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METHOD OF RENDERING TEXTILE MATERIALS
FUNGICIDAL AND THE PRODUCTS THEREBY
PRODUCED

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The present invention relates to textile materials hav-
ing a germicidal precipitate of a water-insoluble quater-
nary ammonium 2-mercaptobenzothiazolate formed in
situ in and upon the fibers thereof and to a two-step
method of rendering such textile materials durably ger-
micidal. This application is, in part, a continuation of
Shibe et al. application Serial No. 402,604, filed January
6, 1954, now abandoned, for "Quaternary Ammonium
Mercaptobenzothiazolates and Process for Preparing the
Same."

It is known to treat textile fabrics with compounds
which are intended to render these materials mildewproof
and germicidal. Insofar as such compounds are water-
soluble, they are of relatively little value and are rapidly
leached by moisture. Insofar as water-insoluble com-
pounds are concerned, it is a difficult problem to apply
these in such manner that the treated fabric has any rea-
sonable amount of germicidal durability. These insoluble
compounds are substantially only in the category of coat-
ing materials as they do not appreciably penetrate into
and become an integral part of the textile materials or
the fibers thereof. It has been the practice, so far as we
are aware, to apply mildewproofing and germicidal agents
to textile materials by passing the textile materials through
a suspension or solution of the chemical compound in a
single step, but we have found that such a procedure is
inferior and is incapable of producing the results of our
present invention.

It is, accordingly, a primary object of the present in-
vention to render textile materials mildewproof, fungi-
cidal and bactericidal in such manner that exceptional
penetration is effected and the treated fabrics retain their
fungicidal properties for a long period of time.

Another object of the invention resides in applying
separate unreacted components to textile materials in suc-
cession so as to produce a precipitate in situ in and upon
the fibers of the textile material while at the same time
achieving exceptional penetration so that the treated fab-
rics retain their properties over a long period of time.

More specifically, an object of the invention resides
in treating a textile material, such as cotton duck, with
an aqueous solution of a germicidal quaternary ammo-
nium compound and then with an aqueous solution of
sodium 2-mercaptobenzothiazolate, the treated fabric
having exceptional mildewproof, germicidal and fungi-
cidal properties with great resistance to leaching, as the
compound is formed and deposited in and on the fibers
in such manner as to be water-insoluble and integrally
bound with the fibers themselves.

Other and further objects and advantages will be un-
derstood from what follows or will be appreciated by those
skilled in this art.

According to the present invention, a first solution is
made up of a germicidal quaternary ammonium com-
pound which may be any of those types or particular
compounds specified in application Serial No. 402,604
aforesaid. Preferably, this solution is made up by dis-
solving alkyl dimethyl benzyl ammonium chloride (benz-

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alkonium chloride) in water, preparing a second solution
containing sodium 2-mercaptobenzothiazolate in water
and then successively passing cotton duck or other textile
fabric through the individual solutions. When this is
done, a water-insoluble precipitate or alkyl dimethyl
benzyl ammonium 2-mercaptobenzothiazolate is formed
in and upon the fibers of the cotton duck or other textile
material in such a manner as to become, for all practical
purposes, an integral part of the textile material.

TABLE 1

Effect of rinsing during 2-bath process upon bacteriostatic
activity of cotton treated with 5% of alkyl dimethyl
3,4-dichlorobenzyl ammonium chloride and sodium 2-
mercaptobenzothiazolate

Treatments	Average zone of inhibition, ¹ mms.
(1) Treated—no rinse	5.3
(2) Treated—air dried overnight—then 3 rinses	4.0
(3) Treated—3 rinses while wet—air dried overnight	3.5
(4) No treatment	0

¹ Average of 4 replicate 10 mm. cloth discs. Assayed November 18,
1954, using *M. pyogenes* var. *aureus* by FDA cir. 198 method.

Conclusions.—The bacteriostatic activity of treatments 2
and 3 in the above table indicates the durability of this anti-
septic treating process. The fact that rinsing the wet cloth
immediately after processing (treatment 3) did not signifi-
cantly affect activity over drying before the rinses (treat-
ment 2) indicates that the chemical is durably deposited in
the fibers of the fabric. Apparently the tenacity of the chemi-
cal in or on the fiber is such that it does not require drying
for durability. (However, some loss results from rinsing as
noted in comparing treatments 2 and 3 with No. 1.) These
results were confirmed in a further test.

Since the precipitate is composed of water-insoluble
material, it resists leaching over long periods of time and,
therefore, the textile material is permanently character-
ized by mildewproof, germicidal and fungicidal properties.

We have found that this two-step method has impor-
tant advantages over the one-step method heretofore used
not only because the treated fabric retains its properties
for an indefinitely long period of time but because the
germicidal character of the quaternary ammonium com-
pound is materially enhanced, being greater than either
the quaternary ammonium compound or the 2-mercapto-
benzothiazolate separately.

TABLE 2

Treatment	Mildew rating after 7 days	
	Unleached	Leached 24 hours
1% benzalkonium chloride	0	2
1% mercaptobenzothiazole	0	5
1% benzalkonium 2-mercaptobenzothiazolate	0	0

Mildew ratings:
0=no growth.
1=trace of mildew; several spots on cloth.
2=slight mildew; up to 25% of area.
3=moderate mildew; up to 50% of area.
4=abundant mildew; 50-100% area covered.
5=overgrown and sporulating.

In addition, by carrying out the procedure in two steps,
as above set forth, the wetting and penetrant properties
of the quaternary ammonium compound can be given full
effect, whereas such are not available in a product of re-
action thereof. The quaternary ammonium 2-mercapto-
benzothiazolate, therefore, contains two functional group-
ings which, in the present invention, serve to enhance and
synergize the active functional groupings of the individual
components, thereby producing results which are vastly

superior to those which can be obtained by applying an already reacted product directly to the fabric or material.

TABLE 3

Comparison of effect of method of application upon bacteriostatic activity of cloth treated with alkyl dimethyl 3,4-dichlorobenzyl ammonium 2-mercaptobenzothiazolate

Percent of chemical in cotton duck, calculated on dry weight of fabric	Average zone of inhibition, mms. ¹	
	One bath	Two bath
2.00	1.8	4.0
1.00	1.3	3.6
0.50	0.8	3.1
0.25	0.4	2.6
0.10	0.2	2.0

¹ Average of 4 replicate 10 mm. cloth discs. Assayed December 2, 1954 using *Micrococcus pyogenes* var. *aureus* by FDA Cir. 198 Method.

Discussion.—Cotton duck was processed by dip-squeezing through solutions of Puratized 1123 which were prepared at various concentrations from 0.1–5% active ingredient. The one-bath solution consisted of the chemical dissolved in benzene. The two-bath consisted first of the aqueous quaternary dip followed by the aqueous mercaptobenzothiazolate. The pickup of the cloth in benzene averaged 62.4% of the dry weight of the fabric and ranged from 60.0–63.8%. The pickup from the aqueous two-bath averaged 55.2% and ranged from 52.4–58.0% for the different chemical concentrations.

For bioassay, 4 random circular discs were punched out of each piece of cloth and placed on agar seeded with the bacterium. The petri plates were incubated 24 hours at 37° C. and zones of inhibition recorded. The bacteriostatic activity was then plotted on log paper against the calculated quantity of chemical in the cloth. For example, for the 1-bath treatment, the wet pickup from the 5% chemical solution was 63.8% of the dry weight of the fabric, or $63.8 \times .05 = 3.19\%$ chemical in the cloth. Unfortunately, no chemical method is available to analyze the cloth directly for concentration of this new chemical.

The plotted bacteriostatic data showed a straight line relationship between the logarithm of the chemical concentration and the germicidal effectiveness. The curves from both methods of application were parallel but the 2-bath process was significantly more effective. The activity shown in the above table was interpolated from the curves at arbitrary concentrations between 0.1–2% to illustrate the superiority of the 2-bath process.

The procedure also is of benefit in that it is extremely simple and economical as it is only necessary to prepare the individual aqueous solutions without being concerned about reacting them and obtaining good yields of the reaction product. The two-step method of the invention is, moreover, carried out at room temperature under ordinary prevailing temperature conditions and thus requires no special apparatus, equipment or control.

The invention is illustrated by the following specific example without limiting it thereto:

EXAMPLE

A first solution was prepared containing 6 grams of alkyl dimethyl benzyl ammonium chloride (benzalkonium chloride) to each 200 milliliters of water.

A second solution was prepared containing 5 grams of sodium 2-mercaptobenzothiazolate to each 200 milliliters of water.

Cotton duck was passed through the first solution at a rate sufficiently slow to permit saturation with the penetrant solution of the quaternary ammonium compound. Excess solution was squeezed out by pressure and the cotton duck then passed through the second solution, whereupon a precipitate of water-insoluble alkyl dimethyl benzyl ammonium 2-mercaptobenzothiazolate was formed in situ in and on the fibers of the cotton duck as a permanent integral part thereof. The thus treated material was allowed to dry in the air and produced a cloth that was bactericidal, fungicidal and resistant to leaching.

It is to be understood from the foregoing that any suitable water-soluble quaternary ammonium compound may be employed so long as it has germicidal or fungicidal properties. While benzalkonium chloride is one of the preferred quaternary ammonium compounds due to its ready availability and low price, the invention is not

limited to the use of such since there are other quaternary ammonium halides which are eminently satisfactory in carrying out the invention. Such include, for instance, lauryl pyridinium chloride, cetyl trimethyl ammonium bromide, dodecylbenzyl trimethyl ammonium chloride and quaternary ammonium compounds which are halogen-substituted in the benzene ring of the benzyl group, such as alkyl dimethyl 3,4-dichlorobenzyl ammonium chloride and alkyl dimethyl 2,4-dichlorobenzyl ammonium chloride, as well as mixtures of such quaternary ammonium compounds. The invention also applies to quaternary ammonium compounds of the type represented by para-diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride (Hyamine 1622) and a mixture of soya trimethyl ammonium chloride and diconut dimethyl ammonium chloride (Arquad S-2C). Likewise, the invention includes the use of 2-mercaptobenzothiazole and its water-soluble salts, such as sodium 2-mercaptobenzothiazolate. When 2-mercaptobenzothiazole is employed in the invention, it is first converted into its sodium or other suitable water-soluble salt as by means of sodium hydroxide.

In the preferred mode of practicing the two-step method in accordance with the invention, it has been found best to pass the textile fabric or material first through the aqueous solution of the quaternary ammonium compound and then through the aqueous solution of the mercaptobenzothiazolate as, in this way, full advantage is taken of the penetrant and wetting properties of the quaternary ammonium compound so that, when the fabric or material is subsequently passed through the mercaptobenzothiazolate solution, reaction occurs to form a water-insoluble precipitate in situ in and upon the fibers. It is, however, within the purview of the invention to reverse the order of steps by first subjecting the textile fabric or material to the mercaptobenzothiazolate solution and then to the quaternary ammonium compound solution, although we have found that this procedure is somewhat less desirable and effective than the preferred procedure but, nevertheless, produces useful and satisfactory results. Instead of treating a finished fabric or material, the procedure may be applied to the fibers or yarn which are then woven or otherwise formed into the finished piece goods or articles.

The invention may also be considered as based upon the impregnation or saturation of the textile fabric or material with a germicidal water-soluble quaternary ammonium compound and the insolubilization of the said germicidal quaternary ammonium compound directly in and upon the fibers of the textile material, this procedure acting to produce a water-insoluble precipitate in situ so that exceptional mildewproof, germicidal and fungicidal properties are imparted to, and conferred upon, the fabric and its fibers by employing a 2-mercaptobenzothiazolate solution as the insolubilizing and fixing agent for the germicidal and fungicidal quaternary ammonium compound which has already been applied to the textile material. Exceptionally good results are obtained due to the fact that the mercaptobenzothiazolate itself has useful pesticidal properties and has a synergistic action on the quaternary ammonium compound. The product of reaction formed in and on the fibers has greatly enhanced fungicidal and pesticidal properties which are retained for an unusual length of time so that it is ordinarily not necessary to re-treat fabric or fibers after treatment in accordance with the invention. The finished fabric also has the advantages that ordinary fluids used for dry cleaning do not have any appreciable solvent action upon the quaternary ammonium mercaptobenzothiazolate and hence, treated fabrics may be dry-cleaned, washed and the like without serious loss of the compound and the properties imparted thereto.

The invention is defined by the appended claims.

We claim:

1. A two-step method of rendering a textile material durably mildewproof, germicidal and fungicidal, which

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comprises forming in situ in and on the fibers of the textile material a water-insoluble quaternary ammonium 2-mercaptobenzothiazolate by passing the textile material successively in either order through separate aqueous solutions, one of which is an aqueous solution of a germicidal quaternary ammonium compound and the other of which is an aqueous solution of a water-soluble 2-mercaptobenzothiazolate, said quaternary ammonium compound synergistically reacting, upon contact with said 2-mercaptobenzothiazolate to form said quaternary ammonium 2-mercaptobenzothiazolate which becomes an integral and leach-resistant part of the textile material.

2. The method of claim 1, in which the textile material is first passed through the aqueous solution of the quaternary ammonium compound to utilize the full penetrant and wetting action thereof.

3. The method of claim 1, in which the quaternary ammonium compound is benzalkonium chloride.

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4. A textile material prepared in accordance with claim 1, and characterized by having in and on the same at least 0.5%, calculated on the basis of the dry weight of the textile material, of water-insoluble quaternary ammonium 2-mercaptobenzothiazolate.

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