4.0

EXAMPLE XI

To test the permanence of the softening agents of the invention, finishing compositions were prepared as described above in Example VIII. Run No. 1 employed a finishing composition containing no softening agent; run No. 2, employed a finishing composition containing 2 percent by weight of N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] stearamide prepared as described above in Example III. The finishing compositions were then employed to treat cellulosic textile material essentially as described above in Example VIII, using ten specimens of cotton percale sheeting with each finishing composition. After calculating the amount of finishing composition retained by the treated material (add-on), samples were cut from the first specimen of each series and subjected to the Elemendorf tear test as described above in Example VIII and the Monsanto crease-recovery test as described in Monsanto Technical Service Bulletin T30–45.1, published by the Monsanto Chemical Co., Springfield, Mass. All of the specimens were placed in a General Electric Filter-Flo washer, given four short cycle washings, allowed to air-dry, ironed, again brought to constant weight and weighed. This process was repeated after 8, 16, and 24 washings. The short cycle washing consisted of a three-minute interval for filling with 17 gallons of water at 48° C., a four-minute agitation with about 100 grams of a commercially available detergent, a three-minute interval during which the wash water was removed, a three-minute interval for filling with 17 gallons of rinse water at 38° C., a two-minute rinse agitation and a three-minute damp-dry spin. The results obtained are indicated below in Table D. In the table the average weight of the fabric specimens and the add-on is indicated in grams.

TABLE D

AFTER PADDING, DRYING AND CURING

Run No.	Average fabric weight	Average add-on	Tear strength	Crease recovery
1	19.664	0.947	432	77.7
2	20.085	1.130	597	84.4

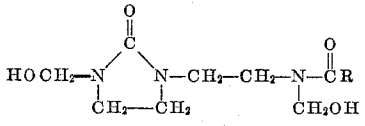
AFTER FOUR WASHINGS

Run No.	Average weight loss	Percent loss of add-on	Tear strength	Crease recovery
1	0.027	2.85	437	78.8
2	0.026	2.30	613	83.3
AFTER EIGHT WASHINGS				
1	0.057	6.02	432	77.7
2	0.055	4.86	608	83.3
AFTER SIXTEEN WASHINGS				
1	0.085	8.99	448	77.2
2	0.085	7.52	640	83.3
AFTER TWENTY-FOUR WASHINGS				
1	0.099	10.45	464	77.2
2	0.097	8.60	624	83.0

In addition, the hand of the cellulosic textile material treated in accordance with the invention as described above was evaluated objectively by manually feeling the fabrics and visually observing their drape. In all cases, an improved hand was found for the material treated in accordance with the invention when compared with the control fabric (no softening agent). This improved hand was still evident after twenty-four washings.

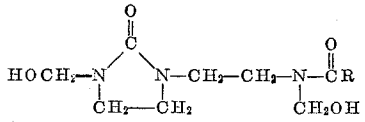
What is claimed is:

1. As new compositions of matter, N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamides of the formula:



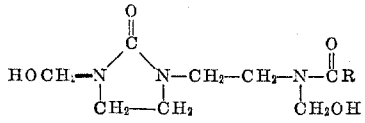
wherein R is a monovalent aliphatic radical selected from the group consisting of alkyl and alkenyl of from 8 to 22 carbon atoms.

2. As new compositions of matter, N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamides of the formula:



wherein R is alkyl of from 12 to 22 carbon atoms.

3. As new compositions of matter, N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamides of the formula:



wherein R is alkenyl of from 12 to 22 carbon atoms.

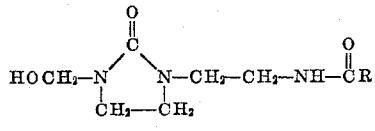
4. As a new composition of matter, N-methylol-N[2-(3-methylol imidazolidon-2-yl-1)ethyl] stearamide.

5. As a new composition of matter, N-methylol-N[2-(3-methylol imidazolidon-2-yl-1)ethyl] lauramide.

6. As a new composition of matter, N-methylol-N[2-(3-methylol imidazolidon-2-yl-1)ethyl] palmitamide.

7. As a new composition of matter, N-methylol-N[2-(3-methylol imidazolidon-2-yl-1)ethyl] myristamide.

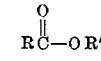
8. A process for the production of an N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamide of the formula



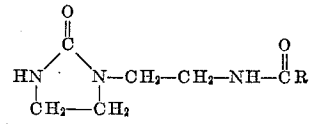
wherein R is a monovalent aliphatic radical selected from the group consisting of alkyl and alkenyl of from 8 to 22 carbon atoms, which process comprises the steps of heating a mixture of 2-(imidazolidon-2-yl-1)ethylamine with a member selected from the group consisting of the aliphatic carboxylic acids of the formula



wherein R is as defined above and the alkyl aliphatic carboxylic acid esters of the formula

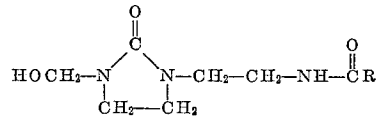


wherein R is as defined above and R'' is an alkyl radical such that the alcohol of the formula R''OH has a boiling point below that of the alcohol of the formula, ROH, at a temperature of from about 30° C. to about 200° C., thereby producing an N-[2-imidazolidon-2-yl-1)ethyl] acylamide of the formula



wherein R is as defined above, and subsequently heating a mixture of said N-[2-(imidazolidon-2-yl-1)ethyl] acylamide with a methylolating agent selected from the group consisting of formaldehyde and paraformaldehyde, at a temperature of from about 20° C. to about 100° C., and recovering the N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamide thereby formed.

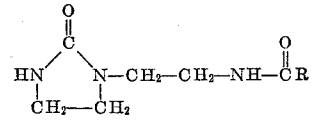
9. A process for the production of an N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamide of the formula



wherein R is a monovalent aliphatic radical selected from the group consisting of alkyl and alkenyl of from 8 to 22 carbon atoms, which process comprises the steps of heating a mixture of 2-(imidazolidon-2-yl-1)ethylamine with an aliphatic carboxylic acid of the formula



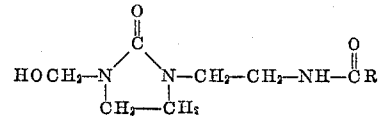
wherein R is as defined above, at a temperature of from about 30° C. to about 200° C., thereby producing an N-[2-(imidazolidon-2-yl-1)ethyl] acylamide of the formula



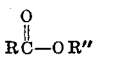
wherein R is as defined above, and subsequently heating a mixture of said N-[2-imidazolidon-2-yl-1)ethyl] acylamide with a methylolating agent selected from the group consisting of formaldehyde and paraformaldehyde, at a temperature of from about 20° C. to about 100° C., and recovering the N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamide thereby formed,

10. The process according to claim 9, wherein R is alkyl of from 12 to 22 carbon atoms.

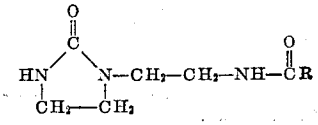
11. A process for the production of an N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamide of the formula



wherein R is a monovalent aliphatic radical selected from the group consisting of alkyl and alkenyl of from 8 to 22 carbon atoms, which process comprises the steps of heating a mixture of 2-(imidazolidon-2-yl-1)ethylamine with an alkyl carboxylic acid ester of the formula



wherein R is as defined above and R'' is an alkyl radical such that the alcohol of the formula R''OH has a boiling point below that of the alcohol of the formula ROH, at a temperature of from about 30° C. to about 200° C., thereby producing an N-[2-(imidazolidon-2-yl-1)ethyl] acylamide of the formula



wherein R is as defined above, and subsequently heating a mixture of said N-[2-(imidazolidon-2-yl-1)ethyl] acylamide with a methylolating agent selected from the group consisting of formaldehyde and paraformaldehyde, at a temperature of from about 20° C. to about 100° C., and recovering the N-methylol-N-[2-(3-methylol imidazolidon-2-yl-1)ethyl] acylamide thereby formed.

12. The process according to claim 11, wherein R is alkyl of from 12 to 22 carbon atoms.

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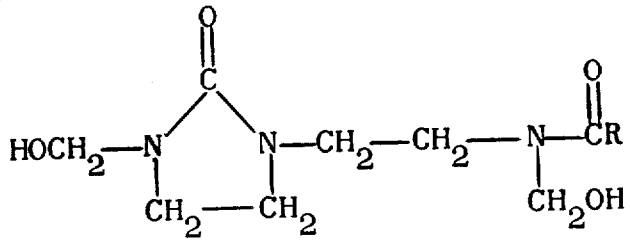
CERTIFICATE OF CORRECTION

Patent No. 3,024,246 March 6, 1962

Henry G. Goodman, Jr.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 13, lines 71 to 75, and column 14, lines 36 to 41 and lines 71 to 75, comprising the first formula of each of the claims 8, 9 and 11, should appear as shown below instead of as in the patent:



Signed and sealed this 27th day of August 1963.

(SEAL)
Attest:
ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents