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DURABLE GERMICIDAL FINISH FOR HYDROPHOBIC POLYAMIDE TEXTILE MATERIALS

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This invention relates to a durable anti-bacterial finish for synthetic hydrophobic polyamide textile materials, to a method of improving the durability of the antibacterial finish when applied to such textile materials, and to the materials thus treated.

In recent years, increased attention has been given to the development of textile finishes which have become known as purifying finishes. These finishes are antibacterial and as such are intended to reduce the number of microorganisms residing in the materials, whereby such materials may be used with less danger from harmful bacteria. These purifying finishes, when applied to articles of clothing worn close to the body, are also helpful in the prevention of development of odor.

Satisfactory purifying finishes should be durable preferably to both laundering and dry cleaning and active at low concentrations against a broad spectrum of microorganisms. It should be non-toxic and non-allergenic. It should not have the tendency to sensitize the wearer of the textile material to the material to be finished. It should not have the quality of allowing strains of bacteria to develop which are resistant to the antibacterial agent of the finish. Still further, it should be resistant to home and commercial laundering conditions and should impart only acceptable modifications of the hand to the textile materials.

At present there are many chemical compounds being used as antibacterial finishes for textile materials. In most instances the methods of applying these have become conventional. A majority of these finishes are known to those skilled in the art of textile finishing as "non-durable" and thus are readily removed from the treated materials by laundering or dry cleaning. Few, if any, are classified as durable finishes specifically on synthetic hydrophobic polyamide textile materials.

Thus, there is a great need for a good, durable antibacterial finish for textile materials of the hydrophobic type and in particular the hydrophobic polyamide type, such as nylon. Neomycin salts are known to be very effective antibacterial compounds and applications of these to textile materials from aqueous solutions of low concentrations have been effective in destroying bacteria and in eliminating odor caused by perspiration. However, on synthetic hydrophobic polyamide fibers such as nylon, while excellent zones of inhibition to *Staph. aureus*, have been obtained initially, these zones are reduced drastically by ordinary washing or laundering operations.

With regard to the use of neomycin salts as purifying finishes, such use is described in U.S. Patent No. 2,830,011, the subject matter of which is incorporated herein by reference.

Accordingly, it is an object of the present invention to provide a process for improving the durability of neomycin salts to synthetic hydrophobic polyamide textile materials and to provide such textile materials having an improved durable antibacterial finish.

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

According to the present invention, a method for providing a durable antibacterial finish on synthetic hydrophobic polyamide textile materials is contemplated, which method comprises treating such materials with neomycin and a polyacrylic acid and thereafter drying the material.

The term "neomycin" is used herein in its ordinary sense to denote the commercially available product which is called neomycin, it actually being a mixture of two very closely related antibiotics known more specifically as neomycin B and neomycin C. The term is also intended to cover neomycin as just defined, the individual components of the complex or its salts, of which the sulfate is most generally available. Other salts of neomycin have been used in finishing textiles of the type contemplated herein with good results. Among these may be mentioned neomycin-parahydroxy benzoate, neomycin sulfanilate, neomycin N-tartrate, neomycin propionate and the like.

By "a polyacrylic acid," as that term is employed herein, it is intended to include polyacrylic acid per se, polymethacrylic acid, polyethacrylic acid, and the like, polyacrylic acid per se being preferred. These polyacrylic acids should be characterized by a molecular weight of from about 2,500 up to about 250,000, although higher molecular weights up to the limit of water solubility are fully contemplated. Preferably the molecular weight is from about 2,500 up to 200,000, while ideally the molecular weight appears to be between about 5,000 and about 20,000. The molecular weight values referred to may be determined by the light scattering technique such as described in Flory's Principles of Polymer Chemistry, Cornell University Press (1953), at pages 283–303, inclusive. These polyacrylic acids have pH's of less than 4 and usually a value of between 1 and 3.

By "synthetic hydrophobic polyamide textile materials" it is meant formed fabrics, whether they be woven, knitted, felted or otherwise formed, containing at least about 30% of nylon and preferably at least 50% of nylon. The balance, if any, may be cellulosic, such as cotton, rayon, linen and the like. In addition, it may be comprised of polyester fibers, acrylic fibers, silk and wool fibers. It will be evident that the balance may be any of the above or other known fibers employed alone or in combination with one another.

By "nylon" it is meant any of the hydrophobic polyamides which are generally and conventionally referred to by this term and which normally are the result of a reaction between a diamine and a dibasic acid, although sometimes prepared by the polymerization of an omega-amino acid. Such nylons include nylons 66, 48, 200, 610, 6, 11 and the like.

The neomycin may be employed within the range of from between 0.001 to 1 inclusive and preferably is employed in amounts of from between about 0.01 to 0.05% based on the dry weight of the synthetic polyamide textile material.

The polyacrylic acids may be employed within the range of from between about 0.5 and 5%, though preferably are employed in amounts of from between 0.5 and 3%, again based on the dry weight of the synthetic hydrophobic polyamide textile material.

We have found it advantageous in some instances to employ a curing accelerator or a catalyst for the polyacrylic acid. Suitable catalysts are those metal salts which are strongly acidic and in particular the metal salts of zinc and aluminum. Illustrative of such accelerators are zinc chloride, zinc nitrate, aluminum chloride, aluminum nitrate and the like. Such accelerators are usually employed in amounts of from between about 3 and 10% and preferably in amounts of from between 5 and 7%, based on the weight of the polyacrylic acid. It should be noted again that the use of such catalysts is optional although their employment in some instances has resulted in improved durability of the antibacterial finish to which this invention is directed.

After application of the neomycin and the polyacrylic acid to the synthetic hydrophobic polyamide textile ma-

terial, the material is normally dried and the material heated to curing temperatures. Normally for drying of the material temperatures within the range of from between 200 and about 300 and preferably temperatures of from between about 215 to about 230° F. are employed. Curing of the finished polyamide textile materials is normally effected within the range of between 225 to 375° F. though preferably within the range of 275 to 325° F.

In the application of the neomycin and the polyacrylic acid, it is preferred that the polyacrylic acid be applied first to the textile material, drying and curing the material and thereafter applying the neomycin solution. Normally thereafter the material is dried. The subsequent heat treatment may include the employment of temperatures within the curing range set forth hereinabove. Alternatively, the neomycin and the polyacrylic acid may be applied simultaneously from a single treating bath or solution. The application of the neomycin first followed by the application of the polyacrylic acid is less desirable than either the above alternatives in view of the fact that the durability of the finish, which is believed to be based on the ability of the polyacrylic acid to associate itself with the textile material fibers, must then be effected through a layer or coating of neomycin. While such procedures do to some extent improve the durability of the finish, it is decidedly less desirable than the preferred alternatives set forth hereinabove.

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

In the examples hereinafter, references will be made to various procedures, methods and tests. In order to facilitate a more thorough understanding of these examples, the following glossary is set forth.

PREPARATION OF TREATING MATERIALS

(1) *One Bath Method*

The polyacrylic acid used is diluted in approximately one half of the required water at room temperature. To this is added the required amount of dilute neomycin sulfate plus additional water to the required total weight. In instances where an accelerator is used, it is entered into the dilution prior to the final addition of water.

Where neomycin is used alone it is diluted with room temperature water to the proper concentration and total weight.

(2) *Two Bath Method*

(*a*) The polyacrylic acid used is diluted in room temperature water to the required concentration and total weight.

(*b*) The neomycin sulfate is diluted with room temperature water to the required concentration and total weight.

The polyacrylic acid (*a*) is applied to the textile material and the treated material is dried for 1 minute at 225° F. and cured. The material is then subjected to the neomycin sulfate treatment (*b*) followed by either drying or curing at desired temperatures.

METHOD OF APPLICATION

The experiments described in this application were performed by applying the treating compositions to the textile materials by means of a conventional three roll padder.

DRYING OR CURING METHODS

Drying or curing the treated materials was accomplished on a pin tenter frame passing through a heating chamber at the desired temperature.

WASHING METHOD

Washing of the treated textile materials was accomplished using an automatic washer set for 140° F. and employing neutral soap as the detergent.

AGAR DIFFUSION TEST METHOD

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

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

"C"—Completely clear area underneath disc.
"P"—At least 75% clear area underneath disc.
"S–VS"—Less than 75% clear area underneath disc.
"N"—None.

Example 1

Applications of 1.0% or 5.0% solids (owf.) polyacrylic acid (5,000–10,000 mol. wt.) plus 6% solids zinc chloride (based on acrylic acid) were made from aqueous solutions on nylon taffeta by normal padding methods.

The swatches were dried for 1 minute at 225° F. followed by curing at 300° F. for 9 minutes. The thus treated fabrics were then padded with aqueous solutions of neomycin sulfate whereby 0.05% solids neomycin sulfate was deposited on the textile materials, followed by drying at 225° F. for 1 minute. A control swatch of nylon treated with 0.05% solids neomycin sulfate alone was also processed. Antibacterial tests were performed by the aforementioned test method. Test results are shown in Table I.

The antibacterial activity after washing is much improved by the use of polyacrylic acid as a pretreatment for neomycin sulfate in comparison to neomycin sulfate treatment alone.

TABLE I.—BACTERICIDAL ACTIVITY—ZONES OF INHIBITION TO *Staph. aureus* (DIA. MM.)

Treatments, Percent Solids (owf.)	Initially	1 Wash [1]	3 Washes [1]	9 Washes [1]
None	N	N-C	VS	VS
0.05% Neomycin Sulfate	22.2		C	P-C
1.0% Polyacrylic acid topped with 0.05% Neomycin Sulfate	23.1	21.7	16.9	13.9
5.0% Polyacrylic acid topped with 0.05% Neomycin Sulfate	20.0	20.1	16.4	16.0

[1] Automatic washer at 140° F. using neutral soap.

Example 2

Applications of 0.3, 0.6, 0.9 or 1.2% solids (owf.) polyacrylic acid (mol. wt. 5,000–10,000) plus 6.0% zinc chloride (based on acrylic acid solids) were made on filament nylon taffeta by padding followed by drying at 225° F. for 1 minute and a subsequent cure at 310° for 9 minutes. The treated swatches were aftertreated with neomycin sulfate solutions depositing 0.045% solids (owf.) on the fabric followed by drying at 225° F. for 1 minute. A control swatch of nylon material treated

with 0.045% solids (owf.) neomycin sulfate only and dried at 225° F. for 1 minute was also run. Antibacterial tests are shown in Table II.

In Table II it is seen that better durability of the zones of inhibition can be obtained after washing by the polyacrylic acid plus neomycin sulfate treatments than can be obtained by neomycin sulfate treatments alone.

TABLE II.—BACTERICIDAL ACTIVITY—ZONES OF INHIBITION TO *Staph. aureus* (DIA. MM.)

Treatment, Percent Solids (owf.)	Initially	After 1 Wash [1]	After 4 Washes [1]	After 9 Washes [1]
None	N	N-C	VS	S
0.045% Neomycin Sulfate	21.6	14.4	12.0	<12.0
0.3% Polyacrylic acid [2] topped with 0.045% Neomycin Sulfate	21.2	20.7	17.7	15.7
0.6% Polyacrylic acid [2] topped with 0.045% Neomycin Sulfate	21.0	21.1	17.9	15.3
0.9% Polyacrylic acid [2] topped with 0.045% Neomycin Sulfate	20.7	20.7	18.8	17.0
1.2% Polyacrylic acid [2] topped with 0.045% Neomycin Sulfate	21.4	21.2	20.0	17.4

[1] Automatic washes at 140° F. using neutral soap.
[2] 6% zinc chloride used based on acrylic acid solids.

Example 3

Applications were made to filament nylon taffeta in which 0.6, 0.9 or 1.2% solids polyacrylic acid (mol. wt. 5,000–10,000) plus 6.0% solids zinc chloride based on weight of polyacrylic acid and 0.045% neomycin sulfate were applied as a one bath combination followed by drying at 225° F. for 1 minute, then curing at 310° F. for 9 minutes.

The results in Table III show better zones of inhibition throughout the washing cycles are obtained by the polyacrylic acid neomycin sulfate treatments than by the neomycin sulfate treatment alone.

TABLE III.—BACTERICIDAL ACTIVITY—ZONES OF INHIBITION TO *Staph. aureus* (DIA. MM.)

Treatments, Percent Solids (owf.)	Initially	1 Wash [1]	4 Washes [1]	9 Washes [1]
None	N	N-C	VS	S
0.045% Neomycin Sulfate	21.6	14.4	12.0	<12.0
0.045% Neomycon Sulfate plus 1.2% Polyacrylic acid	15.1	13.4	13.7	13.6
0.045% Neomycin Sulfate plus 0.9% Polyacrylic acid	16.6	15.2	16.2	15.0
0.045% Neomycin Sulfate plus 0.6% Polyacrylic acid	16.9	17.3	16.3	13.1

[1] Automatic washes at 140° F. using neutral soap.
6% zinc chloride used with polyacrylic acid based on acid wt.

Example 4

Applications of 0.05% solids (owf.) neomycin sulfate alone, in combination with 0.75% solids (owf.) polyacrylic acid (mol. wt. 5,000–10,000) or 0.75% solids (owf.) polyacrylic acid (mol. wt. 5,000–10,000) plus zinc chloride as catalyst were made on filament nylon taffeta. All of the treated fabrics were dried for 1 minute at 225° F. Portions of the materials treated with the combined compounds were subjected to further heating at 290° F. for 6 minutes. Test results after wash cycles are shown in Table IV.

The results show that the use of polyacrylic acid with neomycin sulfate improves the zones of inhibition against *Staph. aureus* over those imparted by neomycin sulfate alone, after cycles of washings. The results also show

that it is not essential to use a catalyst with the polyacrylic acid nor is it necessary to cure the finishes after drying.

TABLE IV.—BACTERICIDAL ACTIVITY OF ZONES OF INHIBITION TO *Staph. aureus* (DIA. MM.)

Treatments on Fabrics, Percent Solids (owf.)	Cure Conditions		Initially	3 Washes
	Time (min.)	Temp. (° F.)		
0.05% Neomycin Sulfate		None	22.1	12.0
0.05% Neomycin Sulfate plus 0.75% Polyacrylic acid.	6	None	19.8	14.3
		290	19.1	15.0
0.05% Neomycin Sulfate plus 0.75% Polyacrylic acid and catalyst. [1]	6	None	20.1	15.7
		290	19.2	15.4
None			N	V-S

[1] 6.0% zinc chloride on solids of acrylic acid—all treatments dried 1 min. at 225° F.

Example 5

Applications of neomycin sulfate at 0.05% solids (owf.) alone or in combination with 0.75% or 1.5% solids (owf.) of four different molecular weight polyacrylic acids from 5,000 to 100,000 were made on filament nylon taffeta by padding, followed by drying at 225° F. for 1 minute. A portion of each treated nylon sample was cured at 300° F. for 6 minutes.

The results of these tests show better initial zones of inhibition were obtained with the neomycin treatments alone. However, those wherein polyacrylic acid is used show greater durability to washing. No appreciable differences were observed in the treatments using different molecular weight polyacrylic acids. Slight reduction in zones were observed on the cured samples when compared with their respective dried counterparts.

It will be noted in Tables I through IV hereinabove that in some instances bactericidal activity seems to be imparted to textile materials which have not been treated or finished with either neomycin or neomycin and polyacrylic acid. This is believed to be the result of the non-treated samples being laundered with the treated samples and to the migration from the treated to the untreated samples of neomycin in the wash cycle. It will be noticed that in all instances such activity appears to be slight.

While the above invention has been described essentially in connection with neomycin and polyacrylic acids, the finished materials may be further treated or finished with other textile agents or auxiliaries to achieve particular effects. Thus, known textile finishing resins may be applied as well as softeners, lubricants and the like.

We claim:

1. A method for providing a durable antibacterial finish on a synthetic hydrophobic polyamide textile material which comprises treating the material with neomycin and a polyacrylic acid and thereafter drying the treated material.

2. A method according to claim 1 in which the textile material is nylon.

3. A method according to claim 1 in which the polyacrylic acid has a molecular weight of about 5,000 to 20,000.

4. A method for providing a durable antibacterial finish on a synthetic hydrophobic polyamide textile material which comprises applying to said material neomycin and a water soluble polyacrylic acid so as to apply from between about .001 to about 1% of neomycin and from between about .5 and about 5% of polyacrylic acid and thereafter drying the treated material.

5. A method for providing a durable antibacterial finish on a synthetic hydrophobic polyamide textile material which comprises applying to said material between about .01 and .05% of neomycin and from between about .5 and about 2% of polyacrylic acid based on the dry weight of the textile material, and from about 5 to about 7% of a

strongly acidic catalyst based on the weight of acrylic acid and thereafter subjecting the material to elevated temperatures to cure the finish on the material.

6. A process according to claim 5 in which the neomycin and polyacrylic acid are applied simultaneously from the same solution.

7. A process according to claim 5 in which the polyacrylic acid is applied first and the material dried, and then the neomycin applied.

8. A synthetic hydrophobic polyamide textile material characterized by an antibacterial finish durable to laundering comprising the reaction product of a neomycin salt and polyacrylic acid.

9. A synthetic hydrophobic polyamide textile material characterized by an antibacterial finish durable to laundering comprising the reaction product of from between .001% to about 1% of neomycin and from between about .5 and about 5% of polyacrylic acid.

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