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METAL CONTAINING COMPOSITIONS, PROCESSES AND PRODUCTS

Domenick Donald Gagliardi and Fred Boswell Shippee, East Greenwich, R.I., assignors to Scientific Chemicals Inc., Chicago, Ill., a corporation of Illinois

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This invention relates to metal containing sanitizing compositions, processes for rendering fibrous materials durably microbiocidal with said compositions and the resulting sanitized products.

It is well known that certain metals or the salts and other compounds of the metals may be applied to fabrics or other substrates to impart thereto microbiocidal properties. For example, silver, copper and various other metal salts have been applied to such materials as fibers, fabrics, animal hides, paper, wood or the like to protect the base against attack from micro-organisms, e.g., to make the base material resistant against mildew, rot, and similar attack by fungi or bacterial. Many forms of metal compositions and processes using these materials have previously been suggested for accomplishing such results.

The prior known compositions and operations have involved one or more practical deficiencies. For example, chlorinated phenols, while initially effective on fibrous materials, lose their mildewproofing and antibacterial effects when exposed to heat and light or when the treated item is repeatedly laundered. Quaternary ammonium compounds, while effective against selected micro-organisms, do not generally render fabrics mildew resistant. Moreover, such quaternary compounds when applied to fibrous materials lose their antimicrobial activity when exposed to soaps, detergents and alkaline washing compounds. Copper containing compounds, such as copper naphthenate or copper 8-hydroxy-quinolate, while effective in rendering cellulosic materials mildew resistant, are not particularly effective against gram negative and gram positive organisms. Moreover, when applied to fibrous materials, such products require solvent application techniques and also produce a greenish color in the treated article.

It has been previously suggested to treat textile materials with silver nitrate complex salts of ethylene thiourea (see U.S. Patent 3,061,469). Such treated textile or other fibrous articles, however, while possessing some limited capacity to resist laundering, lose their antimicrobial effectiveness when exposed to repeated alkaline washing conditions. Further, antimicrobial activity is relatively poor when treated fabrics are buried in soil and the complex salts are sensitive to chlorine upon bleaching to cause a loss of strength when the bleached fabric is ironed. Moreover, fibrous materials treated with such silver ethylene thiourea compounds become brown colored when washed and exposed to heat and light from the formation of metallic silver or silver oxide deposits on the treated fibers. Improved biocidal properties in fibrous substrates have been obtained by impregnation with formaldehyde derivatives of silver-ethylene urea adducts (see U.S. Patent 3,085,909). In this case, however, the presence of small amounts of free formaldehyde may act as a reducing agent for silver and may produce fabric discoloration, although durability to multiple washings may be obtained. The potential formation of color in treated articles is generally undesirable and more foolproof products or processes have been demanded by various industries.

A principal object of this invention is the provision of new and improved metal containing compositions

which may be applied to fibrous substrates to impart thereto durable and broad range microbiocidal properties without detrimentally affecting the color characteristics of the treated substrate or without otherwise adversely affecting the substrate. Further objects include:

(1) The provision of new and improved organometallic compositions that are effective in rendering fibrous materials resistant to mildew, fungi and rot and at the same time producing microbiocidal and self-sterilizing effects against a wide range of gram negative and gram positive organisms as *Staphylococcus aureus, E. coli, Chaetomium globosum, Trichoderma lignorum,* and the like.

(2) The provision of new compositions which comprise water-soluble or water-dispersible compounds which can be readily applied to fibrous materials through conventional treating techniques to impart microbiocidal properties to the fibrous materials.

(3) The provision of metal sanitizing compositions which are not discolored during storage or handling in the treating of fibrous substrates nor by heat or light exposure.

(4) The provision of metal containing compositions and treating processes utilizing them for imparting microbiocidal effects to textiles and other fibrous materials which are durable enough to withstand repeated laundering, dry cleaning, multiple high-temperature alkaline washes or comparable application of cleaning or treating solutions.

(5) The provision of new metal containing compositions which make it possible to produce durable rot-proofing on cotton and rayon duck and awning materials, and self-sanitizing effects on diapers, hospital bedding, bed sheets, undergarments and the like and which retain their strength despite bleaching and ironing.

(6) The provision of new compositions and methods for producing antiseptic cloth for shoe linings, mold-resistant wallpaper, mildew-resistant sailcloth and self-sterilizing non-woven fabric filters.

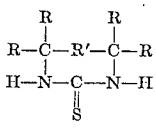
(7) The provision of new compositions and methods for reducing rotting of wood and creating other microbiocidal effects on fibrous substrates.

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 and specific examples, while indicating preferred embodiments of the invention, are 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.

In accordance with the present invention, the organometallic coordination complex is applied to the textile fabric from a physical admixture with a polyfunctional compound or resin capable of reacting with the —NH— groups of the complex to form a water-insoluble reaction product therewith. In addition to the use of physical mixtures, the present invention contemplates a partial prereaction between the coordination complex and the polyfunctional compound or resin, but the prereaction is a limited one which does not destroy water-dispersibility so that, upon deposition of the partial reaction product, it is capable of reacting further with the —NH— groups of the complex to form a water-insoluble reaction product therewith. In this way, water insolubility is achieved by a polymerization reaction with an agent external of the textile being treated providing more extensive insolubilization through polymerization; there is no need to form rather complex chemicals reacted with both metal salt and formaldehyde and which are of limited storage stability and sensitive to formaldehyde release

in the immediate vicinity of the metal causing discoloration; and the active hydrogen atoms of the —NH— groups of the complex are more completely reacted to provide chlorine-resistant finishes when the polyfunctional compound or resin is itself resistant to chlorine.

The organo-metallic coordination complexes embraced by the invention are complexes of salts of metals having biocidal properties with heterocyclic compound having the formula:



wherein R is a radical selected from the group consisting of hydrogen, hydroxyl and alkyl, alkoxy and alkoxyalkyl radicals containing from 1–6 carbon atoms, and R′ is selected from the group consisting of a linking bond and the divalent methylene radical.

The metals which may be used are those having coordination properties and these are particularly illustrated by silver, copper, zinc, iron, cadmium, cobalt, chromium, aluminum and nickel. The invention is especially concerned with silver, copper and zinc, preferably silver.

The organo-metallic coordination complex is conveniently formed by mixing the heterocyclic compound with a salt of the metal in a common solvent, especially water, in a molar ratio of the metal to the heterocyclic compound of from about 1:1 to 1:10.

The polyfunctional compounds or resins which are employed are those which contain a plurality of functional groups capable of reacting with the —NH— groups of the complex to form a water-insoluble reaction product therewith. This reaction is intended to take place under the influence of elevated temperature and after application of the polyfunctional compound or resin to the textile being treated. Preferably, a functionality of at least 2 is intended though higher functionality is preferred and somewhat lower functionality down to about 1.4 may be tolerated.

Various functional groups may be relied upon as indicated below.

Polyepoxides containing the oxirane group illustrated by polyglycidyl ethers of aromatic or aliphatic polyhydric compounds, such as a polyglycidyl ether of glycerin having an epoxy functionality of about 2.3, these being preferred for water dispersibility. Copolymers containing the glycidyl group are also useful such as 95/5 copolymer of ethyl acrylate and glycidyl methacrylate. While terminal oxirane groups are preferred for greater reactivity, this is not essential as in the compound vinyl cyclohexene dioxide.

Polyaldehydes such as dialdehydes and their acetals which release the aldehyde group —CHO when heated. Glyoxal is typical of this class of compounds.

Polymethylol compounds containing a plurality of —CH_2OH methylol groups. It will be understood that the methylol group may be etherified with a volatile alcohol, typically methanol, to release the reactivity of the methylol group upon volatilization of the alcohol, and such ethers are embraced within the term methylol. Numerous polymethylol compounds which are useful are well known, such as polymethylol melamines including dimethylol melamine, trimethylol melamine, hexamethylol melamine, etc.; dimethylol urea, dimethylol ethylene thiourea, dimethylol ethylene urea, tetramethylol acetylene, dimethylol 1,3-propylene urea, tetramethylol acetylene diurea, dimethylol N-ethyl triazone, tris methoxymethyl melamine, dimethylol adducts of polyalkylated monoureins (see French Patent 1,318,810), etc.

It should be particularly noted as a feature of the invention that compounds containing active hydrogen reactive with chlorine, such as dimethylol urea, do not provide bleach-resistant products and are less preferred.

The invention particularly contemplates resinous addition copolymers in which the active group is the methylol group and which is essentially devoid of active hydrogen reactive with chlorine so that, when the —NH— groups of the complex are tied up by the polymerization reaction, the resulting water-insoluble deposit upon the textile material is essentially devoid of groups reactive with chlorine to permit the achievement of superior laundry resistance, color stability, microbiocidal activity, and the capacity to be bleached and then ironed with relative impunity.

From the standpoint of etherified methylol groups, the preference in the invention for at least water dispersible materials carries a corresponding preference for lower alcohols, and particularly methanol, as the etherifying agent. While other ether alcohols are fully operative, their capacity for water miscibility is lowered with respect to methanol and, hence, these are less preferred.

Still other polyfunctional compounds which may be used are compounds containing the ethylene imine group or the aziridinyl group, numerous polyethylene imine compounds and aziridinyl compounds being known as illustrated by tris aziridinyl phosphine oxides. Reactive quaternary ammonium salts such as those produced by the chloromethylation of amides and alcohols and having the general formulae:

$$RCONH.CH_2.NR_3{+}Cl^-$$
$$RO.CH_2.NR_3{+}Cl^-$$

may also be employed as well as vinyl unsaturated compounds having an active terminal methylene group such as divinyl sulfones.

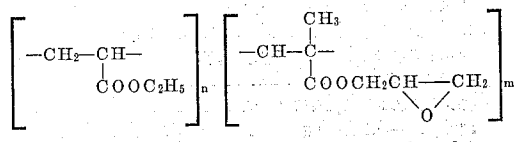
The invention is especially directed to compositions which are capable of water application to textile materials and, from this standpoint, the polyfunctional compound is preferably selected to either possess relatively low molecular weight or a high degree of functionality (2 or more and preferably in excess of 2 for cross-linking) in a water soluble moiety in order to achieve the desired properties of water-insolubility in the reaction product through a thermosetting, cross-linking cure. These materials, which are essentially monomeric, are illustrated by polymethylol ureas and melamines; polymethoxymethyl ureas and melamines; polymethylol and polymethoxymethyl cyclic ureas, thioureas, and iminoureas; dialdehydes as glyoxal and glutaraldehyde; polyglycidyl ethers of polyols; tris aziridinyl phosphine oxides and sulfides; and bis quaternaries of chloromethylated glycols.

A second direction of importance is the utilization of relatively high molecular weight acrylic emulsion copolymers. When these can be formulated in relatively stable aqueous dispersions or emulsion (referred to as latices) they are capable of coreaction with the complexes embraced by the invention to provide the desired properties, despite the fact that these emulsion copolymers are linear copolymers.

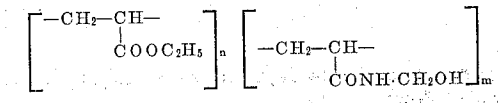
The copolymers which are especially contemplated are those containing a major proportion of acrylic ester with a minor proportion, especially from 1–25% by weight, of what may be termed a reactive acrylate, the term acrylate embracing derivatives of acrylic acid and methacrylic acid. Still more specifically, the acrylic copolymers which are particularly contemplated may be identified by the formula:

where: n is from 75–99% and m is from 25–1%; R is hydrogen or methyl and X is a radical containing a group

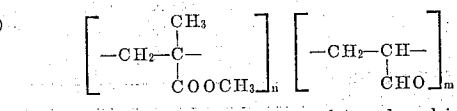
which can react with the —NH— group in the complex. Specific examples of such emulsion copolymers are:

(A) 

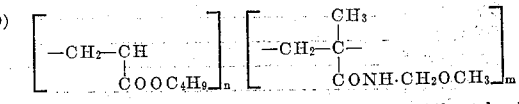
a copolymer of ethyl acrylate and glycidyl methacrylate

(B) 

a copolymer of ethyl acrylate and methylol acrylamide

(C) 

a copolymer of methyl methacrylate and acrolein

(D) 

a copolymer of butyl acrylate and methoxymethyl methacrylamide

In the Examples A, B, C and D above, typical values for *n* and *m* are 95% and 5%, respectively. These may be prepared as illustrated in United States Patent No. 3,100,674.

As will be evident, mixtures of two or more of the polyfunctional compounds with the metal coordination complex or mixtures of two or more of the metal complexes with polyfunctional compounds may be employed.

While application from aqueous medium is preferred as has been previously indicated, it is also possible to employ the mixtures of the invention or partial prereaction products thereof in organic solvent solution or, especially where the mixture is liquid, as an aerosol.

The preferred aqueous treating compositions of the invention will contain between about 0.05 to 5% by weight of the metal-ethylene thiourea complex, and especially 0.1 to 2% by weight of the complex and 1 to 20% by weight of the polyfunctional compound, and especially 3 to 10% of the polyfunctional compound.

Advantageously, the ratio of the metal complex to the polyfunctional compound on a weight basis is in the range of from 1:50 to 2:1.

In treating a fibrous substrate such as paper, woven textiles, non-woven fabrics or the like, between about 0.1 and 30% and, advantageously, 1 to 10% of the combined mixture of metal complex and polyfunctional compound will be impregnated in or applied to the fiber substrate to be treated. Using the preferred aqueous solutions or emulsions described, it is advantageous to control the impregnation or other application of the aqueous composition to give a pick-up of about 50% to 150% by weight thereof, based upon the weight of the fabric or other fibrous substrate to which the aqueous composition is applied.

Advantageously, the treating composition will also contain an acidic catalyst which will aid in the formation of a water-insoluble, heat-cured reaction product between the metal complex and the polyfunctional compound. Between about 1 to 10%, based upon the weight of the polyfunctional compound, of the acidic catalyst is preferably employed.

Following application of the treating composition, the impregnated or otherwise treated fibrous substrate is dried. This is advantageously accomplished by heating to a temperature between about 100 and 150° C. for between about 1 to 60 minutes.

To complete the treatment of the fibrous substrates and to convert the reaction product of the metal complex and polyfunctional compound into a heat-cured condition so that the material is durable against dry-cleaning, laundering or the like, the dried substrate is subjected to a heat-curing step. Preferably, this is accomplished at a temperature between 100 and 200° C. for about 1 to 60 minutes, longer times generally being employed at the lower temperature and vice versa.

A more complete understanding of the new products and methods of this invention may be had by reference to the following working examples of operations conducted in accordance with the invention. In these examples and throughout the remainder of the specification and claims, all parts and percentages are by weight unless otherwise specified.

Example 1

Samples of cotton print cloth were impregnated with about an equal weight of the following solutions, followed by drying for 5 minutes at 120° C. and then curing for 5 minutes at 150° C.:

	Percent
Solution 1:	
Silver-ethylene thiourea complex[1]	0.2
Water	99.8
	100.0
Solution 2:	
Silver-ethylene thiourea complex[1]	0.2
Tris methoxymethyl melamine	5.0
Catalyst—$MgCl_2.6H_2O$	1.0
Water	93.8
	100.0

After curing, the two fabrics were laundered up to 25 times in a home automatic washer using a synthetic detergent. Then they were tested for antibacterial activity against *Staphylococcus aureus* using the AATCC Test Method No. 90–1962T, page B–130, 1962 Technical Manual of AATCC. The following results were obtained:

[1] 1:4 mole ratio of silver nitrate and ethylene thiourea.

Treatment Number	Antibacterial Rating and Halo in mm			
	Initial	5 Washes	10 Washes	25 Washes
Untreated	Poor, 0.0			
Solution 1	Excellent, 1.0	Poor, 0.0	Poor, 0.0	Poor, 0.0.
Solution 2	Excellent, 2.0	Excellent, 2.0	Excellent, 1.0	Good, 0.0.

NOTE.—In the above tabulation, as well as the further tabulations which follow, the remarks "excellent", etc., identify subjective opinion of antibacterial ratings and the numerical ratings, such as 1.0, identify the diameter of the antibacterial halo measured in millimeters. When the test specimen kills the organism under test in the immediate region of the specimen, but without killing the organism at a distance from the specimen, the specimen would have a good rating, but it would have a halo of 0 millimeter.

The samples treated with Solution No. 2 produced durable microbiocidal activity. Moreover, all the samples treated with Solution No. 1 were considerably yellowed by the treatment whereas those treated with solution No. 2 were white and remained white after the various washes. This is shown by percent whiteness retention, measured by a reflectance meter, given below:

Treatment Number	Percent Whiteness	
	Initial	20 Washes
Untreated	80	80
Solution 1	60	51
Solution 2	80	82

Example 2

Samples of cotton duck were treated with the solutions given below to give about 100% pick-up, followed by drying for 10 minutes at 120° C. and then curing for 10 minutes at 150° C. After curing, they were scoured with a synthetic detergent in an automatic home washer to remove any unfixed materials. Then the samples were subjected to 14 days soil burial according to Test Method 5762 of Federal Specifications CCC–T–191b.

Solution 1:	Percent
Silver-ethylene thiourea nitrate complex, 1:4 mole ratio	0.2
Water	99.8
	100.0

Solution 2:	
Silver-ethylene thiourea nitrate complex, 1:4 mole ratio	0.2
Dimethylol, N-ethyl triazone	5.0
Catalyst—$MgCl_2.6H_2O$	1.0
Water	93.8
	100.0

Solution 3:	
Silver-ethylene thiourea nitrate complex, 1:4 mole ratio	0.2
Dimethylol ethylene thiourea	5.0
Catalyst—$MgCl_2.6H_2O$	1.0
Water	93.8
	100.0

Solution 4:	
Silver-ethylene thiourea nitrate complex, 1:4 mole ratio	0.2
Dimethylol melamine	5.0
Catalyst—$MgCl_2.6H_2O$	1.0
Water	93.8
	100.0

Solution 5:	
Copper-ethylene thiourea nitrate complex, 1:4 mole ratio	2.1
Emulsion copolymer of 95 parts ethyl acrylate and 5 parts N-methylol acrylamide	2.5
Catalyst—NH_4Cl	0.3
Water	95.1
	100.0

Solution 6:	
Zinc-ethylene thiourea nitrate complex, 1:2 mole ratio	2.3
Emulsion copolymer of 95 parts ethyl acrylate and 5 parts N-methylol acrylamide	2.5
Catalyst—NH_4Cl	0.3
Water	94.9
	100.0

Solution 7:	
Silver-ethylene thiourea nitrate complex, 1:2 mole ratio	0.2
Emulsion copolymer of 95 parts ethyl acrylate and 5 parts glycidyl methacrylate	2.5
Dimethylol ethylene urea	1.0
Catalyst—0.5% $Zn(NO_3)_2 \cdot 6H_2O$	0.5
Water	95.8
	100.0

The results of the 14 days soil burial test are shown in the table below:

Treatment applied	Percent tensile strength retained after 14 days soil burial
Untreated control	0
Solution 1 control	0
Solution 2	94
Solution 3	82
Solution 4	100
Solution 5	100
Solution 6	95
Solution 7	100

Example 3

Samples of cotton fabric were impregnated with about an equal weight of solutions of silver-ethylene thiourea nitrate complexes and tris methoxymethyl melamine, followed by drying 5 minutes at 120° C. and then curing 5 minutes at 150° C. The treating solutions contained:

Solution 1:	Percent
Silver-ethylene thiourea nitrate complex, 1:8 mole ratio	0.2
Tris methoxymethyl melamine	5.0
Catalyst—$MgCl_2 \cdot 6H_2O$	1.0
Water	93.8
	100.0

Solution 2:	
Silver-ethylene thiourea nitrate complex, 1:4 mole ratio	0.2
Tris methoxymethyl melamine	5.0
Catalyst—$MgCl_2 \cdot 6H_2O$	1.0
Water	93.8
	100.0

The treated samples were then given 10 repeated washes with a synthetic detergent, 10 washes with soap and soda ash, and 10 washes with soap and sodium hypochlorite bleach. The results of antibacterial tests, as previously described, on these specimens are given in the table below.

Treatment Applied	Antibacterial Rating and Halo in mm.		
	10 Detergent Washes	10 Soap and Soda Washes	10 Soap and Chlorine Washes
Solution 1	Very good, 0.0	Fair, 0.0	Excellent, 1.0.
Solution 2	Excellent, 0.0	Good, 0.0	Excellent, 1.0.

Example 4

Samples of cotton fabrics were treated as in Example 1 with various solutions containing the metal-ethylene thiourea-acetate complex (1 to 4 mole ratio) and dimethylol ethylene thiourea at a total loading of 6% solids. The

results of the antibacterial tests are shown in the table below:

Ethylene Thiourea Complex in Mixture	Antibacterial Ratings and Halo in mm.	
	Initial	After 20 Detergent Washes
Zinc	Excellent, 2.5	Very good, 0.0.
Cobalt	Excellent, 0.0	Good, 0.0.
Nickel	Excellent, 4.0	Good, 0.0.
Chromium	Excellent, 2.0	Very good, 0.0.
Aluminum	Excellent, 2.0	Good, 0.0.
Magnesium	Excellent, 3.0	Very good, 0.0.
Copper	Excellent, 0.0	Good, 0.0.
Silver	Excellent, 3.0	Very good, 0.0.

Example 5

Samples of cotton fabrics were treated as in Example 1 with aqueous solutions of 0.2% silver-ethylene thiourea nitrate complexes (1:4 mole ratio) and 2.5% of a polyfunctional reactive acrylic emulsion copolymer of 95% ethyl acrylate and 5% N-methylol acrylamide. The different acid catalysts listed below were used to facilitate the heat-cure of the mixture. The results of antibacterial tests were as shown in the table below:

Catalyst Used	Antibacterial Ratings and Halo in mm.	
	Initial	After 20 Soap and Chlorine Washes
None	Excellent, 2.0	Poor, 0.0.
0.5% $MgCl_2.6H_2O$	Excellent, 2.0	Excellent, 0.0.
0.1% Oxalic Acid	Excellent, 0.5	Excellent, 1.0.
0.3% NH_4Cl	Excellent, 2.0	Very good, 0.0.
0.2% $Zn(BF_4)2$	Excellent, 2.5	Good, 0.0.
0.5% $Zn(NO_3)_2$	Excellent, 3.0	Excelint, 0.0.

These clearly show the influence of the second component polyfunctional compound in fixing the silver compound on the fabric.

Example 6

A variety of textile fabrics were impregnated with about an equal weight of a solution containing 0.3% of silver-ethylene thiourea nitrate complex (1:4 mole ratio), 1.5% dimethylol ethylene urea, 7.5% of the reactive acrylic copolymer identified in Example 5, and 1% catalyst, $MgCl_2 \cdot 6H_2O$. The fabrics were then dried for 10 minutes at 250° F. The results of antibacterial tests are shown in the table below:

Fabric Type	Antibacterial Ratings and Halo in mm.	
	Initial	After 20 Detergent Washes
Spun Acrylic	Excellent, 3.0	Good, 0.0.
Spun Triacetate	Excellent, 3.0	Good, 0.0.
Spun Polyester	Excellent, 2.0	Good, 0.0.
Spun Polyamide	Excellent, 2.0	Excellent, 0.5.
Spun Acetate	Excellent, 4.0	Excellent, 1.5.
Wool Flannel	Excellent, 2.5	Very good, 0.0.

A particular advantage achieved by the invention is the capacity to resist chlorine bleaches and this is an important distinction over the prior art as is illustrated by the materials which follow.

Example 7

Samples of cotton fabrics were treated as follows from aqueous media:

Percent

(A):
- Silver-ethylene thiourea nitrate complex, 1:4 mole ratio — 0.2
- Emulsion polymer of ethyl acrylate — 5.0
- Catalyst—NH_4Cl — 0.3

(B):
- Silver-ethylene thiourea nitrate complex, 1:4 mole ratio — 0.2
- Emulsion copolymer of 95 parts ethyl acrylate and 5 parts N-methylol acrylamide — 5.0
- Catalyst—NH_4Cl — 0.3

(C):
- Silver-ethylene thiourea nitrate complex, 1:4 mole ratio — 0.2
- Vinyl cyclohexane dioxide — 2.0
- Emulsion copolymer of 95 parts ethyl acrylate and 5 parts glycidyl methacrylate — 5.0
- Catalyst—NH_4Cl — 0.3

The fabrics were padded through these treating baths, dried 5 minutes at 250° F. and cured 5 minutes at 300° F. The fabrics were then tested for chlorine resistance by the AATCC chlorine resistance test (see 1960 Technical Manual, page 123, Test Method 92–1958). The tensile strength of the fabrics before and after chlorine test are given below:

	Strip Tensile, Lbs./In.	
	Initial	After Chlorine Test
Sample A	49	0
Sample B	52	44
Sample C	57	53

These results clearly show that the compositions of this invention produce chlorine resistant finishes.

The improved capacity of the invention to provide detergent resistance and light fast finishes is illustrated in the following example.

Example 8

Samples of cotton fabric were treated as above with:

Percent

(D):
- Dimethylol silver-ethylene thiourea nitrate complex, 1:4 mole ratio — 0.2
- Catalyst—NH_4Cl — 0.3
- Dimethylol ethylene thiourea — 4.8

(E):
- Silver-ethylene thiourea nitrate complex, 1:4 mole ratio — 0.2
- Emulsion copolymer of 95 parts ethyl acrylate and 5 parts of N-methylol acrylamide — 5.0
- Catalyst—NH_4Cl — 0.3

After curing as above, the whiteness of the fabrics was measured initially, after 20 alkaline detergent washes and after the washes and 20 hours light exposure in the FadeOmeter. The results are shown below:

	Percent Whiteness		
	Initial	20 Washes	Washes, then Light
Untreated Fabric	80	80	80
Sample D	80	76	68
Sample E	80	80	78

It is desirable to improve the storage stability of the solutions and dispersions which are presently employed and to enhance the laundering and light resistant properties which are obtained upon elevated temperature cure after application of the treating composition to the fabric. This is achieved by partially prereacting the metal complex and the polyfunctional compound as by a heat-blending operation. As heat-blending proceeds, water solubility or dispersibility diminishes and it is merely necessary to stop the prereaction, by discontinuing the application of heat, before the solution or dispersion contains particles of gelatinized material. The prereacted or heat-

blended materials have essentially the same properties reported hereinbefore and these materials are illustrated by the prereaction product of silver-ethylene thiourea nitrate complex (1:4 mole ratio) with tris methoxymethyl melamine (Solution 2 of Example 3). This aqueous solution is prereacted by heating the solution to just below its boiling point.

Example 9

430 grams of an 80% water solution of tris methoxymethyl melamine, 20 grams of silver-ethylene thiourea nitrate (1:4 ratio) and 50 grams of ethylene thiourea (excess) were reacted together for one hour at 65° C. A clear pale yellow viscous product was obtained which was water soluble.

5% of this product was diluted with 94% water to which was added 1% $MgCl_2$—$6H_2O$ as catalyst. This solution was padded onto cotton print cloth, dried 5 minutes at 250° F. and cured 5 minutes at 300° F. Then the cloth was washed 20 times in soap and sodium hypochlorite washing solution. Even after 20 washes, the sample gave a rating of excellent and 1.0 mm. halo in the antibacterial test.

The prepolymer products of the invention may be used alone or in admixture with any of the polyfunctional compounds or resins referred to hereinbefore.

A wide variety of compounds are known to be useful as acidic catalysts for effecting the heat conversion of amino-plasts and similar polyfunctional compounds as involved in this invention. Preferred classes of such catalysts include water-soluble acidic metal salts, water-soluble amine salts and water-soluble acids. Advantageously, the water-solubility of such materials should be at least 1 part in 100 parts of water and preferably, at least 10 parts in 100 parts of water.

Examples of suitable catalysts include 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.

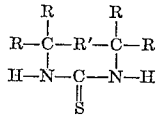
The new metal containing treating compositions of the invention may be used in conjunction with many of other known finishing agents such as water-repellent or waterproofing compounds, polyethylene finishes, cationic softeners, plasticizers and lubricants, coating resins, coloring agents, silicones, sizing materials, e.g., starches and gums, and other agents normally used in the finishing of fibrous materials.

The invention is defined in the claims which follow:

We claim:

1. A microbiocidal composition adapted, when deposited upon fibrous substrates and cured at elevated temperature, to render said substrates durably resistant to attack by fungus and bacteria consisting essentially of:

(a) organo-metallic coordination complex of a biocidal metal having coordination properties with heterocyclic compound having the formula:



wherein R is a radical selected from the group consisting of hydrogen, hydoxyl and alkyl, alkoxy and alkoxyalkyl radicals containing from 1–6 carbon atoms, and R′ is selected from the group consisting of a linking bond and the divalent methylene radical; and

(b) compound containing a plurality of functional groups capable of reacting with the —NH— groups of said complex to produce a water-insoluble reaction product.

2. The microbiocidal composition of claim **1** in which the molar ratio of metal to heterocyclic compound in said complex is in the range of from 1:1 to 1:10.

3. The microbiocidal composition of claim **2** in which the weight ratio of said complex to said compound containing a plurality of functional groups is in the range of from 1:50 to 2:1.

4. The microbiocidal composition of claim **3** in which said biocidal metal is selected from the group consisting of silver, copper and zinc.

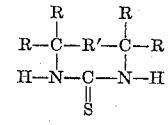
5. The microbiocidal composition of claim **1** in which said heterocyclic compound is ethylene thiourea.

6. The microbiocidal composition of claim **1** in which the functional groups of said compound containing a plurality of functional groups are selected from the group consisting of oxirane, methylol, aldehyde, ethylene imine, aziridinyl, vinyl and quaternary ammonium.

7. The microbiocidal composition of claim **1** in which the functional groups of said compound containing a plurality of functional groups are devoid of active hydrogen reactive with chlorine.

8. An aqueous microbiocidal composition adapted, when deposited upon fibrous substrates and cured at elevated temperature, to render said substrates durably desistant to attack by fungus and bacteria consisting essentially of:

(a) organo-metallic coordination complex of a biocidal metal having coordination properties with heterocyclic compound having the formula:



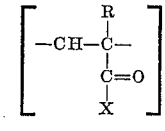
wherein R is a radical selected from the group consisting of hydrogen, hydroxyl and alkyl, alkoxy and alkoxyalkyl radicals containing from 1–6 carbon atoms, and R′ is selected from the group consisting of a linking bond and the divalent methylene radical; the molar ratio of metal to heterocyclic compound in said complex being in the range of from 1:1 to 1:10; and

(b) at least one water-dispersible compound containing a plurality of functional groups capable of reacting with the —NH— groups of said complex to produce a water-insoluble reaction product selected from the group consisting of oxirane, methylol, aldehyde, ethylene imine, aziridinyl, vinyl and quaternary ammonium; the weight ratio of said complex to said compound containing a plurality of functional groups being in the range of from 1:50 to 2:1.

9. The aqueous microbiocidal composition of claim **8** in which said biocidal metal is selected from the group consisting of silver, copper and zinc and said heterocyclic compound is ethylene thiourea.

10. The aqueous microbiocidal composition of claim **8** in which said compound containing a plurality of functional groups is a monomeric compound having a functionality of at least 2.0.

11. The aqueous microbiocidal composition of claim **8** in which said compound containing a plurality of functional groups is an emulsion copolymer consisting essentially of alkyl acrylate and from 1 to 25% by weight of the copolymer of acrylate having the formula:



in which R is selected from the group consisting of hydrogen and methyl and X is a radical containing a functional group reactive with the —NH— group of said complex, said copolymer being dispersed in the aqueous composition.

12. The aqueous microbiocidal composition of claim 8 in which said composition contains from 0.05–5% by weight of said complex and from 1–20% by weight of said compound containing a plurality of functional groups.

13. The aqueous microbiocidal composition of claim 8 in which said complex and said compound containing a plurality of functional groups are partially heat-prereacted with one another.

14. An aqueous microbiocidal composition adapted, when deposited upon fibrous substrates and cured at elevated temperature, to render said substrates durably resistant to attack by fungus and bacteria consisting essentially of:

(a) coordination complex of silver salt with a molar excess up to 10:1 of ethylene thiourea; and

(b) water-dispersible emulsion copolymer of a major weight proportion of alkyl acrylate with from 1–25 weight percent of N-methylol acrylamide;

said composition containing from 0.05–5% by weight of said complex and from 1–20% by weight of dispersed copolymer.

15. An aqueous microbiocidal composition adapted, when deposited upon fibrous substrates and cured at elevated temperature, to render said substrates durably resistant to attack by fungus and bacteria consisting essentially of:

(a) coordination complex of silver salt with a molar excess up to 10:1 of ethylene thiourea; and

(b) water-dispersible emulsion copolymer of a major weight proportion of alkyl acrylate with from 1–25 weight percent of glycidyl methacrylate;

said composition containing from 0.05–5% weight of said complex and from 1–20% by weight of dispersed copolymer.

16. An aqueous microbiocidal composition adapted, when deposited upon fibrous substrates and cured at elevated temperature, to render said substrates durably resistant to attack by fungus and bacteria consisting essentially of:

(a) coordination complex of silver salt with a molar excess up to 10:1 of ethylene thiourea; and

(b) water-dispersible emulsion copolymer of a major weight proportion of alkyl acrylate with from 1–25 weight percent of acrolein;

said composition containing from 0.05–5% by weight of said complex and from 1–20% by weight of dispersed copolymer.

17. A light-stable and durably microbiocidal fibrous article comprising a fiibrous substrate impregnated with the composition of claim 1, said composition being heat-cured in situ to a water-insoluble condition upon said fibrous substrate.

18. An aqueous microbiocidal composition adapted, when deposited upon fibrous substrates and cured at elevated temperature, to render said substrates durably resistant to attack by fungus and bacteria consisting essentially of:

(a) organo-metallic coordination complex of a biocidal metal selected from the group consisting of silver, copper and zinc with ethylene thiourea; the molar ratio of said metal to said ethylene thiourea in said complex being in the range of from 1:1 to 1:10; and

(b) at least water-dispersible compound containing a plurality of functional groups capable of reacting with the —NH— groups of said complex to produce a water-insoluble reaction product selected from the group consisting of oxirane, methylol, aldehyde, ethylene imine, aziridinyl, vinyl and quaternary ammonium; the weight ratio of said complex to said compound containing a plurality of functional groups being in the range of from 1:50 to 2:1; said complex (a) and said compound (b) being partially heat-prereacted with one another.

19. A light-stable and durably microbiocidal textile fabric comprising a textile fabric impregnated with the aqueous composition of claim 8, said aqueous composition being dried and heat-cured in situ to a water-insoluble condition upon said textile fabric.

20. The article of claim 19 in which said fabric comprises cotton fiber.

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MURRAY KATZ, *Primary Examiner.*

WILLIAM D. MARTIN, *Examiner.*

T. G. DAVIS, *Assistant Examiner.*