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3,330,767

GERMICIDAL WASHING POWDER AND METHOD OF MAKING THE SAME

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This invention relates generally to sanitizing detergent compositions and more particularly to such compositions that have been formulated as granular free-flowing powders.

Water solutions of various quaternary ammonium compounds are known to have potent germicidal activity against pathogenic organisms of both the gram negative and the gram positive types. This effect obtains even at high dilutions. Although some quaternary ammonium compounds are classified as solids, these same substances frequently exhibit an unctuousness that causes them to agglomerate rapidly after having been ground or flaked; and as a consequence, such compounds are inconvenient to measure and use in the unformulated state. Other quaternary ammonium salts are viscous liquids and possess the same general disadvantages. Various mineral salts have been proposed for blending with the quaternary compounds to overcome these difficulties, and early attempts were made to produce a fused composition of glassy or crystalline form. Such carriers as urea, alone or in conjunction with sodium acetate, and mixtures of various sodium silicates and polyphosphates have been employed in this regard. These products have overcome the problem of handling and measuring the unctuous quaternary salt, but the fusion temperatures involved have made production both complicated and unduly expensive. To avoid these difficulties, attempts have been made to mix quaternary compounds with dry bulking agents. Numerous materials have been proposed. In this respect, it is known that polyphosphates are capable of sequestering ferric, calcium and magnesium ions which tend to reduce the germicidal effect of quaternary salts. However, many polyphosphates form a germicidally ineffective precipitate with quaternary ammonium compounds. Soaps and surfactants are also theoretically desirable as carriers for the various quaternary salts, but anionic materials such as soaps and anionic synthetic detergents are incompatible with quaternary ammonium compounds. Moreover, simple alkali metal phosphates, silicates, borates, carbonates and sulfates form undesirable precipitates with water hardness ions; and these precipitates appear as scum on washed and sanitized surfaces. In addition, dialkyl dimethyl quaternaries form insoluble precipitates with divalent and trivalent salts, such as phosphates and sulfates for example; and high concentrations of monovalent salts, including the chlorides, may, under certain conditions, cause "salting out" of dialkyl dimethyl quaternary ammonium compounds.

Added to these formulation problems is the difficulty of producing a granular free-flowing composition which does not tend to cake or agglomerate upon storage.

The present invention takes as a principal object the provision of a germicidal detergent composition which overcomes the aforesaid formulation problems and which exists in a permanently granular free-flowing form.

A more particular object of the invention is to provide a germicidal washing powder which can be prepared by simple mixing of the ingredients at room temperature.

Another object of the invention is to provide a new and improved method of making a germicidal washing powder.

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Still another object of the invention is to provide such a method which may be practiced with conventionally available manufacturing equipment.

These and other objects and features of the invention will become more apparent from a consideration of the following descriptions.

The germicidal washing powders of the invention comprise a non-metallic inorganic bulking agent in admixture with the product produced by hydrating a phosphatic material in the presence of a synthetic detergent and a germicidal quaternary ammonium compound. The washing powders of the invention are specifically produced by mixing an anhydrous phosphatic material with water, a non-ionic detergent and a quaternary ammonium germicide. Agitation of the resultant composition is continued until the mixture is no longer a fluid slurry but rather a cohesive mass. At this point in the process, a dry mineral material is added to terminate the hydration of the phosphatic ingredient by quickly absorbing any unbound water. The dry mineral material is added with agitation, and the previously cohesive mass quickly converts into free-flowing granules, the dry mineral material acting as a debinding or glomerating agent as well as a water absorber.

The point in the manufacturing procedures at which hydration is desirably terminated may be determined by visual observation of the mixing ingredients. As stated hereinabove, the dry mineral material is advantageously added when the blending mixture changes from a fluid slurry to a cohesive mass. The relative change in viscosity of the mixture which determines the point in the cycle for addition of the dry mineral material is also capable of identification by observation of the energy required to drive a mixing implement in the blended ingredients.

Exemplary of this change in energy requirement was a 2,000 gm. total weight batch of the composition of the invention that was prepared in a Hobart "Kitchenaid" Mixer, Model K5-A, rated at 115 volts and 3 amperes. The flat beater supplied with this device was employed as the mixing implement. The phosphatic material, synthetic detergent, quaternary ammonium compound and water were blended in the mixer for 7.5 minutes during which time the motor demand varied within the range of 0.6–0.8 ampere. Between 7.5 and 8.0 minutes after mixing had been started, the motor demand rose rapidly into the range of 1.4–1.6 amperes. At this time, the dry mineral material was quickly added; granulation began; and motor demand increased to 2.3 amperes. Motor demand continued at this level until granulation was completed and the mixer stopped.

The compositions of the invention possess superior cleaning efficiency and high germicidal activity against both gram positive and gram negative organisms. These compositions are also characteristically low-foaming and, hence, do not require extensive rinsing for removal from the cleaned surfaces. The compositions of the invention have been found to be readily soluble in water and highly stable during storage. In addition, the compositions of the invention do not tend to form dusts, absorb moisture from the atmosphere or cake. Furthermore, exposure to comparatively high temperatures, on the order of 130° F., does not make the compositions tacky or otherwise produce a reversion from the granular state. Exposure to high temperatures, moreover, does not deleteriously affect the germicidal activity or cause undesirable odors in the product.

In formulating a quaternary ammonium germicide as a free-flowing powder, the present invention contemplates combining the quaternary germicide with a material which is simultaneously hydrated; and the hydrating ingredient is selected to be a phosphatic material, particularly a polyphosphate, because such materials have been found to

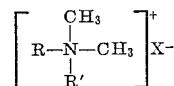
serve a codetergent function and to sequester calcium and other metal ions in an effective manner. When the germicidal washing powder of the invention incorporates a hydrating material of this character, water solutions of the washing powder display a powerful cleaning action. The phosphatic ingredient is advantageously a polyphosphate selected from the class consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate, sodium tetraphosphate and mixtures thereof; and the anhydrous form of the phosphatic ingredient is employed as a starting material in order to permit the contemplated hydration. Of the listed polyphosphates, tetrasodium pyrophosphate has proved to be especially useful because it is generally compatible with quaternary ammonium compounds, because it sequesters iron and other metal ions and because it forms a highly stable decahydrate. The stability of the tetrasodium pyrophosphate decahydrate promotes a permanently granular product free of tackiness and having little propensity to cake during storage.

The phosphatic ingredient may also include sodium tripolyphosphate, and either Phase I or Phase II material may be employed. However, sodium tripolyphosphate tends to precipitate certain quaternary ammonium germicides in water solution. Nonetheless, sodium tripolyphosphate is an effective water conditioning agent, forming soluble complexes with both calcium and magnesium ions. Furthermore, the hydration of sodium tripolyphosphate during manufacture of the instant washing powder has been found to proceed preferentially to the precipitation of the quaternary germicide. Regardless, in order to preserve the germicidal effectiveness of the quaternary compound in the use solutions, a protective material is oftentimes incorporated when sodium tripolyphosphate comprises a component of the instant washing powder. In this regard, sodium carbonate has proved to be particularly effective in protecting the quaternary germicide from precipitation by tripolyphosphate in the use solution. Since sodium carbonate is also capable of serving as a hydration terminating ingredient and since interaction between tripolyphosphate and the quaternary does not occur during the hydration step, the sodium carbonate is desirably incorporated in the final stages of manufacture as will be described more fully hereinafter. Inclusion of sodium carbonate in the composition also permits use of other polyphosphates which have generally deleterious effects on quaternary germicides. However, of these other polyphosphates, sodium hexametaphosphate has been found to form unstable hydrates and is thus of marginal desirability for use as a phosphatic ingredient in the instant washing powder.

In order to preserve the germicidal effectiveness of the quaternary ammonium compound, the active cleaning agent incorporated in the instant washing powder is selected to be a non-ionic synthetic detergent material. The inclusion of even small amounts of anionic synthetic detergent substances has been found to lower the sanitizing power of the quaternary compound rather substantially. Suitable non-ionic surfactants include the polyoxyethylene ether alcohols produced by reacting one mol of a fatty alcohol or a substituted phenol with from eight to fourteen mols of an alkene oxide such as ethylene oxide, propylene oxide or polymers of ethylene and propylene oxides. Both straight chain and branched chain alkyl groups may form the substituent of the described phenols; and suitable fatty alcohols include both primary and secondary alcohols having from eight to eighteen carbon atoms. While these various alcohols may be ethoxylated with from eight to fourteen mols of ethylene oxide or its equivalent, reaction with ten mols of ethylene oxide generally produces more preferable compounds. The polyoxyethylene ether alcohol detergents of the invention are desirably incorporated as 100% active ingredients, and complexing with urea is definitely undesirable because the resultant compositions evolve ammoniacal vapors upon heating and storage. Rep-

resentative non-ionic detergents which are suitable for use in the present invention include alkylphenoxypoly (ethyleneoxy) ethanol and ethoxylated nonylphenol.

The quaternary germicides which are used in the invention include compounds having the general formula:



wherein R is an alkyl group containing from eight to eighteen atoms, wherein X is a halide, and wherein R' is selected from the class consisting of benzyl, ethyl, methyl, ethylbenzyl and halide-substituted benzyl groups. In these quaternary ammonium salts, the length of the chain in the alkyl group is specific to the germicidal effect; and while the alkyl group in this regard may contain from eight to eighteen carbon atoms, germicidal effects in hard water solutions are most pronounced when alkyl groups containing fourteen carbon atoms predominate.

In addition to the aforesaid quaternary ammonium salts, use may be made of such quaternary germicides as the alkyl methylisoquinolium halides in which the alkyl group contains from eight to eighteen carbon atoms. In addition, the quaternary germicide may be di-isobutyl phenoxyethoxyethyl dimethyl benzyl ammonium chloride. Other specific quaternary ammonium salts which fall within the defined compounds include dodecyl dimethyl ethylbenzyl ammonium chloride, tetradecyl dimethyl benzyl ammonium chloride, stearyl methylisoquinolium chloride, cetyl dimethyl ethyl ammonium bromide, cetyl trimethyl ammonium bromide and stearyl (CNO) dimethyl benzyl ammonium chloride.

In producing the germicidal washing powders of the invention, water is added to the phosphatic ingredient in approximately the stoichiometric amount necessary to form a stable hydrate therewith. On the other hand, the quaternary ammonium compound is incorporated in an amount sufficient to produce a washing powder having a minimum Chambers test result of 1:80 in accordance with the procedure described in J.O.A.C., vol. 41, pages 541-543 (August 1958) and a minimum use-dilution test result of 1:80 in compliance with requirements set forth in Official Methods of Analysis of the Association of Official Agricultural Chemists, Ninth Edition, 1960, p. 65, "Use Dilution Method (2)-Official." Preferably, the quaternary germicide is incorporated in an amount sufficient to produce a washing powder having a Chambers test value of 1:100 and a use-dilution test of 1:200.

The dry mineral material which is utilized in terminating the hydration of the phosphatic ingredient also serves as a builder salts or bulking agent; and as used herein, the term "builder salts" includes the sodium carbonate mentioned earlier and such materials as sodium bicarbonate, sodium sulfate, trisodium phosphate and the various polyphosphates. Either as anhydrous or dry hydrates may be employed. Of these various mineral materials, sodium carbonate is particularly desirable because of its protective action relative to the quaternary germicide, because it is relatively inexpensive and may therefore be readily used as a diluent, and because it provides a slight alkalinity and concomitant alkaline cleaning action. Sodium bicarbonate may be used in conjunction with sodium carbonate to reduce the alkalinity of the product, and this alkalinity is preferably controlled to a maximum pH of 10 for household products. Trisodium phosphate is somewhat less desirable because it adds excessive alkalinity, affords no greasing-cutting action and does not serve as a chelating agent. Sodium sulfate is not particularly desirable either because it tends to form unstable hydrates and produces tackiness or adhesiveness in the washing powder, although it may be incorporated in conjunction with other dry ingredients. Polyphosphates generally are too expensive to be used in large quantities as bulking agents, and borax is not gen-

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erally employed in this regard due to the fact that it is not a good absorber of water.

In order to describe the invention more fully, the following specific examples are given without, however, intending to limit the invention to the precises set forth.

Example I

	Percent by weight
Sodium tripolyphosphate (Phase II) -----	12
Tetrasodium pyrophosphate -----	21
Ethoxylated nonylphenol -----	7½
Mixture of 50% N-alkyl dimethyl benzyl ammonium chloride and 50% N-alkyl dimethyl ethylbenzyl ammonium chloride -----	5
Water -----	14½
Sodium bicarbonate -----	5
Sodium carbonate -----	35
	100

A 500-pound batch of the germicidal washing composition was made using the above-described materials in the proportions set forth. A commercial ribbon type blender was employed, and operations were conducted at ambient temperature. The sodium tripolyphosphate and tetrasodium pyrophosphate were charged into the ribbon blender and dry mixed. Thereafter, the non-ionic detergent, the quaternary ammonium ingredient and the water were added in the described order and blended individually into the mixture. As the water was added, the mixture became a fluid slurry; and as the agitation of mixing continued, the composition thickened. When it was visually obvious that the composition was no longer a fluid but rather a cohesive mass, the mixer motor started to stall. At this moment, the previously dry mixed sodium bicarbonate and sodium carbonate were added simultaneously. Blending was continued; and immediately upon addition of the carbonate substances, the cohesive mass began to granulate. Blending was continued until the product reached a dry, powdery state. Specific gravity determinations were made, and a value of 0.97 was established for the loose product and a value of 1.05 for the packed product. Thereafter, the product was size-separated using a 10-mesh screen for removal of larger sized particles followed by a 50-mesh screen to remove fines. Oversize and undersize particles were retained for rebinding with subsequent batches to promote economy of operation.

The cleaning efficiency of the washing composition of Example I was determined using the method described by Liss and Hilton, Soap and Chemical Specialties, 36, 8, 51 (1960); and a value of 96.4% was obtained. The composition had a pH of 10 and passed the use-dilution tests at 1:200 using *S. choleraesuis* as a test organism. The composition of Example I passed the Chambers test at 1:100 and had phenol coefficients of 25 and 16.5 respectively using *S. aureus* and *S. typhosa* as test organisms in the procedure set forth in United States Department of Agriculture "Circular #193." The washing powder of Example I was found to be stable to oven heat at a temperature of 130° F., no softening or melting of the product being observed and no loss of germicidal strength being detected.

Example II

	Percent by weight
Sodium tripolyphosphate (Phase II) -----	7.0
Tetrasodium pyrophosphate -----	11.6
Ethoxylated nonylphenol -----	7.5
Di-isobutyl phenoxyethoxyethyl dimethyl benzyl ammonium chloride -----	5.0
Water -----	8.9
Sodium carbonate -----	25.0
Sodium bicarbonate -----	5.0
Sodium sulfate -----	30.0
	100

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The washing composition of Example II was manufactured in the same manner as that of Example I and various tests were performed on the resulting product. The composition of Example II had a cleaning efficiency of 97.2% using the method of Liss and Hilton; a use-dilution test value of 1:200 using the same test organism as was used for the product of Example I; and phenol coefficients of 33 and 11 respectively with *S. aureus* and *S. typhosa*. The product of Example II had a pH of 9.8 and was stable to oven heat at a temperature of 130° F. However, this material failed the Chambers test and is therefore considered suitable only for dilution and use with soft water.

Example III

	Percent by weight
Sodium tripolyphosphate (Phase I) -----	33
Ethoxylated cetyl alcohol -----	7½
Alkyl methylisoquinolium chloride -----	10
Water -----	9½
Trisodium phosphate -----	10
Sodium tetrphosphate -----	30
	100

The composition of Example III was manufactured in accordance with the same procedures employed for the product of Examples I and II; and similar test procedures were conducted. The pH of the composition of Example III was found to be in excess of the desirable maximum of 10 for a household cleaner, and this product was therefore deemed suitable primarily for industrial use. Otherwise, the washing powder of Example III satisfied the requirements for a suitable product as set forth hereinabove. In manufacturing the washing powder of Example III, the trisodium phosphate and the sodium tetrphosphate were first dry blended and then used to terminate the hydration of the sodium tripolyphosphate (Phase I).

Example IV

	Percent by weight
Sodium tripolyphosphate (Phase I) -----	20
Ethoxylated tallow alcohol -----	5
Cetyl dimethyl ethyl ammonium bromide -----	5
Water -----	10
Sodium carbonate -----	60
	100

The formulation set forth for Example IV proved to be both acceptable and economical for use as a household cleaner, the product of Example IV having been manufactured and examined in manners similar to those set forth for the previous examples.

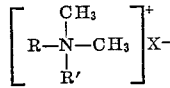
Difficulties were encountered in producing a dry granular product using a mixture of sodium tripolyphosphate (Phase II) and tetrasodium pyrophosphate in conjunction with straight chain rather than branch chain non-ionic surfactants. However, a dry granular product was produced with the straight chain materials when sodium tripolyphosphate (Phase I) alone was selected to be the phosphatic ingredient.

The specific matters herein described are to be considered as being primarily illustrative. Various changes beyond those suggested and described will, no doubt, occur to those skilled in the art; and such changes are to be understood as forming a part of this invention insofar as they fall within the spirit and scope of the appended claims.

The invention is claimed as follows:

1. The method of making a free-flowing germicidal washing powder of stable character which comprises the steps of mixing a substantially anhydrous polyphosphate with a sufficient amount of water to hydrate said polyphosphate, said mixing being caused to take place at substantially room temperature and in the presence of both a non-ionic detergent and a germicidally effective

amount of a quaternary ammonium compound having the general formula.



wherein R is an alkyl group containing from eight to eighteen carbon atoms, wherein X is a halide, and wherein R' is selected from the class consisting of benzyl, ethyl, methyl and ethylbenzyl groups; and terminating the hydration by adding a sufficient amount of dry alkaline detergent builder salts with agitation to absorb unbound water and form the mass into free-flowing granules.

2. The method according to claim 1 wherein said agitation is caused to take place at substantially room temperature.

3. The method according to claim 1 wherein said mixing is continued until the mixture is transformed from a fluid slurry to a viscous cohesive mass.

4. The method according to claim 3 wherein said transformation is indicated by an abrupt increase in the energy needed to turn a mixing implement operating in the mixture.

5. The method according to claim 1 wherein said

water and polyphosphate are present in substantially stoichiometric amounts to produce a stable hydrate.

6. The method according to claim 1 wherein said polyphosphate is tetrasodium pyrophosphate and wherein the hydrate is the decahydrate.

7. The method according to claim 4 wherein said energy increase is about 75%.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,330,767

July 11, 1967

Aaron B. Herrick et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 11, after "eighteen" insert -- carbon --;
line 46, for "incorported" read -- incorporated --; line 56,
for "polyphosuphates" read -- polyphosphates --; same line
56, strike out "as"; line 68, for "greasing-cutting" read
-- grease-cutting --; column 5, line 5, for "precises" read
-- precise details --; line 33, for "cohensive" read -- cohesive
--; column 8, line 11, for "2,365,216" read -- 2,365,215 --.

Signed and sealed this 18th day of June 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents