

UNITED STATES PATENT OFFICE

2,689,809

SELF-STERILIZING ARTICLE AND ITS
PREPARATION

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No Drawing. Application October 8, 1951,
Serial No. 250,386

21 Claims. (Cl. 117—138.5)

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This invention relates to a method useful in treating cloth and other articles to render them antiseptic and self-sterilizing, and to the antiseptic and self-sterilizing articles so produced.

The treatment of articles, such as those made of fabric, rubber goods, paper, leather, felt, synthetic organic plastics, ceramics and other substances to render them lethal over prolonged periods of time and use to microorganisms coming into contact with them has long presented a problem for which no ready or simple solution has heretofore been found. Methods have been devised for impregnating fibrous and, in some instances, non-fibrous articles with solutions or suspensions of germicides or fungicides to give them a measure of self-sterilization until used. A number of conventional germicides and fungicides have been used for such purposes. Bandages supporting germicides on the fibers and in the interstices between the fibers have been prepared which could be stored in the open air without becoming unduly contaminated with microorganisms and which could subsequently be applied to open wounds without danger of carrying air-borne infections into the wound. Although this procedure has met with some success, the practice has not been entirely satisfactory for a number of reasons and has not been used on a wide scale, the usual practice in the case of bandages which are to be stored prior to use being to package the sterilized bandage under aseptic conditions in a germ-proof package, or to sterilize the bandage, e. g. by heat, after it is packaged.

Most of the attempts heretofore made to render fabrics self-sterilizing have been confined to the treatment of bandages and surgical gauze because of the particular necessity for keeping them in a sterile condition until used. Such articles are generally used only once and then discarded so that the question of permanence of the treatment during repeated use and laundering of the article does not generally arise. There are, however, many other instances where the need is apparent for an antiseptic and self-sterilizing cloth or other article which will retain these properties after continued and repeated use and laundering. Thus, clothing, underwear, bedding, stockings, paper, leather goods, towels, shoe linings, diaper cloth, rubber goods, bristles, plastic articles designed for body contact and many other articles invariably carry many kinds of bacteria on their surfaces after even brief exposure to the air and may become potent sources of infection when worn or otherwise contacted with the skin. Bacteria already present on the skin may be picked

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up by clothing and transported to abraded areas with the consequent development of infection in such areas. Frequent laundering or cleaning of such articles serves to clean and sterilize them temporarily but such sterilization has no lasting effect and the articles are subject to re-contamination immediately after laundering.

The need is apparent for a method for treating articles, including those mentioned as well as many others, to impart to them highly effective antiseptic and self-sterilizing properties which are not unduly affected or destroyed by laundering or cleaning or by normal use, and which would thus be effective over a long period of time in devitalizing microorganisms coming in contact therewith. It is likewise apparent that not only would the method itself be of great value, but that the self-sterilizing article itself would be equally valuable provided its self-sterilizing property were sufficiently permanent.

It has now been found, and is herein first disclosed, that an unexpectedly high degree of self-sterilization of a substantially permanent nature for all practical purposes can be imparted to many fibrous and non-fibrous articles by co-precipitating, under controlled conditions hereinafter described, on the surface of or in the interstices of, or even within the body of, the article a mixture of at least two water-insoluble salts or compounds, one of which is a water-insoluble silver compound. The treated article can be stored or used without substantial noticeable alteration in its physical characteristics as compared with the untreated article. Articles treated according to the method can be laundered or cleaned repeatedly, generally with not more than a slight diminution of their antiseptic and self-sterilizing properties. Hypochlorite and chlorine bleaching of laundered treated articles can be effected without harm and actually appears to restore any decreased germicidal activity which may have been caused by repeated laundering under adverse conditions.

An essential feature of the process is the presence in the precipitating bath of a compound or substance, herein referred to as a "solubilizer," which has at least a partial solubilizing effect on the water-insoluble silver compound to the extent that it renders the silver compound more soluble in the bath than in pure water. Solubilizers which can be used include ammonia and organic amines as well as certain inorganic salts. Depending upon its nature, the solubilizer is eventually removed from the article by evaporation or leaching with water, or sometimes by neutraliza-

tion, leaving the co-precipitated salts dispersed in what appears to be substantially molecular inter-dispersion and in a form wherein they are not only extremely difficult to remove from the article but wherein the water-insoluble silver salt is substantially insensitive to discoloration by light. Articles which can be treated using the process to render them substantially self-sterilizing and antiseptic include textiles and clothing of substantially all kinds, leather, paper, dental and face powders, natural and artificial bristles, wood, certain types of rubber, ceramic and plastic articles, catgut, dental cements, guttapercha, casein products, feather products, and many others.

In a preferred procedure for carrying out the process, the article is first dipped in or wetted with an aqueous solution, herein referred to as a "first solution," containing a water-soluble silver salt, e. g. silver nitrate, and a water-soluble metal salt, e. g. magnesium nitrate, herein referred to as a "first salt," the cation of which is capable of forming a water-insoluble salt with the anion of at least one other water-soluble salt, e. g. with a "third" salt to be referred to later. Excess of the first solution over that required to wet the article thoroughly is then usually removed mechanically, e. g. by squeezing, wringing, or wiping, after which the article, usually while still wet, is dipped in or wetted with another aqueous solution, herein referred to as a "second solution," containing ammonia or other suitable solubilizer, a water-soluble salt, e. g. sodium chloride, herein referred to as a "second salt," the anion of which is the anion of a substantially water-insoluble silver salt, and a water-soluble salt, e. g. sodium phosphate, herein referred to as "third salt," the anion of which is capable of forming a water-insoluble salt with the cation of the first water-soluble salt. Excess of the second solution is then generally removed from the article, e. g. by squeezing, wringing or wiping, and the article is then dried thoroughly, after which it can be washed to remove any excess of water-soluble salts and again dried. In some instances the solubilizer is preferably neutralized or otherwise at least partially destroyed, e. g. in the case of ammonia or an amine by adding a dilute acid, either prior to or after removal of the article from the second solution. As a result of these operations there is precipitated on the surface of and in the interstices of the article a tightly adherent deposit of a water-insoluble silver salt comprising the anion of the second water-soluble salt, e. g. silver chloride, together with another water-insoluble salt, e. g. magnesium phosphate, comprising the cation of the first water-soluble salt and the anion of the third water-soluble salt.

Articles treated according to the method described have been found to have an exceptionally high degree of self-sterilization which is retained substantially undiminished after dry cleaning or repeated laundering with hot soap solution. By a proper choice of the water-soluble salts, non-colored water-insoluble salts are formed as a result of the treatment and, unexpectedly, it has been found that the non-colored water-insoluble silver salts, e. g. silver chloride, deposited in this manner are remarkably resistant to darkening or discoloration upon exposure to strong light over long periods of time. The reason for this is not clearly understood and no theory regarding it is presented here. It has been found, however, that whereas a fabric treated according to the method just described can be exposed to light

in an ordinary room for several weeks or months without the slightest tendency to darken, a sample of the same cloth subjected to treatment with the same identical first and second solutions, except for the omission of the first water-soluble salt from the first solution and of the third water-soluble salt from the second solution, begins to darken within a few hours and after a few days acquires the bluish-gray color characteristic of silver chloride which has been exposed to light for some time. Such coloration in the case of treated white goods cannot, of course, be tolerated. When colored fabrics are treated according to the method a considerably greater latitude in the selection of salts to be included in the treating solutions can be exercised, since, in many instances, the formation of a colored salt on the article is not objectionable. Salts which are injurious to the article being treated should, of course, be avoided in both solutions.

In carrying out the preferred process, any convenient water-soluble silver salt can be used in the first solution. The nitrate is generally used because of its ready availability in a state of high purity. Other water-soluble or moderately water-soluble silver salts, such as silver lactate, silver acetate and silver fluoride, can, however, be used, if desired.

The first water-soluble salt should, of course, be one which is compatible in solution with the water-soluble silver salt used to avoid the formation of a precipitate in the first solution. Salts of the alkaline earth metals are often preferred as the first salt because of the generally white nature of their salts and because they react with many relatively inexpensive soluble salts to form insoluble compounds. Water-soluble aluminum salts can often be used with advantage as will become apparent later. Water-soluble zinc salts appear to be of particular value in certain instances, particularly when a fungus-proofing treatment is desired. It also appears that the use of zinc salts is of particular value when exposure of the treated article to sulfur or sulfides may occur. Mixtures of "first" salts can, of course, be used if desired.

The second water-soluble salt, used in preparing the second solution, should, as mentioned previously, contain the anion of a water-insoluble silver salt. For practical reasons, sodium chloride is generally used as the second salt because of its ready availability and low cost and because operation of the process to produce silver chloride as the water-insoluble silver salt has been found to give excellent results. Other salts which can, however, be used as the second salt include potassium bromide, sodium iodide, sodium phosphate, calcium chloride, magnesium chloride and water-soluble halides of the heavy metals, as well as many others. It should be noted that the water-insoluble silver salt which is formed need not be basic in character and, as a matter of fact, non-basic salts, such as the halides and phosphates, are generally preferred in the interest of economy and ease of operation of the process.

The third water-soluble salt, also used in preparing the second solution, should be compatible in aqueous solution with the second water-soluble salt to avoid the formation of a precipitate in the second solution. The choice of the third salt used will, of course, also depend in large measure upon the first salt used in the first solution since it is essential that the cation of the first salt and the anion of the third salt form a water-insoluble compound as a result of the

operation of the process. Salts which have been used successfully as the third salt when the first salt is a water-soluble calcium or strontium salt include the alkali metal and other water-soluble phosphates and sulfates. Sulfates are, of course, unsuited for use as the third salt when the first salt is a magnesium salt because of the solubility of magnesium sulfate in water. A water-soluble phosphate can, however, be used as the third salt in such instances. It is pointed out that it is impossible to give a precise list of salts, any one of which can be used in all cases as the first or second or third salt, because of the interrelationship of properties between these several salts which has been mentioned and which must be maintained by a proper selection of any one of the salts when specific salts have been selected as the other one or two salts.

Another ingredient essential in the process, which has been noted previously and which is generally included in the second solution, is a solubilizer for the water-insoluble silver salt, preferably ammonia or a suitable amine. The function of the ammonia or amine is not entirely understood, but it appears that it is at least related to the greater solubility of the water-insoluble silver salt in the aqueous solution of the solubilizer than in water alone. It is also possible that in some instances, depending upon the particular first and third salts used in the process, the solubilizer may have a significant effect upon the character or solubility of the water-insoluble silver salt formed in the operation of the process. Regardless of the cause, it has been found that satisfactory results are obtained only when a suitable solubilizer is employed in the process. Although ammonia is the preferred solubilizer, other basic nitrogen compounds which can be used include monoethyl amine, dimethyl amine, trimethyl amine, monobutyl amine, diisopropyl amine, monoethanol amine, diethanol amine, ethylene diamine, morpholine, pyridine, picoline and many others. Generally speaking, aliphatic amines, including the substituted alkyl amines having less than about 10 carbon atoms in the molecule, are preferred to amines of higher molecular weight because of their greater volatility and ease of vaporization from the treated article during drying. Insofar as is known, however, any water-soluble basic nitrogen compound can be used in the process.

It is, of course, possible to choose the first, second and third salts so that the same compound can serve as the second and third salts, provided only that the anion of this compound forms a water-insoluble salt both with silver as a cation and with the cation of the first salt. The process can thus frequently be carried out using magnesium nitrate as the first salt and sodium pyrophosphate alone to serve as both the second and third salts. Generally, however, it is preferable to use a halide, preferably a chloride, as the second salt because of the favorable characteristics of the silver halides. It is also possible in some instances, i. e. when the first salt is an aluminum salt, for ammonium hydroxide to serve as the third salt, the insoluble compound deposited with the insoluble silver salt in this instance being aluminum hydroxide.

The proportions of the several salts used in making up the solutions both with respect to the solvent and with respect to one another can be

varied over a wide range. In the interest of economy, however, the water-soluble silver salt and the second salt are used at concentrations in the first and second solutions, respectively, such that the amounts of the solutions used in wetting the article being treated will contain the second salt in at least a stoichiometric ratio to the water-soluble silver salt, and preferably somewhat more. The same applies, in general, to the proportions of the first and third water-soluble salts. It is apparent that an influential factor is the character of the article being treated, including its absorptive capacity and surface characteristics, and that it is substantially impossible to define the first and second solutions in terms of the concentration of the salts therein. It has been found, however, that good results are obtained when the amount of water-insoluble silver salt deposited in or on a fibrous fabric is from about 0.1 to about 0.5 per cent, calculated as silver chloride, of the weight of the fabric, together with from about 0.05 to 1.0 per cent of the weight of the fabric of the other water-insoluble salt deposited with it. Here again, however, it is not possible to define these values quantitatively with any degree of satisfaction because of the number of variables involved in passing from one instance to another and the invention is not limited to the proportions given. For economic reasons, it is seldom desirable to treat the article in such manner that it retains more than about 1.0 per cent of its weight of silver calculated as silver chloride.

Certain other ingredients may often be included in the treating solutions with advantage. In some instances a wetting agent can be included to promote wetting and penetration of the article being treated. In some instances, also, the inclusion of a dispersed resin, e. g., an emulsified polyvinyl acetate, in one or the other of the solutions, usually the second, leads to a more permanently self-sterilizing product. This may be due to the resin acting in the nature of a binder for the co-precipitated salts. Other ingredients which can often be added for specific purposes will be apparent.

Certain other modifications of the process are possible, especially in the preparation of powdered products, it being sometimes possible to use an excess of properly chosen first and third salts to form a product comprising a small proportion of the water-insoluble silver compound as compared to the water-insoluble other compound, the latter functioning also in the final product as the base or treated powder. Such base powders which may be formed in situ include aluminum hydroxide, zinc oxide, calcium sulfate, calcium carbonate, zinc phosphate, magnesium pyrophosphate and many others.

A further modification of the process contemplates the production of highly fungicidal as well as germicidal products using a salt, preferably the calcium salt, of a fungicidal organic acid, such as undecylenic acid, as the fungicidal agent. In carrying out this modification of the process in its preferred form, the article being treated is generally wetted first with a solution of a water-soluble calcium salt, such as calcium chloride, and then with a solution of the ammonium, sodium or other water-soluble salt of undecylenic acid, or vice versa, these treatments being carried out either prior to or subsequent to the treatment with the first and second solutions previously referred to. Somewhat better results appear to be obtained when the treatment with

the first and second solutions is carried out subsequent to the treatments with the calcium salt and undecylenic acid salt solutions. One preferred procedure comprises incorporating a water-soluble calcium salt, such as calcium nitrate, in the first solution along with the water-soluble silver salt and incorporating the water-soluble undecylenate, e. g. ammonium undecylenate, in the second solution along with the second and third water-soluble salts. Under such conditions a desirable co-precipitation of the calcium undecylenate along with the water-insoluble silver salt is realized.

It is apparent from the foregoing description of the preferred procedure that the method in its broadest sense involves the co-precipitation from solution on the article being treated of an intimate mixture of a water-insoluble silver salt and another water-insoluble salt, which other salt, because of the extreme intimacy of the mixture, functions as an effective stabilizer of the silver salt against the effect of light normally tending to discolor silver salts. Although one preferred procedure for carrying out the method has been described in detail, it is apparent that the method of the invention is not limited to the particular preferred procedure described in detail. It is likewise apparent that the product, which has not been described previously, is not limited to that prepared by the particular preferred procedure mentioned but encompasses the product by whatever method prepared.

In the following examples, which are given by way of illustration only and are not to be construed as limiting, there are described the treating of various articles using various procedures and with the formation of corresponding treated articles all of which, unless otherwise noted were found to be antiseptic and self-sterilizing.

Self-sterilizing and antiseptic properties of the treated articles were, in most instances, determined using a modification of a Food and Drug Administration method for assaying penicillin as follows:

A culture medium was prepared in the usual fashion containing the following ingredients:

Bacto-peptone	g--	6.0
Pancreatic digest of casein	g--	4.0
Bacto-yeast extract	g--	3.0
Bacto-beef extract	g--	1.5
Bacto-glucose	g--	1.0
Bacto-agar	g--	15.0
Distilled water	ml--	1000

The pH of the medium was 6.6.

A nutrient broth for preparing inoculum was prepared in the usual fashion using the following ingredients:

Peptone	g--	5.0
Yeast extract	g--	1.5
Beef extract	g--	1.5
Sodium chloride	g--	3.5
Glucose	g--	1.0
Dipotassium phosphate	g--	3.68
Potassium dihydrogen phosphate	g--	1.32
Distilled water	ml--	1000

The pH of the broth was 7.0. Test organisms used were *Staphylococcus aureus* and *Escherichia coli* except as otherwise noted.

The stock culture was maintained on agar slants and transferred to new slants weekly. The inoculum for the plates was prepared by transferring the culture from the agar slant to nutrient broth daily and incubating at 37° C. After 18 hours of incubation 0.2 ml. of the broth cul-

ture was mixed thoroughly with 100 milliliters of the culture medium at 48°-50° C. Plates prepared using this inoculated agar were used for testing the antiseptic properties of the treated articles, a sample of the article being placed near the center of a freshly prepared plate and the clear zone which remained around the sample after incubation for 18 hours at 37° C. being noted. It was found that the width of the clear zone depended to some extent upon the porosity of the treated article. The treated article was said to be antiseptic when a significant clear zone remained in the agar around the test sample but the actual width of the clear zone is not given because of the variation due to the character of the article itself just noted.

The self-sterilizing properties of the treated articles were determined by placing a sample of the treated article after exposure to the air for several hours near the center of a freshly poured sterile agar plate and incubating the plate for 18 hours at 37° C. The article was said to be self-sterilizing when no significant cloudiness developed in the medium around the sample.

In an alternate method for testing treated articles, particularly treated fabrics for germicidal properties, which appeared to be somewhat more reliable than methods employing agar, a 0.5 gram sample of the treated article was placed in a sterile bottle with 20 milliliters of distilled water. The water was then inoculated with 0.1 milliliter of a culture of *Staphylococcus aureus* or *Escherichia coli* in nutrient broth and the bottle and contents shaken mechanically for several hours at room temperature. Cell counts were made of the original culture before inoculation and of the contents of the bottle after each hour of shaking. Controls were run using untreated samples of the article. Using this method large cell populations in the inoculated water were killed by one hour shaking using treated samples which showed a minimum effect when tested on agar. Controls showed large viable cell populations still present after 4 hours' shaking.

The resin emulsion used in certain of the examples is a water-dispersible anionic emulsion of a polyvinyl acetate resin manufactured by American Cyanamid Company and sold under the name of Aerotex 160. The resin emulsion was in some cases mixed with a part of the water used in making up the second solution before being mixed with the solubilizer and salts dissolved in the rest of the water. In other cases the resin and solubilizer were mixed with a part of the water prior to being mixed with the salt or salts dissolved in the remainder of the water. The ammonia used in all cases was, unless otherwise noted, ordinary commercial 28 per cent aqua ammonia.

EXAMPLE 1

A first solution was prepared by dissolving 10 grams of silver nitrate and 20 grams of hydrated magnesium nitrate in 1000 milliliters of distilled water. A second solution was prepared by dissolving 6 grams of sodium chloride, 30 grams of disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) and 200 milliliters of aqua ammonia in 800 milliliters of distilled water. A sample of white cotton sheeting was immersed for a period of 30 to 60 seconds in the first solution and then removed and squeezed tightly to eliminate excess solution. The squeezed cotton sheeting contained about 150 per cent, based on its dry weight, of solution. The still wet cotton sheeting was then immersed in the second solution for 30 to 60 seconds and

then removed, squeezed and dried thoroughly. The dried cotton sheeting was then washed in clear water to remove excess soluble salts and again dried. The product prepared in this manner was found to be both antiseptic and self-sterilizing. It had a hand and feel substantially identical with that of untreated cotton sheeting which had been washed in clear water and dried. The color of the treated fabric was indistinguishable from that of washed untreated fabric. Samples of the treated cotton sheeting exposed to strong sunlight daily for as long as 60 days showed no tendency to become discolored.

A number of samples of the treated cotton sheeting were washed repeatedly in a home washer using a good grade of soap and with the washing bath at about 90° C. The samples were rinsed and dried after each washing. After each period of several washings, one or more of the samples was removed and tested for antiseptic and self-sterilizing properties. After as much as 100 washings and drying cycles the samples still had significant and adequate antiseptic and self-sterilizing properties.

The experiment was duplicated with the cotton sheeting being replaced with cotton gauze, woolen uniform cloth, woolen cloth for civilian use, blended wool and cotton cloth, woolen blankets containing both virgin wool and reprocessed wool, acetate rayon fabrics, surgical masks, surgeons' hats, filter paper, cotton diapers, and woolen, cotton and acetate rayon socks and underwear. In each case the treated product was antiseptic and self-sterilizing, was substantially unchanged in its hand and feel and was not discolored by prolonged exposure to light. In the case of heavy fabrics, such as wool blankets, the samples were soaked in each of the separate solutions for about two minutes. A number of the treated fabrics mentioned were laundered and dry cleaned repeatedly without lowering their antiseptic and self-sterilizing properties appreciably.

Variations of the process were carried out by drying the final washed product in an oven at 60°-70° C., by drying the article after wetting with the first solution and before wetting with the second solution, and by carrying out the dipping steps with the first solution heated at 60°-80° C. None of these variations in the process produced any significant change in the treated article. It was noted that at higher dipping temperatures, e. g. at about 80°-100° C., a small amount of a dark precipitate gradually formed in the first solution upon prolonged exposure to light.

In still other variations of the experiment the squeezing of the sample after wetting with the first solution was varied so as to leave as little as 100 per cent or as much as 200 per cent of the first solution, based on the dry weight of the sample, absorbed on the sample. No significant differences in the results were noted.

EXAMPLE 2

A first solution was prepared by dissolving 10 grams of silver nitrate and 10 grams of crystalline aluminum nitrate in 1000 milliliters of water. A second solution was prepared by dissolving 5 grams of sodium chloride and 300 milliliters of aqua ammonia in 700 milliliters of water. The first procedure described in Example 1 was repeated using these solutions, the results obtained being entirely analogous and comparable to those obtained in Example 1. In this instance aluminum hydroxide was precipitated as the insoluble

aluminum compound along with silver chloride.

EXAMPLE 3

The procedure described in Example 1 was repeated using a variety of first and second treating solutions, the compositions of which are given below in tabular form as treatments "A" to "Q" inclusive:

Table of treatments

Treatment	First Solution	Second Solution
15 A	5 g. AgNO ₃ 5 g. Mg(NO ₃) ₂ ·6H ₂ O 1,000 ml. H ₂ O	3 g. NaCl 5 g. Na ₃ PO ₄ ·12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
B	5 g. AgNO ₃ 5 g. Mg(NO ₃) ₂ ·6H ₂ O 1,000 ml. H ₂ O	3 g. NaCl 5 g. Na ₃ PO ₄ ·12H ₂ O 200 ml. NH ₃ (Aq) 10 g. resin emulsion 800 ml. H ₂ O
20 C	10 g. AgNO ₃ 1 g. Mg(NO ₃) ₂ ·6H ₂ O 1,000 ml. H ₂ O	5 g. NaCl 1.5 g. Na ₃ PO ₄ ·12H ₂ O 150 ml. NH ₃ (Aq) 850 ml. H ₂ O
D	8 g. AgNO ₃ 8 g. Mg(NO ₃) ₂ ·6H ₂ O 1,000 ml. H ₂ O	5 g. KCl 8 g. K ₄ P ₂ O ₇ ·3H ₂ O 125 ml. NH ₃ (Aq) 875 ml. H ₂ O
25 E	10 g. AgNO ₃ 8 g. Ca(NO ₃) ₂ ·3H ₂ O 1,000 ml. H ₂ O	6 g. NaCl 8 g. K ₄ P ₂ O ₇ ·3H ₂ O 150 ml. NH ₃ (Aq) 850 ml. H ₂ O
F	10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1,000 ml. H ₂ O	7 g. NaCl 10 g. Na ₂ SO ₄ 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
30 G	10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1,000 ml. H ₂ O	7 g. NaCl 10 g. Na ₂ SO ₄ 14 g. resin emulsion 180 ml. NH ₃ (Aq) 820 ml. H ₂ O
35 H	10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1,000 ml. H ₂ O	6 g. NaCl 10 g. Na ₂ SO ₄ 15 g. resin emulsion 100 ml. monoethanol amine 100 ml. NH ₃ (Aq) 800 ml. H ₂ O
I	10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1,000 ml. H ₂ O	7 g. NaCl 10 g. Na ₂ SO ₄ 160 ml. monoethanol amine 840 ml. H ₂ O
40 J	10 g. AgNO ₃ 10 g. Al(NO ₃) ₃ ·9H ₂ O 1,000 ml. H ₂ O	5 g. NaCl 200 ml. monoethanol amine 800 ml. H ₂ O
K	10 g. AgNO ₃ 10 g. Al(NO ₃) ₃ ·9H ₂ O 1,000 ml. H ₂ O	5 g. NaCl 100 ml. monoethanol amine 150 ml. NH ₃ (Aq) 750 ml. H ₂ O
45 L	10 g. AgNO ₃ 5 g. Al(NO ₃) ₃ ·9H ₂ O 5 g. Mg(NO ₃) ₂ ·6H ₂ O 1,000 ml. H ₂ O	5 g. NaCl 5 g. Na ₃ PO ₄ ·12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
M	10 g. AgClO ₄ 10 g. Al(NO ₃) ₃ ·9H ₂ O 1,000 ml. H ₂ O	5 g. NaCl 280 ml. NH ₃ (Aq) 720 ml. H ₂ O
50 N	10 g. AgNO ₃ 10 g. Al(NO ₃) ₃ ·9H ₂ O 1,000 ml. H ₂ O	10 g. NaBr 300 ml. NH ₃ (Aq) 700 ml. H ₂ O
O	10 g. Mg(NO ₃) ₂ ·6H ₂ O 1,000 ml. H ₂ O	10 g. Na ₃ PO ₄ ·12H ₂ O 3 g. AgCl 250 ml. NH ₃ (Aq) 750 ml. H ₂ O
55 P	10 g. AgClO ₄ 10 g. Al(ClO ₃) ₃ ·6H ₂ O 1,000 ml. H ₂ O	5 g. NaCl 280 ml. NH ₃ (Aq) 720 ml. H ₂ O
Q	10 g. AgNO ₃ 10 g. Ca(NO ₃) ₂ ·3H ₂ O 1,000 ml. H ₂ O	6 g. NaCl 10 g. Na ₂ SiO ₃ 150 ml. NH ₃ (Aq) 850 ml. H ₂ O

In every instance, except as noted, the treated fabric was antiseptic and self-sterilizing and resistant to discoloration upon exposure to light. The fabric treated using treatment "N" was initially yellowish in color due to the presence of yellow silver bromide on it but it was antiseptic and self-sterilizing. It is noted that in treatment "O" the water-soluble silver salt in the first solution was replaced with silver chloride dissolved in the ammoniacal second solution. Cotton cloth treated according to treatment "O" was not stable against discoloration by light. Furthermore, when ammonia in treatment "O" was replaced with an equivalent quantity of monoethanol amine, the treated sample discolored completely when exposed to sunlight for

three days. No such discoloration occurred in the case of treatments "H," "I," "J" and "K." The antiseptic and self-sterilizing qualities of the treated fabric were, however, satisfactory using either ammonia or monoethanol amine in treatment "O."

EXAMPLE 4

A first solution was prepared by dissolving 10 grams of silver nitrate and 5 grams of crystalline magnesium nitrate in 1000 milliliters of water. A second solution was prepared by dissolving 8 grams of sodium chloride, 10 grams of disodium phosphate and 200 milliliters of aqua ammonia in 800 milliliters of water. Two hundred grams of talcum powder was stirred thoroughly for 10 minutes with 400 milliliters of the first solution. Four hundred milliliters of the second solution was then added and the stirring continued for another 15 minutes. The mixture was filtered, the separated powder was washed with water until free of phosphate ions and then air dried over night and subsequently dried in an oven at 70°-90° C. The dry cake was then pulverized. The powder was pure white in color, did not discolor after 10 days' exposure to sunlight and was antiseptic and self-sterilizing.

In similar manner, and using solutions similar to those described above, titanium dioxide powder, dental magnesium carbonate and powdered aluminum oxide are rendered antiseptic and self-sterilizing.

EXAMPLE 5

Cotton sheeting was treated by the procedure described in Example 1 using first and second treating solutions, the compositions of which are given below in tabular form as treatments "R" to "U," inclusive.

Table of treatments

Treatment	First Solution	Second Solution
R.....	10 g. AgNO ₃ 15 g. Zn(NO ₃) ₂ :6H ₂ O.. 1,000 ml. H ₂ O.....	6 g. NaCl 27 g. Na ₂ P ₂ O ₇ :10H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
S.....	10 g. AgNO ₃ 15 g. Zn(NO ₃) ₂ :6H ₂ O.. 1,000 ml. H ₂ O.....	6 g. NaCl 24 g. Na ₂ P ₂ O ₄ :12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
T.....	10 g. AgNO ₃ 13 g. Al(NO ₃) ₃ :9H ₂ O.. 15 g. Zn(NO ₃) ₂ :6H ₂ O.. 1,000 ml. H ₂ O.....	8 g. NaCl 25 g. Na ₂ P ₂ O ₄ :12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
U.....	10 g. AgNO ₃ 13 g. Al(NO ₃) ₃ :9H ₂ O.. 15 g. Zn(NO ₃) ₂ :6H ₂ O.. 1,000 ml. H ₂ O.....	32 g. CaCl ₂ 200 ml. NH ₃ (Aq) 800 ml. H ₂ O

Nutrient agar was prepared, some of which contained 0.01 per cent of sodium thioglycolate and some of which contained 0.02 per cent cystine. Samples of sheeting which had been subjected to treatments "R," "S," "T" and "U" were tested using each of these nutrients according to the method of Example 1. In each instance the test showed the treated sheeting to be both antiseptic and self-sterilizing even in the presence of the cystine and sodium thioglycolate. No discoloration of any of the treated samples occurred on contact with the agar.

Further tests of the sheeting which had been subjected to treatments "R," "S," "T" and "U" were made using Sabouraud's dextrose agar (10 g. peptone, 40 g. dextrose, 15 g. agar and 1000 ml. distilled water) at pH 5.6 and employing *Trichophyton gypsum* and *Aspergillus itaconicus* (Glaucus group) as the test organisms. Incubation was for seven days at room temperature.

No growth of either organism occurred on the treated sample.

EXAMPLE 6

A modification of treatment "U" of Example 5 was carried out by soaking cotton toweling successively in solutions "a," "b" and "c" having the following compositions:

Solution "a":

8.5 g. Al(NO₃)₃:9H₂O
9.5 g. Zn(NO₃)₂:6H₂O
1000 ml. H₂O

Solution "b":

10 g. AgNO₃
7.5 g. Al(NO₃)₃:9H₂O
7.5 g. Zn(NO₃)₂:6H₂O
1000 ml. H₂O

Solution "c":

30 g. CaCl₂
200 ml. NH₃(Aq)
800 ml. H₂O

Soaking in each of solutions "a" and "b" was continued for five minutes and in solution "c" for four minutes. The toweling was squeezed gently after soaking in each solution and eventually washed thoroughly with distilled water after removal from solution "c" and then dried. Analysis of the washed and dried toweling showed it to contain 0.079 per cent by weight of silver, 0.034 per cent of aluminum and 0.074 per cent of zinc, each calculated as metal.

The treated toweling was antiseptic when tested on agar using *Staphylococcus aureus* as the test organism as described in Example 1. A sample of the treated toweling weighing one gram was boiled for 3 hours in one liter of soap solution and then for 3 hours in water without substantial decrease in its antiseptic value.

Another sample of the treated toweling was tested against *Staphylococcus aureus* on agar containing 0.02 per cent by weight of sodium thioglycolate and found to be antiseptic. Its antiseptic property in this medium was not destroyed by fifteen separate washings in hot soap solution.

Still another sample of the treated toweling was tested against *Staphylococcus aureus* on agar containing one per cent by volume of beef serum and found to be antiseptic both before and after fifteen separate washings in hot soap solution.

EXAMPLE 7

Co-precipitated aluminum hydroxide and silver chloride was prepared in the form of a powder having a strong bactericidal action by a modification of treatment "J" of Example 3. In this modification, a mixture of 6 g. AgNO₃, 241 g. Al(NO₃)₃:6H₂O, 200 ml. aqua ammonia, 6 g. NaCl and 1000 ml. H₂O was stirred thoroughly. Excess ammonia was nearly neutralized by adding dilute HCl slowly while stirring until the mixture was only weakly alkaline. After further efficient agitation for several minutes the mixture was filtered and the precipitate washed thoroughly on the filter with cold distilled water. Analysis of the filtrate and washings showed that 30 per cent of the silver used was retained in the precipitate. The washed precipitate when dried at 100°-110° C. was in the form of a white powder which was not discolored by exposure to strong sunlight. Higher drying temperatures resulted in the formation of rather hard lumps.

The powder was both antiseptic and germicidal. It is suitable for combining mechanically in small

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proportions with other powdered substances, e. g., talcum powder, dentrifice powders and the like, or for incorporating in ointments, to produce antiseptic and self-sterilizing mixtures. In such an instance, 1.0 g. of the powder was mixed thoroughly with 9 g. of dry starch. The mixture was then dispersed in cold water, boiling water was added and a fabric was "starched" using the solution and subsequently ironed in conventional fashion. Samples of the fabric were both antiseptic and self-sterilizing when tested on agar as in Example 1 using *Staphylococcus aureus* as the test organism.

The powder can also be used for sterilizing many types of liquids by stirring a small proportion of it with the liquid and filtering or by percolating the liquid through a bed of the powder.

EXAMPLE 8

A bactericidal powder was prepared by stirring together a mixture of 40 g. of calcium carbonate and a solution of 2 g. of silver fluoride in 200 ml. of water. A solution consisting of 10 g. calcium chloride, 50 ml. aqua ammonia and 150 ml. of water was then added and the mixture stirred for several minutes and then filtered. The precipitate was washed with water and dried at 70-90° C. It was antiseptic and self-sterilizing. The product contained silver chloride and calcium fluoride as the co-precipitated salts.

EXAMPLE 9

A sample of foam rubber was boiled with sodium thiosulfate to remove free sulfur and washed thoroughly with water. It was then boiled with an aqueous solution of copper sulfate to neutralize accelerators, such as sodium dibutyl-dithiocarbamate, and was treated and tested according to the method of Example 1. The sample was self-sterilizing and antiseptic.

EXAMPLE 10

Four solutions were prepared having the compositions given under "d," "e," "f" and "g" below.

Solution "d":

10 g. undecylenic acid
20 ml. ammonia (Aq)
1000 ml. H₂O

Solution "e":

10 g. CaCl₂
1000 ml. H₂O

Solution "f":

10 g. AgNO₃
5 g. Mg(NO₃)₂·6H₂O
1000 ml. H₂O

Solution "g":

8 g. NaCl
10 g. Na₃PO₄·12H₂O
16 g. resin emulsion
150 ml. ammonia (Aq)
850 ml. H₂O

Men's cotton socks were dipped successively in one case in solutions "d," "e," "f" and "g" and in another case in solutions "e," "d," "f" and "g," the socks being wrung fairly dry after each dip. The socks were finally dried and then washed thoroughly with water and again dried. Samples cut from the treated socks were tested by placing them on agar inoculated with *Trichophyton gypsum*. After incubation for 7 days at room temperature no growth of the organism on the sample was apparent. Identical results were obtained on samples of the treated socks after ten launderings in hot soap solution.

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EXAMPLE 11

Four solutions were prepared having the compositions given under "h," "i," "j" and "k" below.

Solution "h":

10 g. AgNO₃
5 g. Mg(NO₃)₂·6H₂O
1000 ml. H₂O

Solution "i":

8 g. NaCl
10 g. Na₃PO₄·12H₂O
200 ml. NH₃(Aq)
800 ml. H₂O

Solution "j":

25 g. CaCl₂
1000 ml. H₂O

Solution "k":

25 g. undecylenic acid
50 ml. NH₃(Aq)
950 ml. H₂O

Two hundred grams of talcum powder was stirred with 400 ml. of solution "h" for about 10 minutes. Four hundred milliliters each of solutions "i," "j" and "k" were then added in this respective order with agitation being continued for 5 to 10 minutes after each addition. The mixture was then filtered and the wet powder washed thoroughly with distilled water, dried and the lumps broken up. The dry treated powder was antiseptic, self-sterilizing and fungicidal when tested according to procedures given in Examples 1 and 5. No discoloration of the treated powder occurred upon exposure to sunlight for several days.

In similar experiments a portion of the free ammonia was neutralized following the addition of solution "k" by the careful addition of dilute hydrochloric acid, care being taken to retain considerable of the free ammonia in the solution up to and during the filtration. In this way a larger proportion of the silver was caused to remain in the powder. It was noted that when substantially all of the free ammonia was neutralized before filtration the light stability of the dry treated powder was seriously affected.

In still another variation of the procedure, solution "j" is replaced with an equal volume of a solution consisting of 20 grams of aluminum chloride in 1000 ml. of water, entirely similar results being obtained.

EXAMPLE 12

Two solutions were prepared having the compositions given under "l" and "m" below.

Solution "l":

100 g. Al(NO₃)₃·9H₂O
83 g. Zn(NO₃)₂·6H₂O
25 g. AgNO₃

500 ml. H₂O

Solution "m":

8 g. NaCl
65 ml. NH₃(Aq)
100 ml. H₂O

Two hundred grams of talcum powder was stirred with solution "l" for several minutes, solution "m" was added to the mixture and stirring was continued for several minutes longer. A portion of the free ammonia was then neutralized by the slow addition of dilute hydrochloric acid to the stirred mixture, care being taken that the final mixture still had a strong odor of ammonia. The mixture was then filtered and the wet powder washed thoroughly with water and dried. The final product was not discolored by exposure to

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light and was antiseptic, self-sterilizing and fungicidal when tested by the methods of Examples 1 and 5. It is useful as an additive for cosmetic and other powders to render them antiseptic, self-sterilizing and fungicidal.

EXAMPLE 13

Samples of cotton fabric and of talcum powder treated substantially as by the methods of Examples 1 and 12, respectively, using a first solution containing silver nitrate, zinc nitrate and water and a second solution containing sodium or ammonium undecylenate, sodium phosphate, free ammonia and water are found to be antiseptic, self-sterilizing and fungicidal when tested according to the methods of Examples 1 and 5. The treated materials are not discolored by exposure to light.

EXAMPLE 14

Silver undecylenate is prepared by mixing a solution of silver nitrate with a solution of sodium or ammonium undecylenate, filtering the mixture, washing the precipitate with water and drying the washed solid. Zinc undecylenate is prepared in a similar manner using zinc nitrate or chloride in place of the silver nitrate. Silver undecylenate is bactericidal and fungicidal and zinc undecylenate has good fungicidal properties. Both of these compounds are soluble in monoethanolamine.

A solution was prepared by dissolving one gram of silver undecylenate and one gram of zinc undecylenate in 60 ml. of monoethanolamine and adding 140 ml. of distilled water. The solution can be diluted with 20 or more times its volume of water without precipitation occurring.

Fifty milliliters of the solution containing about 0.5 per cent each of silver and zinc undecylenates was diluted with 200 ml. of water. Cotton fabric was soaked in the diluted solution for about two minutes and then air dried. The treated fabric is antiseptic, self-sterilizing and fungicidal when tested according to the methods of Examples 1 and 5 but discolors badly upon exposure to light.

It was noted that the above described solution containing 0.5 per cent of silver and zinc undecylenates does not cause discoloration of the skin or fingernails upon prolonged contact therewith. This property, coupled with its germicidal and fungicidal properties, is indicative of its value as a germicide and fungicide for use in contact with body tissues.

Similar results are obtained by replacing the monoethanolamine with diethanolamine, dibutyl amine and other amines in which the silver and zinc undecylenates are soluble. Similarly, also, the undecylenates can be replaced with silver and zinc salts of other aliphatic and unsaturated aliphatic acids, preferably those having a plurality of carbon atoms.

I claim:

1. The method for treating an article to render it antiseptic and self-sterilizing which includes the steps of: contacting the article with a first aqueous solution comprising a water-soluble silver salt and a first water-soluble salt of a metal other than silver; subsequently contacting the thus treated article with a second aqueous solution comprising a second water-soluble salt, the anion of which is selected from the group consisting of halides and phosphates, and a third water-soluble salt, the anion of which forms a water-insoluble compound with the metal cation of the

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first water-soluble salt, and a water-soluble basic nitrogen compound, whereby a water-insoluble silver salt and a water-insoluble metal compound are formed, said metal compound functioning as an effective stabilizer of the silver salt against the effect of light normally tending to discolor said silver salt; and then removing the basic nitrogen compound from said article.

2. The method of claim 1 wherein the basic nitrogen compound is selected from the group consisting of ammonia and amines.

3. The method of claim 1 wherein the basic nitrogen compound is ammonia.

4. The method of claim 1 wherein the second and third water-soluble salts are the same salt.

5. The method of claim 1 wherein the treated article is a fibrous fabric and contains not more than about one per cent of silver, calculated as silver chloride, based on the dry weight of the article.

6. The method of claim 1 wherein the second and third water-soluble salts are different salts.

7. The method of claim 1 wherein the water-soluble silver salt is silver nitrate, the first water-soluble salt is magnesium nitrate, the second water-soluble salt is sodium chloride, the third water-soluble salt is a sodium phosphate and the solubilizer is ammonia.

8. The method of claim 1 wherein the article treated is a fabric and the second and third water-soluble salts are different salts.

9. The method of claim 1 wherein the article treated is a water-insoluble powder.

10. The method for treating an article to render it antiseptic and self-sterilizing which includes the steps of: contacting the article with a first aqueous solution comprising a water-soluble silver salt, a first water-soluble salt of a metal other than silver and a water-soluble salt furnishing fungicidal cations; subsequently contacting the thus treated article with a second aqueous solution comprising a second water-soluble salt, the anion of which is selected from the group consisting of halides and phosphates, a third water-soluble salt, the anion of which forms a water-insoluble compound with the metal cation of the first water-soluble salt, a water-soluble salt whose anion forms a water-insoluble salt with the fungicidal cations, and a water-soluble basic nitrogen compound, whereby a water-insoluble silver salt, a water-insoluble fungicidal salt and a water-insoluble compound of the metal other than silver are formed, said metal compound functioning as an effective stabilizer of the silver salt against the effect of light normally tending to discolor said silver salt; and then removing the basic nitrogen compound from the said article.

11. The method of claim 10 wherein the water-insoluble fungicidal compound is a zinc salt.

12. The method for treating an article to render it antiseptic and self-sterilizing which includes the steps of: contacting the article with a first aqueous solution comprising a water-soluble silver salt, a first water-soluble salt of a metal other than silver and a water-soluble salt furnishing cations of a water-insoluble salt of which the anions are fungicidal; subsequently contacting the thus treated article with a second aqueous solution comprising a second water-soluble salt, the anion of which is selected from the group consisting of halides and phosphates, a third water-soluble salt, the anion of which forms a water-insoluble compound with the metal cation of the first water-soluble salt, a water-

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soluble salt whose anion is the said fungicidal anion, and a water-soluble basic nitrogen compound, whereby a water-insoluble silver salt, water-insoluble fungicidal salt and a water-insoluble compound of the metal other than silver are formed, said metal compound functioning as an effective stabilizer of the silver salt against the effect of the light normally tending to discolor said silver salt; and then removing the basic nitrogen compound from the said article.

13. The method of claim 12 wherein the water-insoluble fungicidal salt is a salt of undecylenic acid.

14. An article having on the surfaces thereof a tightly adherent coating comprising a coprecipitated mixture of a water-insoluble silver salt selected from the group consisting of halides and phosphates and at least one other water-insoluble compound of a metal other than silver, said metal compound functioning as an effective stabilizer of the silver salt against the effect of light normally tending to discolor said silver salt and said article being characterized by being antiseptic and self-sterilizing after repeated washing in hot soap solution and by undergoing substantially no discoloration upon exposure to sunlight.

15. An article as claimed in claim 14 wherein the article is a fibrous article.

16. An article as claimed in claim 14 wherein the insoluble silver salt is a silver halide.

17. An article as claimed in claim 14 wherein the water-insoluble compound other than the silver salt comprises the cation and the anion, respectively, of water-soluble salts.

18. An article as claimed in claim 14 wherein the anions of the water-insoluble silver salt and of the water-insoluble compound of a metal other than silver are the same.

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19. An article as claimed in claim 14 wherein the anions of the water-insoluble silver salt and of the water-insoluble compound of a metal other than silver are different.

20. An article as claimed in claim 14 wherein the article is a fabric and the anions of the water-insoluble silver salt and of the water-insoluble compound of a metal other than silver are different.

21. An article having on the surfaces thereof a tightly adherent coating comprising a coprecipitated mixture of a water-insoluble silver salt selected from the group consisting of halides and phosphates, a water-insoluble fungicidal salt and at least one other water-insoluble compound of a metal other than silver, said metal compound functioning as an effective stabilizer of the silver salt against the effect of light normally tending to discolor said silver salt and said article being characterized by being antiseptic, self-sterilizing and fungicidal after repeated washing in hot soap solution and by undergoing substantially no discoloration upon exposure to sunlight.

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