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TREATMENT OF TEXTILES AND N-HALOGENATED AMINE-ALDEHYDE AGENTS THEREFOR

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The present invention relates to textile finishing agents, to improved methods of finishing textile materials and to the products so produced, and more particularly to textile finishing agents which impart excellent dimensional stability and crease and crush resistance to textile materials. The invention more particularly includes finishing agents for the treatment of textile materials comprising proteinaceous yarns or fibers and/or cellulose derivative staple fibers or filaments; improved methods of finishing such textile materials and the improved textile materials so produced.

Textile materials have been treated, heretofore, with a variety of textile finishing agents for the purpose of improving the dimensional stability and/or crease and crush resistance of such textile materials. For example, cotton, rayon, cellulose derivatives, nylon and other fibers, yarns, and fabrics have been treated with urea-formaldehyde resins, thio urea-formaldehyde resins, melamine-formaldehyde resins and alkylated derivatives thereof, aldehydes such as formaldehyde and the like. Moreover, proteinaceous textile materials such as wool and other keratinous fibers, yarns and fabrics and animal furs have been treated with such finishing agents or have been treated with such other agents as aqueous or anhydrous solutions containing halogen per se, or with a urea-formaldehyde resin which is cured in situ and then followed by a chlorine treatment.

It has also been proposed in the Arsem Patent No. 2,472,361 to prepare organic N-halogen compounds by treating organic nitrogen compounds including melamine, melamine resins and urea-formaldehyde resins with sodium hypochlorite or chlorine under acidic conditions. However, the melamine resins or urea resins thus employed are either water-insoluble prior to the formation of the N-halogen derivative, or the N-halogen derivative thereof is water-insoluble. Moreover, the N-halogen melamine or urea resins prepared as described in the Arsem patent are sometimes obtained as colored precipitates. Because of the water-insolubility of the N-halogen melamine and urea resins of Arsem they are not suitable for the impregnation of textile materials for shrinkproofing and creaseproofing purposes.

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In accordance with the present invention, on the other hand, it is possible to prepare aqueous solutions of water-soluble N-halogenated melamine-aldehyde and urea-aldehyde condensation products which are especially suitable for the treatment of textile materials and particularly textile fabrics. Moreover, in accordance with the present invention an improvement and advance in the textile industry is effected wherein textile materials treated with such solutions and then dried and cured, not only possess improved dimensional stability and crease or crush resistance, but also possess a soft, full and a substantially natural hand or feel, satisfactory tensile strength and wearing qualities.

One object of the present invention is to provide novel, water-soluble finishing agents for textile materials.

A further object of this invention is to provide aqueous solutions comprising a new class of water-soluble condensation products which remain water-soluble for a period of time suitable for textile impregnation.

A further object of this invention is to provide methods of imparting excellent dimensional stability and crease or crush resistance to textile materials without substantially altering the hand or feel of such textile materials.

Still further objects and advantages of this invention will appear in the following description and appended claims. However, before explaining the present invention in detail, it is to be understood that the invention is not limited in its application to the details described herein since the invention is capable of other embodiments and of being carried out in various ways. Also it is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation, and it is not intended to limit the invention claimed herein beyond the requirements of the prior art.

The textile treating methods of this invention are carried out, in general, by impregnating a textile material, particularly a textile fabric, and preferably a fabric containing wool, with a neutral to alkaline aqueous solution comprising a water-soluble N-halogenated amine-formaldehyde condensation product such as a water-soluble N-halogenated melamine-formaldehyde

condensation product or a water-soluble N-halogenated urea-formaldehyde condensation product or a water-soluble N-halogenated methylated derivative of such condensation products, and then curing the condensation product in situ on the textile material. The impregnated textile material is preferably extracted, for example, by centrifuging the material or passing it between squeeze rolls to remove excess solution prior to the curing operation.

The impregnated material may be dried prior to the curing of the condensation product or the material may be dried simultaneously with the curing of the condensation product. The application of from about 2 to 25% by weight of condensation product solids, based on the dry textile material, followed by curing of the condensation product solids to the water-insoluble state provides a textile material having good dimensional stability and a soft, full and substantially natural hand or feel and a satisfactory tensile strength. The application of from about 10 to 25% by weight of condensation product solids, based on the dry material, under such conditions provides a textile material having excellent dimensional stability and crease or crush resistance.

The term "neutral to alkaline aqueous solution" as employed in the description and appended claims is intended to mean a solution having a pH of 7.0 or higher as measured by the glass electrode. The preferred solutions for the purposes of this invention are those which have a pH between about 7.2 and 9.5.

A wide variety of textile materials may be treated in accordance with the present invention. As examples of such textile materials may be mentioned cotton, rayon, cellulose derivatives, such as cellulose esters and ethers and more particularly cellulose acetate, nylon, wool and other keratinous materials, animal furs, protein fibers such as casein fibers, zein fibers, peanut protein fibers and the like. Moreover, textile materials of the above type may be in the form of yarns, fibers, filaments, staple fibers, fabrics and the like, and may contain one of the above materials wholly or may be made up of suitable mixtures of such materials.

The textile treating methods described herein are preferably employed in the treatment of textile fabrics comprising proteinaceous fibers or yarns, particularly all wool fabrics, or in the treatment of textile fabrics comprising cellulose ester staple fibers or filaments, particularly textile fabrics comprising cellulose acetate staple fibers or filaments or both.

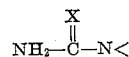
The water-soluble N-halogenated amine-formaldehyde condensates or finishing agents used in the textile treating methods of the present invention may be prepared in a variety of ways. One suitable method of preparing such finishing agents comprises reacting a halogenating agent such as chlorine, bromine and the like, or a compound which contains active halogen, that is, yields free halogen in an aqueous medium, for example, a compound such as chloramine T, in a neutral to alkaline aqueous solution with a water-soluble heterocyclic amine-formaldehyde condensation product, as for example, a water-soluble amino-triazine-formaldehyde condensation product such as a water-soluble melamine-formaldehyde condensation product, or a water-soluble aliphatic amine-formaldehyde condensation product such as a water-soluble urea-formaldehyde condensation product. The aque-

ous solution in which the reaction is carried out should be maintained at a pH of at least 7.0 and preferably between 7.2 and 9.5 to prevent the precipitation of the condensation product from the solution as a water-insoluble polymerizate. In cases where the pH of the solution tends to drop during the reaction between the halogenating agent and the condensation product the pH of the solution is suitably maintained at 7.0 or higher by the addition of sodium hydroxide or sodium carbonate or some other suitable alkali. The reaction between the halogenating agent and the condensation product is normally carried out at room temperature, that is, at a temperature of about 70 to 90° F., but temperatures as low as 40° F. or as high as 110° F. may also be used.

The amine-formaldehyde condensation product employed in the above reaction should be water-soluble, and preferably monomeric or essentially monomeric. Such condensation product should contain at least one nitrogen atom containing at least one replaceable hydrogen atom so that the halogen or the active halogen derived from the halogenating agent can replace such hydrogen atom to form an N-halogen derivative of the condensation product.

As examples of suitable water-soluble heterocyclic amine-formaldehyde condensation products, including amino-triazine-formaldehyde condensation products, which are employed in preparing the finishing agents of this invention in addition to those described above may be mentioned water-soluble condensation products of formaldehyde with 2,4 diamino-6-hydroxy-s-triazine, 2,4 diamino-6-chloro-s-triazine, melam, melem, and the like. Water-soluble thiourea modified melamine-formaldehyde condensation products are also useful. The water-soluble methylated derivatives of the foregoing condensation products, that is, water-soluble methyl ethers of such condensation products derived by reacting the water-soluble heterocyclic amine-formaldehyde condensates with methyl alcohol are particularly useful.

As examples of suitable water-soluble aliphatic amine-formaldehyde condensation products which are employed in preparing the finishing agents of this invention, in addition to those described above, may be mentioned water-soluble condensation products of formaldehyde with thiourea, dicyandiamide, cyanamide, guanidine and the like. In general the water-soluble condensation product of formaldehyde and any aliphatic amine containing the grouping



where X is oxygen, sulfur or an imido group and the free valences of the nitrogen atom are attached to hydrogen or carbon or both are useful. Such amine compound contains from 1 to 4 carbon atoms and no other atoms other than those set forth in the above structural formula.

The preferred finishing agents for the purposes of this invention are those water-soluble N-halogenated condensation products which are derived by replacing a hydrogen atom on one of the nitrogen atoms of a water-soluble melamine-formaldehyde condensation product or a water-soluble methylated melamine-formaldehyde condensation product with a halogen atom and preferably a chlorine atom.

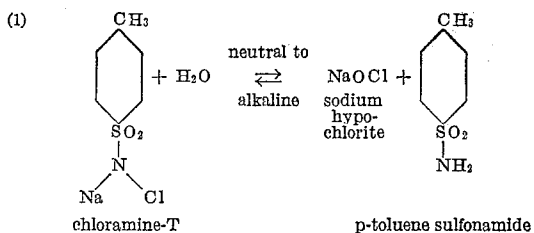
Amine-formaldehyde condensation products of the type used above are suitably prepared by re-

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acting the amine with formaldehyde in a neutral to alkaline aqueous medium until a monomeric or low polymeric condensation product is obtained, that is, it is preferred to avoid condensation products which are difficultly soluble in an aqueous medium. Suitable methylated derivatives of the above resins may be prepared by reacting the monomeric or low polymeric condensation product with methyl alcohol under acidic conditions, after which the solution is made alkaline. Moreover, it is necessary to obtain a water-soluble methylated derivative.

As examples of suitable halogenating agents which are useful in preparing the finishing agents of this invention are the halogens per se, that is, chlorine, bromine, iodine and the like, or compounds which yield active (free) chlorine, bromine, iodine and the like in an aqueous medium under neutral or alkaline conditions as, for example, sodium and calcium hypochlorite or the corresponding bromine, iodine, and fluorine derivatives of such compounds, and compounds such as chloramine B (otherwise known as N, N-sodium chlorobenzene sulfonamide), chloramine T (otherwise known as chlorazene or sodium p-toluene-sulfochloramine), dichloramine T (otherwise known as p-toluene-dichlorosulfamine or N, N-dichloro toluene sulfonamide), N, N'-dichloro dimethyl hydantoin or the corresponding bromine, iodine or fluorine derivatives of such compounds. The halogenating agents employed herein may be water-soluble or water-insoluble. However, it is preferred to use water-soluble halogenating agents since the water solution of the water-soluble N-halogenated amino-formaldehyde condensations obtained by the reaction of such halogenating agents and the water-soluble amino-formaldehyde condensation products are used without further processing. On the other hand, when water-insoluble halogenating agents are employed it is usually necessary to separate the unreacted halogenating agent from the solution prior to the impregnation of the textile materials. Preferred halogenating agents are chloramine T, sodium hypochlorite or alkaline solutions of chlorine in water.

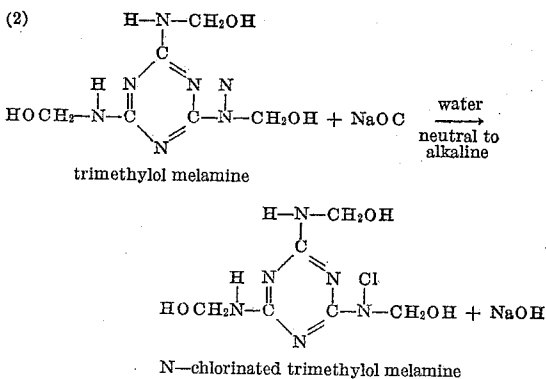
The halogen of the halogenating agent whether it be a halogen per se or free halogen derived from one of the halogenating agents described above reacts in part with the amine-formaldehyde condensation products hereinbefore described by replacing a replaceable hydrogen atom on one of the nitrogen atoms of the amine-aldehyde condensation product to form an N-halogenated condensation product. The mechanism of the reaction varies with the particular halogenating agent employed but the end product is the same. For convenience in description the reaction mechanism between chloramine T and trimethylol melamine is described below but it is to be understood that similar reactions take place between chloramine T and other amine-formaldehyde condensation products containing at least one nitrogen atom having at least one replaceable hydrogen atom:



As is shown in the above equation the chlor-

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amine T dissociates in the presence of water and under neutral to alkaline conditions into sodium hypochlorite and p-toluene sulfonamide. This reaction is reversible and therefore the compounds described in the above equation are present in equilibrium.



The sodium hypochlorite obtained by the dissociation of chloramine T as illustrated in Equation 1 releases free chlorine which replaces one of the replaceable hydrogen atoms on one of the nitrogen atoms of the trimethylol melamine, and sodium hydroxide is also formed. The resulting product is an N-chlorinated trimethylol melamine which is water-soluble in a neutral to alkaline aqueous solution.

The amount of halogenating agent employed may be varied to some extent, but should not be sufficient to provide enough halogen to precipitate the condensation product from solution. In general, the amount of halogenating agent employed to prepare the N-halogenated condensation products varies between about 0.1 and 20% based on the weight of the condensation product in the solution, depending on the molecular weight of the halogenating agent, the amount of active or available halogen present therein and the condensation product used. Thus in those instances where halogen per se is employed it is generally desirable to employ from about 0.1 to 2% by weight of halogen based on the weight of the condensation product. On the other hand when high molecular weight halogenating agents which contain about 10 to 15% of available halogen are used as, for example, chloramine-T, it is generally desirable to employ from about 5 to 20% by weight of such halogenating agent based on the weight of the condensation product in the solution. In most instances when the halogenating agent is a compound which contains active or available halogen as, for example, chloramine-T it is preferred to use from about 5 to 12% by weight of the halogenating agent based on the weight of the condensation product.

The type of textile material on which the N-halogenated condensation product or finishing agent is to be applied also has some influence on the amount of halogenating agent used in preparing the N-halogenated condensation product. While the amounts of halogenating agent described above are generally suitable when the N-halogenated condensation product is to be applied to proteinaceous textile materials and cellulose esters textile materials, it is preferred to use from about 0.05 to about 5% by weight of the halogenating agent based on the weight of the condensation product to prepare the N-halogenated condensation product for use on rayon and cotton textile materials.

Although the preparation of the N-halogenated condensation products or finishing agents

of this invention has been described with reference to the use of a neutral to alkaline aqueous reaction medium, it is to be understood that suitable products may also be prepared by treating solid, water-soluble amine-formaldehyde condensates with halogen gas using the proportions of reactants described above, after which the N-halogenated solid product may be dissolved in a neutral to alkaline aqueous solution.

The N-halogenated condensation products described herein are water-soluble and contain active or available halogen. The halogen is generally released quite slowly under neutral or alkaline conditions and at normal room temperatures. However, under acidic conditions and at elevated temperatures the halogen therein is liberated quite rapidly. The neutral to alkaline aqueous solutions comprising the water-soluble N-halogenated condensation products are stable without precipitation of the condensation product for practical periods of time, usually from 8 to 72 hours or longer. The addition of curing agents or catalysts usually shortens the period of stability but the resulting solutions have suitable stability for textile impregnation.

The above described N-halogenated amine-formaldehyde condensation products may be applied to textile materials in a variety of ways. For example, the material may be immersed, alternately dipped and allowed to drain, or padded one or more times through an aqueous bath containing the N-halogenated condensation product or an aqueous solution of the N-halogenated condensation product may be sprayed on the material. Moreover, other methods of applying the N-halogenated condensation product to textile materials may be used. In order to assist the penetration of the condensation product into the textile materials, a water-soluble wetting agent may be added to the solution containing the N-halogenated condensation product preferably prior to treating such materials. A wide variety of water-soluble wetting agents may be used for the above described purpose. As examples of such wetting agents may be mentioned water-soluble long chain sulfonated aromatic compounds such as the sodium salt of cetyl benzene sulfonic acid, the sodium salt of stearyl benzene sulfonic acid, the sodium salt of octa-hydroanthracene sulfonic acid, 2(β -sulfonaphthyl) stearic acid and the like; water-soluble long chain polyethylene oxides and polyethylene oxide derivatives such as Carbowax (polymerized ethylene oxide), water-soluble sorbitol monolaurate-, sorbitol monopalmitate-, sorbitol monostearate-, and sorbitol monooleate polyethylene oxide derivatives, water-soluble aryl alkyl polyether alcohols, water-soluble organic polyether alcohols and the like. Moreover, suitable mixtures of water-soluble wetting agents may be used.

In addition to the water-soluble N-halogenated condensation product or products, the aqueous solution with or without a water-soluble wetting agent as used for the treatment of textile materials may also contain an appropriate amount of a curing catalyst or catalysts. Although the N-halogenated condensation product can be cured in situ on the textile materials without the aid of catalysts or accelerators, it is generally desirable to employ a suitable catalyst in order to decrease the time required to bring about the cure. It is possible to use a wide variety of curing catalysts or accelerators for this purpose. As examples of these may be mentioned zinc chloride, diammonium hydrogen phosphate,

oxalic acid, ammonium chloride, dilute mineral acids such as, for example, hydrochloric and sulfuric acids, acetic acid, amino-alkylalcohol phosphate salts such as, for example, 2-amino, 2-methyl propanol phosphate and the like. Care should be taken, however, to maintain the solution in a neutral to alkaline condition prior to and during the textile impregnation.

Suitable finishing solutions for use according to the invention may preferably contain from 2 to 30% of N-halogenated amine-formaldehyde condensation product from 0 to 2% of a water-soluble wetting agent, from 0 to 8.0% of a curing catalyst or accelerator, the balance consisting primarily of water. Moreover, the above solutions may be used at any appropriate temperature as, for example, from 10 to 40° C. Furthermore, the textile materials may be treated with such solutions for suitable periods of time as, for example, up to 10 or more minutes. Although the above conditions show a preferred embodiment of the invention, they may be obviously altered to some extent depending upon the type of material treated and/or the type of finish desired.

After the textile material has been treated in a suitable manner as hereinbefore described, it may be dried and then cured, or dried and cured in the same operation. However, it is generally desirable to extract a suitable quantity of excess solution from the textile materials in order to more carefully control the amount of N-halogenated condensation product deposited in the finished material, and also to decrease the length of time required for drying and/or curing. Extraction may be accomplished in a variety of ways as, for example, by padding, wringing, hydroextraction and the like. The degree of extraction is preferably adjusted so that from 2 to 25% solids are deposited on the textile material. The wetted textile materials may be dried and/or cured in any suitable manner as long as substantial injury to the material is avoided. If preliminary drying is desired, suitable temperatures as, for example, from 150 to 225° F. may be used. The resin impregnated textiles may then be cured at appropriate temperatures, preferably at from 240 to 350° F. until the resin has set to the desired extent by the action of heat and/or catalyst. Curing times of from 1 to 60 minutes may be used depending upon the curing temperature and catalyst. Longer curing times may be necessary if a catalyst is omitted.

A further understanding of the invention will be obtained from the following examples, which are intended to be illustrative but not limitative of the invention.

Example I

A low polymeric water-soluble amine-formaldehyde condensation product (hereinafter referred to as Condensate A) is prepared by reacting 4 mols of formaldehyde in the form of a 37% neutral aqueous solution with 1 mol of melamine at a pH of about 9.3. The mixture is maintained at a temperature of approximately 80° C. during the reaction and as soon as it becomes clear the solution is spray dried while the temperature of the solution is maintained at approximately 80° C. An amorphous solid having extreme water-solubility is obtained.

An alkaline aqueous solution comprising a water-soluble N-halogenated amine-formaldehyde condensation product is prepared by stirring the following ingredients (parts shown are

parts by weight) for about 12 minutes at a temperature of approximately 75° F.:

75 parts of Condensate A, prepared as described above.

420 parts of water.

1 part of the condensation product of 1 mol of paraoctyl phenol and 11 mols of ethylene oxide.

0.8 part of ammonium chloride as a curing catalyst.

10 parts of sodium hypochlorite solution containing 12% available chlorine by volume.

The resulting solution comprised a water-soluble N-chlorinated melamine formaldehyde condensate which contains active chlorine. The pH of the solution is approximately 9.3 as measured by the glass electrode.

A piece of wool flannel measuring about 18 inches by 22 inches is padded through the above solution so as to pick up about 12.4% by weight of condensation product solids, based on the dry flannel weight. The flannel is next dried and cured at a temperature of approximately 300° F. for a period of about 30 minutes.

The wool flannel treated in the above manner exhibits excellent dimensional stability or resistance to felting, even after three wool washes, and has a soft and full hand or feel. In addition, the tensile strength of the treated flannel in warp and filling direction is entirely satisfactory.

Example II

An alkaline aqueous solution comprising a water-soluble N-halogenated amine-formaldehyde condensate is prepared by stirring the following ingredients (parts shown are parts by weight) for about 15 minutes at a temperature of approximately 85° F.:

27 parts of the condensate as prepared in Example I (Condensate A).

2.7 parts of chloramine T.

69 parts of water.

4.3 parts of 2-amino, 2-methyl propanol phosphate in the form of a solution containing 35% by weight of a salt prepared by neutralizing 2-amino, 2-methyl propanol with phosphoric acid.

The resulting solution comprised a water-soluble N-chlorinated melamine-formaldehyde condensate which contains active chlorine. This solution has a pH of 7.6 as measured by the glass electrode.

A cut of brown worsted suiting is padded through this solution so as to deposit approximately 12.7% by weight condensation product solids, and it is then plaited on a flat truck in yard lengths. Drying and curing is accomplished in a nine-section carbonizer with the first three sections having a temperature ranging from 160 to 180° F. and the last six sections having a temperature ranging from 262 to 282° F. The cut of suiting is in the carbonizing unit for about 22 minutes and is then scoured in a Dolly Washer at about 100° F. in three pounds of the condensation product of 1 mol of para-octyl phenol and 11 mols of ethylene oxide per 300 gallons of water. The suiting is rinsed and dried on a pin tenter dryer at about 230° F. Drying is followed by decatizing and shearing.

A cut of herringbone woolen suiting is treated in the same manner.

The following results show the effect of the

treatment on the dimensional stability of the worsted and herringbone suitings:

5		Percent Shrinkage		
		Relaxed	After 3 Wool Washes	After 5 Wool Washes
10	Untreated brown suiting:			
	warp.....	0.0	2.3	4.0
	filling.....	7.5	10.0	11.9
	Treated brown suiting:			
15	warp.....	1.1	2.9	3.3
	filling.....	0.6	1.2	1.2
	Untreated herringbone:			
	warp.....	1.8	5.0	6.3
20	filling.....	8.1	11.2	11.9
	Treated herringbone:			
	warp.....	1.2	3.1	3.1
	filling.....	0.7	0.7	0.0

Moreover, in addition to the excellent dimensional stability or resistance to felting as shown in the above table, the fabrics also possessed a soft, full and substantially unaltered hand. Furthermore, the tensile strength of the treated fabrics both in the warp and filling directions is entirely satisfactory.

Example III

An alkaline aqueous solution comprising a water-soluble N-halogenated amine-formaldehyde condensate is prepared by stirring the following ingredients (parts shown are parts by weight) for a period of about 15 minutes at a temperature of approximately 80° F.:

30 parts of the condensate as prepared in Example I (Condensate A).

3 parts of chloramine T.

190 parts of water.

1 part of sodium dodecyl benzene sulfonate containing 30% solids.

2.4 parts of 2-amino, 2-methyl propanol phosphate in the form of a solution containing 35% by weight of the salt formed by neutralizing 2-amino, 2-methyl propanol with phosphoric acid.

The resulting solution comprised a water-soluble N-chlorinated melamine-formaldehyde condensate which contains active chlorine. The pH of this solution is about 7.7 as measured by the glass electrode.

A dry claret crepe fabric having a viscose rayon warp and cellulose acetate filling is padded at open width through this solution so as to pick up about 12% by weight condensation product solids. The fabric is then run through a loop dryer at speed of about 40 to 50 yards per minute and at a temperature of approximately 280° F. Curing is accomplished by heating the fabric for a period of about 3.5 minutes in a loop dryer at a temperature of approximately 350° F. The fabric is then washed for 30 minutes at a temperature of 100 to 110° F. in an aqueous solution containing soda ash and a compound having the formula $C_{17}H_{33} \cdot CO \cdot NCH_3C_2H_4 \cdot SO_3Na$. Finishing is accomplished by drying in a loop dryer, followed by a steam tentering, decatizing and calendaring.

The fabric was observed to have a substantially unaltered hand or feel immediately after the cure, that is, compared to an untreated fabric from the same roll. Moreover, the treated fabric possessed excellent dimensional stability even after three launderings. It also possessed improved resistance to creasing and crushing, and was entirely satisfactory in regards to tensile

strength. The claret fabric had substantially the same shade after treatment as an untreated fabric from the same roll.

Example IV

An all wool houndstooth fabric is treated with the aqueous solution comprising a water-soluble N-chlorinated melamine-formaldehyde condensate, prepared as described in Example III, using the procedure set forth in Example III. The resulting fabric which contains about 12% of cured condensate is subjected to 3 wool washes and shows less than 1% loss in area.

An identical fabric is treated with an aqueous solution of unmodified melamine-formaldehyde condensate, prepared as described in the first paragraph of Example I, according to the procedure described in Example III. The resulting fabric which contains about 12% of cured condensate is subjected to 3 wool washes and shows a loss in area of 38%.

It is thus seen that the N-chlorinated melamine-formaldehyde condensate effects a marked improvement in the resistance to shrinkage of the all wool houndstooth fabric as compared to the unmodified melamine-formaldehyde condensate.

Example V

A low polymeric water-soluble amine-formaldehyde condensation product (hereinafter referred to as Condensate B) is prepared by reacting suitable proportions of formaldehyde in the form of a 37% neutral aqueous solution, melamine and methyl alcohol under refluxing conditions and the resulting water-soluble resin is then further reacted with suitable proportions of thiourea and formaldehyde to yield what is believed to be a monomeric or essentially low polymeric thiourea and formaldehyde modified methyl ether of pentamethylol melamine. The above resin may be concentrated by evaporation and is capable of being diluted with water and/or alcohol.

An alkaline aqueous solution comprising a water-soluble N-halogenated amine-formaldehyde condensate is prepared by stirring the following ingredients (parts shown are parts by weight) for about 10 minutes at a temperature of approximately 85° F.:

- 100 parts of the condensate as prepared above (Condensate B), containing about 60% condensation product solids.
- 3 parts of diammonium hydrogen phosphate.
- 368 parts of water.
- 5 parts of chloramine T.
- 1.25 parts of the condensation product of 1 mol of para-octa phenol and 11 mols of ethylene oxide.

The resulting solution comprises a water-soluble N-chlorinated thiourea and formaldehyde modified methyl ether of pentamethylol melamine which contains active chlorine. This has a pH of about 7.8 measured by the glass electrode.

A skein of wool yarn weighing approximately 12 grams is immersed in this solution and is centrifuged to a pickup of about 7% condensation product solids. The treated wool skein is then dried and cured at a temperature of about 300° F. for a period of approximately 30 minutes.

The wool yarn so treated exhibits excellent resistance to felting, even after 3 wool washes, and has a soft, full and substantially unaltered hand or feel. Moreover, the tensile strength of the treated wool yarn is entirely satisfactory.

Example VI

A water-soluble low polymeric amine-formaldehyde condensation product (hereinafter referred to as Condensate C) is prepared by reacting 1 mol of melamine with 5 mols of formaldehyde in the form of a 37% neutral aqueous solution at a temperature of about 100° C. until solution occurs. The condensation product is separated from the above solution by cooling and is then recovered by filtration and dried. The condensate so separated is alkylated by reaction with 14 mols of methyl alcohol under refluxing conditions in the presence of about 0.1 mol of hydrochloric acid. The reaction is allowed to proceed until solution occurs whereupon said solution is then neutralized with caustic soda to the phenolphthalein endpoint. This solution is concentrated by evaporation to 60% condensation product solids content. The resulting condensation product is obtained in the form of a viscous liquid capable of extreme dilution with water and/or alcohol.

An alkaline aqueous solution comprising a water-soluble N-halogenated amine-formaldehyde condensation product is prepared by stirring the following ingredients (parts shown are parts by weight) for about 10 minutes at a temperature of approximately 80° F.:

- 20 parts of condensate as prepared above (Condensate C), containing 60% condensation product solids.
- 78 parts of water.
- 1 part of chloramine T.
- 1.9 parts of 2-amino, 2-methyl propanol phosphate in the form of a solution containing 35% by weight of a salt prepared by neutralizing 2-amino, 2-methyl propanol with phosphoric acid.
- 0.5 parts of sodium dodecyl benzene sulfonate, containing 30% solids.

The resulting solution comprises a water-soluble N-chlorinated methyl ether of melamine-formaldehyde condensation product which contains active chlorine. The pH of this solution is about 7.7 as measured by the glass electrode.

A piece of folded, but split tubular knit, all-wool jersey is padded through this solution at the rate of about 20 yards per minute, and the pickup is adjusted so as to deposit 8.4% condensation product solids on the jersey. After padding, the piece is opened to full width, and dried at about 150° F. for a period of approximately 30 minutes in a loop drier. The treated jersey is then cured in the same dryer at a temperature of approximately 280° F. for a period of about 17 minutes. After the curing operation, the jersey is steam framed twice. The original width of the piece is 56 inches and it is steam framed as above at 52 inches.

The treated jersey has a soft, full hand or feel, and possesses excellent dimensional stability or resistance to felting as shown by the results in the following table:

	Percent Shrinkage		
	Relaxed	After 3 Wool Washes	After 5 Wool Washes
Untreated jersey:			
length.....	15.1	38.2	40.2
width.....	0.5	13.4	17.0
Treated jersey:			
length.....	4.7	5.7	11.5
width.....	6.3	13.0	12.1

¹ Stretch.

In addition, the treated jersey possesses a satisfactory tensile strength in the length and width directions.

Compositions were prepared as described in Examples 8, 9 and 10 of the Arsem patent, No. 2,472,361 except that Condensate C, prepared as described above, was used instead of the succinimide and melamine, respectively, of Arsem's examples. In each case the condensation product immediately precipitated from the solution as a water-insoluble gummy product which was not suitable for the impregnation of textile materials. The compositions thus obtained were acid and had a pH of 5.1, 4.4 and 4.9, respectively.

Example VII

An alkaline aqueous solution comprising a water-soluble N-halogenated aliphatic amine-formaldehyde condensation product is prepared by stirring the following ingredients (parts shown are parts by weight) for about 10 minutes at a temperature of about 75° F.:

125 parts of an aqueous urea-formaldehyde paste having a pH of 8 and comprising 55% by weight of a water-soluble urea-formaldehyde condensate.

375 parts of water.

7 parts of a sodium hypochlorite solution containing 12% available chlorine by volume.

1 part of the condensation product of 1 mol of para-octyl phenol and 11 mols of ethylene oxide.

1.9 parts of ammonium chloride as a curing catalyst.

The resulting solution comprises a water-soluble N-chlorinated urea-formaldehyde condensate which contains active chlorine. The pH of this solution was about 8.8 as measured by the glass electrode.

A cut of brown worsted suiting is padded through this solution so as to deposit approximately 12% by weight of condensation product solids, based on the dry weight of the suiting. The suiting is then dried at a temperature of about 160 to 180° F. and finally cured at a temperature of about 300° F. for 30 minutes to insolubilize the condensate therein.

The worsted suiting treated in the above manner exhibits good dimensional stability or resistance to felting, even after three wool washes, and has a soft and full hand or feel. In addition, the tensile strength of the suiting in warp and filling direction is entirely satisfactory.

The water-soluble N-halogenated amine-formaldehyde condensation products of this invention may be employed alone or as mixtures thereof. Furthermore, they may be employed in combination with other amine-formaldehyde condensates which have not been halogenated. It is intended that such modifications and variations be included within the scope of this invention.

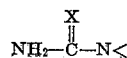
The term "cure" as used herein is intended to cover a variety of degrees of polymerization to which the N-halogenated amine-formaldehyde condensates of the present invention may be submitted. Thus, the polymeric form of the finish may range from a slightly polymerized to a completely polymerized state depending upon the type of finish desired. If a substantially non-wash resistant finish is contemplated, for example, the condensate need only be slightly polymerized, that is, it need only be cured for a short period of time at relatively low temperatures. On the other hand, an N-halogenated amine-formaldehyde condensate of the type herein em-

ployed may be highly polymerized or substantially thoroughly cured to yield a textile finish which is substantially resistant to washing.

This application is a continuation-in-part of our co-pending application Serial No. 770,168 filed August 22, 1947 and now abandoned.

What is claimed:

1. A finishing composition for textile materials comprising a neutral to alkaline aqueous solution comprising a water-soluble N-halogenated condensation product selected from the group consisting of water-soluble N-halogenated aminotriazine-formaldehyde condensation products, water-soluble N-halogenated aliphatic amine-formaldehyde condensation products, and water-soluble N-halogenated methylated derivatives of said condensation products, said aliphatic amine containing from 1 to 4 carbon atoms and having the grouping



where X is selected from the group consisting of oxygen, sulfur, and an imido group and the free valences on the nitrogen are attached to atoms selected from the group consisting of hydrogen and carbon atoms, said aliphatic amine being further characterized in that it contains no atoms other than those defined in the foregoing formula, said N-halogenated condensation product being further characterized in that it contains available halogen and is prepared by contacting a compound selected from the group consisting of free halogen and compounds capable of liberating free halogen in a neutral to alkaline aqueous solution with the corresponding water-soluble unhalogenated condensation product, which contains a replaceable hydrogen atom on a nitrogen atom thereof, in a neutral to aqueous solution.

2. A finishing composition for textile materials comprising a neutral to alkaline aqueous solution comprising a water-soluble N-halogenated amino-triazine-formaldehyde condensation product which contains available halogen, said condensation product having been prepared by contacting a compound selected from the group consisting of free halogen and compounds capable of liberating free halogen in a neutral to alkaline aqueous solution with a water-soluble amino-triazine-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution.

3. A finishing composition for textile materials comprising a neutral to alkaline aqueous solution comprising a water-soluble N-halogenated melamine-formaldehyde condensation product which contains available halogen, said condensation product having been prepared by contacting a compound selected from the group consisting of free halogen and a compound capable of liberating free halogen in a neutral to alkaline aqueous solution with the corresponding water-soluble unhalogenated condensation product, which contains a replaceable hydrogen atom on a nitrogen atom thereof, in a neutral to alkaline aqueous solution.

4. A finishing composition for textile materials comprising an aqueous solution having a pH between about 7.2 and 9.5 and comprising a water-soluble N-chlorinated melamine-formaldehyde condensation product which contains available chlorine, said condensation product having been prepared by contacting a compound

capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble melamine-formaldehyde condensation product, which contains a replaceable hydrogen atom on a nitrogen atom thereof, in a neutral to alkaline aqueous solution.

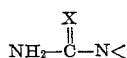
5. A finishing composition for textile materials comprising a neutral to alkaline aqueous solution comprising a water-soluble N-halogenated methylated melamine-formaldehyde condensation product which contains available halogen, said condensation product having been prepared by contacting a compound selected from the group consisting of free halogen and compounds capable of liberating free halogen in a neutral to alkaline aqueous solution with a water-soluble methylated melamine-formaldehyde condensation product, which contains a replaceable hydrogen atom on a nitrogen atom thereof, in a neutral to alkaline aqueous solution.

6. A finishing composition for textile materials comprising an aqueous solution having a pH between about 7.2 and 9.5 and comprising a water-soluble N-chlorinated methylated melamine-formaldehyde condensation product which contains available chlorine, said condensation product having been prepared by contacting a compound capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble methylated melamine-formaldehyde condensation product, which contains a replaceable hydrogen atom on a nitrogen atom thereof, in a neutral to alkaline aqueous solution.

7. A finishing composition for textile materials comprising a neutral to alkaline aqueous solution comprising a water-soluble N-halogenated urea-formaldehyde condensation product which contains available halogen, said condensation product having been prepared by contacting a compound selected from the group consisting of free halogen and a compound capable of liberating free halogen in a neutral to alkaline aqueous solution with a water-soluble urea-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution.

8. A finishing composition for textile materials comprising an aqueous solution having a pH between about 7.2 and 9.5 and comprising a water-soluble N-chlorinated urea-formaldehyde condensation product which contains available chlorine, said condensation product having been prepared by contacting a compound capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble urea-formaldehyde having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution.

9. A method of finishing textile materials which comprises impregnating said materials with a neutral to aqueous solution comprising a water-soluble N-halogenated condensation product selected from the group consisting of water-soluble N-halogenated aminotriazine-formaldehyde condensation products, water-soluble N-halogenated aliphatic amine-formaldehyde condensation products and water-soluble N-halogenated methylated derivatives of said condensation products, said aliphatic amine containing from 1 to 4 carbon atoms and having the group-



where X is selected from the group consisting

of oxygen, sulfur, and an imido group and the free valences on the nitrogen atom are attached to atoms selected from the group consisting of hydrogen and carbon atoms, said aliphatic amine being further characterized in that it contains no atoms other than those defined in the foregoing formula, said N-halogenated condensation product being further characterized in that it contains available halogen and is prepared by contacting a compound selected from the group consisting of free halogen and compounds capable of liberating free halogen in a neutral to alkaline aqueous solution with the corresponding water-soluble unhalogenated condensation product, which contains a replaceable hydrogen atom on a nitrogen atom thereof, in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% by weight of condensation product solids based on the dry textile material weight and curing the condensation products in the textile material.

10. A method of finishing a textile material comprising proteinaceous yarns or fibers which comprises impregnating said material with a neutral to alkaline aqueous solution comprising water-soluble N-halogenated melamine-formaldehyde condensation products which contain available halogen, said condensation product having been prepared by contacting a compound selected from the group consisting of free halogen and compounds capable of liberating free halogen in a neutral to alkaline aqueous solution with a water-soluble melamine-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof, in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% by weight of condensation product solids based on the dry weight of the textile material, and heating the textile material to dry the same and cure the condensation products therein to the water-insoluble state.

11. A method of finishing a textile fabric comprising proteinaceous yarns or fibers which comprises impregnating said fabric with an aqueous solution having a pH between about 7.2 and 9.5 and comprising a curing catalyst and water-soluble N-chlorinated melamine-formaldehyde condensation products which contain active chlorine, said condensation product having been prepared by contacting a compound capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble melamine-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% of condensation product solids based on the dry weight of said fabric, and heating the fabric to dry the same and cure the condensation products therein to the water-insoluble state.

12. A method of finishing a textile material comprising proteinaceous yarns or fibers which comprises impregnating said material with a neutral to alkaline solution comprising water-soluble N-halogenated methylated melamine-formaldehyde condensation products which contain available halogen, said condensation product having been prepared by contacting a compound selected from the group consisting of free halogen and a compound capable of liberating

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free halogen in a neutral to alkaline aqueous solution with a water-soluble methylated melamine-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% of condensation product solids, based on the dry textile material, and heating the textile material to dry the same and cure the condensation products therein to the water-insoluble state.

13. A method of finishing a textile fabric comprising proteinaceous yarns or fibers which comprises impregnating said fabric with an aqueous solution having a pH between about 7.2 and 9.5 and comprising a curing catalyst and water-soluble N-chlorinated methylated melamine-formaldehyde condensation products which contain available chlorine, said condensation product having been prepared by contacting a compound capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble methylated melamine-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% of condensation product solids based on the dry weight of the fabric, and heating the fabric to dry the same and cure the condensation products therein to the water-insoluble state.

14. A method of finishing a textile material comprising proteinaceous yarns or fibers which comprises impregnating said fabric with a neutral to alkaline aqueous solution comprising water-soluble N-halogenated urea-formaldehyde condensation products which contain available halogen, said condensation product having been prepared by contacting a compound selected from the group consisting of free halogen and compounds capable of liberating free halogen in a neutral to alkaline aqueous solution with a water-soluble urea-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% of condensation product solids based on the dry weight of said textile material, and heating the fabric to dry the same and cure the condensation products therein to the water-insoluble state.

15. A method of finishing a textile fabric comprising proteinaceous yarns or fibers which comprises impregnating said fabric with an aqueous solution having a pH between about 7.2 and 9.5 and comprising a curing catalyst and water-soluble N-chlorinated urea-formaldehyde condensation products which contain available chlorine, said condensation product having been prepared by contacting a compound capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble urea-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2

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to 25% of condensation product solids based on the dry fabric weight, and heating the fabric to dry the same and cure the condensation products therein to the water-insoluble state.

16. A method of finishing a textile material comprising cellulose ester staple fibers or filaments which comprises impregnating said material with an aqueous solution having a pH between about 7.2 and 9.5 and comprising a curing catalyst and water-soluble N-chlorinated melamine-formaldehyde condensation products which contain available chlorine, said condensation product having been prepared by contacting a compound capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble melamine-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% of condensation product solids based on the dry textile material, and heating said textile material to dry the same and cure the condensation products therein to the water-insoluble state.

17. A method of finishing a textile material comprising cellulose ester staple fibers or filaments which comprises impregnating said material with an aqueous solution having a pH between about 7.2 and 9.5 and comprising a curing catalyst and a water-soluble N-chlorinated methylated melamine-formaldehyde condensation products which contain available chlorine, said condensation product having been prepared by contacting a compound capable of liberating free chlorine in a neutral to alkaline aqueous solution with a water-soluble methylated melamine-formaldehyde condensation product having a replaceable hydrogen atom on a nitrogen atom thereof in a neutral to alkaline aqueous solution, said first mentioned solution being supplied in an amount sufficient to provide from about 2 to 25% of condensation product solids based on the dry weight of said textile material, and heating said textile material to dry the same and cure the condensation products therein to the water-insoluble state.

18. A textile material prepared according to process of claim 9.

19. A finishing composition as in claim 6, but further characterized in that the compound capable of liberating free chlorine is sodium p-toluene-sulfochloramine.

20. A process as in claim 13, but further characterized in that the compound capable of liberating free halogen is sodium p-toluene-sulfochloramine.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,368,451	D'Alelio	Jan. 30, 1945
2,373,191	Landolt	Apr. 10, 1945
2,395,724	Cowley	Feb. 26, 1946
2,472,361	Arsem	June 7, 1949
2,518,266	Baird	Aug. 8, 1950
2,561,814	Novotny	July 24, 1951