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# IMPARTING ANTI-MICROBIAL PROPERTIES TO FORMED ARTICLES

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This invention relates to processes for imparting antimicrobial properties to formed articles of synthetic linear condensation polymers, and more particularly to treating the surface of such formed articles with a water soluble aryl mercury compound in the presence of dilute aqueous phenol, and drying. The treatment is continued until the resulting article shows a zone of inhibition of at least 5 mm. under standard test conditions.

The art is familiar with various formed articles made from synthetic polymeric materials, including such materials as nylon and the like. The art is also familiar with processes for treating nylon bristles and the like with phenyl mercuric acetate in the presence of aqueous nitric acid. Generally, the latter process is disadvantageous from the operational or economical viewpoint, inasmuch as the corrosive nature of the materials used requires rather costly corrosion-resistant material. The art is confronted by the problem of providing a process for imparting antimicrobial properties to formed articles of nylon and the like materials in an economic and effective manner.

The discoveries associated with the invention and relating to the solution of the above problem, and the objects achieved in accordance with the invention as set forth herein include: the provision of a process for imparting antimicrobial properties to formed synthetic linear condensation polymer articles by treating the same with an aqueous solution of an aryl mercury compound and a phenol at a temperature in the range of about 0 to 100° C. and a time in the range of about 5 to 300 minutes, until the resulting product (after drying) shows a zone of inhibition under standard test conditions of at least 5 mm., the solution containing per 100 parts by weight of water about 0.5 to 10 parts of the phenol and 0.001 up to about 0.5 part of the mercury compound; the provision of such a process wherein the article is made of a polyamide and a saturated solution of phenyl mercuric acetate is used; the provision of such a process wherein nylon toothbrush bristle stock is treated and the solution contains about 2 parts of phenol; and other objects which will be apparent as details or embodiments of the invention as set forth hereinafter.

In order to facilitate a clear understanding of the invention, the following preferred specific embodiments are described in detail.

*Example 1*

Into a suitable reaction vessel having an inner surface of stainless steel, glass, polyethylene, or the like, there are mixed:

2 parts by weight of phenol
100 parts of water
0.2 parts of phenyl mercuric acetate

and into the resulting mixture (the pH of which is 4.3), there is placed a hank of nylon (of toothbrush bristle stock of 0.008 inch, or 0.010 inch, or 0.013 inch in diameter), about 46 inches long weighing about 2.5 pounds, clamped at one end with a metal hose clamp, and it is maintained in the solution at 25° C. for about 15 minutes; removed and hung up by the clamp and allowed to drain for 15 minutes; immersed in tap water at 25° C. for 15 minutes, removed and allowed to air dry for about 48 hours. Alternatively, it may be force dried by means of warm air in a shorter period, such as two hours.



The resulting treated nylon is cut into segments of the appropriate length and fed into a standard bristling machine for manufacturing toothbrushes. In the usual brush manufacturing procedure, the bristle stock is cut, and a tuft thereof is bent double and the bent end is inserted into an appropriate hole in the brush handle, together with a wire staple or the like means for holding the tuft therein. The resulting inserted tufts may be trimmed to give a brush of desired shape. If desired, the bristle or bristle stock may be treated with a conventional lubricant, antistatic agent or the like; e.g., sorbitol monolaurate antistatic agent.

The resulting toothbrushes are subjected to the following standard test for antimicrobial activity (a modified version of the test set forth in the United States Food and Drug Administration Methods of Testing Antiseptics and Disinfectants outlined in the United States Department of Agriculture Circular No. 198, dated December 1931). A flask of melted cooled nutrient agar is seeded with a 1 percent inoculum of a twenty-four hour broth culture of the appropriate test organism and then poured into standard petri dishes. While the agar is still fluid, the articles to be tested, such as a toothbrush head, is embedded therein and the agar allowed to harden (the toothbrush head is set in lying on its side). The test materials are then incubated at 37° C. for 48 hours and then examined visually for zones of growth inhibition; i. e., distance between the end or side of the bristle and the nearest uninhibited growth area.

A series of brushes prepared in accordance with this example were subjected to accelerated use tests analogous to actual use of a toothbrush by setting the brush onto a plate having a knobbed surface (the plate being about 4.5 inches in diameter and the knobs being provided by hemispherical slotted screw heads of about 0.3 inch diameter in close packed relationship in circular patterns), together with about 1 cc. of tap water and a ribbon of conventional toothpaste (2.5 inches in length and about 0.25 inch in diameter) and the brush and plate moved relative to each other in a circular path of about 1.5 inch radius for about 12 cycles per minute; this treatment was continued for 100 minutes with interruptions to replenish the toothpaste as needed to maintain an ample supply thereof between the bristles and the plate.

The data in the following table are typical of results obtained with several samples of brushes prepared in accordance with this example.

| Material Tested | Zone of Inhibition | |
|---|---|---|
| | *Micrococcus pyogenes* var. *aureus* 209, mm. | *Escherichia coli*, mm. |
| Control (untreated) | 0.0 | 0.0 |
| New Brush: | | |
| Sample A | 31.0 | ---- |
| Sample B | 27.3 | ---- |
| Sample C | 33.0 | ---- |
| Sample D | 36.0 | ---- |
| Sample E | ---- | 7.3 |
| Sample F | ---- | 8.0 |
| Sample G | ---- | 7.6 |
| Sample H | ---- | 7.6 |
| Used Brush—100 minutes: | | |
| Sample I | 18.6 | ---- |
| Sample J | 22.6 | ---- |
| Sample K | 33.0 | ---- |
| Sample L | 25.0 | ---- |
| Sample M | ---- | 4.3 |
| Sample N | ---- | 6.0 |
| Sample O | ---- | 6.0 |
| Sample P | ---- | 6.0 |

A zone of inhibition of at least 5 mm. is desirable, and the materials of this example clearly meet this requirement even for the *Escherichia coli* organism which is regarded as much more resistant than that of the above-mentioned bulletin. Compared to commercially available mercury containing toothbrushes, the materials of this example are about twice as good; i.e., show similar efficiency for about one-half as much extractable mercuric content. This can be regarded as an indication of synergistic action between phenol and phenyl mercuric acetate. In this connection, leaving phenyl mercuric acetate out of the treating solution gives a product which is substantially no better than the untreated control, and this is also true if the phenol is left out of the treating solution.

A most remarkable feature of the products of the invention is their retention of the antimicrobial activity even after the very severe use or scrubbing, as described above. Compared to the heretofore proposed nitric acid treatment method, the process of the invention is much more easily carried out, avoids the undesirable personal hazards of nitric acid and avoids the need of special apparatus to offset such hazards.

*Example 2*

Conventional combs made of nylon are treated in accordance with the procedure of Example 1 and comparable results are obtained.

*Example 3*

Completed toothbrushes are treated in accordance with the procedure of Example 1 and similar results are obtained as to the nylon bristles (but not as to the cellulose acetate or the like handles).

*Example 4*

Similar results to Example 3 are obtained using phenyl mercuric chloride instead of the acetate.

Comparable results to the foregoing may be achieved with various modifications thereof including the following. The phenol concentration may be in the range of 0.5 to 10 parts per 100 parts of water (the pH of this mixture being in the range of 5.7 to 4.0), desirably 0.5 to 4.0 and preferably 2.0 parts. Phenol itself is particularly effective from the viewpoint of imparting the desired properties, and avoiding deleterious discoloration or softening of the nylon or the like materials. However, where all the advantages thereof are not necessarily required, substituted phenols such as those containing a chloro, methyl, or the like groups may be used.

The temperature may be in the range of about 0 to 100° C., preferably about 20 to 40° C. The time may be in the range of about 5 to 300 minutes, preferably up to about 15 minutes. The preferred water soluble aryl mercuric compound is phenyl mercuric acetate, and



the concentration thereof may be in the range of about 0.001 part up to about 0.5 part (saturation point) per 100 parts of water. Other desirable materials are phenyl mercuric chloride, or nitrate, or the like.

The formed articles treated may be bristles or bristle stock, finished articles such as molded combs and the like, personal brushes, textile fibers or textile material, or formed textile articles or garments and the like. The treatment is particularly effective for nylon or the like synthetic linear polyamide articles having fiber forming properties, i.e., an intrinsic viscosity above about 0.4. Such materials are known and, in general, are prepared from appropriate organic diamines and dicarboxylic acids, or amino carboxylic acids or their derivatives; e.g., from polyhexamethylene adipamide, caprolactam, and the like. Where all the advantages thereof are not necessary, articles of other condensation polymers may be treated in accordance with the invention.

In view of the foregoing disclosure, variations or modifications thereof will be apparent, and it is intended to include within the invention all such variations and modifications except as do not come within the scope of the appended claims.

I claim:

1. A process of imparting antimicrobial properties to a formed synthetic linear condensation polymer article which comprises treating said article with an aqueous solution of a water soluble aryl mercury compound and a material selected from the group consisting of phenol, chlorphenol and methylphenol, at a temperature in the range of 0 to 100° C., a pH in the range of about 5.7 to about 4.0 and a time in the range of about 5 to 300 minutes until the resulting treated article gives a minimum zone of inhibition of 5 mm. under standard test conditions with an organism of the group consisting of *Micrococcus pyogenes* var. *aureus* 209 and *Escherichia coli*, said solution containing 100 parts by weight of water, 0.5 to 10 parts of the phenol and 0.001 part up to saturation of the aryl mercury compound.

2. A process of claim 1 wherein the polymer is a polyamide, the aryl mercury compound is phenyl mercuric acetate and a saturated solution thereof is used.

3. A process of claim 2 wherein nylon bristle stock is treated and the solution contains about two parts of phenol.

4. A process of claim 2 wherein a nylon comb is treated and the solution contains about two parts of phenol.

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