United States Patent Office

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# ANTISEPTIC SOAP COMPOSITION

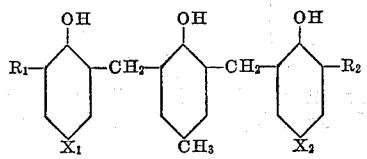
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10 Claims. (Cl. 252—107)

This invention relates to new and useful compositions of matter.

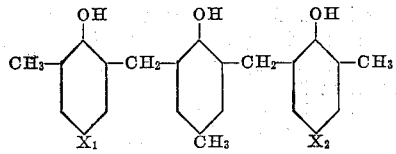
In accordance with this invention it has been found that halogenated tris-phenols of the general formula



where $R_1$ and $R_2$ are like or unlike short chain alkyl radicals such as methyl, ethyl, propyl, isopropyl, butyl, etc., and where $X_1$ and $X_2$ are like or unlike halogen atoms, and their corresponding alkali metal salts comprise a family of highly useful compounds.

The new compounds have been found to have exceptional antiseptic properties in cosmetic formulations and in particular it has been found that the new compounds 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 are readily incorporated in a detergent whether the latter be liquid or solid. The halogenated tris-phenols of this invention and their alkali metal salts 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 compounds of this invention when compounded with a detergent produce a non-skin irritating detergent composition.

In its preferred embodiment the invention relates to halogenated tris-phenols of the general formula



and their corresponding mono-alkali metal salts where $X_1$ and $X_2$ are either chlorine or bromine atoms. These tris-phenols and their corresponding mono-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 and in cosmetic formulations.

As exemplary of the preferred halogenated tris-phenols of this invention are

4-methyl-a,a'-bis(2 - hydroxy - 3 - methyl-5-chlorophenyl)-2,6-xylenol

4-methyl-a,a'-bis(2-hydroxy-3-methyl - 5 - bromophenyl)-2,6-xylenol

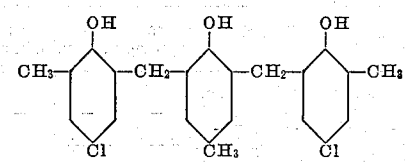
and their corresponding mono-alkali metal salts.

As exemplary of the preparation of the new compounds the following is illustrative:



## EXAMPLE I

Approximately 16.8 parts by weight of 5-methyl-2-hydroxy-m-xylene-a,a'-diol and approximately 50.0 parts by weight of 4-chloro-o-cresol are intimately mixed with approximately 2.0 parts by weight of conc. hydrochloric acid in a suitable reaction vessel, the temperature rising to about 95° C. Upon standing the mass cools and solidifies, which solid mass 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 being subsequently filtered off and dried. A yield of approximately 67.3% by weight is obtained. The recrystallized product is a white needle-like solid possessing a melting point of 230–231° C. Upon analysis, the product is found to contain 16.93% chlorine and is believed to be 4-methyl-a,a'-bis(2-hydroxy-3-methyl-5-chlorophenyl)-2,6-xylenol,



The white solid mono-sodium salt derivative thereof is obtained upon heating the phenol with an equimolecular amount of sodium hydroxide in an aqueous medium.

## EXAMPLE II

Employing the process of Example I but replacing 4-chloro-o-cresol with an equimolar amount of 4-bromo-o-cresol a good yield of a solid believed to be 4-methyl-a,a'-bis(2-hydroxy-3-methyl - 5 - bromophenyl)-2,6-xylenol is obtained.

The following examples in tabular form are presented to illustrate the variety of new halogenated tris-phenols which can be prepared according to the process of Example I.

*Products of reaction of 5-methyl-2-hydroxy-m-xylene-a,a'-diol with a 4-halo-o-alkyl phenol*

| 4-Halo-o-Alkyl Phenol | Product |
|---|---|
| 4-chloro-2-ethyl-phenol | 4-methyl-a,a'-bis(5-chloro-3-ethyl-2-hydroxy-phenyl)-2,6-xylenol. |
| 4-bromo-2-ethyl-phenol | 4-methyl-a,a'-bis(5-bromo-3-ethyl-2-hydroxy-phenyl)-2,6-xylenol. |
| 4-chloro-2-n-propyl-phenol | 4-methyl-a,a'-bis(5-chloro-3-n-propyl-2-hydroxy-phenyl)-2,6-xylenol. |
| 4-chloro-2-n-butyl-phenol | 4-methyl-a,a'-bis(5-chloro-3-n-butyl-2-hydroxy-phenyl)-2,6-xylenol. |
| 4-bromo-2-sec. butyl-phenol | 4-methyl-a,a'-bis(5-bromo-3-sec. butyl-2-hydroxy-phenyl)-2,6-xylenol. |

Any of the above halogenated tris-phenols when admixed with a detergent composition form efficient antiseptic detergent compositions. The corresponding alkali metal salts of these halogenated tris-phenols when incorporated in detergent compositions also produce satisfactory antiseptic detergent compositions.

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-methyl-a,a'-bis(2-hydroxy-3-methyl-5-chlorophenyl)-2,6-xylenol is compounded in a detergent composition and compared to detergent compositions which, respectively, contain analogous halogenated tris-phenols. The tris-phenols listed below are, respectively, incorporated in an "Ivory" brand white high grade soap (a mixture of 80% sodium soap and 20% potassium soap produced from a 70% tallow and 30% coconut oil glyceride blend in accordance with U. S. 2,295,594) 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 1.25 p. p. m., 2.5 p. p. m., 5 p. p. m., and 10 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 I*

| Halogenated Tris-Phenol | 10 p. p. m. | 5 p. p. m. | 2.5 p. p. m. | 1.25 p. p. m. |
|---|---|---|---|---|
| 4-methyl-a,a'-bis(2-hydroxy-3-methyl-5-chlorophenyl)-2,6-xylenol | – | – | – | ½+ |
| 4-t-butyl-a,a'-bis(2-hydroxy-3-methyl-5-chlorophenyl)-2,6-xylenol | +++ | +++ | 0 | 0 |
| 4-methyl-a,a'-bis(3,5-dichloro-2-hydroxy-phenyl)-2,6-xylenol | – | ½+ | +++ | +++ |
| 4-methyl-a,a'-bis(5-chloro-2-hydroxy-phenyl)-2,6-xylenol | +++ | +++ | 0 | 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 4-methyl-a,a'-bis(2-hydroxy-3-methyl-5-bromophenyl)-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-methyl-a,a'-bis(5-chloro-3-ethyl-2-hydroxy-phenyl)-2,6-xylenol, or 4-methyl-a,a'-bis(5-chloro-3-n-propyl-2-hydroxy-phenyl)-2,6-xylenol. Good control of Staphylococci is obtained also by the usage of the mono-sodium salt of 4-methyl-a,a'-bis(2-hydroxy-3-methyl-5-chlorophenyl)-2,6-xylenol and the mono-potassium salt of 4-methyl-a,a'-bis(3-allyl-5-chloro-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.

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.

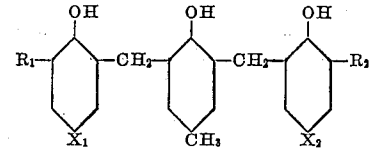


The halogenated tris-phenols of this invention or the alkali metal salts thereof or mixtures thereof may be added to the detergent composition in any suitable manner during the crutching or milling or similar operation. The antiseptic agents of this invention may be first dissolved in a suitable solvent 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.

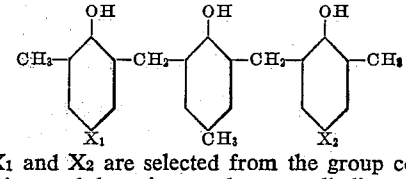
What is claimed is:

1. A halogenated tris-phenol of the formula



where $R_1$ and $R_2$ are short chain alkyl radicals and where $X_1$ and $X_2$ are halogen atoms, and alkali metal salts thereof.

2. A halogenated tris-phenol of the formula



where $X_1$ and $X_2$ are selected from the group consisting of chlorine and bromine, and mono-alkali metal salts thereof.

3. 4-methyl-a,a'-bis(2-hydroxy-3-methyl-5-chlorophenyl) 2,6-xylenol.

4. 4-methyl-a,a'-bis(2-hydroxy-3-methyl-5-bromophenyl)-2,6-xylenol.

5. The monosodium salt of the tris-phenol of claim 3.

6. An antiseptic detergent composition comprising the combination of a detergent soap and 0.5 to 10% by weight based upon the detergent soap of a halogenated tris-phenol of claim 1.

7. An antiseptic detergent composition comprising the combination of a detergent soap and 0.5 to 10% by weight based upon the detergent soap of a halogenated tris-phenol of claim 2.

8. An antiseptic detergent composition comprising the combination of a detergent soap and 1 to 3% by weight based upon the detergent soap of a halogenated tris-phenol of claim 3.

9. An antiseptic detergent composition comprising the combination of a detergent soap and 1 to 3% by weight based upon the detergent soap of a halogenated tris-phenol of claim 4.

10. An antiseptic detergent composition comprising the combination of a detergent soap and 1 to 3% by weight based upon the detergent soap of a halogenated tris-phenol of claim 5.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,353,724 | Gump | July 18, 1944 |
| 2,544,826 | Craige | Mar. 13, 1951 |

OTHER REFERENCES

Ziegler et al.: Monatshefte für Chemie, vol. 43 (1948) (pages 334–342).

Megson et al.: Jour. Soc. Chem. Industry, vol. 49 (1930) (pages 251T–257T).