United States Patent Office 2,730,502 Patented Jan. 10, 1956

2,730,502

ANTISEPTIC DETERGENT COMPOSITION

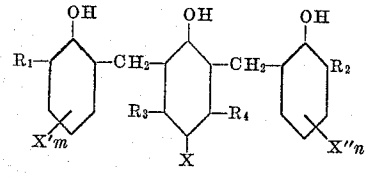
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No Drawing. Application March 31, 1951, Serial No. 218,704

10 Claims. (Cl. 252—107)

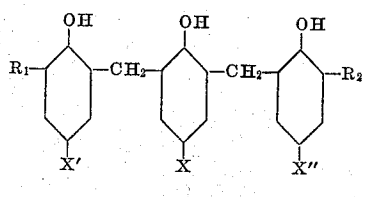
This invention relates to new and useful detergent compositions. More particularly it relates to detergent compositions containing a halogenated tris-phenol or a salt thereof possessing antiseptic properties.

In accordance with this invention it has been found that halogenated tris-phenols of the general formula



where R_1 and R_2 are like or unlike hydrocarbon radicals, such as methyl, ethyl, propyl, butyl, cyclohexyl, benzyl, phenyl, and the like, where R_3 and R_4 are like our unlike substituents selected from the group consisting of hydrogen atoms and short chain alkyl radicals, where X, X′ and X″ are like or unlike halogen atoms and where *m* and *n* are like or unlike whole numbers from 1–3, and their corresponding alkali metal salts comprise a family of compounds which when admixed with detergents in minor proportions form detergent compositions exhibiting antiseptic properties. The halogenated tris-phenols of this invention and their corresponding alkali metal salts, hereafter referred to as antiseptic agents, are readily incorporated in a detergent whether the latter be liquid or solid. The antiseptic agents of this invention remain permanently in the detergent composition and they neither affect the lathering, cleansing or physical properties of the detergent nor do they impart an unpleasant odor nor discolor the finished detergent composition. The new antiseptic detergent compositions are non-skin irritants.

In its preferred embodiment the invention relates to antiseptic detergent compositions containing a tris-phenol of the general formula



or its corresponding alkali metal salt where R_1 and R_2 are like or unlike short chain alkyl radicals such as methyl, ethyl, propyl and butyl radicals, and where X, X′ and X″ are like or unlike halogen atoms. These tris-phenols and their corresponding alkali metal salts, e. g., the sodium, potassium and lithium salts, are readily prepared and are characterized by exceptional antiseptic properties when in admixture with a detergent.

As exemplary of the preferred antiseptic agents of this invention are:

4 - chloro - a,a′ - bis(5 - chloro - 2 - hydroxy - m - tolyl) - 2,6-xylenol
4 - chloro - a,a′ - bis(5 - bromo - 2 - hydroxy - m - tolyl) - 2,6-xylenol
4 - bromo - a,a′ - bis(5 - bromo - 2 - hydroxy - m - tolyl) - 2,6-xylenol
4 - chloro - a,a′ - bis(5 - chloro - 3 - ethyl - 2 - hydroxy - phenyl)-2,6-xylenol
4 - chloro - a,a′ - bis(5 - chloro - 3 - n - propyl - 2 - hydroxy-phenyl)-2,6-xylenol
4 - chloro - a,a′ - bis(3 - n - butyl - 5 - chloro - 2 - hydroxy-phenyl)-2,6-xylenol

and their corresponding alkali metal salts. Of this preferred group the most effective antiseptic agents are the 4 - halo - a,a′ - bis(5 - halo - 2 - hydroxy - m - tolyl) - 2,6-xylenols and their corresponding alkali metal derivatives.

As exemplary of other tris-phenols of this invention which when admixed with a detergent form an efficient antiseptic detergent composition are:

4 - chloro - a,a′ - bis(5,6 - dichloro - 2 - hydroxy - m - tolyl)-2,6-xylenol
4 - bromo - a,a′ - bis(5,6 - dichloro - 2 - hydroxy - m - tolyl)-2,6-xylenol
4 - chloro - a,a′ - bis(4,5,6 - trichloro - 2 - hydroxy - m - tolyl)-2,6-xylenol
4 - bromo - a,a′ - bis(4,5,6 - trichloro - 2 - hydroxy - m - tolyl)-2,6-xylenol
4 - chloro - a,a′ - bis(5 - bromo - 6 - chloro - 2 - hydroxy - m-tolyl)-2,6-xylenol
4 - chloro - a,a′ - bis(5,6 - dichloro - 3 - ethyl - 2 - hydroxy-phenyl)-2,6-xylenol
4 - chloro - a,a′ - bis(5,6 - dichloro - 2 - hydroxy - m - tolyl)-3-methyl-2,6-xylenol
4 - chloro - a,a′ - bis(5,6 - dichloro - 2 - hydroxy - m - tolyl)-3-n-butyl-2,6-xylenol
4 - chloro - a,a′ - bis(5,6 - dichloro - 2 - hydroxy - m - tolyl)-3,5-dimethyl-2,6-xylenol
4 - chloro - a,a′ - bis(5 - chloro - 2 - hydroxy - m - tolyl) - 3,5-dimethyl-2,6-xylenol
4 - chloro - a,a′ - bis(5,6 - dichloro - 3 - ethyl - 2 - hydroxy-phenyl)-3,5-dimethyl-2,6-xylenol
4 - bromo - a,a′ - bis(3 - benzyl - 5 - chloro - 2 - hydroxy - phenyl)-2,6-xylenol
4 - chloro - a,a′ - bis(5 - chloro - 3 - cyclohexyl - 2 - hydroxy-phenyl)-2,6-xylenol
4 - chloro - a,a′ - bis(5 - chloro - 3 - phenyl - 2 - hydroxy - phenyl)-2,6-xylenol

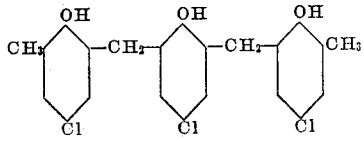
The corresponding alkali metal salts of these halogenated phenols when incorporated in detergents also produce satisfactory antiseptic detergent compositions.

As exemplary of the preparation of the antiseptic agents of this invention the following is illustrative:

EXAMPLE I

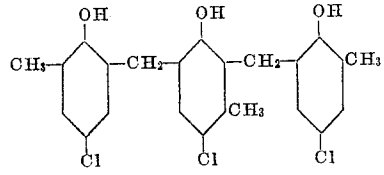
Approximately 9.5 parts by weight of 5-chloro-2-hydroxy-m-xylene-a,a′-diol and approximately 28.5 parts by weight of 4-chloro-o-cresol are intimately mixed with approximately 2.2 parts by weight conc. hydrochloric acid in a suitable reaction vessel and heated at 90° C. for approximately 15 minutes. The resultant semi-viscous mix is then slurried with approximately 35 parts by weight of a petroleum hydrocarbon (sp. gr. 0.7) consisting chiefly of heptanes, allowed to stand, the solids subsequently filtered off and dried. A yield of approximately 62.4% by weight is obtained. The recrystallized product is a white needle-like solid possessing a melting point of 194–195° C. Upon analysis, the product is found to con-

tain 24.1% chlorine and is believed to be 4-chloro-a,a'-bis(5-chloro-2-hydroxy-m-tolyl)-2,6-xylenol,



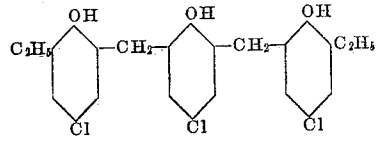
EXAMPLE II

Approximately 10.1 parts by weight of 5-chloro-2-hydroxy-4-methyl-m-xylene-a,a'-diol and approximately 28.5 parts by weight of 4-chloro-o-cresol are intimately mixed with approximately 2.2 parts by weight of conc. hydrochloric acid in a suitable reaction vessel and heated at 90° C. for approximately 15 minutes. The resultant semi-viscous mix is then slurried with approximately 35 parts by weight of a petroleum hydrocarbon (sp. gr. 0.7) consisting chiefly of heptanes, allowed to stand, the solids subsequently filtered off and dried. A yield of approximately 65.1% by weight is obtained. The recrystallized product is a white needle-like solid possessing a melting point of 166–167° C. Upon analysis the product is found to contain 23.8% chlorine and is believed to be 4-chloro-a,a'-bis(5-chloro-2-hydroxy-m-tolyl)-3-methyl-2,6-xylenol,



EXAMPLE III

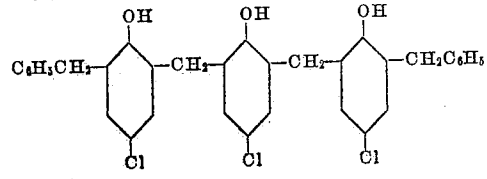
Approximately 9.4 parts by weight of 5-chloro-2-hydroxy-m-xylene-a,a'-diol and approximately 30.0 parts by weight of 2-ethyl-p-chlorophenol are intimately mixed with approximately 3.3 parts by weight of conc. hydrochloric acid in a suitable reaction vessel and heated at 90° C. for approximately 30 minutes. The resultant semi-viscous mix is then slurried with approximately 22 parts by weight of toluene, allowed to stand, and the solids subsequently filtered off and dried. Upon recrystallization a 34.6% yield of a white crystalline material possessing a melting point of about 222–223° C. believed to be 4-chloro-a,a'-bis (5-chloro-3-ethyl-2-hydroxy phenyl)-2,6-xylenol,



is obtained.

EXAMPLE IV

Approximately 9.4 parts by weight of 5-chloro-2-hydroxy-m-xylene-a,a'-diol, approximately 30.0 parts by weight of 2-benzyl-p-chlorophenol, approximately 25 parts by weight of glacial acetic acid, and approximately 9 parts by weight of conc. sulfuric acid are intimately mixed in a suitable reaction vessel and heated on a steam bath for three hours. Upon steam distilling the reaction mix the viscous mass obtained is slurried with toluene, allowed to stand, and the solids subsequently filtered off and dried. Upon recrystallization a white crystalline product possessing a melting point of 177–178° C. believed to be 4-chloro-a,a'-bis(5-chloro-3-benzyl-2-hydroxy-phenyl)-2,6-xylenol



is obtained.

By replacing 4-chloro-o-cresol of Example I with an equimolar proportion of 4-bromo-o-cresol and carrying out the condensation with 5-chloro-2-hydroxy-m-xylene-a,a'-diol in substantially the same manner a good yield of 4-chloro-a,a'-bis(5-bromo-2-hydroxy-m-tolyl)-2,6-xylenol is obtained. Similarly by the employment of 4-bromo-o-cresol and 5-bromo-2-hydroxy-m-xylene-a,a'-diol as reactants a good yield of 4-bromo-a,a'-bis(5-bromo-2-hydroxy-m-tolyl)-2,6-xylenol is obtained.

The alkali metal salts, particularly the mono-alkali metal salts, of the halogenated tris-phenols of this invention are conveniently prepared by heating in suitable proportions a halogenated tris-phenol with an aqueous solution of an alkali metal hydroxide, such as potassium hydroxide, sodium hydroxide or lithium hydroxide. However, the di- and tri-alkali metal salts in many instances require more drastic conditions, as for example refluxing the tris-phenol with a mixture of alcohol and the alkali metal hydroxide in the necessary proportions.

As exemplary of this invention 4-chloro-a,a'-bis(5-chloro-2-hydroxy-m-tolyl)-2,6-xylenol and 4-chloro-a,a'-bis(5-chloro-2-hydroxy-m-tolyl)-3-methyl-2,6-xylenol are, respectively, compounded in a detergent composition and compared to a detergent composition containing a similar halogenated tris-phenol. The halogenated tris-phenols listed below are, respectively, incorporated in an "Ivory" brand white high grade tallow soap to form 2% by weight compositions, that is a ratio of one part of halogenated tris-phenol to 49 parts soap. Aliquots of each are added to a nutrient agar so as to give concentrations of 0.17 p. p. m., 0.34 p. p. m., 0.67 p. p. m., 1.25 p. p. m. and 25 p. p. m. of the halogenated tris-phenol in the nutrient agar. The agar in each case is then poured into a petri dish, allowed to harden and then is streaked with a 24 hour old culture of *Staphylococcus aureus* of standard resistance. The incubation in each case is made at 37° C. for 72 hours and the degree of growth is noted below:

Table

Halogenated Tris-Phenol	2.5 p. p. m.	1.25 p. p. m.	0.67 p. p. m.	0.34 p. p. m.	0.17 p. p. m.
4-chloro-a,a'-bis(5-chloro-2-hydroxy-m-tolyl)-3-methyl-2,6-xylenol	–	–	–	½+	+
4-chloro-a,a'-bis(5-chloro-2-hydroxy-m-tolyl)-2,6-xylenol	–	–	–	–	–
4-chloro-a,a'-bis(5-chloro-2-hydroxy-p-tolyl)-2,6-xylenol (M. P. 236° C.)	+++	+++	+++	+++	0

Legend:

–	No growth.
½+	Extremely light growth.
+	Very light growth.
++	Light to moderate growth.
+++	Normal heavy growth.
0	Not tested.

By replacing any one of the aforementioned halogenated tris-phenols of the aforedescribed detergent compositions with an equal weight of either 4-chloro-a,a'-bis(5-bromo-2-hydroxy-m-tolyl)-2,6-xylenol or 4-bromo-a,a'-bis(5-bromo-2-hydroxy-m-tolyl)-2,6-xylenol and similarly evaluating excellent control of *Staphylococcus aureus* is obtained. Good control of *Staphylococci* is obtained by the usage of either 4-chloro-a,a'-bis(3-benzyl-5-chloro-2-hydroxy-phenyl)-2,6-xylenol, or 4-chloro-a,a'-bis(5-chloro-3-ethyl-2-hydroxy-phenyl)-2,6-xylenol.

Relatively small amounts of the halogenated tris-phenols of this invention or their alkali metal salts or mixtures of said phenols and said alkali metal salts in a detergent composition have been found to yield efficient antiseptic detergent compositions. Amounts as low as 0.5–1% by weight based upon the detergent of a halogenated tris-phenol of this invention or its alkali metal salt or mixtures

thereof have proved satisfactory in some instances. However, it is preferred to employ amounts in the order of 1–3% by weight. While larger amounts can be employed, as for example up to 10% by weight, the upper limit is determined by practical considerations.

Other antiseptic agents may be incorporated where desired as well as emollients, water softeners, and the well known "vehicles" of the detergent trade. Various colors, antioxidants, perfumes, and the like can be included also.

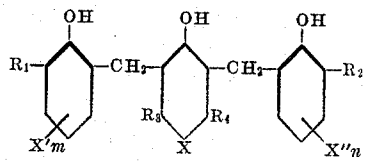
The term "detergent" includes soap and synthetic detergents, particularly the anionic detergents such as the substituted amides and the alkylated aryl sulfonates. The term "detergent" includes also mixtures of synthetic detergents and soap. The term "soap" or "detergent soap" as used herein is employed in its popular or ordinary meaning, that is, those cleansing compositions prepared from an alkali metal compound such as potassium or sodium hydroxide and a fat or fatty acid, both saturated and unsaturated.

The halogenated tris-phenols of this invention or the alkali metal salts thereof or mixtures thereof may be added to the detergent composition in any suitable manner during the crutching or milling or similar operation. The antiseptic agents of this invention may be first dissolved in a suitable solvent and then incorporated in the detergent if so desired. In general any method which results in the halogenated tris-phenols of this invention or their alkali metal salts thereof or mixtures of said phenols and said salts being uniformly incorporated in the final detergent composition is satisfactory.

While the invention has been described relative to several particular embodiments it is not so limited but that many variations and modifications which are obvious to those skilled in the art to which this invention appertains may be made without departing from the spirit or scope of the invention.

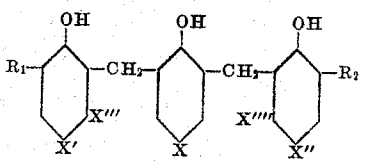
What is claimed is:

1. An antiseptic detergent composition possessing cleansing properties consisting essentially of a detergent soap and 0.5 to 10% by weight based upon the detergent soap of a halogenated tris-phenol of the formula



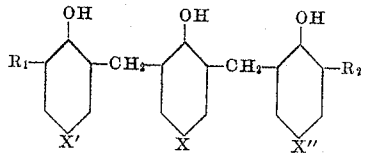
where R_1 and R_2 are hydrocarbon radicals selected from the group consisting of alkyl radicals containing from 1 to 4 carbon atoms, cyclohexyl, benzyl and phenyl, where R_3 and R_4 are selected from the group consisting of hydrogen atoms and alkyl radicals containing not more than 4 carbon atoms, where X, X′ and X″ are halogen atoms having an atomic weight greater than 20 but less than 80, and where *m* and *n* are whole numbers from 1–3.

2. An antiseptic detergent composition consisting essentially of a detergent soap and 0.5 to 10% by weight based upon the detergent soap of a halogenated tris-phenol of the formula



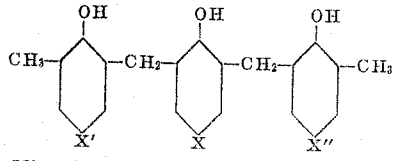
wherein R_1 and R_2 are alkyl radicals containing not more than 4 carbon atoms and where X, X′, X″, X‴ and X⁗ are halogen atoms having an atomic weight greater than 20 but less than 80.

3. An antiseptic detergent composition consisting essentially of a detergent soap and 0.5 to 10% by weight based upon the detergent soap of a halogenated tris-phenol of the formula



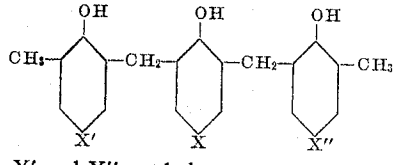
where R_1 and R_2 are alkyl radicals containing not more than 4 carbon atoms and where X, X′ and X″ are halogen atoms having an atomic weight greater than 20 but less than 80.

4. An antiseptic detergent composition consisting essentially of a detergent soap and 0.5 to 10% by weight based upon the detergent soap of a halogenated tris-phenol of the formula



where X, X′ and X″ are halogen atoms having an atomic weight greater than 20 but less than 80.

5. An antiseptic detergent composition consisting essentially of a detergent soap and 1 to 3% by weight based upon the detergent soap of a halogenated tris-phenol of the formula



where X, X′ and X″ are halogen atoms having an atomic weight greater than 20 but less than 80.

6. An antiseptic detergent composition consisting essentially of a detergent soap and 1 to 3% by weight based upon the detergent soap of 4-chloro-a,a′-bis(5-chloro-2-hydroxy-m-tolyl)-2,6-xylenol.

7. An antiseptic detergent composition consisting essentially of a detergent soap and 1 to 3% by weight based upon the detergent soap of 4-chloro-a,a′-bis(5-bromo-2-hydroxy-m-tolyl)-2,6-xylenol.

8. An antiseptic detergent composition consisting essentially of a detergent soap and 1 to 3% by weight based upon the detergent soap of 4-bromo-a,a′-bis(5-bromo-2-hydroxy-m-tolyl)-2,6-xylenol.

9. An antiseptic detergent composition consisting essentially of a detergent soap and 1 to 3% by weight based upon the detergent soap of 4-chloro-a,a′-bis(5-chloro-2-hydroxy-m-tolyl)-3-methyl-2,6-xylenol.

10. An antiseptic detergent composition consisting essentially of a detergent soap and 1 to 3% by weight based upon the detergent soap of 4-chloro-a,a′-bis(5-chloro-3-ethyl-2-hydroxy-phenyl)-2,6-xylenol.

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