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POLYAMIDE FIBERS HAVING MICROBIOCIDAL ACTIVITY

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This invention relates to nylon fibers having microbicidal activity and to fabrics prepared therefrom. This invention relates also to a novel composition of matter for use in preparing the fibers of this invention.

Attempts have been made in the past to produce members from nylon or polyamide resins which would retard effectively the growth of various microorganisms. These attempts have been directed primarily to the preparation of fibers of polyamide resins which have the property of retarding effectively the growth of various microorganisms. These attempts have not been entirely satisfactory.

One particular method that has been employed in the art in an attempt to produce polyamide or nylon fibers having the property of effectively retarding the growth of various microorganisms has been to treat separately fibers prepared from polyamide resins by applying to the surface thereof a resinous material containing a microbicide. Such treatments have proved to be relatively ineffective owing to the fact that the applied resinous coating tends to flake off the fiber in normal use, and laundering or dry cleaning operations usually destroy, in a relatively short period of time, whatever microbicidal properties that might be present on the surface of the fibers. In addition, resinous coatings on nylon or polyamide fibers tend to change the hand of fabrics prepared therefrom in an undesirable manner.

Another prior art method consists of treating nylon fibers in an aqueous solution comprised of a microbicide. Fibers treated in this manner have not proved to be entirely satisfactory owing to the fact that the microbicidal agent is held so loosely by the fibers that it can be easily and readily removed during laundering of fabrics prepared therefrom.

The selection of a satisfactory microbicidal agent has also posed a problem for those skilled in the art. The microbicidal agent employed, while it must be of sufficient potency to kill or to at least inhibit the growth of microorganisms, must not be toxic or poisonous to the individual wearing clothing prepared from fabrics treated therewith. Further, the microbicidal agent must not have any untoward effects on the fibers per se. That is, they must not affect adversely the physical properties of the individual fibers, the dyeing characteristics of the fibers, and the like.

It is desirable to have available in the art polyamide fibers and the like that have a substantial permanence of microbicidal activity, this result being accomplished without affecting adversely the physical properties of the fibers or the appearance of fabric prepared therefrom.

An object of this invention is to provide a novel polyamide composition suitable for use in preparing formed members having improved microbiological growth inhibition.

Another object of this invention is to provide polyamide fibers having improved microbiological growth inhibition.

A further object of this invention is to provide novel polyamide fibers which, with respect to dyeability, appearance, and the like, are not significantly different from corresponding fibers not possessing microbicidal activity.

Another object of this invention is to provide fabrics comprised of the novel fibers of this invention which

fabrics, with respect to hand, appearance, and the like, are not significantly different from fabrics prepared from nylon fibers not possessing microbicidal activity.

A still further object of this invention is to provide novel polyamide fibers capable of inhibiting microbiological growth, and which are amenable to the various phases of fiber processing without loss of this inhibitory power.

Another object of this invention is to provide novel polyamide fibers which will resist the formation of obnoxious odors after having been contaminated by perspiration or like soiling agents.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

For a complete understanding of the nature and the objects of this invention, reference is made to the following detailed description.

In accordance with this invention it has been determined that relatively small amounts of 3,4,4'-trichlorocarbanilide can be admixed with a polyamide resin in finely divided form, such as in the form of granules, flakes and the like to provide a composition that can be subsequently melt spun, extruded, or otherwise drawn into fibers by conventional methods to produce fibers having substantially improved microbicidal activity. The 3,4,4'-trichlorocarbanilide is employed in an amount sufficient to provide a fiber containing, by weight, from about 0.2% to 1.2% thereof.

The novel fibers of this invention have the 3,4,4'-trichlorocarbanilide substantially uniformly distributed and dispersed therein, and the fibers have the 3,4,4'-trichlorocarbanilide microbicide built in or locked in. Hence, the fibers of this invention and fabrics prepared therefrom are quite unlike natural and synthetic fibers and fabrics which have been superficially surface-treated with various microbicidal agents.

The microbicide in the polyamide fibers of this invention is available to render its microbicidal effect and yet, cannot be completely removed by repeated washings, dry cleanings, and abrasions, which properties are not possessed by conventional surface-treated fabrics and fibers.

Further, and in accordance with this invention, there is provided a novel composition of matter suitable for use in preparing fibers that can be subsequently formed into fabrics and the like possessing microbicidal activity. The novel composition of this invention is comprised of, by weight, from about 0.2% to 1.2% of 3,4,4'-trichlorocarbanilide and from about 99.8% to 98.8% of a polyamide resin.

The microbicide, 3,4,4'-trichlorocarbanilide, employed in carrying out this invention, can be prepared by refluxing substantially equimolar proportions of 3,4-dichloroaniline and 4-chlorophenylisocyanate in an inert solvent such as diethyl ether. This microbicide is admixed with a polyamide resin to provide an intimate admixture of the two components which is thereafter spun by conventional methods into textile fibers. The microbicide, 3,4,4'-trichlorocarbanilide, is substantially uniformly distributed throughout the individual fibers. Such fibers can be woven into fabrics or they can be combined with other fibers, natural or synthetic, and woven into fabrics.

The polyamide or nylon resins employed in carrying out this invention can be of the type derived by the copolymerization of dibasic acids and diamines, or by the polymerization of alpha,omega-amino acids, or by the polymerization of caprolactam or substituted derivatives of such materials or their modifications. These resins and their method of preparation are well known in the art.

Particularly suitable polyamide or nylon resins useful in preparing the novel fibers of this invention include those commonly referred to in the art as type 6 nylon and type

66 nylon. Type 6 nylon is sometimes referred to as polycaprolactam and can be prepared by polymerizing 6-aminocaproic acid. Usually, however, 6-caprolactam is employed as the starting material in the polymerization process. Type 66 nylon is polyhexamethylene adipamide and is derived by the polymerization of hexamethylene diammonium adipate which is a salt formed from hexamethylenediamine and adipic acid. Nylon resins of the fiber-forming type can also be prepared by the polymerization of diammonium salts derived from other diamines and other dicarboxylic acids. Examples of suitable diamines include decamethylenediamine, octamethylenediamine, pentamethylenediamine, and tetramethylenediamine. Examples of suitable dicarboxylic acids include azelaic acid, suberic acid, and sebacic acid. Nylon fibers are usually prepared by melt-spinning methods well known in the art. The nylon fibers of this invention can be similarly prepared by first preparing an intimate admixture of nylon granules or flakes and 3,4,4'-trichlorocarbanilide in the desired amounts, melting the admixture and melt spinning the same.

The fibers of this invention have substantial microbicidal activity against such microorganisms as *Micrococcus pyogenes* var, *aureus, Micrococcus epidermidis, Micrococcus pyogenes, Diplococcus penumoniae, Corynebacterium diptheriae, Streptococcus viridans, Lactobacillus casei,* and related microorganisms. The synthetic fibers of this invention and the fabrics prepared therefrom show particular microbicidal activity toward gram positive microorganisms; however, while the fibers and fabrics of the invention have microbicidal activity, they are substantially non-toxic and non-irritating to humans and thus can be used in the manufacture of clothing, blankets, carpeting, and for numerous other uses.

A particularly desirable property of the fibers of this invention is the permanence of the 3,4,4'-trichlorocarbanilide distributed therein. Even in view of the substantial surface area of fabrics prepared from the fibers of this invention, these fabrics can be subjected to more than 25 washings in household washing machines in the usual manner and still exhibit satisfactory microbicidal activity. Likewise, this microbicidal activity is not substantally lost by mechanical abrasion of the fibers or of the fabrics such as normally results in the processing and use thereof. The permanence of the microbicidal activity is attributed to the fact that the 3,4,4'-trichlorocarbanilide is substantially uniformly distributed throughout the fiber and forms an integral part thereof as distinguished from those fibers carrying a superficial coating of a microbicidal agent.

The incorporation of 3,4,4'-trichlorocarbanilide in the above-defined amounts does not affect adversely the physical properties of the fibers of this invention and fabrics prepared therefrom such, for example, as strength, elongation, hand and lustre. In addition, this microbicide is compatible in the fibers as it does not oil out and does not cause discoloration thereof under usual processing and usage. Also, the presence of this microbicide in the nylon melt creates no difficulty in spinning of fibers therefrom, and its presence in the thus-prepared fiber creates no difficulty in the dyeing of the fiber.

The following examples are illustrative of this invention. All parts are by weight unless otherwise indicated.

Example I

A mixture of about 95.5 parts of polyhexamethylene adipamide and about 0.5 part by weight of 3,4,4'-trichlorocarbanilide is fed into a nitrogen filled chamber onto a melting grid maintained at a temperature of about 285° C. to form a fused or molten mass comprised of the polyhexamethylene adipamide and the 3,4,4'-trichlorocarbanilide. The fused mass is subsequently spun through a spinnerette in the form of yarn. The total denier of the yarn is about 175 and consists of 12 filaments. The denier of the yarn has a standard variable deviation of about 1.2%. After drawing the yarn 400%, it has a strength of about 4.9 grams per denier and an elongation of about 23%. The denier variation is less than 1% when calculated on 10-inch section which is considered satisfactory for this type of yarn.

Example II

A polyhexamethylene adipamide resin similar to that employed in Example I above, having a melt viscosity of about 300 poises and containing no 3,4,4'-trichlorocarbanilide is melt-spun in the same manner as that described in Example I above. Essentially no difference is noted in the spinning conditions, the denier variations, and the breaks during drafting of this yarn from those of Example I above.

Example III

Yarns prepared in accordance with Example I and II above are knitted into fabric and tested in accordance with the test procedure used for the evaluation of bacteriostatic activity of nylon, Tentative Test Methods 90–958, Technique of Antibacterial Properties of Fabrics, Agar Plate Method, published in the Technical Manual of the American Association of Textile Chemists and Colorists, XXXV, 1959, pp. 75–77. Essentially, the test consists of placing discs of the fabrics on the surface of a nutrient agar innoculated with the organism *Micrococcus aureus* (Staphylococcus) Strain FDA 209, ATCC 6538. The *Micrococcus aureus* is inhibited in growth for a distance of about 1½ mm. from the bacteriostatic yarn of Example I, but the control yarn of Example II does not inhibit the growth of the organism at all.

Example IV

Fabrics are prepared from yarns prepared in accordance with Example I above and fabrics are prepared from the yarns prepared in accordance with Example II above. Some of the prepared fabrics are washed 20 times in an automatic home washer in water maintained at a temperature of about 120° F. using a neutral soap, and others are dry cleaned 20 times at 95° F. in a commercial dry cleaning unit using a perchloroethylene solvent. The fabrics prepared from the fibers of Example II, after washing and dry cleaning, showed no inhibition of *Micrococcus aureus* while the bacteriostatic fabrics prepared from the yarns of Example I above showed a ¾ mm. wide zone around the washed fabric and a 1 mm. zone around the dry cleaned fabric.

Example V

A mixture of 95.5 parts of type 6 nylon (polycaprolactam) and about 0.5 part by weight of 3,4,4'-trichlorocarbanilide is fed into a nitrogen filled chamber onto a melting grid maintained at a temperaure of about 285° C. to provide a molten composition comprising the nylon and the 3,4,4'-trichlorocarbanilide. From the melting grid the molten mass is forced through a spinnerette to form yarn having a total denier of about 175 and consisting of 12 filaments.

Example VI

Polycaprolactam (type 6 nylon) containing no 3,4,4'-trichlorocarbanilide is melt-spun in a manner similar to that described in Example V above. There is substantially no difference in the spinning conditions from those of Example V. Denier variations and breaks during drafting are substantially the same as those of the yarn of Example V.

Example VII

Yarns prepared in accordance with Example V and VI above are knitted into fabrics and tested for bacteriostatic activity by the test method described in Example III above. *Micrococcus aureus* is inhibited in the growth of the yarn of Example V while in the yarn of Example VI there is no evidence of inhibition of organism growth at all.

Example VIII

Fabrics are prepared from yarns prepared in accordance with Example V above and fabrics are prepared from yarns prepared in accordance with Example VI above. Some of the fabrics are washed 20 times in an automatic home washer containing water maintained at a temperature of about 125° F. using a neutral soap, and other fabrics are dry cleaned 20 times at 95° C. in a conventional dry cleaning unit using a perchloroethylene solvent. Fabrics prepared from the yarns containing no 3,4,4'-trichlorocarbanilide, after washing and dry cleaning, show no inhibition of *Micrococcus aureus* while the fabrics prepared from the fibers containing 3,4,4'-trichlorocarbanilide show a ¾ mm. wide zone around the washed fabric and a 1 mm. zone around the dry cleaned fabric.

It is to be noted in the above examples that the spinning and drafting operations in the forming of the fibers of this invention are not materially altered by the presence therein of the 3,4,4'-trichlorocarbanilide.

The microbicide of this invention can be prepared by the method described in the following example.

Example IX

Into a suitable reaction vessel equipped with a thermometer, agitator and reflux condenser and containing 8.1 parts by weight of 3,4-dichloroaniline in 57 parts by weight of diethyl ether, there is added, dropwise, a solution of 7.7 parts by weight of 4-chlorophenylisocyanate in 15 parts by weight of diethyl ether at a rate sufficient to maintain gentle reflux. Upon completion of the isocyanate addition, the reaction mass is agitated for about 1 hour. The mass is filtered and the residue washed with diethyl ether. The dried product is a fluffy white solid. The resulting 3,4,4'-trichlorocarbanilide product can be further purified by recrystallization from ethanol, if desired, to give fine white plates of 3,4,4'-trichlorocarbanilide having a melting point of from about 255.2° C.–256.0° C.

The present invention provides novel nylon fibers which have considerable utility because of their built-in or locked-in microbicidal activity, this microbicidal activity having a permanence in the fibers of this invention and the fabrics prepared therefrom not heretofore possessed by conventional surface-treated fibers and fabrics. In addition, the 3,4,4'-trichlorocarbanilide additive of this invention does not adversely affect the processing, physical appearance, and physical properties of the subject fibers and fabrics.

While the above description of this invention has been directed primarily to the preparation of nylon fibers having microbicidal activity and to fabrics prepared therefrom, it is to be understood that other members can be prepared from the novel composition of this invention. Thus, for example, this invention makes possible the production of nylon bristles for hairbrushes and toothbrushes, the preparation of surgical bandages, gauzes and the like. Further, the novel composition of this invention can be employed in the manufacture of other articles such, for example, as teething rings, tongue depressors, combs, hairbrush backs, toothbrush handles, and the like.

It is to be understood that the above description and examples are illustrative of this invention and not in limitation thereof.

We claim:

1. A composition of matter comprised of, by weight, from about 0.2% to 1.2% of 3,4,4'-trichlorocarbanilide and from about 99.8% to 98.8% of nylon, said 3,4,4'-trichlorocarbanilide being substantially uniformly dispersed throughout the nylon.

2. A composition of matter comprised of, by weight, from about 0.2% to 1.2% of 3,4,4'-trichlorocarbanilide and from about 99.8% to 98.8% of polycaprolactam, said 3,4,4'-trichlorocarbanilide being substantially uniformly dispersed throughout the polycaprolactam.

3. A composition of matter comprised of, by weight, from about 0.2% to 1.2% of 3,4,4'-trichlorocarbanilide and from about 99.8% to 98.8% of polyhexamethylene adipamide, said 3,4,4'-trichlorocarbanilide being substantially uniformly dispersed throughout the polyhexamethylene adipamide.

4. An article of manufacture having microbicidal activity comprising nylon having substantially uniformly dispersed therein from about 0.2% to 1.2% by weight of 3,4,4'-trichlorocarbanilide.

5. An article of manufacture having microbicidal activity comprising polycaprolactam having substantially uniformly dispersed therein from about 0.2% to 1.2% by weight of 3,4,4'-trichlorocarbanilide.

6. An article of manufacture having microbicidal activity comprising polyhexamethylene adipamide having substantially uniformly dispersed therein from about 0.2% to 1.2% by weight of 3,4,4'-trichlorocarbanilide.

7. A textile fiber having microbicidal activity comprised of nylon having substantially uniformly dispersed therein from about 0.2% to 1.2% by weight of 3,4,4'-trichlorocarbanilide.

8. A textile fiber having microbicidal activity comprised of polycaprolactam having substantially uniformly dispersed therein from about 0.2% to 1.2% by weight of 3,4,4'-trichlorocarbanilide.

9. A textile fiber having microbicidal activity comprised of polyhexamethylene adipamide having substantially uniformly dispersed therein from about 0.2% to 1.2% by weight of 3,4,4'-trichlorocarbanilide.

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