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CELLULOSIC SPINNING SOLUTION

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The present invention relates to a process of producing artificial silk of cellulosic origin having bactericidal properties, especially when being contacted by vapors or liquid substances.

The primary object of this invention relates to the production of antiseptic, cellulosic filaments and yarns containing one or more colloidal metals in combination with one or more dissimilar, colloidal metal salts.

Another object of my invention has to do with a process of increasing the bactericidal powers of colloidal metals and colloid metal compounds by irradiating them with ultra-violet rays prior to their incorporation into cellulosic spinning solutions.

Other objects of my invention will become apparent to those skilled in the art after a study of the following specification.

I am well aware that it has, heretofore, been proposed to use colloidal metals as disinfectants (vide Rideal, "Disinfection and Sterilization", 1921, pages 206–9), and to impregnate textile fibers with metallic salts and colloidal hydroxides (vide U. S. Patents Nos. 22,362, 1,482,416, 1,536,254, and 1,717,483) to prevent fungous growth thereon.

However, I have found by experimentation that a colloidal metal or a colloidal metal compound does not have a sufficient sterilizing power after being imbedded into cellulosic fibers. After a thorough investigation of the effect of colloidal metals as well as colloidal metal compounds upon non-pathogenic and pathogenic microorganisms, such as bacteria and molds, I have found that the bactericidal effect of the aforementioned substances can be substantially increased and accelerated by distributing a combination of colloidal metals and colloidal metal compounds in a spinning solution or filament of cellulosic origin.

In order to increase and/or accelerate the bactericidal properties of colloidal metals and metal compounds, it is necessary to select at least one metal in combination with a metal compound to form a bactericidal agent, i. e., disinfectant. Thus, I may combine, for example, copper with cuprous oxide or sulfide, cupric selenide with cuprous oxide, etc. I may also combine an electro-positive element chosen from the lighter metals of the second and third periodic groups and an electro-negative electrode element chosen from the oxygen family in the sixth periodic group, for example, magnesium as the electro-positive electrode element and a selenide of a copper alloy as the electro-negative electrode element, all of these elements being colloidally dispersed.

When microorganisms, such as bacteria, molds, etc., are distributed in a liquid phase and subsequently a solid phase, such as a colloidal metal added thereto, they are killed after a while and the liquid phase becomes sterile. The time consumed to paralyze the protoplasma of microorganisms depends naturally upon the species of microorganisms treated, the chemical composition and temperature of the nutritive solution and the amounts and chemical properties of the colloidal metals and metal compounds used as disinfectants. The physico-chemical principles underlying this sterilization are unknown, although the theory has been advanced that the colloidal metal particles become adsorbed to the membranes of the microorganisms and in turn prevent proper assimilation of nutritive substances. Other investigators have claimed that invisible rays are emitted by the colloidal particles which paralyze protoplasma. I have been unable to definitely find the cause why cells of microorganisms are much more rapidly killed in the presence of a colloidal metal and a dissimilar colloidal metal compound. Whether or not this theory is correct, I have definitely found that microorganisms are much more rapidly killed by disinfectants comprising one or more dissimilar metals in combination with one or a plurality of colloidal metal compounds, than by a single colloidal metal, two or more colloidal metals unable to set up a potential difference, a single colloidal metal salt or a plurality of colloidal metal salts unable to set up a potential difference.

Table I depicts the results obtained by using various colloidal substances, in accordance with the present invention, to sterilize aqueous suspensions of *Bacillus coli*. To obtain comparable results, aqueous suspensions of *Bacillus coli* were prepared by inoculating it into sterile water. Subsequently equal amounts of this bacterial suspension were transferred by means of a platinum loup into test tubes containing identical quantities

of sterile beef broth-gelatine. After thoroughly shaking each inoculated test tube to evenly distribute the bacterial cells in the nutritive, molten gelatine, an equal amount of disinfectant was added to the test tubes and the same incubated, after thorough shaking, at a temperature of about 37.5° C. To determine the exact period of time necessary to sterilize the cultures, each tube was opened at five minute intervals under sterile conditions and a loop of the cultures inoculated into new sterile beef broth-gelatine tubes. The first tube of each series, showing no growth on incubation for several days, was considered the characteristic one for each disinfectant tested.

Table I

Bacillus coli cultivated in beef broth-gelatine at 37.5° C.

One loop of bacterial suspension inoculated into every test tube containing 10 cc. of gelatine, 0.1 g. of disinfectant in 1 cc. of distilled water and 0.01 g. gelatine as protective colloid.

Disinfectant	Times of treatment in minutes								
	0	10	20	30	40	50	60	70	80
Colloidal copper	×	×	×	×	–	–	–	–	–
Colloidal silver	×	×	×	×	×	×	–	–	–
Colloidal copper plus cuprous oxide in dark	×	×	×	×	×	×	×	–	–
Colloidal copper plus cuprous oxide in diffused light	×	×	–	–	–	–	–	–	–
Colloidal gold	×	×	×	×	×	–	–	–	–
Colloidal gold plus cuprous oxide plus copper	×	–	–	–	–	–	–	–	–

× indicates that *Bacillus coli* is growing.
– indicates that *Bacillus coli* is dead.
When using composite disinfectants, equal amounts of each ingredient were used to make up 0.1 g. of disinfectant, for example 0.05 g. copper plus 0.05 g. cuprous oxide, etc.

I have, furthermore, found that colloidal metals and metal salts, irradiated with ultra-violet rays, prior to being used as disinfectants, have a greater bactericidal power than non-irradiated ones. Although ultra-violet rays stimulate the aforementioned colloidal disinfectants to a higher degree than day light, it is to be noted that a prolonged irradiation fails to increase the bactericidal effect of a disinfectant beyond a fixed limit. This limit varies for each metal, metal salt and compositions thereof and must be determined by experiment, in other words, each colloidal agent has a definite optimum time of irradiation. Overexposure to ultra-violet rays does not deleteriously effect the colloidal disinfectants, but it should be avoided for reasons of economy. I am unable to define the complex reactions which evidently take place in such irradiated dispersions, but I have definitely found that the agents, cited above, substantially increase their bactericidal power after being irradiated. This stimulation by means of irradiation is so pronounced that even the walls of glass flasks in which they are kept acquire bactericidal properties. When, for example, all colloidal metals and/or colloidal metal salts are removed from such a flask by rinsing and the same filled with a suspension of virulent bacteria, they will be killed after standing for some time. This experiment can be repeated several times, the glass walls acting as disinfectants in the absence of colloidal particles, at least I have been unable to detect with the microscope any particle adsorbed to the glass walls of such flasks. Although I am unable to explain this phenomena, a marked increase of the bactericidal power of my agents is obtained by pre-irradiation. Table II depicts some results obtained by this method.

Table II

Effect of irradiation

All dispersions were irradiated with ultra-violet rays in open glass dishes prior to being used as disinfectants. After inoculation the tubes were kept in a dark incubator (see Table I).

Disinfectant	Periods of time required for complete sterilization in minutes	
	Irradiated	Not irradiated
Colloidal copper	20	30
Colloidal silver	55	60
Colloidal copper plus colloidal cuprous sulfide	12	60
Glass flask after removing all disinfectants with water, first trial	120	----------
Second trial after removing bacterial suspension and addition of living bacteria	About 4 hours.	----------

Similar results were obtained with spores of *mucor* and *oidium* species, although they are more resistant to destruction. After standing in the dark for 14 days the irradiated colloidal disinfectants were again compared with the non-irradiated ones. The pre-irradiated disinfectants had retained a higher sterilizing power than the non-irradiated ones. It is to be noted, however, that the stimulation, obtained by pre-irradiation, slowly abates on standing, and that it may be revived by a second irradiation, etc.

The colloidal dispersions may be prepared by well known processes to form suitable disinfectants. The metals may be dispersed by electrical means and held in aqueous suspension by adding thereto suitable protective colloids, such as gelatine, agar, gums, alginates, casein, soluble silicates, protalbic acid, etc, Colloidal metals may also be formed by chemical precipitation in aqueous solutions. Subsequently the byproducts may be removed by dialysis, the colloidal particles suspended in water and protective colloids added thereto as stabilizing agents. Colloidal salts may be prepared by grinding, for example, oxides, hydroxides, sulfides, etc., in pebble or colloid mills to microscopic fineness. They may also be formed by chemical reaction and purified by dialysis. Colloidal copper, for example, may be prepared in the following manner. A 20% aqueous solution of copper sulphate, containing about 10 to 20% saccharose is boiled for a few minutes and subsequently diluted with an equal amount of distilled water, this comprising solution No. 1. Solution No. 2 consists of a 14% aqueous solution of sodium or potassium hydroxide. Solution No. 3 is prepared by adjusting sulphuric acid that 1 cc. thereof corresponds to 2 ccs. of the hydroxide solution. Solution No. 4 is obtained by dissolving approximately 5 g. of gelatine in 100 ccs. of distilled water. After having prepared solutions 1 to 4, 10 ccs. of solution No. 1 are mixed with 40 ccs. of solution No. 4 and the mixture boiled on a water bath for a few minutes. About 5 to 6 ccs. of solution No. 2 are added to the hot mixture to precipitate colloidal cuprous hydroxide. This cuprous oxide may be purified by dialysis and used in combination with colloidal metals according to my invention. To form colloidal copper from cuprous hydroxide, the solution is again boiled and subsequently about 3 ccs. of solution No. 3 added. Red colloidal copper is spontane-

ously precipitated which is purified by dialysis. The colloidal copper dispersion tends to coagulate on prolonged standing, but it may be stabilized by a small addition of alcoholic potassium citrate solution, etc. Instead of using sulphuric acid to form colloidal copper, any acid may be employed in which colloidal copper is insoluble. Such colloidal metals may be also prepared by reducing water-soluble metal salts with aldehydes, p-aminophenol, etc., 1 g. of gold chloride, for example, is dissolved in a few ccs. of distilled water and added to 500 ccs. of a 10% aqueous solution of vinyl alcohol. After addition of a mixture of 40 ccs. of formaldehyde and 40 ccs. of n-sodium carbonate solution, colloidal gold is precipitated which may be purified by dialysis. Instead of vinyl alcohol, other protective colloids may be used. Ammonia added to water-soluble chromium chloride, for example, in the presence of vinyl alcohol results in the formation of colloidal chromium hydroxide. In a similar manner other colloidal metal hydroxides may be formed. Colloidal metals and metal compounds may be also prepared in the following manner. 10 g. of silver nitrate is mixed with 100 g. of cholesterine or phytosterine and the mixture heated to about 250° C. until a silver mirror appears on the surface of the composition. The composition containing colloidal silver may be dissolved in oils, such as olive oil, Turkey red oil, etc. When lead peroxide is treated in this manner in the presence of silver nitrate, a mixture of colloidal lead and silver is obtained which may be dissolved in oils. By melting, for example, cobalt nitrate with uranyl nitrate in cholesterine, colloidal cobalt oxide and uranyl oxide is obtained, which may be taken up in chloroform or oils. When such metal organosols are incorporated into cellulosic spinning solutions, bactericidal filaments are obtained which are simultaneously delustered.

Example

By incorporating metal salts, which are insoluble in the spinning solution per se, together with colloidal metals, for example colloidally dispersed titanium dioxide in combination with colloidal copper, silver, gold, etc., not only antiseptic but delustered products are obtained. It is to be noted that only such colloidal metal salts can be used which are substantially insoluble in the spinning solution to which they are added. Metallic salts which dissolve as crystalloids in spinning solutions cannot be used in accordance with my invention.

This invention is naturally not limited to the production of filaments or yarns, but also antiseptic ribbons, sheets and the like may be formed from the spinning solutions. In this manner it is possible to produce sterile sausage casings, wrapping materials, filter cloths, etc.

I wish to point out that the above example is merely illustrative, and I do not wish to be limited to the exact proportions set forth above, which are typical combinations, since certain of these ingredients may be omitted or replaced by others of similar nature, and the proportions within wide limits may be varied. In other words, while I have found that the colloidal metals and metal salts, above mentioned, give the desired results, I do not wish to be limited to the use of all of these substances and no others, nor the exact proportions and concentrations, set forth above, as the omission of some ingredients or a slight variation of proportions will not adversely affect the final products, although it may somewhat vary the relative characteristics of such products, resulting from such variations. The expression "colloidal metal salts" in the specification as well as in the claims means: metal salts which are substantially insoluble in cellulosic spinning solutions, which are, thus, dispersable therein and which are able to set up a more or less large potential difference with a dissimilar, colloidal metal in the presence of minute quantities of electrolytes. Modifications may be made in details of the method and the product without departing from the spirit and scope of my invention, as defined by the appended claims.

I claim:

1. A spinning solution for the manufacture of products having bactericidal properties comprising a cellulosic spinning solution of the group consisting of viscose, cuprammonium cellulose, cellulose esters and cellulose ethers, a colloidal metal and a dissimilar colloidal metal salt dispersed therein, said metal salt being able to set up a potential difference in the presence of a colloidal metal and an electrolyte, and said metal and metal salt being chemically inert to said spinning solution.

2. A spinning solution for the manufacture of products having bactericidal properties comprising a cellulosic spinning solution of the group consisting of viscose, cuprammonium cellulose, cellulose esters and cellulose ethers, a colloidal metal and a dissimilar metal salt, said metal and metal salt being pre-irradiated with ultra-violet rays and able to set up a potential difference in the presence of an electrolyte, and said metal and metal salt being chemically inert to said spinning solution.

3. A spinning solution for the manufacture of products having bactericidal properties comprising a viscose spinning solution, a colloidal metal and a dissimilar colloidal metal salt, said metal salt being able to set up a potential difference in the presence of a colloidal metal and an electrolyte, and said metal and metal salt being chemically inert to said spinning solution.

4. A spinning solution for the manufacture of products having bactericidal properties comprising a viscose spinning solution, a colloidal metal and a dissimilar colloidal metal salt, said metal salt being pre-irradiated with ultra-violet rays and able to set up a potential difference in the presence of a colloidal metal and an electrolyte, and said metal and metal salt being chemically inert to said spinning solution.

5. A bactericidal cellulosic product of the group consisting of viscose, cuprammonium cellulose, cellulose esters and cellulose ethers containing a colloidal metal and a dissimilar colloidal metal salt uniformly dispersed therein.

6. A bactericidal cellulosic product of the group consisting of viscose, cuprammonium cellulose, cellulose esters and cellulose ethers containing a colloidal metal and a dissimilar colloidal metal salt uniformly dispersed therein, said metal and metal salt being pre-irradiated with ultra-violet rays.

7. A bactericidal viscose product containing a colloidal metal and a dissimilar colloidal metal salt uniformly dispersed therein.

8. A bactericidal viscose product containing a colloidal metal and a dissimilar colloidal metal salt uniformly dispersed therein, said metal and metal salt being pre-irradiated with ultra-violet rays.

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