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3,087,861

PROCESS AND COMPOSITION FOR ANTI-MICROBIAL TREATMENT

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No Drawing. Filed Dec. 18, 1959, Ser. No. 860,327
11 Claims. (Cl. 167-84)

Our present invention relates to a treatment of fabrics and other materials with metallic compounds designed to impart antimicrobial properties to such materials.

In co-pending applications Ser. Nos. 738,967 and 760,857, filed by Meyer Mendelsohn (one of the present applicants) on June 2, 1958, and September 15, 1958, respectively, both now abandoned, there has been disclosed a treatment of this character in which a zinc compound is caused to react on the fibers of a material to be treated, notably a cellulosic or proteinaceous material, so that the zinc will firmly adhere to the fibers and exert its antimicrobial action even after repeated washings. More particularly, the treatment disclosed in these pending applications involves the immersion of the material in an aqueous bath at high temperatures, the bath including as its principal ingredients a chelating agent, a catalyst such as sodium acetate, and optionally a detergent along with a suitable zinc compound such as zinc chloride. A fixing agent rich in amine groups, such as urea, is applied to the material either in the same bath or in a second treatment solution to help lock the zinc in place on the fibers of the material.

Although the treatment just described is satisfactory with respect to both the safety of operation and the quantity of zinc fixed in the fibers, the material so obtained has a rather limited range in which it can exert an antimicrobial effect upon its environment as established by inhibition-zone measurements carried out with pieces of fabric treated in this manner.

It is, therefore, an important object of our present invention to provide an improved process for the treatment of organic fibrous or film materials in such manner as to render those materials not only resistant to microbial attack and destructive of the resident flora thereon, but also effective in exerting growth-inhibiting action upon nearby surfaces even after repeated washings.

A more specific object of this invention is to provide a process for carrying out such treatment on a commercial scale in the mass production of fabric, paper and similar organic sheet materials.

In accordance with this invention we admix a water-soluble zinc salt, a chelating agent, a catalyst, an aminating agent and preferably a detergent and a buffering agent with a small amount of an organic solvent, advantageously a low-boiling ketone such as acetone, and dissolve the mixture in an aqueous medium (preferably water). When this mixture is applied to the material to be treated, it is surprisingly found that the zinc compound reacts with other ingredients to form a complex which remains fixed to the fiber over prolonged periods of use and causes the treated material to exhibit distinct halos or zones of inhibition against micro-organisms even after many washings in hot or cold water.

It is further found that similar results are obtained where, in accordance with a modified process according to the invention, the aminating agent is dissolved in a second bath in which the material to be treated is steeped separately, preferably prior to its immersion in the active bath containing the other ingredients enumerated above.

Following is a list of ketones found suitable for the process of our invention.

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TABLE 1

Compound:	Boiling point (° C.)
Acetone	56
Hexafluoroacetyl acetone	63-65
2-butanone (ethyl methyl)	80
3-buten 2-one (methyl vinyl)	81
Biacetyl acetone	88
Methyl isopropyl ketone	94.3
Diethyl acetone	102
Methyl propyl ketone	102.3
Pinacolone	106
Methyl isobutyl ketone	116.8
Cyclohexanone	156

The following proportions, by weight of solution, have been found to give a satisfactory mixture:

TABLE 2

	Percent
Zinc salt	0.5 to 90
Aminating agent	0.5 to 30
Chelating agent	0.1 to 10
Catalyst	0.1 to 35
Detergent	0 to 15
Buffering agent	0 to 25
Volatile organic solvent	0.1 to 30

The zinc salt is preferably zinc chloride but may also be any other water-soluble organic or inorganic salt such as zinc sulfate, or zinc nitrate, zinc bromide or zinc acetate.

Sufficient quantity of the aforementioned ingredients are dissolved in water to obtain a solution where concentration preferably ranges between about one and ten parts of total solids per one hundred parts of water.

Following is a list of aminating agents adapted to be used in the process of the invention:

TABLE 3

Urea	Triethanolamine
Isopropylamine	Aniline
n-Propylamine	Toluidine
t-Butylamine	p-Phenylene diamine
Monoethanolamine	Morpholine
Diethanolamine	Melamine

Suitable sequestrants or chelating agents are the alkalimetal (e.g. sodium, potassium, lithium) salts of the following acids:

TABLE 4

Ethylene diamine tetraacetic acid
Methylimino diacetic acid
Phenylimino diacetic acid
Ammonia triacetic acid
1,2-diamino-cyclohexanetetraacetic acid
Uramildiacetic acid

A variety of detergents, of both the non-ionic and the quaternary type, have been found suitable for purposes of the invention. Typical among them are the following.

TABLE 5

Non-ionic detergents:
Sorbitan Sesquileate (Arlacel C)
Polyethanolamine condensate of a fatty acid (Cerfak N-100)
Alkoxypolyglycol fatty-acid ester (Dergon PX)
Sulfated glyceryl trioleate (Drutone SE)
Polyoxyethylene alkyl phenol (Energetic W-100)
Fatty-acid condensate of N-Methyl glucamine and coconut fatty acids (Glucaterge 12)
Isooctyl phenoxy polyoxyethylene ethanol (Igepal CA-630)
Nonyl phenoxy polyoxyethylene ethanol (Igepal Co-633)

Polyoxyethylene sorbitol stearate (Morosol SI)
 Polyoxyethylene stearate (Myrj 45)
 Quaternary detergents:
 Alkyl (fatty acid) benzyl dimethyl ammonium chloride (Benzalkonium chloride)
 Tallow trimethyl ammonium chloride (Arquad T)
 Soya trimethyl ammonium chloride (Arquad S)
 Dodecyl trimethyl ammonium chloride (Arquad 12)

Example 1

A dry mixture is prepared as follows:

	Parts
Anhydrous zinc chloride, $ZnCl_2$ -----	220
Sodium acetate, 60% crystalline -----	50
Boric acid (anhydrous) -----	10
Anhydrous sodium ethylene diamine tetra-acetate --	10
Ethylene cycloimido 1-alkyl (fatty acid), 2-hydroxy ethylene sodium alcoholate, methylene sodium carboxylate (a detergent commercially known as Miranol CM Concentrate) -----	20

Ninety-five parts of the above mixture are admixed with five parts of acetone. Five parts of the latter mixture and an equal amount of urea are next dissolved in two-hundred parts of water. The resulting solution is used as a treatment liquor at 90° C. A piece of cotton is immersed therein for fifteen minutes, removed and allowed to dry.

A sample of the textile so treated is washed forty times in a household washing machine with soap or detergent and is then placed on a Petri dish containing agar streaked with a culture of *Staphylococcus aureus*. After an incubation period of twenty-four hours a distinct 0.5-mm. halo or zone of inhibition is observed.

Similar halo effects are noted when either wool or nylon is treated in accordance with the procedure set forth in this Example 1.

Example 2 (Control)

Example 1 is repeated in every material respect except that acetone is not employed.

No zone of inhibition against *Staphylococcus aureus* is observed after forty washings.

Example 3

Methyl isobutyl ketone is used as a solvent in lieu of that given in Example 1 above which is repeated in every other detail. The same zone of inhibition is observed as in Example 1. Substitution of cyclohexanone for methyl isobutyl ketone in the above composition yields inhibition zone around the treated material of 0.4 mm.

Example 4

One-hundred and fifty parts of zinc chloride, seventy parts of sodium acetate (60% crystalline), ten parts of boric acid, ten parts of sodium ethylene diamine tetra-acetate and ten parts of detergent (Miranol CM Concentrate) are mixed together. To ninety-five parts of this mixture we add five parts of acetone. Five parts of the resultant composition are next dissolved in 100 parts of water. The solution constitutes the first treating bath.

A second solution is prepared by dissolving five parts of urea in about one-hundred parts of water.

A piece of cotton is immersed in the first treating bath heated to about 90° C. for about ten minutes. It is next immersed in the second solution, heated to about 90° C., and held in the bath for an additional five minutes before removal and drying. Thereafter, it is washed for about forty times with soap or detergent.

The washed cotton swatch is tested for the presence of a halo in the manner described in Example 1. An 0.5-mm. zone of inhibition is observed after an incubation period of twenty-four hours. In general, organic fibrous or film-forming materials such as cotton, wool, paper, regenerated cellulose or polyamide sheets can be subjected to either a one-step process, as in Examples 1 and

3, or a two-step process, as in Example 4. In the latter case the order of immersions can be reversed, with the treatment in the aminating solution preceding the immersion in the active zinc bath. In each case, inhibition of bacterial growth occurs around the treated sample even after the many washings described. Small amounts of ketonic solvent upwards of about 0.1% and up to approximately 30%, by weight of the dry treatment composition are apparently sufficient to intensify the antimicrobial action of the mixture to the extent necessary for the attainment of this result.

It should be noted that the addition of a detergent or wetting agent, while not essential, is especially desirable where the composition according to the invention is to be used on synthetic fibers, such as nylon.

Other alkali-metal acetates, such as potassium or lithium acetates, may be used as the catalyst in lieu of sodium acetate.

The proportions of catalyst and buffering agent, if any, should be so selected as to result in a pH of 3 to 9, preferably within a range of 5 to 7. Any of a number of commercially available buffering agents may be employed for this purpose.

The bath temperatures may be maintained, in general, between approximately 65° and 100° C. Lower bath temperatures are possible, as disclosed in commonly assigned application Ser. No. 858,871, filed December 11, 1959, by Meyer Mendelsohn and Carl Horowitz, by the dissolution of a natural or synthetic gum (e.g. polyvinyl alcohol) in the bath, in proportions ranging between 1% and 50% of the solids. The length of the immersion may vary from upwards of five minutes in a one-step process to a few seconds in a two-step treatment.

It should be noted that treatments corresponding in every respect to those described above, save for the addition of a volatile solvent such as acetone, result in fabrics or other articles initially displaying a zone of inhibition similar to that shown by an article treated in accordance with our present invention, e.g. from 3 to 5 mm. After about five washings, however, the control samples treated by the solvent-free bath no longer exhibit a detectable halo around their circumference, even though there is absence of growth under each sample, whereas those subjected to the herein disclosed process still manifest a relatively large zone, of about 2 mm., which only gradually decreases to the aforesaid value of 0.5 mm. after about forty washings. The invention is thus shown to be effective in maintaining the antimicrobial activity of a treated article over a surprisingly long period, compared with processes heretofore developed.

We claim:

1. A treatment composition for imparting antimicrobial properties to organic fiber and sheet materials, comprising a predominantly aqueous solution of a zinc salt and a chelating agent, and a volatile organic solvent in said solution.

2. A composition according to claim 1 wherein said solution further includes an alkali-metal acetate.

3. A composition according to claim 1 wherein said solvent is present in a proportion ranging between substantially 0.1% and 30%, by weight, of said solution.

4. A composition according to claim 1 wherein said solvent is a ketone having a boiling point below substantially 160° C.

5. A composition according to claim 4 wherein said ketone is acetone.

6. A treating composition for imparting antimicrobial properties to material which comprises a predominantly aqueous solution of a water soluble zinc salt, an N-substituted acetic acid chelating agent, and a low boiling ketone in said solution.

7. A treating composition for imparting antimicrobial properties to material which comprises a predominantly aqueous solution of zinc chloride, sodium ethylene diamine tetra-acetate and acetone in said solution.

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8. A treating composition for imparting antimicrobial properties to material which comprises a predominantly aqueous solution of zinc chloride, sodium ethylene diamine tetra-acetate and methyl isobutyl ketone.

9. A treating composition for imparting antimicrobial properties to material which comprises a predominantly aqueous solution of zinc chloride, sodium ethylene diamine tetra-acetate and cyclohexanone.

10. An antimicrobial composition of matter comprising a zinc salt, a chelating agent and a volatile organic solvent.

11. A process for imparting antimicrobial properties to organic fiber and sheet materials, comprising the steps of immersing the material to be treated in an aqueous solution of a zinc salt at an elevated temperature, said solution further containing a chelating agent and a volatile

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organic solvent having a boiling point higher than said temperature, and drying said material.

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