

UNITED STATES PATENT OFFICE

2,510,510

GERMICIDAL DETERGENT COMPOSITION

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No Drawing. Application October 3, 1945,
Serial No. 620,172

9 Claims. (Cl. 252-107)

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This invention relates to improved germicides and germicidal detergents and water softening compositions, and more particularly to silver-containing glassy systems of value for such uses.

The usefulness of silver as a germicide has long been recognized. Numerous silver-containing compounds have been used as antiseptics, such as silver acetate, silver bromide, silver chloride, and silver citrate. Silver iodide has been used in preparing colloidal silver preparations, and silver nitrate has also been used for this and numerous other purposes. Various silver vitellin preparations have been used as antiseptics in the treatment of the eyes, nose and throat.

Most such silver compounds are possessed of certain undesirable characteristics which detract from their usefulness. For the most part, they are sensitive to light and tend to precipitate free silver upon exposure to light. This property is a distinct disadvantage in the use of these compounds and compositions as antiseptics. The shelf life of most silver-containing germicides is short and somewhat undependable. Further, it has been considered impractical to use silver preparations in or with natural water solutions because of incompatibility. So far as I am aware no satisfactory germicidal detergent or germicidal water softening composition, in which the germicidal properties are due to silver, have been heretofore suggested.

The products of the present invention are glassy systems comprising the phosphates and polyphosphates of silver, the complex phosphates and polyphosphates of silver and another metal or metals, advantageously an alkali metal or alkaline earth metal, or both, and compositions which contain one or more such glassy materials along with other materials which are useful from the standpoint of imparting detergent or water softening properties to the compositions, or enhancing the germicidal properties of the silver.

The glassy products of the invention are essentially fusion products which may be regarded as formed of one or more metal oxides and phosphorous pentoxide, although not necessarily or even desirably produced from metal oxide and phosphorous pentoxide, and in which the atomic or molecular arrangement is that typical of glassy systems as distinguished from crystalline systems. The invention includes products which are predominantly or primarily glassy in nature but which may include a considerable proportion of crystalline material imbedded in the glassy matrix. The products may be in the form of powder, granules, globules or beads, flakes or the like, and the term "glassy" is not intended to denote the gross physical form of the products, but rather their atomic or molecular arrangement.

The glassy silver-containing phosphates of the

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invention are not noticeably affected by light, and do not stain the skin. They may be used with soaps, in acid, neutral or alkaline solution, and are resistant to precipitation on contact with organic materials found in wash or other solutions. For these reasons, and in view of the high activity of the compositions, that is, high germicidal effectiveness with low concentration of silver, they are of benefit as germicides and of particular advantage in germicidal detergents and as germicidal water softening agents.

The new compositions themselves may be effective water softening agents and may have effective detergent properties, as when the compositions consist of complex glassy phosphates containing some silver and substantial proportions of alkali metal, or the compositions may be essentially germicidal in nature as in the glassy products in which silver is the sole or predominating metal and in either case they may be associated with appropriate detergent or water softening materials, such as alkaline salts, soaps, synthetic detergents such as sulfated alcohols, sulfated monoglycerides, sulfonated alkyl naphthalene derivatives, meta or polyphosphates and the like. The glassy silver-containing phosphates exhibit high activity over a wide range of pH, and therefore may be used with advantage to impart germicidal properties to water softening or detergent compositions which may be acid, neutral or alkaline in character, thus embracing substantially the entire range of the recognized water softening and detergent materials.

The germicidal compositions of the invention include the glassy silver phosphates, ranging from fused silver metaphosphate



up to the fused silver pyrophosphate



and complex fused glassy products, having in addition to a silver content a content of other metal or metals, advantageously alkali metal or alkaline earth metal, although products containing other metals than these are included. The exact composition or structure of these fused or glassy products is not known, but it is common practice to designate products of this type (i. e. "glasses") in terms of their content of metal oxide and phosphorous pentoxide, as, for example in the case of glassy silver tetrapolyphosphate, which may be designated as $3\text{Ag}_2\text{O}:\text{P}_2\text{O}_5$, and in general this system of nomenclature will be followed in this specification.

The invention includes, as new products, the fused silver phosphates in which the $\text{Ag}_2\text{O}:\text{P}_2\text{O}_5$ ratio is between about 1.1:1 and about 1.9:1, which products are advantageous for use as germicides, or as ingredients of germicidal deter-

gents or water softeners, and the complex fused products which contain, considered analytically, in addition to silver oxide and phosphorous pentoxide, the oxide of another metal or metals, particularly of an alkali metal or metals or combinations of the alkali metals and the alkaline earth metals, although glassy products containing other metals, such as the heavy metals, are included.

While the glassy silver phosphates themselves exhibit remarkably high germicidal activities, the products in which the silver is associated with another metal or metals, particularly one or more of the alkali metals, because they show even more pronounced germicidal activity, calculated on the basis of silver content required for effective killing action against typical microorganisms, and because the inclusion of a proportion of alkali metal in the glassy product has the effect of substantially increasing solubility or rate of solubility, are of particular advantage for use in or as germicidal detergents and water softening agents, where the expense of the silver is an item of consequence. Thus, complex glassy phosphate systems containing both silver and sodium which show highly effective germicidal activity, as exhibited by the killing of 99.5% of *E. coli* by standardized tests with silver concentrations as low as 1 or 2 parts per million, are readily prepared in accordance with the invention and are of great value for use in germicidal detergents or water softening materials.

Furthermore, in these complex products containing an alkali metal in addition to the silver, and which contain but a small proportion of silver such as is economically feasible in a germicidal detergent or water softener, the silver seems to reduce the hygroscopicity of the product well below that of the alkali metal metaphosphates and polyphosphates more or less commonly used today in detergents and water softening agents, and the glassy compositions of this invention are less susceptible to caking than are these present day commercial products, in addition to the fact that they are remarkably effective germicidally.

In contrast with the previously known silver germicides the products of the present invention are quite reliable, and their germicidal action is quite reproducible. They do not exhibit the erratic action frequently observed with silver nitrate, for example. They are also quite lacking in caustic properties, and are not irritating or caustic as are many of the known silver germicides, such as silver nitrate. They may therefore be used even in solutions to which the skin is subjected for prolonged periods, such as in compositions for hand dish-washing, without producing undue irritation or caustic effects.

The new compositions are effective against both gram positive and gram negative organisms, in contrast with many germicidal materials, which are effective against one or the other but not both types. The new compositions may be used in water of relatively high temperature, as their germicidal activity is not destroyed at temperatures normally experienced with detergents, water softeners or the like.

In general, for simple germicidal compositions, consisting essentially of silver oxide and phosphorous pentoxide, to be used as germicides or disinfectants, the silver concentration in the products may be quite high, ranging as high as about 71%, compositions which correspond to a silver oxide, phosphorous pentoxide ratio of 1.1:1 to 1.9:1 being particularly valuable. Such glassy

compositions, consisting essentially of silver oxide and phosphorous pentoxide (fused as a glass) may also be used in germicidal detergent compositions and germicidal water softening compositions by admixture with appropriate detergent or water softening ingredients such as soaps, synthetic detergents, sodium phosphates, particularly metaphosphates and polyphosphates, alkaline salts such as sodium metasilicate and the like, but in general for these latter purposes, the complex products containing an alkali metal, or an alkali metal and an alkaline earth metal, in addition to the silver, are advantageous. Extensive tests have shown that on the basis of silver content of the solution tested, the complex phosphates containing silver oxide, sodium oxide or the like and phosphorous pentoxide, as by fusing together a mixture of materials which gives a glassy phosphate containing a relatively small percentage of silver, such as about 2%, are more effective germicidally than are the compositions consisting essentially of silver oxide and phosphorous pentoxide. This we attribute to the fact that the phosphate radical exerts an enhancing action in compositions containing silver as the effective germicidal material and substantially promotes the activity of the silver, such as to make it more effective, or effective in a lower concentration, or more resistant to inactivating influences of other materials, such as the constituents of natural water, organic matter, and the like.

For industrial germicidal detergent purposes, as for materials intended for use in washing dishes or other utensils, for disinfecting purposes, and the like, the final detergent compositions will ordinarily not contain more than about 2% of silver, and effective compositions containing substantially less silver than this may be readily prepared in accordance with the invention. In general, it is advantageous to have the silver present, not as a simple glassy silver phosphate, but as a glassy complex phosphate containing silver and alkali metal or alkali metal and alkaline earth metal, and to include along with this complex glassy phosphate, which itself may have, and usually will have, effective water softening properties, one or more of the commonly used detergents such as sodium metasilicate, trisodium phosphate, a synthetic wetting agent, such as one of the Nacconols, or the like. Effective detergents with a soap base may be produced by mixing one of these complex phosphates with a soap, such as a white soap flake, white floating soap, or a laundry soap, consisting of soap plus alkaline salts, usually silicate. For special germicidal detergent purposes, as for a product adapted for surgical and hospital use, as in the washing of hands of surgeons, cleaning of surgical instruments, operating rooms, etc., products containing considerably more silver, for example up to 5% of silver, are practical from a cost standpoint and may be regarded as effective germicidal detergents within the scope of this invention. Again it is advantageous to use the complex silver-alkali metal or alkali metal-alkaline earth metal phosphates rather than the simple silver phosphates, in all cases the phosphate being in the form of the glassy systems previously described.

For germicidal detergent and water softening compositions, the solubility of the product is a factor of some importance. The alkali metal silver phosphates of the invention, probably because of the influence of the alkali metal and the lower content of silver, are, particularly where the alkali

metal content is relatively high, relatively soluble and advantageous for that reason. In some cases, a product which dissolves slowly is of advantage and for such purposes, products which contain but a small amount of alkali metal and have correspondingly increased content of silver or of alkaline earth metal or both are advantageous.

The products used in accordance with the invention may be prepared by mixing together appropriate metal phosphates for any desired composition and then fusing them and quenching the melt to obtain a glassy product. Compounds other than phosphates may be included in the mixture which is fused providing harmful elements are not used or such undesired element or elements are volatile under the conditions of fusion. Thus the silver polyphosphates may be prepared by fusing together in appropriate proportions such materials as silver orthophosphate, silver pyrophosphate, silver metaphosphate, phosphoric acid or phosphorous pentoxide, silver oxide, silver compounds in which the undesired element or elements are volatile under the conditions of fusion, or selected groups of such materials.

The silver phosphate to be obtained may be considered as consisting of the oxides Ag_2O and P_2O_5 in the desired ratio and by appropriate selection of the mixture to be fused the desired glassy phosphate may be obtained. Thus it will be noted that the compound silver metaphosphate may be considered as consisting of the oxides Ag_2O and P_2O_5 in a one to one ratio (1:1) and that the compound silver pyrophosphate may be considered as consisting of the oxides Ag_2O and P_2O_5 in the ratio of two to one (2:1). Thus, by using appropriate quantities of silver metaphosphate and silver pyrophosphate, compositions consisting of any ratio of the oxides between one to one and two to one (1:1 and 2:1) may be obtained. Likewise it will be seen that by using silver orthophosphate, which has a metal oxide to P_2O_5 ratio of three to one (3:1) and another silver phosphate or phosphorous pentoxide in appropriate proportions, it will be possible to prepare a silver phosphate of any desired metal oxide to P_2O_5 ratio.

It has long been known that the alkali-metal polyphosphates, and in particular sodium polyphosphates, may be prepared by fusing together appropriate quantities of NaOH and H_3PO_4 (or certain sodium phosphates), and then quickly chilling the melt. Glassy polyphosphates of various compositions are obtained. By inclusion of an appropriate amount of silver oxide, a silver phosphate or other suitable silver-containing compound in a mixture so fused, complex phosphates containing silver and alkali metal are readily prepared, while by the addition of calcium oxide or phosphate or magnesium oxide or phosphate or the like, the corresponding complex phosphates of silver, alkali metal and alkaline earth metal may be prepared. Manifestly, such materials as sodium carbonate may be used as constituents in preparing the materials in accordance with well known practice, as may other metal oxides or metal compounds as those of the heavy metals.

The invention will be illustrated by the following examples, but it is not limited thereto:

EXAMPLE 1

A mixture consisting of 74.752 parts by weight of silver metaphosphate, and 60.552 parts of silver pyrophosphate was intimately mixed and fused. The melt was quickly chilled by pouring

it upon a cooled stainless steel slab in small beads. The composition of the above fusion may be considered as Ag_2O and P_2O_5 in the ratio 4:3, and corresponds to the hypothetical compound $\text{Ag}_4\text{P}_3\text{O}_{13}$, having a silver content of 63.75%.

EXAMPLE 2

A mixture consisting of 37.376 parts by weight of silver metaphosphate and 60.552 parts of silver pyrophosphate was treated as in Example 1, by mixing, fusing, and chilling. The composition yielded consists of Ag_2O and P_2O_5 in the ratio of 3:2 and corresponds to the formula $\text{Ag}_3\text{P}_2\text{O}_{11}$ having a silver content of 66.09%. The chilling slab is ordinarily maintained as close to room temperature as is possible.

EXAMPLE 3

A mixture of 18.688 parts of silver metaphosphate and 60.552 parts of silver pyrophosphate was treated as in Example 1, by mixing, fusing and chilling. The resulting product contains Ag_2O and P_2O_5 in the ratio of 5:3 and corresponds to the formula $\text{Ag}_5\text{P}_3\text{O}_{16}$ having a silver content of 68%.

EXAMPLE 4

27.73 grams of silver metaphosphate was treated with 10 ml. of 85% orthophosphoric acid (having a specific gravity of 1.689, and being equivalent to 10.39 grams of P_2O_5). Upon strong heating a clear fusion was obtained. The product was quenched by pouring onto a cold steel slab. It has a composition corresponding to the formula $\text{Ag}_2\text{O} \cdot 2\text{P}_2\text{O}_5$ and contains 40.5% silver.

EXAMPLE 4A

A glassy sodium silver polyphosphate with a $\text{MO}:\text{P}_2\text{O}_5$ ratio of 1.1:1 and a silver content of 0.5% was made as follows. 24.75 grams of silver nitrate was dissolved in a small amount of water and added to 2484 milliliters of 75% phosphoric acid. This solution was then poured slowly over, and thoroughly mixed with, 1750 grams of sodium carbonate in a steel pan. This mixture was then dehydrated and the dry material transferred to a crucible, placed in a furnace and melted and held at above the melting temperature for a short time. The melt was then quenched by pouring onto a cooled stainless steel slab.

EXAMPLE 5

An intimate mixture consisting of 20 parts by weight of a sodium polyphosphate ($4\text{Na}_2\text{O} \cdot 3\text{P}_2\text{O}_5$) and 0.6 part of Ag_3PO_4 was prepared. It was then fused, the temperature required being about 700°C . The mass was then quickly chilled by pouring in a thin layer or in small beads upon a chilled or cooled stainless steel slab. The product is a glassy material, and contains 2.26% silver.

EXAMPLE 6

A mixture of 9.415 parts by weight of a sodium polyphosphate ($4\text{Na}_2\text{O} \cdot 3\text{P}_2\text{O}_5$) together with 4.16 parts of $\text{Ag}_4\text{P}_3\text{O}_{17}$ and 5.0 parts AgPO_3 , after being intimately ground together, was fused. The mass was then quickly chilled by pouring in a thin layer or in small beads upon a stainless steel slab. The resulting glassy product contains 31.3% silver.

EXAMPLE 7

A mixture of 5 parts by weight of KH_2PO_4 , 7.5 parts by weight of K_2HPO_4 and 0.573 part by

weight of AgPO_3 , after being intimately ground together was fused. The mass was then quickly chilled by pouring in a thin layer or in small beads upon a cold stainless steel slab. The resulting product is a glassy material approximating the composition of potassium-silver tetraphosphate in which the metal oxide to P_2O_5 ratio is 3:2, and the silver content equal to 2.75%.

The alkaline earth metal silver polyphosphates are for the most part difficultly soluble, which is advantageous for some uses as where it is desired to employ a germicide which goes into solution slowly and over a rather long period of time, or where it is to be used in a filtering operation, for example, where a germicide is desired and where the product must dissolve slowly. These materials are not well fitted for use as simple germicides, or as ingredients of germicidal detergents or water softening compositions, but are useful for such purposes as those just referred to. Such materials are illustrated by the following two examples.

EXAMPLE 8

A mixture of 25.4 parts by weight of anhydrous calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$) and 148.5 parts of anhydrous silver metaphosphate (AgPO_3) was intimately ground together. The mixture was heated to well above the fusion temperature and then the mass was quenched by pouring in a thin film or in small beads upon a stainless steel slab which is water cooled. The resulting product is a glassy composition having the following oxide ratios $2\text{CaO}:4\text{Ag}_2\text{O}:5\text{P}_2\text{O}_5$ and contains 47.6% silver.

EXAMPLE 9

A mixture of 10.9 grams of $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and 0.268 gram of AgPO_3 was fused and quenched. The product is a magnesium silver metaphosphate containing 13.36% magnesium and 1.66% silver.

The alkali-metal alkaline earth-metal silver polyphosphates in general possess solubilities somewhat intermediate to the solubilities of the alkali-metal silver polyphosphates and the alkaline earth silver polyphosphates. The greater the proportion of alkali-metal, the greater is the solubility. Thus by varying the proportions of the metals used, the solubility of the product may be varied. This fact enables the manufacturer to tailor the product to fit the desired situation.

In general these substances are prepared in a manner similar to that previously described for the alkali-metal silver polyphosphates. The appropriate alkali-metal phosphate, alkaline earth-metal phosphate, and silver phosphate in proper amounts are intimately mixed together, fused, and quenched. As examples of alkali-metal alkaline earth-metal silver polyphosphates, we may cite the following:

EXAMPLE 10

18 parts by weight of $\text{Mg}(\text{H}_2\text{PO}_4)_2$, magnesium monobasic (primary) phosphate, was intimately mixed with 3.24 parts of Ag_3PO_4 and 95.5 parts of a sodium polyphosphate ($4\text{Na}_2\text{O}:3\text{P}_2\text{O}_5$) and the mixture fused and quenched. The resulting glassy product contains metal oxides and P_2O_5 in a molecular ratio of approximately 4:3, a silver content equal to 2.21%, and a Mg content of 1.76%.

EXAMPLE 11

10 parts by weight of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, calcium monobasic phosphate was first dehydrated, then mixed with 5.89 parts of sodium polyphosphate (having a $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratio of 4:3) and 0.433 part of silver orthophosphate. The mixture was then fused and quenched. The product is a glassy composition containing 1.12% calcium and 2.36% silver.

Another convenient method for the preparation of certain of these silver products is by electrolysis of the appropriate phosphate in the fused condition, using a silver anode and an inert metal or carbon as cathode. In this manner the silver is introduced into the fusion in a highly active germicidal condition. When the desired concentration of silver in the product is attained the electrolysis is discontinued and the fused material is chilled in the usual manner. Thus, sodium silver polyphosphates, potassium silver polyphosphates, sodium magnesium silver polyphosphates, and other alkali and/or alkaline earth silver polyphosphates have been prepared and have been found to possess strong germicidal activity.

The extreme effectiveness of the glassy silver phosphates, and particularly those having a silver oxide: phosphorous pentoxide ratio in the range of 1.1:1 to 1.9:1, and of the complex silver-containing glassy phosphates has been demonstrated by appropriate tests against a number of bacteria, and in general, as measured by the concentration of silver in the test solution required to kill the bacteria by standardized test, is substantially higher than that observed with other silver-containing materials.

The germicidal activity of the various preparations under consideration was tested by a modified F. D. A. procedure quite similar to the method of testing germicidal detergents which is described by Cade and Halvorson on page 17 of vol. 10, No. 8, 1934, issue of "Soap." The exact procedure used is as follows:

A 10 ml. sample of the solution to be tested is placed in a 1" x 6" test tube. A series of these tubes of solutions to be tested is placed in a rack in a water bath maintained at a temperature of $40 \pm 0.2^\circ \text{C}$. When these medication tubes have attained the temperature of the water bath a 0.3 ml. portion of a 24 hour broth culture is added to each at a known time and the contents of each tube mixed thoroughly immediately after addition of the culture. (It is understood of course, that proper bacteriological technique is to be followed in all of the operations involved in this method of testing.) At the end of the desired time-of-medication interval a 4 mm. loopful of medicated solution is introduced into a tube of molten ($43-45^\circ \text{C}$.) nutrient agar (when *Streptococcus hemolyticus* or *Diplococcus pneumoniae* is used as the test organism, 5 ml. of whole blood per 100 ml. of nutrient agar is added) and thoroughly mixed, poured into a petri plate and incubated at 37°C . The colonies resulting from unkilld organisms are counted after 24 hours of incubation.

Other special tests indicated that the results obtained by the above method were due to the germicidal action of the materials being tested and not to bacteriostatic effects.

The extreme effectiveness of the compositions is illustrated by the results tabulated in Table I below. Included are tests using the germicidal solution alone and tests on certain of the materials in the presence of salt and in the presence

of peptone. The table shows the amount of silver in parts per million required to kill 99.5% of the bacterial population of *E. coli* in the time indicated.

TABLE I

Compound	Alone		With NaCl		With Peptone	
	3.5 min.	7.0 min.	3.5 min.	7.0 min.	3.5 min.	7.0 min.
S-22	5.7	2.3			11.5	5.7
S-69	2.3	1.15	5.7	1.15	5.7	2.3
S-111	46.0	11.5				

The compound S-22 is that described in Example 5 above. S-69 is a composition made by fusing together and then quenching a mixture of 15 parts by weight of a sodium polyphosphate ($4\text{Na}_2\text{O} \cdot 3\text{P}_2\text{O}_5$) and 0.2867 part of silver orthophosphate (Ag_3PO_4), and contains 1.36% silver. S-111 is a composition made by fusing together and then quenching a mixture of 0.9439 part by weight of silver metaphosphate (AgPO_3) and 0.6034 part of silver pyrophosphate ($\text{Ag}_2\text{P}_2\text{O}_7$). The composition of this compound corresponds approximately to that of silver tetraphosphate ($\text{Ag}_4\text{P}_4\text{O}_{13}$), and has a silver content of 62.4%.

The silver preparations of this invention are very consistent and reliable in germicidal action and give results which are quite reproducible. In Table II below the results of a series of tests made with the silver-containing product of the invention designated as S-69, described above, under as nearly identical conditions as it was possible to maintain are given. In each test a series of concentrations of the germicide was tested and from the results there were selected those concentrations which gave a 99.5% reduction in the bacterial population of *E. coli* in the time shown, the results being expressed in terms of parts per million of silver. It will be noted that the results obtained are almost identical for each test, an unusual observation for a silver germicide.

TABLE II

Test	S-69	
	3.5 min.	7.0 min.
1	2.3	2.3
2	2.3	2.3
3	2.3	1.15
4	2.3	2.3
5	2.8	2.8
6	1.15	1.15

As previously pointed out the compositions of the invention are well adapted for use in germicidal detergents. One of the requirements for such uses is compatibility with the common detergent materials; another, compatibility or effectiveness in the conditions under which such detergents are commonly used. The glassy phosphates of the invention have these compatibilities to a marked extent. Thus they are effective over a wide range of pH, that is, may be used with neutral or alkaline materials, or even acid materials, are not inactivated in the presence of salt or organic matter, by high temperatures, etc. They may be used as ingredients in germicidal detergents containing carbonates, silicates, chlorides, organic compounds, or in conjunction with such materials in solution, are relatively free from inactivation by organic matter, are effective

at high temperatures, etc. Typical germicidal detergents included within the scope of the invention which are effective as detergents and also effective germicidally in the concentrations in which the detergents are used, for example, in 1% or more dilute solution, are shown in the following examples.

EXAMPLE 12

- 10 27% Nacconol NR (a proprietary product, being a sodium alkyl benzene sulfonate the alkyl side-chain of which is derived from a kerosene fraction containing hydrocarbons having an average carbon content of at least 12 and not more than 16 carbon atoms per molecule)

15 15% bentonite

20% sodium sesquicarbonate

37% sodium chloride

1% S-69 (a sodium silver polyphosphate containing 1.36% silver, described above)

- 20 The total composition contains 0.0136% silver. When such a detergent composition is used in a 1% solution the silver is present in 1.36 P. P. M. Such a wash solution has a pH of 9.3 and is highly germicidal, giving a 99.99% kill of *E. coli* at 40° C. in 3.5 min. (when tested according to the procedure previously described). This is suitable as a hand dishwashing compound.

EXAMPLE 13

23.5% sodium pyrophosphate

25.0% sodium bicarbonate

25.0% borax

10.0% sodium carbonate

- 35 15.0% Nacconol NR

1.5% S-22

- 40 The total composition contains 0.0339% silver. When this detergent composition is used in a 0.1% solution, the solution contains 0.5 P. P. M. of silver. Such a wash solution has a pH of 9.27 and is highly germicidal, giving a 99.98% kill of *E. coli* at 40° C. in 3.5 minutes (when tested according to the procedure previously described).

EXAMPLE 14

20% sodium polyphosphate

40% sodium metasilicate

35% sodium carbonate

- 50 5% S-22 (a sodium silver polyphosphate containing 2.26% silver described above)

- 55 The total composition contains 0.113% silver. When this detergent composition is used in a 0.2% solution, the solution contains 2.3 P. P. M. of silver. When tested according to the procedure previously described this solution gave a 99.95% kill in 3½ minutes at 40° C. The pH of this solution is 10.

EXAMPLE 15

82% white soap flakes

18% S-69

- 65 The total composition contains 0.245% silver. When used in a 0.1% solution, the solution contains 2.4 P. P. M. of silver. This 0.1% solution has a pH of 8.9 and gave a 99.99% kill of *E. coli* in 3.5 minutes at 40° C. (when tested according to the procedure described above).

EXAMPLE 16

99% white floating soap

1% S-69

- 75 The total composition contains 0.0136% of silver. A 0.1% solution of the above composition has

a pH of 9.3 and contains 0.136 P. P. M. silver. Such a solution gave a 99.99% kill in 3.5 minutes when tested against *E. coli* at 40° C. according to the procedure described above.

Tests conducted on a wide range of other glassy silver-containing phosphates similarly showed their remarkable effectiveness germicidally. Thus products obtained by fusing together appropriate quantities of the respective silver and sodium phosphates with silver contents ranging from as little as 0.59 to as much as 31.3% and with metal oxide ($\text{Na}_2\text{O} + \text{Ag}_2\text{O}$) : phosphorous pentoxide ratios ranging from 1:1 to 2:1 showed remarkably high effectiveness. With compositions containing silver in proportions ranging around 10% or higher, the germicidal activity was in general, as measured by the quantity of silver required for effective killing with the test described above, lower than that of the compositions in which the silver content ranged from a fraction of 1% to 2 or 3% but in nearly all cases addition of a phosphate, such as a sodium polyphosphate, enhanced the activity of the glassy silver-containing phosphate with the relatively high silver contents to an extent such that it became nearly as active based on the silver content of the test solution as the compositions with the relatively low silver content.

In the following table are shown the results obtained with a large number of glassy sodium silver phosphates. In each case, the compound tested was made by fusing together appropriate quantities of selected silver and sodium phosphates by the method described above. In the first column is shown the percentage of silver in the compound. In the second column is shown the ratio of metal oxide, that is $\text{Ag}_2\text{O} + \text{Na}_2\text{O}$ to phosphorous pentoxide. In the third and fourth columns are shown the parts per million of silver in the test solution required to kill 99.5% of the bacteria (*E. coli*) by the method described above in 3.5 and 7 minutes respectively.

TABLE III

No.	Per Cent Ag	MO/P ₂ O ₅	Germicidal Activity, P. P. M.	
			3.5'	7'
1	.59	1/1	2.5	1
2	.83		2.5	1
3	1.13		2.0	1.0
4	1.19		2	1
5	1.49		2	1
6	.57		2	1
7	.57		5	5
8	1.55		2	2
9	1.90			
10	2.24			
11	10.00	1.08/1	10	5
12	.70		1	.5
13	.58		2	1
14	.57		1	.5
15	1.30		2.5	1
16	10.00	1.25/1	5	.5
17	.85		5	2
18	1.28		2.3	1.2
19	1.52		5.0	2.5
20	2.26		5.7	2.3
21	2.26	1.33/1	2.3	2.3
22	7.07		11.5	5.7
23	10.00		20	5
24	31.3		5.7	5.7
25	.85	1.375/1	1	1
26	.85		5	2
27	1.35	1.4/1	5	2
28	1.52		2	1
29	1.63	1.5/1	2	1
30	2.24		2	1
31	1.30	1.6/1	2.5	2.5
32	1.47		5	2
33	1.51	1.67/1	2	2
34	2.24		2	2
35	1.34	7/4	2.5	2.5
36	10.00		5	5

Addition of a sodium polyphosphate with an $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratio of 4:3 in quantity equivalent to 300 parts per million of phosphorous pentoxide to the test solution of the compound No. 5 decreased the quantity of silver required for the corresponding germicidal activity to 0.5 and 0.5 P. P. M. for 3½ and 7 minutes respectively. A similar addition to the test solution of compound No. 11 reduced the concentration of silver required to 5 and 5 P. P. M. for 3½ and 7 minutes. Addition of the same quantity of sodium polyphosphate to the test solution of compound No. 16 reduced the concentration for the 3.5 minute kill to 0.5 P. P. M., the concentration for the 7 minute kill remaining the same. The same addition of sodium polyphosphate to the test solution of compound No. 23 reduced the respective effective concentrations to 1 and 1 P. P. M., while the same addition to the test solution of compound No. 24 reduced the concentrations required to 2.3 and 2.3 P. P. M.

Similar tests carried out on glassy silver phosphates containing no metal other than silver showed that the concentration required for a phosphate with an $\text{Ag}_2\text{O}:\text{P}_2\text{O}_5$ ratio of 1.5:1 was 46% of that for a compound with a ratio of 1:1 and 50% of that for a compound with a ratio of 2:1 for the 3½ minute kill, with respectively corresponding figures of 11.5% and 100% for the 7 minute kill, illustrating the increased effectiveness of the simple glassy silver phosphates in the $\text{Ag}_2\text{O}:\text{P}_2\text{O}_5$ ratios between 1:1 and 2:1 as compared with the compounds corresponding to fused silver metaphosphate and fused silver pyrophosphate.

The following table gives the results of tests carried out on potassium silver phosphates, the columns having the same significance as in Table III.

TABLE IV

Potassium silver phosphates

No.	Per cent Ag	MO/P ₂ O ₅	Germicidal Activity	
			3.5'	7'
37	3.48	1/1	25	5
38	1.32	1/1	5	2
39	1.47	4/3	5	2
40	.57	4/3	2	2
41	3.38	1.5/1	2.5	2.5

Similar data are given for glassy lithium silver phosphates in the following table.

TABLE V

Lithium silver phosphates

42	2.03	1/1	2.5	2.5
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Similar data are given for glassy magnesium silver phosphates in the following table.

TABLE VI

Magnesium silver phosphate

43	34.94	1/1	50	50
44	1.80	1/1	50	50

Similar data are given in the following table for 75 glassy calcium silver phosphates.

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TABLE VII

Calcium silver phosphates

45.....	2.14	1/1	50	50	5
46.....	2.54	4/3	100	100	10

It will be noted that with the magnesium and calcium silver phosphates there is a substantial increase in the quantity of silver required to be present for germicidal effectiveness in the test used. This is compensated for, for certain purposes, by their desirable properties of relative insolubility, and non-hygroscopicity, which make them of value for purposes referred to above.

The following table gives similar data with respect to glassy silver sodium magnesium phosphates.

TABLE VIII

Silver sodium magnesium phosphates

No.	Per cent Ag	Per cent Mg	MO/P ₂ O ₅	Germicidal Activity	
				3.5'	7'
47.....	8.54	0.10	1/1	100	50
48.....	1.55	1.00	1/1	50	10
49.....	2.3	1.57	4/3	2	2
50.....	1.97	6.57	4/3	20	5

Again it will be noted that in general the activity is less than it is in the simple sodium phosphates, a factor which for certain uses is offset by the considerations outlined above.

The following table gives similar data for a glassy sodium barium silver phosphate containing 12% barium.

TABLE IX

Sodium barium silver phosphate

51.....	1.36	-----	4/3	5.7	2.3
---------	------	-------	-----	-----	-----

The following table gives similar data for a glassy potassium calcium silver phosphate containing 3.4% calcium.

TABLE X

Potassium calcium silver phosphate

52.....	6.56	-----	1/1	20	10
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The following table gives similar data for a glassy sodium copper silver phosphate.

TABLE XI

Sodium copper silver phosphate

		Per cent Cu			
53.....	1.82	2.18	4/3	5	5
54.....	.68	8.50	4/3	5.7	2.3

The following table gives similar data for a glassy sodium mercury silver phosphate.

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TABLE XII

Sodium mercury silver phosphate

No.	Per cent Ag	Per cent Hg	MO/P ₂ O ₅	Germicidal Activity	
				3.5'	7'
55.....	2.19	1.915	4/3	2.5	2.5
56.....	2.24	1.18	4/3	11.5	2.3

The following table gives data for glassy sodium copper mercury silver phosphate containing 2.2% copper and 1.87% mercury.

TABLE XIII

Sodium copper mercury silver phosphate

		Per Cent Hg	Per Cent Cu			
57.....	2.13	1.87	2.20	4/3	2.5	1

The following table gives data for glassy sodium manganese silver phosphate.

TABLE XIV

Sodium manganese silver phosphate

		Per Cent Mn				
58.....	1.09	4.16	4/3	5.7	5.7	
59.....	2.25	1.31	4/3	5.7	2.3	
60.....	0.6	0.93	4/3	5.7	2.3	

35

TABLE XV

Sodium iron silver phosphate

		Per Cent Fe				
61.....	.88	4.20	4/3	2.6	2.8	
62.....	2.18	3.36	4/3	5.7	2.3	

45

The following table gives similar data for a glassy sodium nickel silver phosphate containing 4% nickel.

TABLE XVI

Sodium nickel silver phosphate

		Per Cent Ni				
55 63.....	1.99	4.06	4/3	11.5	2.3	

50

The following table gives similar data for a glassy sodium cerium silver phosphate, containing 5.6% of cerium.

TABLE XVII

Sodium cerium silver phosphate

No.	Per Cent Ag	MO/P ₂ O ₅	Germicidal Activity	
			3.5'	7'
64.....	2.2	4/3	11.5	2.3

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From the foregoing it is obvious that not only do the complex glassy phosphates of silver and alkali metals have unexpected high germicidal activity but these properties are shared by other silver-containing complex glassy phosphates.

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These glassy silver phosphates may be used for germicidal purposes in a number of ways according to the particular need or purpose at hand. The variety of compositions available, each with good germicidal properties, but with controlled differences in respect to other properties such as pH, solubility, etc., make these materials adaptable to many different uses.

When used for germicidal detergent purposes these products may be used in a number of ways. For instance, these silver phosphates or solutions thereof may be added to solutions of detergents at the time of use. This enables one to use his favorite detergent and at will make its solution germicidal by adding to the wash solution the proper proportion of a selected silver phosphate. Or one may mix the dry powdered or granular glassy silver phosphate with the desired detergent composition to provide a complete germicidal detergent composition ready for use, as illustrated in Examples 12, 13, and 14. The powdered glassy silver-containing phosphate also may be added to soap in the crutching operation to provide a product of composition such as is illustrated in Example 16. Thus these materials have the distinct advantage of being usable in many different ways.

An important feature of my silver germicides is the fact that they are effective against both gram positive and gram negative organisms. This is not generally the case with other germicides. Many germicides are effective against either gram positive or gram negative organisms, but not against both.

I have found compositions of the invention to be active against the following gram positive organisms commonly used in determining germicidal activity:

Staphylococcus aureus
Streptococcus hemolyticus
Diplococcus pneumonia
Corynebacterium diphtheriae

as well as the following gram negative organisms also commonly used in determining germicidal activity:

Eshcherichia coli
Eberthella typhosus
Salmonella paratyphi
Shigella dipenteriae (Flexner)

My silver containing polyphosphates have been found not only to have extraordinary bactericidal properties, based on silver content, but it has also been shown that the inclusion of silver in another polyphosphate improves their properties. The solubility of the resulting complexes may be regulated by varying the proportions of the metals. These glassy silver-containing phosphates are less hygroscopic than similar phosphates not containing silver. Some phosphates such as sodium polyphosphates are relatively unstable at higher temperatures, changing to the less effective orthophosphates. My silver polyphosphates are considerably more stable in hot water than many other germicidal compositions, such for instance as the hypochlorites, rendering them useful in a greater variety of conditions.

In accordance with the patent statutes, I have described the principles of composition of my silver-containing glassy systems, and while I have endeavored to set forth the best embodiments thereof, I desire to have it understood that ob-

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vious changes may be made within the scope of the following claims without departing from the spirit of my invention.

I claim:

1. A glassy phosphate having a metal oxide to phosphorous pentoxide ratio of 1:1 to 2:1 and having a silver content effective to impart germicidal properties to the material when dissolved in water, said silver content not exceeding 5%.
2. A product as in claim 1 in which the remaining metal content is alkali metal.
3. A product as in claim 1, in which the remaining metal content is sodium.
4. A germicidal detergent composition which consists essentially of a water-soluble soap and a minor proportion of a glassy phosphate having a metal oxide to phosphorous pentoxide ratio of 1:1 to 2:1 and having a silver content effective to impart germicidal properties to said glassy phosphate when dissolved in water, said silver content not exceeding 5%.
5. A composition as in claim 4 in which the remaining metal content of the glassy phosphate is sodium.
6. A germicidal detergent composition which consists essentially of an inorganic alkaline detergent sodium salt and a minor proportion of a glassy phosphate having a metal oxide to phosphorous pentoxide ratio of 1:1 to 2:1 and having a silver content effective to impart germicidal properties to said glassy phosphate when dissolved in water, said silver content not exceeding 5%.
7. A composition as in claim 6 in which the remaining metal content of the glassy phosphate is sodium.
8. A germicidal detergent composition which consists essentially of a detergent and a minor proportion of a glassy phosphate having a metal oxide to phosphorous pentoxide ratio of 1:1 to 2:1 and having a silver content effective to impart germicidal properties to said glassy phosphate when dissolved in water but not exceeding 5%, said detergent being composed of an inorganic alkaline detergent sodium salt and a sodium alkyl benzene sulfonate the alkyl group of which has from 12 to 16 carbon atoms.
9. A composition as in claim 8 in which the remaining metal content of the glassy phosphate is sodium.

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