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BASE FABRIC COATED WITH RESIN HAVING MIXTURE OF QUATERNARY AMMONIUM GERMICIDES

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This invention relates to a material containing an active germicide and more particularly to a plastic or rubber coated fabric impregnated with a germicide.

This application is a continuation-in-part of copending application Serial No. 126,459, filed June 26, 1961, now abondoned.

The primary object of the invention is to provide a germicidally treated material for use in the control of pathogenic microorganisms. The treated material has particular use in hospitals, restaurants, dairies, laundries and the like where it is necessary to control and reduce bacteria activity. More specifically, the material can be used for hospital and other laboratory purposes as draw sheets, laundry basket liners, laboratory aprons, hamper bags, mattress covers and the like, and also has domestic use as diaper bags, mattress covers, sweat suits and other similar articles.

Accordingly to the invention, the germicidally treated article comprises a base fabric coated with a thermoplastic resin or natural rubber. Finely divided particles of a germicide are dispersed within the thermoplastic material or rubber coating and the thermoplastic coating not only serves to hold or retain the germicide, but also presents a smooth surface which can be readily cleaned. The germicidal material to be used is an organic ammonium quaternary salt, and it has been found that the combination of an alkyl dimethyl benzyl ammonium halide with the alkyl group containing from 8 to 18 carbon atoms and a diisobutyl phenoxyethoxy ethyl dimethylbenzyl ammonium halide is particularly effective as the germicide. This combination of germicidal materials provides an effective protection against bacteria and other micro-organisms, such as *Staphylococcus aureus, Brucella abortus, Clostridium welchii, Proteus vulgaris, Pseudomonas aeruginosa, Salmonella choleraesuis, Salmonella typhosa, Streptococcus fecalis,* and the like.

As the germicidal material is dispersed within the thermoplastic coating, the germicide will be retained in the material and be effective for long periods of time. The fabric can be repeatedly washed in either cold or hot water and the germicidal effect will be relatively unimpaired.

The fabric backing material can be any reinforcing material which will provide the necessary tensile strength for the article and can take the form of fabric made of synthetic fibers, such as nylon, Dacron, Orlon or rayon; animal fibers such as wool; vegetable fibers such as cotton; or mineral fibers such as glass or asbestos; and the like.

The coating material can be natural rubber or any thermoplastic resin or elastomer which, in the cured state, is sufficiently flexible to permit the composite article to be readily handled and fabricated. The coating can be applied as a natural rubber or synthetic latex in which the particles of natural rubber or resin are suspended in a liquid carrier such as water or other evaporable liquid. The latex can be applied to the fabric backing by spraying, dipping or the like, and subsequently dried to form the smooth surface coating on the fabric backing. Butadiene - styrene, butadiene - acrylonitrile, neoprene, polyvinyl chloride acrylic resins, and the like can be used to form the synthetic latex.

The thermoplastic resin coating can also be applied to

the fabric backing by conventional spread-coating processes. In this process the fabric passes over a table or counter and then over a supporting roll. An adjustable coating knife or doctor blade is located between the supporting roll and a following roll. The coating material, in a soft state, is introduced just behind the blade and the blade spreads a film of the coating material on the fabric. The thickness of the film is determined by the adjustment of the blade and the speed of travel of the fabric.

The particular method of applying the thermoplastic coating to the fabric backing is not critical to the invention and any method commonly used for coating fabrics or similar sheet material can be employed.

The germicide, distributed as fine particles throughout the coating, is an organic ammonium quaternary salt in which the hydrogen atoms attached to the nitrogen atom in the normal ammonium quaternary salt are replaced by organic groups. In general, the germicide may be an alkyl trimethyl ammonium halide with the alkyl group having from 8 to 18 carbon atoms, a dialkyl dimethyl ammonium halide with the alkyl group having from 8 to 18 carbon atoms, an alkyl dimethyl benzyl ammonium halide with the alkyl group having from 8 to 18 carbon atoms, a diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium halide, a diisobutyl cresoxy ethoxy ethyl dimethylbenzyl ammonium halide, and mixtures thereof.

Typical germicides which can be used are

Methyl dodecyl benzyl trimethyl ammonium chloride;

Methyl dodecyl xylylene bis-trimethyl ammonium chloride;

Alkyl trimethyl ammonium chloride with the alkyl group comprising 90% dodecyl and 9% tetradecyl and 1% octadecenyl;

Alkyl trimethyl ammonium chloride where the alkyl group comprises 90% hexadecyl, 6% octadecyl and 4% octadecenyl;

Alkyl trimethyl ammonium chloride where the alkyl group comprises 8% octyl, 9% decyl, 47% dodecyl, 18% tetradecyl, 8% hexadecyl, 5% octadecyl and 5% octadecenyl;

Normal alkyl dimethyl benzyl ammonium chloride where the alkyl group comprises 50% dodecyl, 30% tetradecyl, 17% hexadecyl and 3% octadecenyl;

Dialkyl dimethyl ammonium chloride where the alkyl group comprises 8% octyl, 9% decyl, 47% dodecyl, 18% tetradecyl, 8% hexadecyl and 10% octadecyl;

Dialkyl dimethyl ammonium chloride where the alkyl group comprises 24% hexadecyl, 4% octadecyl, 30% octadecenyl and 42% octadecadienyl;

Normal alkyl dimethyl benzyl ammonium chloride where the alkyl group comprises 50% dodecyl, 30% tetradecyl, 17% hexadecyl and 3% octadecyl;

Normal alkyl dimethyl ethyl benzyl ammonium chloride where the alkyl group comprises 50% dodecyl, 30% tetradecyl, 17% hexadecyl and 3% octadecyl;

Alkyl dimethyl 3,4-chlorobenzyl ammonium chloride where the alkyl group comprises 50% dodecyl, 30% tetradecyl, 17% hexadecyl and 3% octadecyl;

Diisobutyl phenoxyethoxy ethyl dimethylbenzyl ammonium chloride;

Diisobutyl cresoxy ethoxy ethyl dimethylbenzyl ammonium chloride and mixtures thereof.

The corresponding bromides can be substituted for the chlorides in the quaternary salts set forth above. However, if a combination of quarternary salts is to be used as the germicide, all of the germicides in a given combination should either be chlorides or bromides and not mixtures thereof.

The germicide comprises about 5% to 25% by weight of the thermoplastic coating, based on 100% active ma-

terials. In addition, a small amount in the range of .01% to 1.0% by weight of the coating of boric acid can be included to increase the adherence between the thermoplastic material and the fabric, and from 0.01% to 1.5% of a defoaming agent, such as 2-ethyl hexanol, can also be employed in the coating mixture to reduce the foaming action of the germicide during mixing and to prevent a "bubbly-type" of coating.

It has been found that the combination of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride or diisobutyl cresoxy ethoxy ethyl dimethylbenzyl ammonium chloride and an alkyl dimethylbenzyl ammonium chloride, with the alkyl group having from 8 to 18 carbon atoms, such as lauryl-dimethylbenzyl ammonium chloride, provides a particularly effective and lasting germicidal combination for the article of the invention.

In the coating diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride comprises from 50 to 80% by weight of the total germicidal material and the germicides are preferably added to the elastomer or thermoplastic material in a two batch operation. For example, a first batch of the uncured latex or resin is prepared and 1.3 to 10.0% by weight of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and 0.8 to 6.0% by weight of an alkyl dimethylbenzyl ammonium chloride, based on 100% active ingredients, are then added to the resin and mixed thoroughly therein. Diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride is normally used in a weight ratio of 1.5:1 to 2.5:1 with respect to the alkyl dimethylbenzyl ammonium chloride in the first batch.

A second batch of the latex or resin of substantially the same weight as the first batch is prepared and 2.0 to 10.0% of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and from 0.4 to 4.0% of an alkyl dimethylbenzyl ammonium chloride, based on 100% active ingredients, are added to the second batch and thoroughly mixed in. Diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride is preferably used in a weight ratio of about 3.5:1 to 4.5:1 with respect to the alkyl dimethylbenzyl ammonium chloride in the second batch. After thoroughly mixing the germicidal materials in each separate batch, the two batches are combined to provide the final mixture of the latex or resin to be applied to the fabric as a coating by conventional procedures. The elastomer coating is then cured by conventional methods such as heating the article to a temperature in the range of 300 to 425 degrees F.

When using the combination of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and an alkyl dimethylbenzyl ammonium chloride as the active germicidal materials, it has been found that the above two batch mixing procedure is important in providing the desired germicidal characteristics in the cured material. The combination of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and alkyl dimethylbenzyl ammoniuum chloride provides an unexpected germicidal activity which cannot be achieved by either germicide separately. Moreover diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride appears to remain on or near the surface of the coating while alkyl dimethylbenzyl ammonium chloride penetrates within the coating so that the combination of germicides provides a uniform distribution of germicidally effective material throughout the coating which will remain active for long periods.

EXAMPLE NO. 1

As a specific example of the process, 0.3 pound of boric acid, 3.30 pounds of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride (50% active ingredients) and 2.40 pounds of lauryl dimethylbenzyl ammonium chloride (50% active ingredients) were mixed with 94.0 pounds of polyvinyl chloride resin which was in a thick, paste-like consistency. A second batch was made up by adding 0.3 pound of boric acid, 4.70 pounds of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride (50% active ingredients) and 1.20 pounds of lauryl dimethylbenzyl ammonium chloride (50% active ingredients) to 93.8 pounds of polyvinyl chloride resin. After thoroughly mixing the separate batches, the two batches were mixed together in a vat and the resulting mixture was then applied to one surface of nylon fabric by a spread-coating process. After the resin has been applied to one surface of the nylon fabric, the coated fabric was passed through an oven at a temperature of 400 degrees F. to partially cure the resin. After the precuring treatment, the resin containing the germicidal materials was applied to the opposite side of the fabric and subsequently the fabric was passed through a curing oven at a temperature of 400 degrees F. to completely cure the resin coating on both surfaces.

The germicidal materials were dispersed throughout the resin coating and provided exceptional effectiveness against various types of bacteria and other micro-organisms for extended periods of time.

EXAMPLE NO. 2

As a second example .10 pound of boric acid, .75 pound of 2 ethyl hexanol, 14.917 pounds of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride (50% solution) and 8.66 pounds of lauryl dimethylbenzyl ammonium chloride (50% solution) were mixed with 75.573 pounds of polyvinyl chloride resin which was in a thick paste-like consistency. A second batch was prepared by mixing .10 pound of boric acid, .103 pound of 2 ethyl hexanol, 10.917 pounds of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride (50% solution) and 8.66 pounds of lauryl dimethylbenzyl ammonium chloride (50% solution). After separately mixing the two batches, the batches were mixed together and the resulting mixture was applied to nylon fabric as set forth in Example No 1.

The antibacterial activity of the material of the invention is illustrated by the following tests.

Test No. 1

A sample of the nylon sheeting prepared as in Example No. 1 was cut into one inch squares and the squares were inoculated by spreading 0.1 ml. of a 50% serum in saline suspension of *Staphylococcus aureus* No. 6538 over the surface of the squares. After an appropriate time interval, the squares were cultured by shaking in 100 ml. of Difco neutralizing buffer solution. Decimal dilutions of these solutions were plated upon Difco fluid thioglycolate medium containing 1.5% agar. The inoculum was a 24-hour nutrient broth culture of the test organism. The test squares were inoculated with 370,000 organisms. The results of the test are as follows:

Sampling time	Count per square			Percent reduction
	Test No. 1	Test No. 2	Average	
30 Min	280,000	260,000	270,000	27
60 Min	190,000	210,000	200,000	46
2 Hrs	15,000	18,000	17,000	95
4 Hrs	600	400	500	99.9

The results of the above test indicate that the sheet material of the invention reduced the organism count by 99.9% in a four hour period.

Test No. 2

This test was substantially similar to Test No. 1 except that each square was inoculated with 35,000,000 or-

ganisms instead of 370,000 organisms as in Test No. 1. The results of this test are as follows:

Sampling time	Count per square			Percent reduction
	Test No. 1	Test No. 2	Average	
30 Min	23,000,000	26,000,900	24,000,000	31
60 Min	13,000,000	14,000,000	13,500,000	61
2 Hrs	6,000,000	6,800,000	6,400,000	82
4 Hrs	1,700,000	800,000	1,200,000	97

This test indicates that the sheeting material of the invention was 97% effective in destroying the organism count in a four hour period, and it is to be noted that inoculated organism count of 35,000,000 was far greater than that which would be present in any hospital, dairy or other sanitary type location.

Test No. 3

In this test the nylon sheeting prepared as in Test No. 1 was hand washed in detergent and dried 40 times. After this extensive wash procedure the sheeting was cut into one inch square and inoculated as in the manner of Test No. 1 with 460,000,000 organisms. The antibacterial results are as follows:

Sampling time	Count per square			Percent reduction
	Test No. 1	Test No. 2	Average	
30 Min	360	420	390	15
60 Min	380	390	385	16
2 Hrs	300	320	310	33
4 Hrs	9.7	12	11	98

In this test 98% of the Staphylococcus aureus organisms were destroyed in a four hour period, even though the sheeting had been subjected to 40 washings prior to the testing.

Test No. 4

Sheeting prepared as in Example No. 2 was tested to determine the ability of the sheeting to inhibit the production of ammonia from urea. Each test sample was tested by the method of Latlief, Goldsmith, Friedl and Stuart, J. Pediatrics 30, 1951. The test oragnism was *Proteus mirabilis* No. 9921. The results of the tests were as follows:

Tube number	Contents, g. of fabric	Time of first Ammonia Production, hours
1	1.5	>24
2	1.5	>24
3	1.5	>24
4	1.9	>24

To be of practical value for the inhibition of ammonia from urine, a material must demonstrate a delay of at least 6 hours in the appearance of ammonia production. The samples tested far exceeded the requirements, for there was no evidence of ammonia production in a 24-hour period.

These tests illustrate the effectiveness of the sheeting material in controlling micro-organisms and reducing bacteria activity. As the germicidal materials are dispersed within the thermoplastic coating the germicidal properties will be retained for long periods of time and will not be impaired by repeated washings.

While the above description is directed to a sheeting material including a fabric backing, it is contemplated that the thermoplastic material can be fabricated into articles without the fabric backing. Also, the thermoplastic material can be natural rubber or a thermoplastic resin and can be in a foamed or non-foamed type.

Various modes of carrying out the invention are contemplated as being within the scope of the following claims particularly pointing out and distinctly claiming the subject matter which is regarded as the invention.

I claim:

1. A germicidally treated article, comprising a fabric sheet-like backing member, a layer of an elastomer bonded to a surface of the backing member, and finely divided particles of a germicide uniformly distributed throughout said elastomer, said germicide consisting essentially of 50% to 80% by weight of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and the balance being an alkyl dimethylbenzyl ammonium chloride with said alkyl group having from 8 to 18 carbon atoms, said germicide comprising from 5% to 25% by weight of the combined weight of the elastomer and said germicide.

2. A germicidally treated article, comprising a sheet of nylon fabric, a layer of polyvinyl chloride resin bonded to a surface of said fabric, and a germicide distributed throughout the layer of polyvinyl chloride resin, said germicide consisting essentially of 50% to 80% by weight of material selected from the group consisting of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and diisobutyl cresoxy ethoxy ethyl dimethylbenzyl ammonium chloride, and the balance being an alkyl dimethylbenzyl ammonium chloride with said alkyl group having from 8 to 18 carbon atoms, said germicide comprising from 5% to 25% by weight of the combined weight of the elastomer and said germicide.

3. A method of preparing a germicidally treated article, comprising the steps of preparing an uncured elastomer, mixing a substance selected from the group consisting of diisobutyl phenoxy ethoxy ethyl dimethyl ammonium halide and diisobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium halide, and an alkyl dimethyl-benzyl ammonium halide with said alkyl group having from 8 to 18 carbon atoms with a quantity of said elastomer in a weight ratio of 1.5:1 to 2.5:1 of said substance to said alkyl dimethylbenzyl ammonium halide to provide a first mixed batch, mixing a material selected from the group consisting of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium halide and diisobutyl cresoxy ethoxy ethyl dimethylbenzyl ammonium halide, and an alkyl dimethylbenzyl ammonium halide with said alkyl group having from 8 to 18 carbon atoms with a second quantity of said elastomer in a weight ratio of 3.5:1 to 4.5:1 of said material to said alkyl dimethylbenzyl ammonium halide to provide a second batch, mixing the first and second batches together to provide a combined mixture, applying the mixture to a surface of a backing member in a form of a thin film, and thereafter curing the elastomer to provide a composite article.

4. A method of preparing a germicidally treated article, comprising the steps of preparing an uncured elastomer, mixing with a quantity of said elastomer from 1.3% to 10.0% by weight of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and from 0.8% to 6.0% by weight of an alkyl dimethylbenzyl ammonium chloride with said alkyl group having from 8 to 18 carbon atoms to provide a first batch, mixing with a second quantity of said elastomer from 2.0% to 10.0% by weight of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride and from 0.4% to 4.0% by weight of an alkyl dimethylbenzyl ammonium chloride with said alkyl group having from 8 to 18 carbon atoms to provide a second batch, mixing the first and second batches together to provide a combined mixture, applying the mixture to a surface of a backing member in a form of a thin film, and heating the elastomer to cure the same and provide a composite article having effective and lasting germicidal activity.

5. A germicidally treated article, comprising an elastomer, and finely divided particles of a germicidal composition embedded within and uniformly distributed throughout said elastomer, said germicidal composition

consisting essentially of lauryl dimethylbenzyl ammonium halide and a material selected from the group consisting of diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium halide and diisobutyl cresoxy ethoxy ethyl dimethylbenzyl ammonium halide, said last named material comprising from 59% to 69% by weight of the composition the balance of the composition being said lauryl dimethylbenzyl ammonium halide.

6. A germicidally treated article, comprising an elastomer, and finely divided particles of a germicidal composition embedded within and uniformly distributed throughout said elastomer, said germicidal composition consisting essentially of the combination of an alkyl dimethylbenzyl ammonium halide with said alkyl group having from 8 to 18 carbon atoms and a material selected from the group consisting of diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium halide and diisobutyl

cresoxy ethoxy ethyl dimethylbenzyl ammonium halide, said last named material comprising from 50 to 80% by weight of the combination and the balance of the combination being said alkyl dimethylbenzyl ammonium halide.

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