Patented Sept. 26, 1944

2,359,240

UNITED STATES PATENT OFFICE

2,359,240

GERMICIDAL COMPOSITIONS

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No Drawing. Application July 31, 1941, Serial No. 404,893

11 Claims. (Cl. 167—31)

The present invention is concerned with new germicidal compositions, and is particularly directed to mixtures comprising water-soluble phenolates and alkaline reacting salts.

The water-soluble phenolates are well known as germicidal toxicants and have found wide application in such use. These compounds are employed in dispersions, solutions, emulsions, and powders adapted to be diluted with or dissolved in water or other solvents to produce germicidal, bactericidal, and antiseptic compositions.

The phenolates as a class have a tendency to break down on contact with water to liberate free phenols which may be water-insoluble, less toxic to microorganisms, and more irritating to humans than the salts themselves. To prevent such hydrolysis and dissociation, it is common practice to maintain an appreciable excess of alkali or alkaline reacting salt in compositions comprising the phenolates. Free alkali or alkaline detergent salts are frequently employed in combination with phenolates especially in germicidal cleansing powders, washing compositions, and the like. Several disadvantages accrue to such practice. In the first place an excessively high alkalinity materially limits the application of a germicidal composition. More important is the fact that in mixtures with many alkaline reacting materials, the germicidal effectiveness and phenol coefficient of the phenolate is reduced.

According to the present invention, germicidal compositions are provided which comprise as an active toxic ingredient a mixture of a water-soluble phenolate with an alkali metal pyrophosphate. It has been found that water solutions of pyrophosphate-phenolate mixtures are of relatively lower pH yet resistant to hydrolysis and dissociation of the phenolate. The toxicity of the phenolate in such pyrophosphate-phenolate mixture, measured in terms of phenol coefficient, is much higher than that accruing to phenolates in mixture with other alkaline reacting salts. A further embodiment of the invention resides in the pyrophosphate-phenolate mixtures modified with certain preferred groups of wetting and detergent agents.

In preparing the new compositions, the water-soluble phenolate and pyrophosphate are mixed together in any suitable fashion with or without the inclusion of such wetting, dispersing, and detergent agents as further increase the efficiency of the phenolate in the mixture. While the use of pyrophosphate results in a somewhat lower pH for dilute aqueous solutions of the compositions than is obtained when tri-sodium phosphate, sodium carbonate, or excess free alkali are employed, the pH of such aqueous solution may be somewhat raised by the addition of free alkali without materially affecting the germicidal activity of the solution.

The pyrophosphate and phenolate are compatible in any proportions and any suitable amounts of the two materials may be combined. Aqueous solutions of the pyrophosphates alone have no appreciable germicidal power at concentrations as high as 15 per cent by weight and the solid alkali pyrophosphates have phenol coefficients of less than 0.05. In mixtures, however, of the pyrophosphates with phenolates in widely varying proportions, the apparent phenol coefficient of the phenolate is appreciably in excess of that observed for the phenolate alone. The preferred percentage composition of the germicidal mixture with which the present invention is concerned varies somewhat with the particular phenolate and pyrophosphate employed. A percentage range of general utility is that found specifically for sodium ortho-phenyl-phenolate and sodium pyrophosphate and consists of a mixture of 1 part by weight of phenolate with from 0.33 to 49 parts of pyrophosphate, i. e., a mixture containing from 2 to 75 per cent by weight of the phenolate. Preferred embodiments of the invention are compositions comprising potassium or sodium pyrophosphate. The latter has been found particularly useful in the compositions as defined. Sodium ortho-phenyl-phenolate constitutes a preferred phenolate for use therewith.

The method for determining the phenol coefficients as set forth in the following examples is one developed by the United States Public Health Service, Hygenic Laboratory, and described in Circular 198 of the Food and Drug Administration, United States Department of Agriculture. These values are based upon a coefficient of 1.0 for pure phenol. The phenol coefficient of ortho-phenyl-phenol as the sodium salt according to this method is 16–17.0.

The following examples are not to be construed as limiting either with respect to the proportions employed or the particular phenolates disclosed.

Example 1

Finely ground sodium ortho-phenyl-phenolate was mixed with sodium pyrophosphate

($Na_4P_2O_7.10H_2O$)

to obtain a series of dry white powders containing from 2.5 to 50 per cent by weight of the

phenolate. These compositions were dissolved in water to obtain detergent and germicidal solutions useful for the sterilization of drinking glasses, dishes, and silverware. Analogous series of mixtures were prepared in which tri-sodium phosphate, sodium carbonate and other alkaline reacting salts were substituted for the sodium pyrophosphate initially employed. The following table sets forth the comparative efficiencies of the sodium ortho-phenyl-phenolate in the mixtures:

Table A

Composition of the test mixture	Phenol coefficient against *E. typhi* at 20° C.
Sodium ortho-phenyl-phenolate:	
Alone	17
With 1 part Na_2CO_3	9.5
With 3 parts Na_2CO_3	5.5
With 5 parts Na_2CO_3	7.2
With 10 parts Na_2CO_3	8.3
With 1 part $Na_3PO_4.12H_2O$	16.7
With 3 parts $Na_3PO_4.12H_2O$	5.5
With 5 parts $Na_3PO_4.12H_2O$	7.1
With 10 parts $Na_3PO_4.12H_2O$	9.6
With 1 part $Na_4P_2O_7.10H_2O$	18.5
With 3 parts $Na_4P_2O_7.10H_2O$	20.2
With 5 parts $Na_4P_2O_7.10H_2O$	20.0
With 10 parts $Na_4P_2O_7.10H_2O$	23
With 15 parts $Na_4P_2O_7.10H_2O$	19
With 25 parts $Na_4P_2O_7.10H_2O$	20
With 40 parts $Na_4P_2O_7.10H_2O$	22
With 5 parts $Na_2SiO_3.9H_2O$	2.5
With 5 parts Borax and 1.2 grams NaOH	10

In a similar manner portions of sodium ortho-phenyl-phenolate were mixed with 2 and 5 parts by weight of potassium pyrophosphate

($K_4P_2O_7.10H_2O$)

In both of the compositions so obtained the phenolate was found to have a phenol coefficient of 22. In check compositions employing tri-potassium phosphate in mixture with the sodium-ortho-phenyl-phenolate, the compositions containing 2 and 5 parts of the phosphate per 1 part by weight of the phenolate the latter had phenol coefficients of 6.2 and 8.9, respectively.

Example 2

1 part by weight of sodium carvacrolate was mixed with 5 parts of sodium pyrophosphate to obtain a composition in which the phenolate had a phenol coefficient of 31 against *E. typhi* at 20° C. In compositions containing an equivalent amount of tri-sodium phosphate and sodium carbonate the carvacrolate had phenol coefficients of 13 and 18, respectively. The sodium carvacrolate alone has a phenol coefficient of 26 against *E. typhi*.

Experiments were also made to determine the phenol coefficient of sodium carvacrolate against *E. typhi* when dissolved in 0.5 per cent solutions of various alkali reacting salts. Such dilutions are the equivalent of those encountered in detergent sterilizing solutions as frequently employed in eating places. In 0.5 per cent tri-sodium phosphate solution, sodium carvacrolate had a phenol coefficient of 12. In 0.5 per cent sodium carbonate solution, the phenol coefficient of the carvacrolate was 18.5. In 0.5 per cent solution of sodium pyrophosphate, the phenol coefficient of the carvacrolate was 29.

Example 3

In a similar manner sodium monochloro-carvacrolate was mixed with 10 parts by weight of sodium pyrophosphate to obtain a composition in which the phenolate had a phenol coefficient of 150 against *E. typhi* at 20° C. The sodium monochloro-carvacrolate alone had a phenol coefficient of 95. In combination with 10 parts of sodium carbonate and of tri-sodium phosphate, this compound had a phenol coefficient of 27 and 22, respectively.

The phenol coefficient of the sodium monochloro-carvacrolate in 0.5 per cent aqueous sodium pyrophosphate solution was 120. In similar aqueous compositions comprising 0.5 per cent sodium carbonate and tri-sodium phosphate, the phenol coefficients of sodium monochloro-carvacrolate were found to be 30 and 27, respectively.

Example 4

1 part by weight of sodium monochloro-ortho-phenyl-phenolate was ground with 10 parts of sodium pyrophosphate to obtain a composition in which the phenolate had a phenol coefficient against *E. typhi* at 20° C. of 92. Sodium monochloro-ortho-phenyl-phenolate alone had a phenol coefficient of 85. In combination with 10 parts by weight of sodium carbonate and of tri-sodium phosphate, the phenolate had phenol coefficients of 19 and 18, respectively.

In the presence of 0.5 per cent aqueous solution of sodium pyrophosphate, the sodium monochloro-ortho-phenyl-phenolate had a phenol coefficient of 75. In an analogous composition in which sodium carbonate was substituted for the sodium pyrophosphate, the phenol coefficient of the phenolate was but 13.0.

Example 5

The phenol coefficients of sodium para-chloro-thymolate in mixture with several alkaline reacting salts were determined against *E. typhi* at 20° C. substantially as described above. In combination with 10 parts by weight of sodium pyrophosphate, the sodium para-chloro-thymolate had a phenol coefficient of 155. In combination with sodium carbonate and tri-sodium phosphate, the apparent coefficients of the phenolate were 63 and 30, respectively.

In 0.5 per cent aqueous solutions of sodium carbonate and tri-sodium phosphate, sodium para-chloro-thymolate in each instance showed a phenol coefficient of 33. In a 0.5 per cent aqueous solution of sodium pyrophosphate, the apparent coefficient of the sodium para-chloro-thymolate was over 150.

The pyrophosphate-phenolate mixtures as illustrated by the foregoing examples may further be modified to impart even higher phenol coefficients to the phenolate contained therein by the addition of certain types of detergent and wetting agents. This preferred group of addition agents are the water-soluble salts of alkyl-aryl-sulfonates, higher fatty alcohol sulfates, and alkyl-phenyl-phenol sulfonic acids. The addition of wetting and detergent agents generally to the pyrophosphate mixture does not cause an increase in the apparent pH of the phenolate, nor does the addition of the preferred agents to phenolate mixtures with common alkaline reacting salts other than the pyrophosphates operate to the benefit of the ultimate composition. It is believed that the chemical constitution of the ternary mixtures as hereinafter set forth is critical.

Example 6

Mixtures of sodium ortho-phenyl-phenolate with sodium pyrophosphate were ground with a water-soluble salt of an alkyl-aryl-sulfonate

marketed as Santomerse #1. The following table sets forth the composition of the several mixtures and the phenol-coefficient of the phenolate therein.

Table B

Parts of sodium ortho-phenyl-phenolate	Parts of sodium pyrophosphate	Parts of Santomerse #1	Phenol coefficient of sodium ortho-phenyl-phenolate
0	6	1	Less than 0.1 (for composition)
1	6	0.2	21
1	6	1	25
1	6	3	24
1	6	6	24
1	2	3	20
1	4	3	25
1	6	3	24
1	8	3	24
1	10	3	26

EXAMPLE 7

In a similar manner compositions were prepared by mixing sodium ortho-phenyl-phenolate and sodium pyrophosphate with a water-soluble salt of an alkyl-phenyl-phenol sulfonic acid sold as Aresklene 400 and believed to consist essentially of dibutyl-phenyl-phenol sodium sulfonate. In a mixture of 1 part phenolate, 6 parts sodium pyrophosphate, and 3 parts of Aresklene 400, the phenolate had a phenol coefficient of 25.

EXAMPLE 8

A similar beneficial result was obtained when the sodium pyrophosphate mixture with sodium ortho-phenyl-phenolate was modified with water-soluble salts of higher fatty alcohol sulfates and particularly proprietory materials sold as Orvis, Dreft, and Grasselli IN-181-P, all of which are believed to consist essentially of sodium lauryl sulfate. The following table sets forth representative results obtained, and also illustrates the non-equivalence of compositions in which other alkaline reacting salts are substituted for sodium-pyrophosphate.

Table C

Parts of sodium ortho-phenyl-phenolate	Parts of alkaline reacting salt	Parts of wetting and dispersing agent	Phenol coefficient of sodium ortho-phenyl-phenolate
1	6 of sodium pyrophosphate	3 of Dreft	30
1		3 of Orvis	18.5
1	6 of sodium pyrophosphate	do	35
1	1 of sodium pyrophosphate	1 of Grasselli IN-181-P	32
1	do	2 of Grasselli IN-181-P	30
1	2 of sodium pyrophosphate	do	31
1	4 of sodium pyrophosphate	do	31
1	6 of sodium pyrophosphate	3 of Grasselli IN-181-P	30
1	1 of sodium metasilicate	2 of Grasselli IN-181-P	16
1	2 of sodium metasilicate	do	13
1	1 of sodium carbonate	do	18.5
1	4 of sodium carbonate	do	17
1	2 of sodium carbonate	4 of Grasselli IN-181-P	19.5
1	2 of tri-sodium phosphate	2 of Grasselli IN-181-P	19.5
1	do	4 of Grasselli IN-181-P	13.3

Any of the other water-soluble salts of the phenols disclosed or the sodium, potassium, lithium, calcium, barium, ammonium, or magnesium salts of such other phenols as 4-hexyl resorcinol, 2-chloro-4-phenyl-phenol, 2.4.5-trichlorophenol, 2.4.6-trichlorophenol, 2.4.5.6-tetrachlorophenol, pentachlorophenol, 2-chloro-4-tertiaryamyl-phenol, 4-chloro-symmetrical-xylenol, or mixtures of 2 or more of such water-soluble phenolates may be employed in place of those compounds shown in the examples. Similarly, mixed sodium and potassium pyrophosphate may be substituted for the substantially pure compounds shown in the examples. It is also sometimes advantageous to employ combinations of 2 or more of the wetting and detergent agents as set forth above.

I claim:

1. A germicidal composition comprising as an active toxic ingredient a mixture of from 2 to 75 per cent by weight of a water-soluble phenolate with an alkali metal pyrophosphate, and substantially free of alkaline reacting salts which reduce the germicidal effectiveness of the water-soluble phenolate.

2. A germicidal composition comprising as an active toxic ingredient a mixture of a water-soluble phenolate with an alkali metal pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

3. A germicidal composition comprising as an active toxic ingredient a mixture of a water-soluble phenolate with a detergent salt selected from the group consisting of sodium and potassium pyrophosphates, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

4. A germicidal composition comprising as an active toxic ingredient a mixture of a water-soluble phenolate with sodium pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

5. A germicidal composition comprising as the active toxic ingredient a mixture of a water-soluble phenolate with potassium pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

6. A germicidal composition comprising as the active toxic ingredient a mixture of a water-soluble sodium phenolate with sodium pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

7. A germicidal composition comprising as the active toxic ingredient a mixture of sodium ortho-phenylphenolate with an alkali metal pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

8. A germicidal composition comprising as the active toxic ingredient a mixture of sodium ortho-phenylphenolate with sodium pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the pheonalte and being free from other inorganic alkaline detergent salts.

9. A germicidal composition comprising an

organic wetting and detergent agent selected from the group consisting of water-soluble salts of alkyl-aryl-sulfonates, higher fatty alcohol sulfates, and alkyl-phenyl-phenol sulfonic acids, and as an active toxic ingredient a mixture of a water-soluble phenolate with an alkali metal pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

10. A germicidal composition comprising an organic wetting and detergent agent selected from the group consisting of the water-soluble salts of alkyl-aryl-sulfonates, higher fatty alcohol sulfates, and alkyl-phenyl-phenol sulfonic acids, and as an active toxic ingredient a mixture of sodium ortho-phenylphenolate with sodium pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

11. A germicidal composition comprising sodium lauryl sulfate and as an active toxic ingredient a mixture of a water-soluble phenolate with sodium pyrophosphate, said mixture containing from 2 to 75 per cent by weight of the phenolate and being free from other inorganic alkaline detergent salts.

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