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## NYLON ARTICLE RENDERED SELF-STERILIZING BY TREATMENT WITH AN ARYL MERCURIC COMPOUND AND METHOD OF MAKING IT

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This invention relates to nylon and articles produced therefrom which are self-sterilizing or bacteriostatic throughout their normal useful life and to a method for rendering nylon substantially permanently bacteriostatic.

Because of the lasting self-sterilizing property or bacteriostatic power of nylon treated in accordance with the present invention the invention makes the use of nylon desirable in the production of many articles which, prior to the present invention, had been produced from other materials. For example, nylon fibres or threads may be treated in accordance with the present invention and fabrics formed for use in the preparation of surgical bandages, gauzes, etc. or the fabrics may be produced from nylon fibres or threads and the fabric treated in accordance with the invention. The invention also makes desirable the use of nylon in the production of various other articles, such as teething rings, tongue depressors, combs, hair brush backs, tooth brush handles, etc. Furthermore, the invention makes possible the production of nylon bristles for hair brushes and tooth brushes, nylon filaments, fibres or threads for use in dental floss all of which are bacteriostatic throughout their useful life.

We have made the very surprising discovery that solid nylon when impregnated with an aryl mercuric compound in the presence of nitric acid may be rendered bacteriostatic and remain bacteriostatic throughout the useful life of the nylon.

The term "nylon" is used herein to mean a superpolyamide of the type produced from dibasic acids and diamines, or $\alpha,\omega$— aminoacids or caprolactam or substituted derivatives of such materials or their modifications.

In the practice of the invention, the solid nylon may be impregnated with a dilute solution of nitric acid and thereafter impregnated with a solution of an aryl mercuric compound. Preferably, the nylon is impregnated with a dilute solution of nitric acid to which the aryl mercuric compound, such as phenyl mercuric acetate, phenyl mercuric nitrate, etc. has been added. The concentration of the nitric acid solution should not exceed about 25 percent. Good results have been obtained using a solution containing a concentration of nitric acid as small as about 5 percent. After the nylon has been impregnated with the solution of an aryl mercuric compound, it may be treated, if desired, with a dilute solution of a hydrogen halide or a halide salt, such as hydrochloric acid, sodium iodide, etc., to convert the aryl mercuric compound to an aryl mercuric compound which is less soluble in water. This after-treatment, however, is not essential to the production of self-sterilizing nylon possessing an effective basteriostatic power after long use.

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As illustrative of other aryl mercuric compounds which may be used are phenyl mercuric benzoate, borate, gluconate, hydroxide, phthalate, salicylate, etc., aminophenyl mercuric acetate, dimethyl amino phenyl mercuric acetate, α-naphthyl mercuric acetate, tolyl mercuric acetate, tolyl mercuric nitrate, etc.

The bacteriostatic effectiveness of the treated nylon can be determined by comparison with ammoniated mercury ointment. Ammoniated mercury ointment, which is known to be an effective antiseptic ointment, when tested by the serum-agar plate method of George F. Reddish described in the Journal of Laboratory and Clinical Medicine, Vol. XIV, No. 7 beginning on page 649, shows a clear zone of 0.5 cm. The capacity of the treated nylon to retain its bacteriostatic power is best illustrated by testing the bristles of a brush after the equivalent of several years normal use. Such bristles have produced a clear zone as great as about 0.9 cm. when tested by the method above mentioned.

In testing treated nylon by this method, staphylococcus aureus is employed as the microorganism since this is the most resistant of the pyrogenic organisms. The germicidal efficiency is indicated by the size of the clear zone around the specimen which is in marked contrast to the turbidity of the surrounding medium caused by the heavy growth of the organism. The clear zone is the zone of sterilization in which the growth of staphylococcus aureus is inhibited.

In order to determine the germicidal efficiency of the brush bristles after any desired period of use, a brush is subjected to scrubbing conditions similar to those of actual use of a toothbrush for a predetermined period, because under such conditions, the bristles are subjected to great potential leaching and wear. After being subjected to such scrubbing conditions, several representative bristles are selected from the brush and tested by the serum-agar plate method previously referred to. The average measurement of the clear zones is taken as representative of the bacteriostatic power of the bristles of the brush. Thus, a brush having bristles treated in accordance with the invention is subjected to scrubbing by moving it in a substantially circular path of about four inches in diameter at the rate of about 60 R. P. M., over a corrugated glass plate in the presence of toothpowder and water for a period of 5 minutes. The brush and glass plate

then are washed to remove the toothpowder. This cycle of operations is repeated a desired number of times. Assuming that the average person uses a toothbrush about one minute each day, 70 to 75 of the above described scrubbing cycles is equivalent to about 1 year of normal use of a toothbrush. Brushes treated in accordance with the present invention when subjected to 500 scrubbing cycles of 5 minutes each as above described and then tested to determine the germicidal efficiency of the bristles have shown an average uniform clear zone of about 0.9 cm.

The practice of the invention is illustrated further by the following specific examples:

*Example I*

Eleven toothbrushes having nylon bristles were immersed for 10 minutes in the following solution:

| | | |
|---|---|---|
| Nitric acid (conc.) | c. c. | 34.2 |
| Water | c. c. | 65.8 |
| Phenyl mercuric acetate | grams | 3.6 |

The above solution contains about 25 percent nitric acid and was filtered before using. After immersion in the above solution, the brushes were dried at room temperature for 30 minutes and then immersed for 20 minutes in a 5 percent water solution of hydrochloric acid. The brushes then were rinsed in distilled water and dried in an oven at 60° C. for 1 hour. One of the thus treated brushes was saved as a control sample and the remaining ten brushes each were subjected to scrubbing for a different number of scrubbing cycles of 5 minutes each as previously described. Several representative bristles then were selected from each of the brushes including the control sample and tested as previously described to determine their average germicidal efficiency. The results of the tests are indicated in the following table:

| Brush No. | No. of Scrubbing Cycles | Bacteriostatic Zone in cm. |
|---|---|---|
| | | *Min.* *Max.* |
| 1 | [1] none | 1.4 to 1.5 |
| 2 | 50 | 1.2 to 1.3 |
| 3 | 60 | 1.2 |
| 4 | 70 | 0.9 to 1.0 |
| 5 | 80 | 0.7 to 0.8 |
| 6 | 100 | 0.7 to 0.8 |
| 7 | 150 | 0.8 to 0.9 |
| 8 | 200 | 0.8 to 0.9 |
| 9 | 300 | 0.7 to 0.8 |
| 10 | 400 | 0.9 to 1.0 |
| 11 | 500 | 0.9 |

[1] Control sample.

It will be noted that after 500 scrubbing cycles, which is equivalent to approximately 7 years average normal use, the bristles possess a bacteriostatic power substantially greater than ammoniated mercury ointment which is known to be an effective antiseptic ointment. The bristles after 500 scrubbing cycles were worn down to approximately one-half their original length.

*Example II*

Four toothbrushes having nylon bristles were immersed for 20 minutes in a 10 percent solution of nitric acid in water and then dried at room temperature for 30 minutes. The brushes then were immersed for 30 minutes in a solution prepared as follows:

| | | |
|---|---|---|
| Formic acid | c. c. | 18 |
| Phenyl mercuric acetate | grams | 3.6 |



To each 5 c. c. of this solution, 20 c. c. of ethyl alcohol and 25 c. c. of distilled water was added. The solution was filtered before use. After immersion in this solution for 30 minutes, the brushes were rinsed in distilled water and dried in an oven at 60° C. for 1 hour. One of the thus treated brushes was saved as a control sample and the remaining three were scrubbed for 200, 300 and 400 cycles of 5 minutes each as previously described. Several representative bristles then were selected from each of the brushes including the control sample and tested as previously described to determine their average germicidal efficiency. The results of the tests are indicated in the following table:

| Brush No. | No. of Scrubbing Cycles | Bacteriostatic Zone in cm. |
|---|---|---|
| | | *Min.* *Max.* |
| 1 | [1] none | 0.9 |
| 2 | 200 | 0.4 to 0.5 |
| 3 | 300 | 0.4 |
| 4 | 400 | 0.4 |

[1] Control sample.

It will be noted that while the bacteriostatic power of brushes treated as described in this example is not as great as that of brushes prepared as described in Example I, nevertheless, it compares favorably with that of the ammoniated mercury ointment previously referred to, which is known to be an effective antiseptic ointment.

*Example III*

Ten toothbrushes having nylon bristles, were immersed for 10 minutes at room temperature in a solution of 3.6 grams of phenyl mercuric acetate in 100 ml. of water containing 25 percent of nitric acid. The brushes were removed from the solution and dried at room temperature for 30 minutes. The brushes then were rinsed with distilled water and dried in an oven at 60° C. for one hour. One of the treated brushes was saved as a control sample and the remaining nine brushes each were subjected to scrubbing for a different number of scrubbing cycles of 5 minutes each as previously described. Several representative bristles then were selected from each of the brushes including the control sample and tested as previously described to determine their average germicidal efficiency. The results of the tests are indicated in the following table:

| Brush No. | No. of Scrubbing Cycles | Bacteriostatic Zone in cm. |
|---|---|---|
| | | *Min.* *Max.* |
| 1 | [1] none | 0.8 to 1.1 |
| 2 | 5 | 0.8 to 1.0 |
| 3 | 10 | 0.7 to 0.8 |
| 4 | 20 | 1.0 |
| 5 | 25 | 0.7 to 0.8 |
| 6 | 50 | 0.7 to 0.8 |
| 7 | 75 | 0.5 |
| 8 | 100 | 0.5 |
| 9 | 125 | 0.5 to 0.7 |
| 10 | 150 | 0.5 to 0.7 |

[1] Control sample.

*Example IV*

A brush having nylon bristles was immersed for 20 minutes in a 10 percent solution of nitric acid in water, and was then rinsed in distilled water and dried in an oven at 60° C. for 1 hour. A second brush having nylon bristles was immersed for 20 minutes in a 10 percent solution of nitric

acid in water and dried for 30 minutes at room temperature. The second brush then was immersed for 30 minutes in the following solution:

| | C. c. |
|---|---|
| Formic acid | 5 |
| Water | 25 |
| Ethyl alcohol | 20 |

The second brush then was rinsed in distilled water and dried in an oven for 1 hour. Several representative bristles were selected from each brush and then tested by the serum-agar plate method and none showed any bacteriostatic zone. This example indicates that while nitric acid, formic acid, and ethyl alcohol have some antiseptic properties they do not themselves contribute to the bacteriostatic power of the brushes produced as described in Examples I, II or III.

*Example V*

13 toothbrushes were immersed in a 15% solution of hydrochloric acid in water for 5 minutes, and then allowed to dry partially at room temperature for 30 minutes. The brushes then were immersed for 10 minutes in a solution prepared as follows:

| | | |
|---|---|---|
| Formic acid | c.c. | 18 |
| Phenyl mercuric acetate | grams | 3.6 |

To each 5 c.c. of this solution, 20 c.c. of ethyl alcohol and 25 c.c. of distilled water was added. The solution was filtered before use. After immersion in this solution the brushes were rinsed in distilled water and then dried in an oven at 60° C. for 1 hour. One of the thus treated brushes was saved as a control sample and the remaining 12 were subjected to scrubbing for a different number of scrubbing cycles of 5 minutes each as previously described. Several representative bristles then were selected from each of the brushes including the control sample, and tested as previously described to determine their average germicidal efficiency. The results of the tests are indicated in the following table:

| Brush No. | No. of Scrubbing Cycles | Bacteriostatic Zone in cm. |
|---|---|---|
| | | *Min.* *Max.* |
| 1 | [1] None | 0.2 to 0.4 |
| 2 | 1 | 0.2 to 0.3 |
| 3 | 2 | 0.2 |
| 4 | 3 | 0.2 to 0.3 |
| 5 | 4 | 0.2 to 0.3 |
| 6 | 5 | 0.2 to 0.3 |
| 7 | 10 | [2] 0.2 |
| 8 | 15 | [2] 0.0 to 0.2 |
| 9 | 20 | [2] 0.0 to 0.2 |
| 10 | 25 | [3] 0.0 to 0.2 |
| 11 | 30 | [3] 0.0 to 0.2 |
| 12 | 35 | 0.0 |
| 13 | 40 | 0.0 |

[1] Control sample.
[2] Partial.
[3] Slight.

This example illustrates that the antiseptic cannot be satisfactorily impregnated in the presence of either hydrochloric or formic acid. In the above table the terms "partial" and "slight" indicate that there were bacterial colonies within the zone and that the bacteriostatic action was not complete and definite. It will be noted that in this example such a condition existed after ten scrubbing cycles and that after thirty-five scrubbing cycles the brush bristles had no bacteriostatic power.



In each of the foregoing examples the composition of the bristles of the brushes used was the reaction product of hexamethylene diamine and sebacic acid. Comparable results were obtained with the reaction product of hexamethylene diamine with adipic acid. Similar results were obtained with each of these types of nylon modified with aminocaprylic acid or with caprolactam.

It will be understood that the treatment of nylon as described herein is applicable to solid nylon regardless of its shape, size or the method used for shaping the nylon to the shape of the article desired. Thus, the invention is applicable for treating solid nylon before or after it has been shaped by molding, extrusion, casting, etc. to form the article desired. For example, the nylon may be treated after being molded to form a comb, a brush bristle block such as a hair brush back or tooth brush handle, or extruded to form monofilaments either of the multifilament size such as are used in the preparation of fabrics, or the larger monfilament size such as are used in the preparation of bristles, rattans, etc.

This application is a continuation-in-part of our copending application Serial No. 664,440, filed April 23, 1946, now abandoned.

We claim:

1. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a solution of an aryl mercuric salt in the presence of nitric acid.

2. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a dilute solution of nitric acid, and thereafter treating the nylon with a solution of an aryl mercuric salt.

3. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a dilute solution of nitric acid to which an aryl mercuric salt has been added.

4. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a solution of a phenyl mercuric salt in the presence of nitric acid.

5. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a solution of phenyl mercuric acetate in the presence of nitric acid.

6. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a solution of nitric acid to which phenyl mercuric acetate has been added.

7. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a solution of phenyl mercuric acetate in the presence of nitric acid, and treating the nylon with a solution of a hydrogen halide.

8. The method of making nylon self-sterilizing, which comprises treating nylon in solid form with a solution of nitric acid to which phenyl mercuric acetate has been added, and treating the nylon with a solution of a hydrogen halide.

9. The product produced by the method of claim 1.

10. The method of making nylon bristles of a brush self-sterilizing which comprises treating the bristles of the brush with a solution of an aryl mercuric salt in the presence of nitric acid.

11. A brush produced by the method of claim 10.

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