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3,082,118

NOVEL MERCURATED ACRYLAMIDE COMPOUNDS AND GERMICIDAL TEXTILE FINISHES

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This invention relates to novel germicidal or bactericidal compounds, to their use on textile materials as durable germicidal finishes and to processes for applying such compounds as finishes to textile materials and to the textile materials so treated.

More particularly, this invention relates to novel mercurated derivatives of acrylamides as germicidal or bactericidal compounds, to their use on textile materials as durable germicidal finishes, to the processes of applying said compounds as finishes to textile materials, and to the materials so treated.

An object of the present invention is to provide a novel class of mercurial derivatives of acrylamides, their formaldehyde condensates or methylol derivatives and their alkylated methylol derivatives.

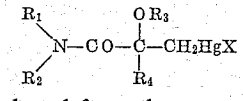
A further object of this invention is to provide a durable antibacterial finish for textile materials and in particular a finish which is durable to laundering in the presence of soaps and/or chlorine such as is normally employed as chlorine in bleach.

A further object of this invention is to provide an antibacterial finishing composition which is compatible with known textile finishing agents or resins, which resins contribute dimensional stability and wrinkle resistance to cellulosic substrates.

A still further object of this invention is to provide a water soluble or water dispersible antibacterial finish which can be applied by standard textile finishing methods, i.e., those normally employed by the textile finishing industry to impart wrinkle resistance and shrinkage control to cellulosic textile material.

These and other objects and advantages of the present invention will become more apparent from the detailed description thereof set forth hereinbelow.

According to the present invention novel mercurial compounds and more specifically mercurial compounds that are derivatives of an acrylamide are prepared having the following general formula:



wherein R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is selected from the group consisting of hydrogen, alkyl, $—CH_2OR_5$ and aryl, R_3 and R_4 are selected from the group consisting of hydrogen or lower alkyl, R_5 is hydrogen or lower alkyl, and X is any monovalent electronegative component or anionic radical such as CH_3COO, Cl or OH and the like.

These compounds may be preformed and then applied to the textile substrates or materials or they may be formed in situ on such materials.

In general, these mercurated derivatives of acrylamide are prepared by reacting an acrylamide with mercuric acetate or a similar mercuric salt in an alcohol or water medium acidified with a weak acid such as acetic acid. The reaction mixture is stirred and heated until the reaction is completed.

In an alternative procedure, an acrylamide is applied to a suitable textile substrate and the fabric subsequently treated with a hot acidic alcoholic solution of mercuric acetate or similar salt and acetic acid.

The values for R_1, R_2 and R_4 in the general formula above will depend on the substituents in the corresponding positions of the starting compounds. However, the value for R_3, is determined by the solvent medium in which the reaction is carried out. If the medium is an alcohol, R_3 will be the alkyl radical of that alcohol. When the medium is water, R_3 will be hydrogen.

The value of X, the anionic radical, will depend on the anion of the mercury salt used. If mercuric acetate is employed, the anion will be acetate. If mercuric propionate is employed, the anion will be propionate. However, X may be changed to another electronegative component by reacting the original reaction product such as the acetate with a salt such as sodium chloride or silver nitrate whereby the acetate will be converted to a new salt such as the chloride or nitrate.

In general, the acrylamides used as starting materials in this invention are well known and readily prepared. Among the acrylamides which may be used are acrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-methyl-N-n-propylacrylamide, and alpha-methylacrylamide.

The mercuric salts are preferably salts of such aliphatic organic acids as acetic, propionic, butyric and the like.

The solvent medium in which the mercurated propionamides of this invention are prepared is preferably an alcohol such as methanol, ethanol, propanol or butanol, water or alcohol-water solutions.

Whether the mercurating medium is alcoholic, aqueous or a mixture, the medium is acidified with a weak, preferably organic, acid such as acetic acid, propionic acid, butyric acid and the like, in order to facilitate the mercuration and prevent hydrolysis of the mercuric salt.

While the acrylamides of this invention may be mercurated prior to methylolation and alkylation, if the latter is carried out, it is greatly preferred that the mercuration be effected on the methylolated or alkylated methylolated acrylamides of this invention. Mercuration of these formaldehyde condensates, as noted above, is carried out on the acid side in an alcoholic or aqueous medium normally at a temperature of from 25 to 100° C. and preferably at a temperature of from 60–80° C. for from two to forty-eight hours and preferably from sixteen to twenty-four hours. The mercury compound is preferably employed in an amount equal to one equivalent of the acrylamide compound. Excesses of the mercury compound on the acrylamide may be employed but without advantage. In fact, excesses of the mercury compound present recovery problems.

The acrylamides of this invention may be condensed with formaldehyde and thereby introduce methylol groups on the amino nitrogen atom which bears a labile hydrogen atom. These formaldehyde condensates are prepared by reacting the acrylamide with formaldehyde preferably under alkaline conditions as, for example, at a pH of from 8 to 11. In general, methylolation of the acrylamide is conducted in accordance with procedures known to those skilled in the art for preparing the formaldehyde condensates of amino compounds. Thus, a mole of formaldehyde for each amino hydrogen sought to be methylolated is introduced into a reaction vessel and under alkaline conditions the reaction mixture is normally heated at temperatures up to reflux until condensation is complete. Normally a slight excess of formaldehyde is employed to insure the degree of methylolation sought. Additionally, as is well known in the field of textile finishing resins and in particular aminoplast resins as textile finishing resins the methylol group may be subsequently alkylated and formed into an alkoxymethyl group such as N-methoxymethyl by reacting a methylol compound with a suitable alcohol under acidic conditions,

normally in the presence of a mineral acid. Suitable acids for such a condensation may be hydrochloric, sulfuric, nitric and the like. Suitable alcohols that may be employed in the process of this invention would include the saturated aliphatic monohydric alcohols and particularly those containing 1 to 4 carbon atoms as, for example, methyl, ethyl, propyl, butyl and the like.

As examples of suitable methylol or formaldehyde condensates of the mercurated acrylamides of this invention the following are illustrative:

3-acetoxymercuri-2-methoxy-N-hydroxymethylpropionamide and
3-acetoxymercuri-2-methyl-2-methoxy-N-hydroxymethylpropionamide.

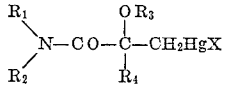
As examples of the alkylated methylol derivatives of the mercurated acrylamides of this invention the following are illustrative:

3-acetoxymercuri-2-methoxy-N-methoxymethylpropionamide and
3-acetoxymercuri-2-methyl-2-methoxy-N-methoxymethylpropionamide.

By formaldehyde condensates of the mercurated acrylamides of this invention it is meant the formaldehyde or alkylated formaldehyde condensates thereof.

As will be more evident from the disclosure hereinafter these are the materials employed to provide a durable germicidal finish to textile materials. These compounds should contain at least one methylol or alkylated methylol group.

These formaldehyde condensates have the following general formula:



where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is $—CH_2OR_5$, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl and X is a monovalent electronegative component.

The N-methylol and N-alkoxymethyl derivatives are the preferred germicidal agents of this invention since their use insures maximum durability as compared with the unmethylolated mercurated acrylamides of this invention. It should be noted, however, that the unmethylolated acrylamides and for that matter the methylolated ones when applied with a thermosetting creaseproofing resin (including topping with such resins) are as durable as the methylolated acrylamides alone and in many instances are more so. These methylolated acrylamides are particularly the preferred bactericidal finishes when the base textile material is of a cellulosic character as, for example, cotton, rayon and the like. This is so in that the presence of the methylol group renders the acrylamide "fiber reactive" when the fiber is of cellulosic origin.

The compounds of this invention are either water soluble or water dispersible and are readily applied to textile materials from aqueous media by any of the well known methods for applying water-soluble textile resin finishes. Thus, for example, they may be padded, sprayed, applied by immersion, dipping or any of the other well known finishing techniques.

If desired, a thermosetting aminoplast resin, as for example of the type well known to the textile finishing industry, may be applied with the antibacterial agents, either from the same bath or subsequently from a second treating bath or solution. As examples of suitable thermosetting aminoplast resins contemplated by this invention, the water-soluble melamine-formaldehyde resins prepared in accordance with U.S. Patents Nos. 2,197,357 and 2,529,856 are fully contemplated. Examples of such

resins are tris(methoxymethyl) melamine, tris(methoxymethyl) dimethylol melamine, hexakis (methoxymethyl) melamine, and the like. In addition to these melamine-formaldehyde resins, the urea and thiourea-formaldehyde condensates are contemplated, as are their alkylated derivatives. Thus, for example, dimethylol urea, methylated dimethylol urea and thiourea, dimethylol ethylene urea, dimethylol 1,2-propylene urea and thiourea, dimethylol 1,3-propylene urea and thiourea and other related homologous compounds are contemplated. Additionally, the formaldehyde condensates of dicyandiamide, biuret and the like are contemplated, as are the water-soluble formaldehyde condensates of thiobis amides of the type described in U.S. Patent No. 2,887,408.

Guanamine formaldehyde condensates, as for example, those described in U.S. Patent No. 2,887,409, including the formaldehyde condensates of methoxy acetoguanamine, ethoxy acetoguanamine, tertiary butoxy acetoguanamine, and the like are contemplated.

Urons may also be employed with the compounds of this invention as, for example, N,N'-bis(methoxymethyl) uron and various other and closely related compounds such as are described in U.S. Patent No. 2,373,135. Additionally, tetrahydro triazones such as tetrahydro-5-(β-hydroxyethyl)-s-triazone and compounds of the type described in U.S. Patent No. 2,304,624 are also fully contemplated.

It has been our experience that when the antibacterial agents of this invention do not contain methylol groups, that greater durability of the germicidal finish is normally obtained by applying a textile resin, as for example, any of the water-soluble potentially thermosetting aminoplast resins identified hereinabove in conjunction with the germicidal compounds.

When the germicidal compound contains methylol groups or when a thermosetting aminoplast textile finishing resin is employed in conjunction with the germicidal compounds of this invention, it is advantageous to employ a suitable acid-acting curing catalyst or accelerator such as ammonium sulfate for effecting the cure of these aminoplasts (mercurated methylol compound and thermosetting aminoplast textile finishing resins) on the textile finishing resins. It will be apparent that if the mercurated acrylamide does not contain methylol or alkylated methylol groups a catalyst or curing accelerator is not required to fix it upon the textile material and if a thermosetting aminoplast resin is not subsequently applied all that is required is that the treated material be dried. Examples of catalysts that may be employed are free acids, acid salts, alkanolamine salts, metal salts and the like of the well known types. The concentration of catalyst employed may range from about 0.1 to about 25% or higher based on the weight of resin solids, depending upon the particular catalyst type employed. Thus, for example, from between about 0.1 and about 10% of free acids, such as phosphoric, tartaric, oxalic and the like may be employed, while in the case of ammonium chloride amounts of from between 0.5 and about 10% are used. In the case of amine salts including alkanolamine salts such as diethanolamine hydrochloride, from about 1 to about 10% are most useful, while with respect to salts such as magnesium chloride, amounts of from between about 5 and 25% have been successfuliy employed. In addition to magnesium chloride, zinc nitrate, zinc borate, aluminum chloride and other known conventional metal salts are normally employed in amounts corresponding to from between 5 and 25% based on the weight of the resin solids.

After the application of the methylolated mercurated acrylamides of this invention, with or without the addition of a thermosetting aminoplast resin, the treated textile material is dried and subjected to temperatures normally considered to be the drying and curing temperatures employed for drying and curing for creaseproofing resins in the textile finishing industry. Thus, for exam-

ple, the treated material may be subjected to temperatures of from between about 180° F. to about 450° F. or higher. Generally speaking, the time of drying and/or curing operations is inversely proportional to the temperature employed and of course is influenced by whether or not separate or combined drying and curing steps are employed. Generally, when drying and curing is carried out in a combined operation, a time of from about 1 minute to about 10 minutes may be employed at temperatures of from 450 to 250° F., respectively. When the fabric has been dried preliminary to curing, curing times of the order of about 5 minutes to about ¼ minute at a temperature of from about 250 and 450° F., respectively, have been successfully employed.

The germicidal finish of this invention may be applied to textile materials or bases, usually in the form of fabric which may be knitted, woven, non-woven or otherwise formed, and which may be prepared from cellulosic or non-cellulosic fibers or mixtures of the two. Thus, the textile material may be a formed fabric of cellulosic fibers, as for example, cotton, linen or viscose rayon or mixtures thereof, or it may be a textile fabric prepared from acetate rayon, nylon, the polyester fibers and acrylic fibers, wool, silk and the like. Additionally, the textile material may be prepared from mixtures of these and other cellulosic and non-cellulosic fibers.

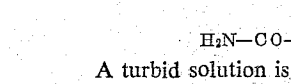
Preferably, the textile material is a cellulosic material formed principally from cellulosic fibers. In this regard, for purposes of this invention, the term "cellulosic fabric" shall mean to include fabrics containing at least 50% by weight of cellulosic fibers, whether they be cotton, viscose rayon, linen or the like.

The antibacterial compounds of this invention are normally applied in an amount of from between 0.0001% to 2.5% on the weight of the textile material. The preferable amount is from between .01 to 1% based on the dry weight of the textile material to which it is applied. In applications where the water-soluble thermosetting aminoplast resin is employed in conjunction with the acrylamides of this invention, these resins are normally applied in amounts of from between about 1 and about 25% and preferably in amounts of from 2.5 to 10% based on the dry weight of the textile material.

In order that the present invention may be more fully understood, the following examples are given primarily by way of illustration. No specific details or enumerations contained therein should be construed as limiting of the present invention except insofar as they appear in the appended claims. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

3-Acetoxymercuri-2-Methoxypropionamide



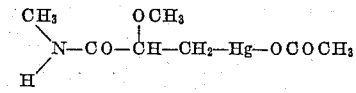
A turbid solution is obtained by dissolving 7.1 parts of acrylamide (0.1 mole) in 48.6 parts of methanol. After filtering, the filtrate is heated to reflux while stirring, and to the refluxing mixture a hot solution consisting of 72.9 parts of methanol, 6.29 parts of glacial acetic acid and 30.2 parts (0.09 mole) of mercuric acetate is added. After refluxing for 18 hours the solution is filtered and the filtrate is concentrated in vacuo to 20–30 parts by volume. The residue is treated with 24 parts of acetone and 576 parts of ether, at which time an oil is formed. The ether layer is decanted from the oil and 216 parts of fresh ether is then added to the oil. After chilling and triturating, a solid is formed. The solid is filtered, washed with ether and dried in vacuo over phosphoric anhydride.

The yield is 21.7 parts.

Analysis.—Calculated for $C_6H_{11}HgNO_4$: C, 19.95; H, 3.04; N, 3.88; Hg, 55.3. Found: C, 20.01; H, 2.80; N, 3.86; Hg, 54.6.

EXAMPLE 2

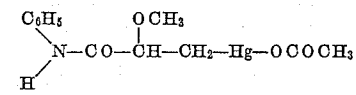
3-Acetoxymercuri-2-Methoxy-N-Methylpropionamide



The procedure of Example 1 is followed substituting 8.5 parts of N-methylacrylamide for the 7.1 parts of acrylamide.

EXAMPLE 3

3-Acetoxymercuri-2-Methoxy-N-Phenylpropionamide



The procedure of Example 1 is followed substituting 14.7 parts of N-phenylacrylamide for the 7.1 parts of acrylamide.

EXAMPLE 4

Procedures of Application, Drying and Washing of Fabrics Treated with Product of Example 1

Application.—All applications are made from aqueous solutions by padding through a two roll micro-set padder.

The product of Example 1 is applied at various concentrations and by several different methods, i.e.

Method "A"—Product applied alone.
Method "B"—Product plus creaseproofing resins.
Method "C"—Product applied alone and topped with creaseproofing resin.

Drying and curing.—The drying or curing of the various treated fabrics is accomplished in hot, circulating air ovens.

Fabrics treated by method "A" are dried for 2 minutes at 225° F.

Fabrics treated by method "B" are predried for 2 minutes at 225° F. and then cured for 1.5 minutes at 350° F.

Fabrics treated by method "C" are predried for 2 minutes at 225° F., then repadded with the creaseproofing resin, dried for 2 minutes at 225° F. and then cured for 1.5 minutes at 350° F.

Laundering.—The cotton fabrics treated with the product of Example 1 are laundered in a Laundromat washer as follows and are designated in the tables by code, i.e.

LW=0.1% neutral soap at 140° F.
LWC=0.1% neutral soap plus 0.02% available chlorine at 140° F.

The synthetic or wool fabrics are laundered in a Najort reversing washer employing 0.1% neutral soap at 100° F. followed by rinsing and drying.

Agar diffusion test method.—Bacterial inhibition tests are made on treated fabrics by the following method.

Discs (11.5 mm.) of the treated fabrics are placed on an agar plate inoculated with bacterial culture. After several hours of contact, the discs are removed and the plate incubated overnight. The activity of the compound used on the fabric discs is recorded as the diameter (in mm.) of the clear area at the site of the discs. An effective agent will show a clear area with a diameter greater than that of the disc itself (11.5 mm.).

The larger the clear area, the greater is the compound's activity. The activity under the fabric disc is also noted where there is no zone outside the area covered by the fabric. The area under the disc of the fabric is rated as follows:

"C"—Completely clear area underneath disc.
"P"—At least 75% clear area underneath disc.
"S-VS"—Less than 75% clear area underneath disc.
"N"—No clear area.

EXAMPLE 5

The product of Example 1 is applied to 80 x 80 cot-

ton percale by both methods "A" and "B" as described under Example 4.

Solutions of 1% solids are applied and drying/curing carried out as previously described.

Results are shown in Table I.

No durability of germicidal activity is obtained by use of product alone. When topped with thermosetting resin plus catalyst, excellent durability is obtained.

TABLE I

[Germicidal effects of 3 acetoxymercuri 2 methoxy-propionamide alone or in combination with a thermosetting aminoplast resin]

Percent Solids (OWF)	Zones of Inhibition (Dia. mm.)					
	E. Coli			*Staph. Aureus*		
	Initial	25LW	25LWC	Initial	25LW	25LWC
1	23.4	N	N	27.6	N	N
1 [a]	17.3	12.6	13.6	19.7	14.0	14.8

[a] Topped with 5% solids (OWF) tris(methoxymethyl) melamine + 3.5% ammonium sulfate on weight of resin solids in the bath.

EXAMPLE 6

N-Methoxymethyl-3-Acetoxymercuri-2-Methoxy-propionamide

The procedure of Example 1 is followed, only 11.5 parts of N-methoxymethylacrylamide is substituted for the acrylamide there used.

Applications of the thus obtained product to cotton using conventional drying and curing finishing procedures yields a durable germicidal finish.

EXAMPLE 7

Methylol Acrylamide Pretreated 80 x 80 Cotton Percale Aftertreated With Mercuric Acetate

A swatch of 80 x 80 cotton percale is treated with an aqueous solution of methylol acrylamide plus 12% magnesium chloride (based on the resin solids), then dried and cured. A portion of the treated fabric is Soxhlet extracted with hot dimethylol formamide for 4 hours, rinsed in water at 140° F. and air dried. Percent N on fabric=0.74 (equivalent to 5.4% of methylol acrylamide).

A 20 gram sample of this treated fabric (containing 0.01075 mole of compound durably fixed thereon) is heated at reflux with stirring in a solution of 203 parts of methyl alcohol, 1.57 parts of acetic acid and 6.84 parts (0.0215 mole) mercuric acetate for 31 hours, then rinsed several times in methanol/water (acidified with a little HOAc) and air dried.

Results are shown in Table II.

TABLE II

[80 x 80 cotton percale pretreated with methylol acrylamide, then aftertreated with mercuric acetate]

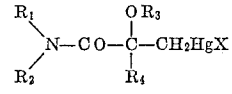
Treatments	Washes	Zones of Inhibition (mm.)		Percent Hg on Fabric
		E. Coli	*S. Aureus*	
Fabric pretreated with methylol acrylamide, aftertreated with mercuric acetate.	none	sample lost		
	25LW	15.4	19.7	[1] 4.51
	25LWC	19.2	22.0	

[1] Theory on basis of nitrogen analysis=6.28% Hg.

It will be apparent that the compositions of this invention may be employed in combination with other textile finishing agents, auxiliaries and assistants, as for example, lubricants, dyes, antistatic agents and the like insofar as these materials do not diminish the effects sought to be achieved thereby.

We claim:

1. A compound having the following general formula:



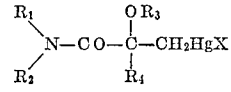
where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is selected from the group consisting of hydrogen, $—CH_2OR_5$, alkyl and phenyl, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl, and X is a monovalent electronegative component.

2. 3-acetoxymercuri-2-methoxypropionamide.

3. 3-acetoxymercuri - 2 - methoxy - N - methylpropionamide.

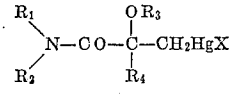
4. 3-acetoxymercuri - 2 - methoxy - N - phenylpropionamide.

5. Mercurial compounds having the following general formula:



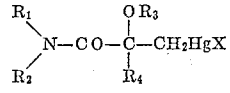
where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is $—CH_2OR_5$, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl, and X is a monovalent electronegative component.

6. The method of applying a germicidal finish to textile materials which comprises applying thereto from between 0.0001% and 2.5% of a mercurated acrylamide of the general formula:



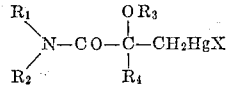
where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is selected from the group consisting of hydrogen, $—CH_2OR_5$, alkyl and phenyl, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl, and X is a monovalent electronegative component and thereafter subjecting the textile material to elevated temperatures to cure said compound on said material.

7. The method of applying a germicidal finish to textile materials which comprises applying thereto from between 0.0001% and 25% of a mercurated acrylamide of the general formula:



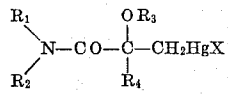
where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is $—CH_2OR_5$, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl, and X is a monovalent electronegative component and thereafter subjecting the textile material to elevated temperatures to cure said compound on said material.

8. Textile material having a germicidal finish thereon comprising a mercurated acrylamide having the following general formula:



where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is selected from the group consisting of hydrogen, $—CH_2OR_5$, alkyl and phenyl, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl, and X is a monovalent electro-negative component.

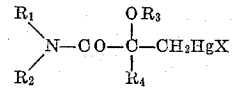
9. Textile material having a germicidal finish thereon which comprises a heat cured mercurated acrylamide having the following general formula:



where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is $—CH_2OR_5$, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl, and X is a monovalent electro-negative component.

10. The method of applying as a germicidal finish to

textile materials from .0001% and 2.5% of a mercurated acrylamide of the formula:



where R_1 is selected from the group consisting of hydrogen and alkyl, R_2 is selected from the group consisting of hydrogen, $—CH_2OR_5$, alkyl and phenyl, R_3 and R_4 are members selected from the group consisting of hydrogen and lower alkyl, R_5 is a member selected from the group consisting of hydrogen and lower alkyl, and X is a monovalent electro-negative component, which comprises applying to said material from .0001% and 2.5% of an appropriate acrylamide moiety and thereafter treating said acrylamide containing textile material with an acidic alcohol solution of a mercury salt to react the acrylamide with said salt, and then drying the material.

11. The method according to claim 10 in which a thermosetting aminoplast creaseproofing resin and a curing accelerator therefor are applied after drying the mercurated acrylamide treated material, and the material is thereafter subjected to elevated temperatures to dry and cure the aminoplast resin, whereby a germicidal wrinkle resistant finish is achieved.

No references cited.