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WATER SOLUBLE IODINE-PHOSPHORIC-ACID-SYNTHETIC DETERGENT COMPOSITION

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This invention relates to water soluble compositions of phosphoric acid and iodine-synthetic detergent complex having detergent-germicidal and sanitizing properties wherein the components exhibit synergistic action, and the method of preparing such compositions. The invention is more particularly directed to compositions adapted for rapid dilution in the field for use in the cleaning and sanitizing in one operation, of apparatus such as food handling equipment, where the use dilution must have highly efficient cleaning properties as well as highly efficient germicidal and sanitizing properties in reducing the micro-organism count of the treated surface. The compositions of the present invention can be marketed either in powder or liquid form for dilution in water by the user.

Essentially the present invention is directed to dispersing iodine and phosphoric acid, together with a synthetic surface active agent or agents having detergent properties in water, so as to render the iodine effective as a germicide and/or as a fungicide for treating food handling equipment. In such use it is desirable that the iodine and phosphoric acid be associated with an amount of synthetic detergent which will be effective in the removal of the organic and inorganic soil from the apparatus. It is also essential that the user receive the composition as a concentrate so that a measured amount can be added to the available water in providing an adequate quantity of use solution. It is also essential that there be no substantial loss of strength, particularly of the iodine, for normal periods of shelf life, and it is equally important that the composition rapidly disperses in the wash and/or rinse water used to provide the use dilution, and that the hardness ingredients of this water, as well as the organic soil of the apparatus being cleaned, do not materially reduce the effective strength of the iodine as a germicide or fungicide.

In the compositions of the present invention the iodine is loosely bound or carried by the synthetic detergent in what will hereinafter be referred to as an iodine-synthetic detergent complex. This complex together with phosphoric acid as hereinafter described is mixed with water or a solid water soluble diluent to provide a liquid or solid composition in concentrate form adapted for addition to water in providing use solutions thereof. The synthetic detergent can comprise one or more nonionic and/or anionic synthetic surface active agents having strong detergent and wetting properties.

In general any nonionic and/or anionic synthetic detergent which is itself an effective iodine carrier can be employed in our improved compositions wherein the carrier-iodine complex is stabilized and made more effective as a source of iodine by the presence of phosphoric acid. As preferred synthetic detergents, however, we employ one or more of the following:

Nonionics which are alkyl aryl polyethylene glycols and which are sold by General Aniline and Film Corporation under the trademark "Antarox." An example of such nonionic is "Antarox" A-400, which is a nonyl phenol ethylene oxide condensate containing 8 to 9 mols of ethylene oxide per mol of phenol.

Nonionics which are distributed by Wyandotte Chem-

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icals Corporation under the trademark "Plurionics," and which are disclosed and claimed in U.S. Patent No. 2,674,619 dated April 6, 1954, issued to Wyandotte Chemicals Corporation, as compounds according to the formula $\text{HO}-(\text{C}_2\text{H}_4\text{O})_x(\text{C}_3\text{H}_6\text{O})_y(\text{C}_2\text{H}_4\text{O})_x-\text{H}$ where y equals at least 15, and $(\text{C}_2\text{H}_4\text{O})_{x+y}$ equals 20 to 90% of the total weight of the compound. Examples of such nonionics are "Plurionics" L-62, liquid condensate of polypropylene oxide and ethylene oxide wherein the polyoxypropylene group has a molecular weight within the range of 1501 to 1800 and the condensate contains 20 to 30% by weight of ethylene oxide; and "Plurionics" F-68, a condensate of polypropylene oxide and ethylene oxide in the form of flakes wherein the polypropylene oxide group has a molecular weight within the range of 1501 to 1800 and the condensate contains from 80 to 90% by weight of ethylene oxide.

Anionics which are alkyl aryl sulfonates and which are sold by National Aniline Division, Allied Chemical and Dye Corporation under the trademark "Nacconol." Examples of such anionics are "Nacconol" 60, "Nacconol" Z and "Nacconol" NRSF. In these products the active component or anionic is alkyl benzene sulfonate wherein the alkyl substituent contains 12 to 18 carbon atoms. They differ in concentration or amount of water associated with the active component. "Nacconol" 60 is a 60% concentration. "Nacconol" Z is an 85% concentration, and "Nacconol" NRSF is a 92½% concentration of the active component with water.

The compositions include phosphoric acid, preferably orthophosphoric acid. Pyro, meta and hypophosphoric acids can be used instead of orthophosphoric acid, but orthophosphoric acid is preferred because of its inherent stability and its acceptability in food processing. The phosphoric acid has numerable functions. It functions not only to counter-act the salts or hard water minerals present in the waters used to dilute the composition, but also to counter-act the organic and inorganic soil on the apparatus being cleaned and/or sanitized by the use solution. It has been found to greatly increase the effect of a given amount of iodine in so acting as a buffer against water impurities and soil on the apparatus which would normally interfere with the action of the iodine. Also the acid has the further effect of adjusting the pH to that low value of about 2.0 to 4.0, and suitably about pH 3.0, needed to maintain the stability of the iodine in the compositions and in the use dilutions thereof.

The phosphoric acid in the compositions also has the further effect of acting as a synergistic agent upon the iodine by extending the activity of the iodine to higher values than that which would be obtained by using the detergent-iodine complex without this acid. While any acid, organic or inorganic could be employed to adjust the pH of the concentrate to that value which stabilizes the iodine content, phosphoric acid has been found to exhibit novel synergistic activity. In addition, the phosphoric acid provides a physically stable or homogeneous composition both as concentrate and in use solutions, which cannot be attained with other mineral acids such as hydrochloric and sulfuric acids.

Where the water soluble phosphoric acid iodine-synthetic detergent composition is produced in liquid form, we have found the following to be the range of amounts by weight of the ingredients:

	Percent
Iodine	0.5-6.0
Phosphoric acid (85%)	4.0-30
Synthetic surface active detergent	1.5-25
Inert carrier (water)	Balance

Where the water soluble phosphoric acid iodine-synthetic detergent composition is produced as a powder, urea is an essential ingredient. The urea acts as a car-

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rier of the acid in the powdered composition and also exhibits synergistic activity by increasing the detergency of the surface active agent or agents. In preparing the phosphoric acid iodine-synthetic detergent compositions in powder form, it is also desirable to effect an initial solution of the iodine and a part of the carrier in ethyl alcohol. Ethyl alcohol is preferred for this purpose because it acts as a common solvent for both the iodine and the synthetic detergents.

Where the water soluble phosphoric acid iodine-synthetic detergent composition is produced in powder form, we have found the following to be the range of amounts by weight of the ingredients:

	Percent
Iodine -----	0.5-7.0
Phosphoric acid (85%) -----	4.0-10
Synthetic surface active detergent -----	1.5-10
Urea -----	Balance

The following examples will serve to show how typical compositions of phosphoric acid and iodine-synthetic detergent complex in accordance with the present invention can be prepared. It is to be understood however, that these examples are given by way of illustration and not of limitation.

Example 1

As an example of producing in liquid form a water soluble phosphoric acid iodine-synthetic detergent composition in accordance with the present invention and using both a nonionic and an anionic synthetic surface active agent, the nonionic agent or carrier was "Antarox" A-400 a product of General Aniline & Film Corporation as above defined and the anionic synthetic surface active agent or carrier was "Nacconol" Z, a product of National Aniline Division, Allied Chemical & Dye Corporation as above defined.

In preparing this composition, 21 parts of elemental iodine were mixed with 66 parts of the "Antarox" A-400. To this mixture were added 81 parts of the "Nacconol" Z, 175 parts of phosphoric acid (85%), and 607 parts of water. In providing the use solution one fluid ounce of this composition was diluted in five gallons of water, the use solution having 25-30 p.p.m. active iodine, a pH of 3.1, and being highly effective as a germicide, a sanitizer and as a detergent in treating dairy equipment. The parts indicated are by weight.

Example 2

As an example of producing in liquid form a water soluble phosphoric acid iodine-synthetic detergent composition in accordance with the present invention and using an anionic synthetic surface active agent or carrier for the iodine, the anionic agent or carrier was "Nacconol" 60, a product of National Aniline Division, Allied Chemical and Dye Corporation as defined above.

In preparing this composition, 21 parts of elemental iodine were mixed with 230 parts of the "Nacconol" 60. To this mixture were added 175 parts of phosphoric acid (85%) and 524 parts of water. In providing the use solution one fluid ounce of this composition was diluted in five gallons of water, the use solution having 25-30 p.p.m. active iodine, a pH of 3.1, and being highly effective as a germicide, a sanitizer and as a detergent in treating dairy equipment. The parts indicated are by weight.

Example 3

As an example of producing in liquid form a water soluble phosphoric acid iodine-synthetic detergent composition in accordance with the present invention and using a nonionic synthetic surface active agent or carrier for the iodine, the nonionic agent or carrier was "Antarox" A-400, as described in Example 1.

In preparing this composition, 35 parts of elemental iodine were mixed with 111 parts of "Antarox" A-400. To this mixture were added 175 parts of phosphoric acid

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(85%) and 629 parts of water. In providing the use solution, one fluid ounce of this composition was diluted in five gallons of water, the use solution having 47-50 p.p.m. active iodine, a pH of 3.1, and being highly effective as a germicide, a sanitizer and as a detergent in treating dairy equipment. The parts indicated are by weight.

Example 4

As an example of producing a powdered or substantially dry, water soluble phosphoric acid iodine-synthetic detergent composition in accordance with the present invention and using both a nonionic and anionic synthetic surface active agent or carrier for the iodine, the nonionic agent or carrier was "Pluronic" F-68, a product of Wyandotte Chemicals Corporation as above defined, and the anionic agent or carrier was "Nacconol" NRSF, a product of National Aniline Division, Allied Chemical & Dye Corporation as above defined.

The various ingredients were used in the following percentages, it being noted that the ethyl alcohol evaporated out so that the remaining ingredients total 100%. The percentages are by weight:

	Percent
Elemental iodine -----	2.5
"Pluronic" F-68 -----	4.3
"Nacconol" NRSF -----	4.6
Phosphoric acid (85%) -----	10.0
Urea -----	78.6
Ethyl alcohol -----	12.4
	112.4

In compounding the above 2½ parts by weight of the "Pluronic" F-68 and 2½ parts by weight of the iodine were dissolved in 12.4 parts by weight of ethyl alcohol. This solution was then deposited on a mixture of 1.8 parts by weight of the "Pluronic" F-68, 4.6 parts by weight of the "Nacconol" NRSF, 10 parts by weight of the phosphoric acid, and the 78.6 parts by weight of urea. Upon evaporation of the alcohol the composition was in the form of a cake which was readily reduced to a fine powder highly soluble in water.

In preparing an aqueous solution of the above composition, the ratio by weight, of the composition to the water was 1 to 320. This provided a use dilution having a pH of 3.0 and 49 p.p.m. of titratable iodine by weight. The use dilution was highly effective as a germicide, a sanitizer and as a detergent in treating dairy equipment.

Example 5

As an example of producing a powdered or substantially dry, water soluble phosphoric acid iodine-synthetic detergent composition in accordance with the present invention and using a nonionic synthetic surface active agent or carrier for the iodine, the nonionic agent or carrier was "Pluronic" F-68, as described in Example 4.

The various ingredients were used in the following percentages, it being noted that the ethyl alcohol evaporated out so that the remaining ingredients total 100%. The percentages are by weight:

	Percent
Elemental iodine -----	2.5
"Pluronic" F-68 -----	8.5
Phosphoric acid (85%) -----	10.0
Urea -----	79.0
Ethyl alcohol -----	12.4
	112.4

In compounding the above 2½ parts by weight of the "Pluronic" F-68 and 2½ parts by weight of the iodine were dissolved in 12.4 parts by weight of ethyl alcohol. This solution was then deposited on a mixture of the remaining ingredients, namely 6 parts by weight of the "Pluronic" F-68, 10 parts by weight of phosphoric acid and 79 parts by weight of urea. Upon evaporation of the

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alcohol the composition was in the form of a cake which was readily reduced to a fine powder highly soluble in water.

In preparing an aqueous use solution of the above composition, the ratio, by weight, of the composition to the water was 1 to 320. This provided a solution having a pH of 3.05 and 47 p.p.m. of titratable iodine by weight. The use dilution was highly effective as a germicide, a sanitizer and as a detergent in treating dairy equipment.

Example 6

As an example of producing in liquid form a water soluble phosphoric acid iodine-synthetic detergent composition in accordance with the present invention using a "Pluronic" type of nonionic surface active agent or carrier for the iodine, the nonionic agent or carrier was "Pluronic" L-62 as defined above.

In preparing this composition 33 parts of elemental iodine were mixed with 111 parts of "Pluronic" L-62. To this mixture were added 175 parts of phosphoric acid (85%) and 629 parts of water. In providing the use solution, one fluid ounce of this composition was diluted in 5 gallons of water, the use solution having about 47-50 p.p.m. of active iodine, a pH of 3.1, and being highly effective as a germicide, a sanitizer and as a detergent in treating dairy equipment. The parts indicated are by weight.

Various changes and modifications in the phosphoric acid iodine-synthetic detergent compositions herein disclosed will occur to those skilled in the art, and to the extent that such changes and modifications are embraced by the appended claims, it is to be understood that they constitute part of our invention.

This application is a continuation-in-part of our prior application Serial No. 298,828, filed July 14, 1952 (now abandoned).

We claim:

1. A water soluble iodine-synthetic detergent-phosphoric acid composition having detergent, germicidal and sanitizing properties, said composition consisting essentially of an iodine-synthetic detergent complex with phosphoric acid, the amount of iodine present being such as to provide a germicidally effective amount of iodine in the intended use dilution of said composition, the amount of phosphoric acid in said composition being in excess of four times the amount of iodine present and being sufficient to provide a pH within the range of about 2.0 to 4.0 in said use dilution, and the synthetic detergent in said composition being selected from the group consisting of acid stable, organic nonionic and anionic surface active agents having detergent properties and which are themselves effective iodine carriers.

2. A water soluble iodine composition as defined in claim 1 wherein the nonionic synthetic detergent is an alkyl aryl polyethylene glycol.

3. A water soluble iodine composition as defined in claim 1 wherein the nonionic synthetic detergent is a compound according to the formula



where y equals at least 15, and $(\text{C}_2\text{H}_4\text{O})_{x+x'}$ equals 20 to 90% of the total weight of the compound.

4. A water soluble iodine composition as defined in claim 1 wherein the anionic synthetic detergent is an alkyl aryl sulfonate.

5. A water soluble iodine composition as defined in claim 1 in the form of a liquid concentrate consisting of 0.5 to 6.0% iodine, 4.0 to 30% phosphoric acid of 85% concentration, 1.5 to 25% of acid synthetic detergent, and water to 100%.

6. A water soluble iodine composition as defined in claim 1 wherein the detergent consists of a mixture of said nonionic and anionic synthetic detergents.

7. A water soluble iodine composition as defined in claim 2 wherein the nonionic synthetic detergent is a nonyl

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phenol ethylene oxide condensate containing 8 to 9 mols of ethylene oxide per mol of phenol.

8. A water soluble iodine composition as defined in claim 3 wherein the nonionic synthetic detergent is a liquid condensate of polypropylene oxide and ethylene oxide wherein the polyoxypropylene group has a molecular weight within the range of 1501 to 1800 and the condensate contains 20 to 30% by weight of ethylene oxide.

9. A water soluble iodine composition as defined in claim 3 wherein the nonionic synthetic detergent is a condensate of polypropylene oxide and ethylene oxide in the form of flakes wherein the polypropylene oxide group has a molecular weight within the range of 1501 to 1800 and the condensate contains 80 to 90% by weight of ethylene oxide.

10. A water soluble iodine composition as defined in claim 4 wherein the anionic synthetic detergent is alkyl benzene sulfonate wherein the alkyl substituent contains 12 to 18 carbon atoms.

11. A water soluble iodine composition as defined in claim 6 wherein the nonionic synthetic detergent is in alkyl aryl polyethylene glycol and the anionic synthetic detergent is an alkyl aryl sulfonate.

12. A water soluble iodine composition as defined in claim 6 wherein the nonionic synthetic detergent is a compound according to the formula



where y equals at least 15, and $(\text{C}_2\text{H}_4\text{O})_{x+x'}$ equals 20 to 90% of the total weight of the compound and the anionic synthetic detergent is an alkyl aryl sulfonate.

13. A water soluble iodine composition as defined in claim 11 wherein the nonionic synthetic detergent is a nonyl phenol ethylene oxide condensate containing 8 to 9 mols of ethylene oxide per mol of phenol and the anionic synthetic detergent component is alkyl benzene sulfonate wherein the alkyl substituent contains 12 to 18 carbon atoms.

14. A water soluble iodine composition as defined in claim 12 wherein the nonionic synthetic detergent is a condensate of polypropylene oxide and ethylene oxide in the form of flakes wherein the polypropylene oxide group has a molecular weight within the range of 1501 to 1800 and the condensate contains 80 to 90% by weight of ethylene oxide and the anionic synthetic detergent is alkyl benzene sulfonate wherein the alkyl substituent contains 12 to 18 carbon atoms.

15. A water soluble iodine-synthetic detergent-phosphoric acid composition having detergent, germicidal and sanitizing properties, said composition consisting essentially of an iodine-synthetic detergent complex with phosphoric acid, the amount of iodine present being such as to provide a germicidally effective amount of iodine in the intended use dilution of said composition, the amount of phosphoric acid in said composition being in excess of four times the amount of iodine present and being sufficient to provide a pH of about 3.0 in said use dilution, and the synthetic detergent in said composition being selected from the group consisting of acid stable, organic nonionic and anionic surface active agents having detergent properties and which are themselves effective iodine carriers.

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