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3,085,909

SILVER CONTAINING REACTION PRODUCTS, METHODS FOR THEIR PRODUCTION AND USE IN FORMING PERMANENT SILVER CONTAINING DEPOSITS ON BASE MATERIALS

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This invention relates to new improvements in silver containing reaction products, to methods for the production of such products, to the use of these new products in forming permanent deposits comprising silver on textiles and other base materials, and to the resulting treated base materials.

It has long been known that metallic silver and many silver containing compounds, when applied to a base material, can impart a number of beneficial properties to the base material. For example, colloidal silver and certain silver compounds, when applied to base materials, such as fibers, fabrics, animal hides, leather, wood and the like, protect the base against attack by micro-organisms, such as fungi and bacteria. Also, silver and some of its compounds possess certain catalytic properties which may be most efficiently utilized by affixing the silver or the silver compound on a base material so as to provide the maximum surface area for the active silver catalyst.

The utility of silver and silver compounds as referred to above has not been fully exploited because of certain problems which have been experienced in connection with the application of silver and its compounds to base materials. In the first place, it has been found to be difficult to form a silver containing deposit on a base material and have the deposit remain intact when subjected to the disturbing conditions encountered in the use of the product. It is quite easy to impregnate base materials with silver compounds when no concern need be given to the permanency of the deposit, but it is extremely difficult to form on textiles or other base materials silver containing deposits which are relatively permanent in nature, i.e., which will not be quickly removed by ordinary laundering, dry-cleaning or the like.

The problem of forming relatively permanent silver containing deposits on base materials is referred to in numerous prior patents and publications, e.g., see U.S. 2,459,896 and 2,459,897.

Another serious problem encountered in using silver and its compound as biocides for treatment of textiles is their tendency to discolor the textile. If the silver is applied to a fabric in the form of the metal colloid, the fabric will be discolored by the applied silver colloid from the very beginning, since such silver deposits are themselves colored, varying from yellow through brown to gray. It is possible to use silver compounds which are substantially colorless, but usually when such materials are exposed to light, or laundered the silver containing deposits discolor, e.g., turn gray or brown. Accordingly, although it is possible using such silver compounds, to initially prepare textiles or other impregnated fibrous materials which possess the same color and appearance as the unimpregnated base, on exposure to light or laundering such textile or fibers as have been available heretofore generally become discolored.

A principal object of this invention is the provision of new silver containing reaction products which may be used to create on textiles or other base materials, substantially permanent silver containing deposits. Further objects include:

(1) The provision of new silver containing reaction

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products which are substantially colorless and which are highly stable to light, so that they may be applied to cloth or other base materials and subjected to light exposure without appreciable decomposition or discoloration.

(2) The provision of new methods for making silver containing reaction products which are particularly useful in rendering textile fabrics resistant to attack by micro-organisms.

(3) The provision of new forms of textiles and other base materials which carry a relatively permanent silver containing deposit.

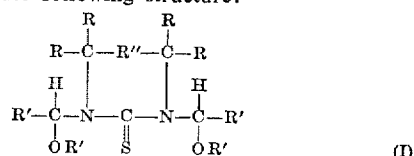
(4) The provision of new forms of biocidal finishes for textiles, which do not discolor on exposure to light and which are durable to laundering and dry cleaning without discoloration so that the sanitizing effects provided to the textiles by the biocidal finishes, are substantially fully retained throughout the useful life of the finished textile.

(5) The provision of new methods for applying relatively permanent silver containing deposits to textiles and other base materials.

(6) The provision of new forms of silver containing deposits on base materials in which the silver content of the deposit is in a highly reactive form, providing biocidal, catalytic or other desirable properties to the structure.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

These objects are accomplished according to the present invention by forming silver containing reaction products from monovalent silver ions and heterocyclic compounds having the following structure:



In the foregoing formula, R represents radicals selected from the group consisting of hydrogen, hydroxyl, alkyl, alkoxy and aryl, R' represents radicals selected from the group consisting of hydrogen, alkyl and aryl, and R'' is selected from the group consisting of a linking bond and the divalent $-\text{CR}_2-$ radical. Preferred silver containing reaction products are those formed from heterocyclic compounds having the structure as indicated above wherein R represents radicals selected from the group consisting of hydrogen, hydroxyl, 1 to 6 carbon alkyl and 1 to 6 carbon alkoxy, R' is a radical selected from the group consisting of hydrogen and 1 to 6 carbon alkyl and R'' is selected from the group consisting of a linking bond and the divalent $-\text{CR}'_2-$ radical.

In addition to the use of monomeric compounds having a structure as defined above, the new silver containing reaction products may be formed from monovalent silver ions and polymers of the described heterocyclic compounds. Also, reaction products may be formed from mixtures of such polymers or mixtures of polymers with the monomeric heterocyclic compounds.

The total quantity of silver ions combined with the heterocyclic compounds to form the new reaction products may be varied. As little as 0.01 mol of silver ions per mol of the heterocyclic compound may be employed, or as much as a mol or more of silver ions per mol of heterocyclic compound is useable. Thiouronium salts are formed and with dimethylol ethylene thiourea as the heterocyclic compound and silver nitrate providing the sil-

ver ions, reacted in equal molecular proportions, the resulting product is silver dimethylol ethylene thiouronium nitrate. When less than an equal molecular amount of silver ions are reacted with the heterocyclic compound, the reaction product constitutes a silver containing complex which comprises some free, unreacted heterocyclic compound. Silver containing reaction products of the best light stability are the complexes made with an excess of the heterocyclic compound and preferably between about 0.01 and 0.2 mol of silver salt are used for each mol of heterocyclic compound.

The formation of the reaction products may be accomplished under varied conditions and in different ways. For example, various reaction temperatures may be used. The reaction proceeds effectively at temperatures between 10° to 100° C. although temperatures in a broader range, e.g., 0° to 175° C. may be used if suitable provision is made for condensation of vaporized fluids, etc.

Silver nitrate is the preferred silver salt used to furnish silver ions in the production of the new reaction products of this invention. However, other water-soluble and water-insoluble silver salts may be employed, e.g., silver chloride, silver iodide, silver bromide, silver acetate, silver citrate, silver fluoride, silver sulfate, silver sulfite and silver ortho-phosphate.

As far as procedural steps are concerned, the reaction products may be obtained in any one of the following ways:

a. First a complex is prepared by mixing together a cyclic thiourea compound and a silver salt. This complex is then reacted with formaldehyde or other aldehyde in water or in the presence of lower alcohols to produce water-soluble precondensates comprising the N,N'-dioxo thiouronium salt.

b. As a first step, condensing, in an aqueous or alcoholic solution, a cyclic thiourea with an aldehyde, such as formaldehyde, by reacting 1 to 2 mols of the aldehyde with 1 mol of the ethylene urea at a temperature of between about 25 to 100° C. at times for a few minutes to several hours and at pH's from 1 to 12 until the aldehyde has fully reacted with the thiourea compound. When the ethylene thiourea-formaldehyde precondensate has been prepared, this is then reacted with an aqueous solution or dispersion of the silver salt.

c. As a third procedure, one prepares separately solutions of the heterocyclic compound and solutions or dispersions of the silver salt. At the time of use, such as finishing of textiles, these individually prepared solutions are mixed in water of dilution to prepare an application solution.

Solutions and dispersions of silver containing reaction products as described above can be used to treat a large variety of base materials, including the following:

- A. Hospitals bed sheets and linen.
- B. Hospital blankets.
- C. Clothing materials,
- D. Sanitary napkins.
- E. Military fabrics for biological warfare.
- F. Tent ducks and tarpaulins.
- G. Sail cloth and awnings.
- H. Shoe liners.
- I. Leather and leather products.
- J. Filters in biological warfare masks.
- K. Wood and wood products.
- L. Solid painted surfaces.
- M. Carpet and rugs.
- N. Paper and paper products.

The treatment of the base materials with the silver containing reaction product solutions can be accomplished in a variety of ways. Dilute solutions, e.g., solutions containing 0.01 to 10 parts of reaction product per 100 parts of solution, can be applied to fibrous materials by padding, impregnation, coating, spraying or other techniques, followed by drying and curing. Drying conditions normally employed for converting amino-aldehyde

resins to the thermoset conditions are usable, e.g., curing temperatures from about 25 to 175° C. for varying periods of time, and preferably in the presence of acidic catalysts, may be used.

The valuable properties created in the base material by incorporation of the silver containing deposits include the following:

(1) Self sterilizing effects against toxic organisms such as *Staphylococcus aureus*, *E. coli*, etc.

(2) Prevention of spread of air-borne bacteria in contaminated surfaces.

(3) Prevention of the formation of objectionable odors on textile garments in use.

(4) Prevention of the growth of and damage by mildews, molds and rot on treated surfaces such as textiles, paper, wood, leather, plastics, and painted surfaces.

All of these effects are produced by the products of this invention on a durable basis, i.e., they are not lost by water and rain leaching, by laundering, by drycleaning, by scrubbing, and by other conditions of end-use.

EXAMPLES

A more complete understanding of the new compositions, products and processes provided by this invention may be had by reference to the following examples, which describe the best modes contemplated for carrying out the invention. All parts and percentages in the examples are by weight unless otherwise specified.

Example I

A concentrated solution of dimethylol ethylene thiourea is prepared by charging into a reaction vessel equipped with an external heater, an internal stirrer, a cover and a reflux-condenser, 1250 parts of 37% formaldehyde and 455 parts of water. While this formaldehyde solution is stirred, there is added 787 parts of ethylene thiourea and 7.5 parts of 10% sodium hydroxide solution. The ensuing reaction is exothermic and the temperature of the reaction mixture rises rapidly from 22° C. to 45° C. By the application of external heat, the temperature of the reaction mixture is raised to 50° C. and maintained there for one hour. The contents of the reaction vessel are then cooled and the solution is neutralized to a pH of 7.5 by the addition of a small amount of nitric acid. The resulting product is a clear solution containing 50% by weight of dimethylol ethylene thiourea.

Example II

Complexes of dimethylol ethylene thiourea and silver nitrate in various mole ratios are prepared as follows:

II-A.—Four parts of AgNO₃ are dissolved in 196 parts of water with stirring. Then there are added 200 parts of the solution from Example I and stirring is continued at 25° C. until a clear solution is obtained. The pH is 6.75.

II-B.—To 196 parts of the solution from Example I, there are added 4 parts of dry AgNO₃ crystals. Stirring is continued until a clear solution is obtained. The pH is 7.15.

II-C.—Four parts of AgNO₃ are dissolved in 296 parts of water. Then there are added 100 parts of the solution from Example I and stirring is continued until a clear product is formed. The pH is 6.33.

II-D.—To 192 parts of the solution from Example I, there are added 8 parts of AgNO₃ crystals. Stirring is continued until a clear solution is formed. The pH is 6.22.

II-E.—Into 346 parts of water, there is mixed 4 parts of AgNO₃ and stirred until dissolved. To this solution, there is added 50 parts of the product from Example I and stirring is continued until a clear solution is obtained. The pH is 5.95.

II-F.—To 184 parts of the product from Example I, there is added 16 parts of silver nitrate crystals and the mixture is stirred until a clear solution is obtained. The pH is 5.38.

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Example III

Samples of white, bleached cotton 80 x 80 print cloth are padded to 80% wet pick-up through solutions of various concentrations of the products from Example II. The impregnated cloth samples are dried at 100° C. and then cured at 120° C. for five minutes. After curing, a portion of each sample is washed in an automatic home washer at 60° C. with soap and washing soda twenty consecutive times. The color of the samples before and after washing is measured by a Photovolt Reflectance Meter and is reported in percent reflectance of the measured value of magnesium oxide.

The germicidal properties of the samples before and after twenty washings were evaluated by the AATCC Tentative Test Method 90-1958, page 8, "American Dye-stuff Reporter," January 12, 1959, using *Staphylococcus aureus* as the bacterial agent. The results of killing efficiencies are reported in terms of percent inhibition of the growth of the organism by the test samples using the following ratings:

	Percent inhibition
Excellent -----	100
Good -----	75
Fair -----	50
Poor -----	25
Unsatisfactory -----	0

In the same series of tests, untreated fabric samples are subjected to the color and germicidal property determinations. Also, samples of the fabric are padded in the same fashion as just indicated using a 0.2% solution of AgNO₃ and, separately, a solution containing 0.2% AgNO₃ and 0.2% ethylene thiourea.

The results of these tests are shown in Table I. After each rating, there is also included the value for zone of inhibition in mm. This is equal to:

$$ZI = \frac{DI - DS}{2}$$

where

DI=Diameter of inhibition

DS=Diameter of test sample

Table I

Percent Bath Solids of Various Products	Percent Whiteness		Percent Inhibition	
	Orig.	20 Washes	Orig.	20 Washes
2.60 II-A -----	93	88	E 6.6	E 1.0
1.30 II-A -----	92	90	E 5.3	E 0.0
0.26 II-A -----	92	92	E 2.5	E 0.0
1.35 II-B -----	92	87	E 5.9	E 1.0
0.67 II-B -----	92	90	E 5.5	E 0.0
0.14 II-B -----	92	92	E 2.0	P 0.0
0.72 II-C -----	92	88	E 5.6	E 1.0
0.35 II-C -----	91	90	E 4.3	P 0.0
0.07 II-C -----	92	93	F 0.0	P 0.0
0.40 II-D -----	89	84	E 4.8	G 0.0
0.20 II-D -----	89	83	E 3.6	G 0.0
0.04 II-D -----	90	91	E 3.8	P 0.0
2.60 II-E -----	91	87	E 9.1	E 1.0
1.30 II-E -----	92	88	E 5.5	E 0.0
0.26 II-E -----	92	91	E 1.5	P 0.0
1.35 II-F -----	91	84	E 6.0	E 1.0
0.30 II-F -----	90	87	E 5.0	E 0.0
0.14 II-F -----	92	92	F 2.0	P 0.0
Untreated Fabric -----	93	93	U 0.0	U 0.0
0.20 AgNO ₃ -----	55	34	E 4.5	P 0.0
0.20 AgNO ₃ +0.2% ETU -----	92	72	E 4.0	U 0.0

The results reported in Table I show that while impregnation of textile fabric with silver nitrate provides appreciable germicidal activity to the fabric, even after twenty washings, such impregnated fabric is very critically discolored even at the beginning, and this becomes increasingly worse as the fabric is washed. On the other hand, the results show that where textile is treated with a silver complex formed of silver nitrate and ethylene thiourea, initial color of the fabric is good and the

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germicidal properties are excellent, but after twenty washings, the germicidal activity of the cloth is completely destroyed and at the same time, the color of the fabric is relatively poor. Textile treated with the new silver-dimethylol ethylene thiourea complexes exhibits appreciable initial and final germicidal activity without any significant discoloration.

Example IV

Samples of cotton fabrics are treated with solutions containing varying amounts of dimethylol ethylene thiourea and AgNO₃ using the general procedures described in Example III. The results of the color and germicidal tests on the resulting cloth samples are reported in Tables II and III. In these tables, the data under the columns 10W and 20W are those recorded on the samples washed ten times and twenty times respectively.

TABLE II
UNCATALYZED

Percent Bath Solids		Percent Whiteness			Percent Inhibition		
AgNO ₃	ETU-F	Orig.	10 W.	20 W.	Orig. ²	10 W.	20 W.
0.20	0.00	60	34	30	E	P 0.0	U 0.0
0.20	0.25	88	87	87	E	F 4.9	E 3.1
0.20	0.50	87	85	85	E	E 4.1	E 1.5
0.20	0.75	88	84	84	E	E 3.5	E 0
0.20	1.00	88	80	79	E	E 3.5	E 1.3
0.20	2.00	87	76	76	E	E 2.1	E 2.0
CATALYZED ¹							
0.20	0.25	88	80	77	E	E 3.5	E 3.1
0.20	0.50	89	81	79	E	E 2.0	E 2.0
0.20	0.75	88	82	80	E	E 1.0	E 1.5
0.20	1.00	89	81	80	E	E 2.0	E 0.5
0.20	2.00	89	82	81	E	E 0.2	E 0.0
Untreated Fabric -----		89	89	89	U	U	U

¹ 0.5% Zn(NO₃)₂·6H₂O used as catalyst.

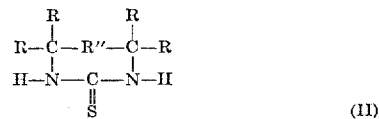
² Zone of inhibition not measured in this case.

TABLE III

Percent Bath Solids		Percent Whiteness			Percent Inhibition		
AgNO ₃	ETU-F	Orig.	10 W.	20 W.	Orig. ¹	10 W.	20 W.
0.10	0.12	88	87	87	E	G 0.0	P 0.0
0.02	0.25	87	85	85	E	E 1.0	G 0.0
0.04	0.50	88	84	84	E	E 1.5	E 0.0
0.10	1.20	88	80	79	E	E 3.0	F 1.2
0.20	2.50	87	76	76	E	E 3.7	E 2.5
0.10	1.00	88	80	77	E	E 3.2	E 2.0
0.10	1.25	89	81	79	E	E 2.5	F 0.8
0.10	1.50	88	82	80	E	E 2.5	F 1.0
0.10	2.00	89	81	80	E	E 3.0	E 1.0
0.10	2.50	89	82	81	E	E 3.4	E 1.0

¹ Zone of inhibition not measured in this case.

The heterocyclic compounds from which the products of this invention are formed may be produced in a variety of ways. Preferably, they are prepared by condensing an aldehyde with a cyclic thiourea having the following structure:



wherein R and R' have the significance previously stated. Ethylene thiourea having the following structure is a preferred material:



Another usable material is propylene thiourea which

may also be called, tetrahydro-2(1H) thiopyrimidone. Additional examples of 5 and 6 member ring cyclic thioureas include 4,5-dimethyl ethylene thiourea; 4-phenyl ethylene thiourea; tetramethyl ethylene thiourea; 4-ethyl, 5-hydroxy ethylene thiourea; 4,5-diethoxy ethylene thiourea; 4-octyl ethylene thiourea; 4-methoxy, 5-tolyl ethylene thiourea; 4-hydroxy ethylene thiourea; 4,5-dihexyl ethylene thiourea; 4-methyl, 4-ethoxy ethylene thiourea; 4-hydroxy, 5-naphthyl ethylene thiourea; tetrahydro-4-methyl-2(1H)-pyrimidone; tetrahydro-4-ethoxy-2(1H) pyrimidone; tetrahydro-4-methyl-5-hydroxy-6-phenyl-2(1H) pyrimidone; tetrahydro-4-hydroxyl-6-butoxy-2(1H) pyrimidone and tetrahydro-4-dimethyl-5-hydroxy-6-hexyl-2(1H) pyrimidone.

The preferred aldehyde for use in producing the heterocyclic compounds used to form the silver containing reaction products of this invention is formaldehyde. Commercial formalin, which contains about 37% active formaldehyde, is a good source of HCHO for use in conducting the condensation reactions, but other sources and formaldehyde donors may be used, e.g., paraformaldehyde, hexamethylene tetramine or the like. Other aldehydes which may be used to form condensation products with these heterocyclic compounds include acetaldehyde, propionaldehyde, acrolein, methacrolein, benzaldehyde, cinnaldehyde and the like.

The amount of aldehyde used for reaction with the cyclic thioureas as indicated above may be varied from about 0.5 to 2 mols for each mol of the cyclic thiourea. When less than 2 mols of aldehyde per mol of cyclic thiourea is used, the mono-N-oxy or a mixture of the mono- and N,N'-dioxy cyclic thiourea is obtained. Solutions resulting from use of formaldehyde with an average of 1.2 to 2.0 methylol groups are particularly useful in forming the new silver containing reaction products.

The initial condensation between the aldehyde and the cyclic thiourea compound is preferably carried out at a temperature between about 25 to 100° C. in an aqueous medium having a pH from 1 to 12, and preferably between about 8 to 11, until all of the aldehyde is reacted. The pH in this initial condensation reaction may be adjusted to the desired value by addition of suitable alkaline, acidic or buffer materials including sodium or other alkali metal hydroxides or carbonates, ammonium hydroxide, a magnesium carbonate, alkali metal phosphates, nitric acid, hydrochloric acid, or the like. The condensation reaction is conducted under the conditions indicated for a sufficient time to permit substantial reaction to occur, less time being required the higher the temperature, e.g., when formaldehyde is used in the preferred range of 25 to 100° C., the reaction time will be between about 5 to 120 minutes. This condensation reaction produces N-oxy derivatives of the cyclic thioureas, e.g., methylol, ethylol, propylol, hexylol, phenylol, and similar derivatives of the cyclic thioureas, i.e., heterocyclic compounds (I) previously referred to.

The condensation reaction involving the cyclic thioureas may be carried out in the presence of alcohols or the resulting N-oxy derivatives may be reacted with alcohols to form the corresponding ethers. For example, reaction of dimethylol ethylene thiourea with ethanol will yield the N,N'-diethyl ether. Alcohols suitable for the process include 1 to 6 carbon monohydric alcohols, e.g., methanol, ethanol, propanol, butanol, hexanol, allyl alcohol, methallyl alcohol, etc., and 1 to 6 carbon polyhydric alcohols, e.g., ethylene glycol, propylene glycol, glycerol and the like. Mixtures of alcohols may be used to give products which are mixed ethers.

The alcohol modification of the condensation products can be accomplished simultaneously with the reaction between the aldehyde and the cyclic thiourea compound (II), but alcohol modification is better obtained by carrying out the initial condensation between the aldehyde and the cyclic thiourea compound (II) under the conditions specified above, then adding the alcohol thereafter,

along with sufficient acid to bring the pH of the reaction mixture below 7, preferably about 4 to 6, and condensing the alcohol with the preformed reaction product at an elevated temperature between about 50 and 100° C. The maximum amount of alcohol which can be made to react is 2 mols for each mole of initial cyclic thiourea, but less than this may be employed, e.g., 0.5 to 2 mols of alcohol per mol of cyclic thiourea.

No special equipment or unusual procedural methods are required for treating textiles with the new silver containing reaction products of this invention. Thus, established padding or impregnation procedures may be used and these may be carried out in standard textile processing equipment. Likewise, the drying and curing may be carried out on standard textile handling apparatus. Furthermore, these treating agents may be applied in conjunction with other textile processing operations such as waterproofing, calendering, embossing, pressing and the like.

After the dilute solutions of the new silver containing reaction products are applied to the textile or other base material by padding, impregnation, coating, spraying or similar technique, the wet base is dried at a temperature of, for example, 50 to 150° C. and it is then heated to convert the active resin forming material, i.e., the silver containing reaction products of this invention with or without any added aminoplasts or other resin forming condensates, into a thermoset resinous product, preferably at a temperature of about 25 to 200° C. and especially 100 to 175° C. for varying periods of time, e.g., 1 to 30 minutes. Drying and curing can take place at the same temperature and in the same oven or dryer, if desired. It is preferable to use aqueous solutions of the new silver containing reaction products in a state of condensation that they are water-soluble, e.g., capable of being dissolved in water to form solutions of about 1 to 10% concentration.

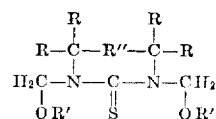
The new silver containing reaction products may be condensed to form high molecular weight thermoset silver containing aminoplasts without the use of catalysts, but preferably acidic-aminoplast-forming catalysts are used. Examples of suitable catalysts includes free acids, e.g., hydrochloric, citric, phthalic and tartaric acids, acid-reacting metal salts, e.g., zinc chloride, zinc nitrate, zinc fluoroborate, magnesium chloride, and acid-reacting salts of ammonia or amines, e.g., ammonium silico fluoride, diammonium acid phosphate, monoethanolamine hydrochloride and the like. Usually 1 to 10% by weight of the catalysts based upon the weight of the silver containing reaction product is an effective amount.

The new silver containing reaction products may be used alone to treat base materials or may be used in conjunction with many of other known finishing agents such as amino-aldehyde resins, epoxy resins, water-repellent or waterproofing compounds, polyethylene finishes, cationic softeners, plasticizers and lubricants, coating resins, coloring agents, silicones, sizing materials, e.g., starches and gums, and other agents normally used in the finishing of fibrous materials.

Having provided a complete description of the invention in such manner as to distinguish it from other inventions and from what is old, and having provided a description of the best mode contemplated of carrying out the invention, the scope of patent protection to be granted the invention is defined by the following claims.

We claim:

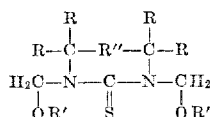
1. A water-soluble silver containing reaction product of monovalent silver ions and a heterocyclic compound selected from the group consisting of compounds having the structure:



and water-soluble polymers thereof, wherein R'' is selected from the group consisting of a linking bond and the divalent —CR'₂— radical, R' is a radical selected from the group consisting of hydrogen and one to six carbon alkyl, and R represents radicals selected from the group consisting of hydrogen, hydroxyl, one to six carbon alkyl and one to six carbon alkoxy.

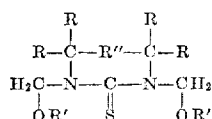
2. The process of rendering a base material durably biocidal and light stable which comprises applying to a base material a silver containing composition as defined in claim 1, drying the base material with the applied composition to leave a residue of a silver containing reaction product on the base material and heating the resulting structure to cure the silver containing reaction product to a water-insoluble state.

3. A durable and light stable biocidal resin-forming composition comprising an aqueous solution of an acidic aminoplast-forming catalyst and a resin forming material selected from the group consisting of reaction products of mono-valent silver ions and a heterocyclic compound selected from the group consisting of compounds having the structure:



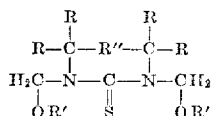
and water-soluble polymers thereof, wherein R'' is selected from the group consisting of a linking bond and the divalent —CR'₂— radical, R' is a radical selected from the group consisting of hydrogen and one to six carbon alkyl, and R represents radicals selected from the group consisting of hydrogen, hydroxyl, one to six carbon alkyl and one to six carbon alkoxy.

4. A light stable and durably mildew-resistant cotton textile fabric comprising a fabric made of cotton fibers impregnated with a thermo-set resinous material of the silver containing reaction product of monovalent silver ions and a heterocyclic compound selected from the group consisting of compounds having the structure:



and water-soluble polymers thereof, wherein R'' is selected from the group consisting of a linking bond and the divalent —CR'₂— radical, R' is a radical selected from the group consisting of hydrogen and one to six carbon alkyl, and R represents radicals selected from the group consisting of hydrogen, hydroxyl, one to six carbon alkyl and one to six carbon alkoxy.

5. A process of forming an aqueous solution of a silver containing reaction product which may be used to treat fibrous materials to impart biocidal properties thereto which comprises forming an aqueous solution of a heterocyclic compound selected from the group consisting of compounds having the structure:



and water-soluble polymers thereof, wherein R'' is se-

lected from the group consisting of a linking bond and the divalent —CR'₂— radical, R' is a radical selected from the group consisting of hydrogen and one to six carbon alkyl, and R represents radicals selected from the group consisting of hydrogen, hydroxyl, one to six carbon alkyl and one to six carbon alkoxy, adding to said solution a substance which will provide monovalent silver ions in the solution, the total quantity of silver ions added being between about 0.01 and 1 mol of silver ions per mol heterocyclic compound and agitating the resulting mixture until a substantially clear solution is obtained.

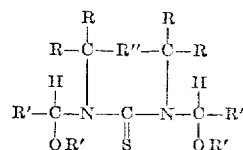
6. A process of forming an aqueous solution of a silver containing reaction product which may be used to treat fibrous materials to impart biocidal properties thereto which comprises forming an aqueous solution of dimethylol ethylene thiourea, adding to said solution a silver salt which will provide monovalent silver ions in said solution, the total quantity of silver salt added being between about 0.01 and 1 mol of salt per mol of said dimethylol ethylene thiourea, and agitating the resulting mixture until a substantially clear solution is obtained.

7. A process of forming an aqueous solution of a silver containing reaction product, which solution may be used to treat textiles to impart durable biocidal properties thereto and without fabric discoloration which comprises forming an aqueous solution of dimethylol ethylene thiourea, adding silver nitrate thereto in an amount between about 0.01 and 0.2 mol of silver nitrate per mol of the dimethylol ethylene thiourea and agitating the resulting mixture until a substantially clear solution is obtained.

8. An aqueous solution for use in treating textiles to impart durable biocidal properties thereto and without fabric discoloration comprising silver dimethylol ethylene thiouroneum nitrate and dimethylol ethylene thiourea.

9. An aqueous solution for use in treating textiles to impart durable biocidal properties thereto and without fabric discoloration comprising silver dimethylol propylene thiouroneum nitrate and dimethylol propylene thiourea.

10. A silver containing reaction product of monovalent silver ions and a heterocyclic compound selected from the group consisting of the monomers and polymers of compounds having the structure:



wherein R represents radicals selected from the group consisting of hydrogen, hydroxyl, alkyl, alkoxy, and aryl, R' represents radicals selected from the group consisting of hydrogen, alkyl and acryl and R'' is selected from the group consisting of a linking bond and the divalent —CR'₂— radical.

11. Silver dimethylol ethylene thiouroneum nitrate.

12. Silver dimethylol propylene thiouroneum nitrate.

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