

UNITED STATES PATENT OFFICE

2,535,077

GERMICIDAL SOAPS CONTAINING
HALOGENATED DIHYDROXY DI-
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N. J., assignors, by mesne assignments, to Sin-
dar Corporation, a corporation of New JerseyNo Drawing. Application January 20, 1944,
Serial No. 519,000

14 Claims. (Cl. 252-107)

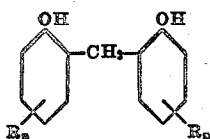
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This invention relates to germicidal soaps, and more particularly to soaps, whether in solid or liquid form, that combine the detergent properties of ordinary soaps and the germicidal properties of certain phenolic materials.

This application is a continuation-in-part of our co-pending application, Serial Number 324,054, filed March 15, 1940, now abandoned.

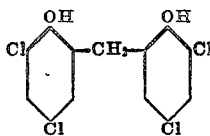
According to this invention, soaps such as washing, toilet, or liquid soaps may be rendered germicidal by incorporating therein a small amount of a 2,2'-dihydroxy halogenated diphenyl methane.

The 2,2'-dihydroxy halogenated diphenyl methanes used in this invention may be represented according to their chemical structure as follows:

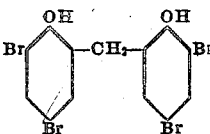


where R is halogen and n is an integer from 1 to 4 inclusive.

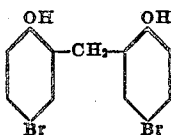
As examples of specific members of the foregoing class of compounds the following may be noted:



melting point 166°-167° C.,

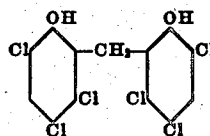


melting point 198°-199° C.,

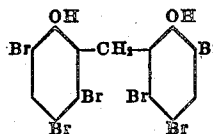


melting point 182°-183° C.,

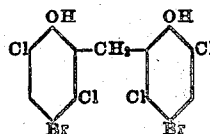
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melting point 164°-165° C.,



melting point 180° C., and



melting point 166-166.5° C.;

their mono-sodium (or potassium or lithium) salts.

All of the 2,2'-dihydroxy halogenated diphenyl methanes thus far prepared are white, crystalline solids. The alkali metal salts are white, substantially odorless substances that do not possess clearly-defined melting points, but decompose at varying temperatures upon heating.

Relatively small amounts of the germicidal agents of the invention are sufficient to render soap germicidal. Amounts as low as 1/2 of 1% of the germicidal agent, based on the weight of the soap content of the final soap product, have proved satisfactory in some cases. However, we prefer to use amounts of the order of 1 to 3% on the same basis. The upper limit of the amount of agent which may be used is determined by practical considerations. As a general rule, increasing the concentration of agent in the soap increases the germicidal activity of the resulting soap. However, the cost of the agent relative to the cost of the soap itself mitigates against the use of too large an amount of the agent in soap. Moreover, large amounts of the agent in soap are to be avoided since it is desired to obtain a resulting soap product with satisfactory detergent properties.

The invention may be practiced by adding the agents to the soap in any suitable manner during the crutching or milling or similar operation. Care should be taken to obtain a uniform distribution of the agents throughout the soap. They may be dissolved in a small amount of a suitable solvent, for example, acetone or alcohol. If desired, however, the agents may be added directly to the soap without dissolving them previously. In the case of "frame" soaps, we prefer to add the agents to the soap during the crutching operation. With milled soaps, we prefer to make the addition during the milling operation. In the case of liquid soaps, we prefer to effect the addition while the agent is in solution. In general, any method which results in the agent being uniformly incorporated into the final soap product is satisfactory.

We are aware that it is already known to combine soap and phenolic materials to make soap-containing disinfectants. Such compositions are not contemplated by this invention and indeed are materially distinguishable from germicidal soaps. Soap-containing disinfectants are not ordinarily used for detergent purposes. Their soap content is primarily used to solubilize the phenols and is present normally in no greater amount than the phenolic material. On the other hand, the germicidal soaps of this invention are both detergents and germicides. They combine the properties of both types of materials, and thus can be used as toilet, washing or liquid soaps, unlike the soap-containing disinfectants. Moreover, the instant germicidal soaps contain only a small amount of phenolic material in comparison to the soap content.

We are also aware that soaps allegedly possessing both detergent and germicidal properties have been suggested. However, so far as we have been able to ascertain, such soaps which do appear to combine these two properties depend upon the presence of mercury-containing compounds. Such compounds have certain disadvantages not possessed by the phenolic materials of this invention. In this connection we may mention the widely-held view that mercury compounds are toxic and that they are cumulative poisons. Indeed, we have noted that all commercial soaps containing mercury that we have seen are labelled "Poison." In addition, soaps containing mercury compounds are irritating to the skin of the user.

We believe our invention to have been most unexpected. This conclusion is reached by a consideration of the prior art relating to the use of phenolic materials in soaps. As to the latter, we believe a fair picture can be obtained from some excerpts taken from Hampil, *Journal of Bacteriology*, vol. XVI, pp. 287-300, (1928). In the introduction of this article, the author states:

"It has been abundantly shown that soaps in general have a limited germicidal value, . . . and various workers have expressed the idea that this is due for the most part to their detergent properties. The literature indicates that a large variety of organisms have been tested, at time intervals of exposure from two and one-half to sixty minutes. Soaps prepared from various types of oils have shown more or less selective action. The typhoid, diphtheria and colon bacilli, the spirochetes, the gonococcus, the meningococcus and different types of the streptococci are easily destroyed. On the other hand, it is significant that *Staphylococcus aureus* is particularly resistant. It is no doubt because of this

selective action that efforts have been made from time to time to incorporate certain germicidal substances into soaps, and thereby manufacture a product which will not only cleanse but at the same time destroy organisms found on the skin, regardless of the type present. There are numerous commercial soaps on the market at the present time, to many of which have been added phenolic derivatives. The soaps are labelled as antiseptic, and a phenol coefficient is often determined. As yet there are no scientific data to show that the incorporation of the phenolic substances has added to the intrinsic germicidal activity which the soap itself may possess. The determination of the phenol coefficient for such a so-called 'antiseptic soap' is in practice the measure of its activity against *Bacillus typhosus*, which organism has been shown by several workers to be very susceptible to the disinfectant action of soaps."

After an investigation "undertaken to determine the effect of pure individual soaps on the germicidal activity of certain representative phenolic substances," the author reached these conclusions, inter alia:

"From a practical standpoint, this work indicates the unsuitability of phenolic compounds as germicidal agents in soaps. A germicidal soap is expected to perform a double function. It must cleanse the surface, whether this surface be the skin, floors, or walls, etc. . . .

"The marked inhibitory action of sodium oleate, sodium myristate, potassium palmitate and potassium stearate on the bactericidal properties of phenol, metacresol, secondary butyl phenyl, n-butyl resorcinol and n-hexyl resorcinol has been demonstrated. The relationship appears to be more or less quantitative and indicates the impossibility of producing a germicidal soap by adding small quantities of a phenolic compound to soap. The addition of large quantities of a phenolic disinfectant is not feasible, since the cost of production precludes the use of any but very crude and irritating phenols. Phenols are therefore unsuitable as disinfectant agents in the production of germicidal soaps."

It is noted that the Hampil article was published in 1928 and thus would seem to be too old to represent the present state of the art. However, a diligent search of the scientific and patent literature to bring the matter up to date indicates that this is not so and that the Hampil article as above stated is a fair statement of the position of the present prior art.

The method employed to test the germicidal properties of the soaps of this invention is that of the U. S. Food and Drug Administration. (Circular 198, December 1931.) The liquid soap employed had a 40% soap content and was prepared from a mixture of 75% coconut oil and 25% castor oil. The solid soap used was a neutral white toilet soap of the "Lux" type. The fatty acids in this soap were of the following composition:

	Per cent
Oleic and linoleic acids-----	About 45
Palmitic acid-----	About 30
Stearic acid-----	About 10
Lower fatty acids (lauric, etc.)-----	About 15

The table which follows gives the results obtained. A minus (—) sign means all bacteria were killed. A plus (+) sign means some bacteria survived. Unless otherwise indicated, the compounds were tested in liquid soap.

Compound	Amount of Compound in Soap	Concentration of Compound as tested	Exposure to <i>Staph. aureus</i> at 20° C.	
			2 min.	10 min.
2,2'-dihydroxy-3,5,5'-dibromo diphenyl methane.....	Per cent 3	1:1000 1:2000	----- -----	----- +
2,2'-dihydroxy-3,5,3',5'-tetrabromo diphenyl methane.....	2	1:1000 1:1500	----- +	----- -----
2,2'-dihydroxy-3,5,6-3',5',6'-hexabromo diphenyl methane.....	2	1:1500 1:2000	----- +	----- -----
2,2'-dihydroxy-3,5,3',5'-tetrachloro diphenyl methane.....	2	1:1000 1:1500	----- +	----- -----
2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane.....	1	1:2000 1:3000	----- +	----- -----
1 at 37° C.				
2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane.....	1.5	1:2000 1:3500	----- +	----- -----
Sodium Salt of 2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane.....	1.5	1:2000 1:3500	----- +	----- -----

¹ A temperature of 20° C. was found to yield a jelly-like mass when solid soap was tested. Accordingly, 37° C. was adopted as the temperature of test.

² In white solid soap.

The foregoing data indicate the practical applicability as germicidal soaps of soaps containing small amounts of a 2,2'-dihydroxy halogenated diphenyl methane compound. For example, these results show that 2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane is capable of killing *Staphylococcus aureus* in a concentration of 1 to 3500 in the presence of large excess of soap. Since soap is usually diluted about 20 times in making a lather for normal toilet purposes, it follows that the 2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane need be present in the soap in a concentration of only 1 part to 175 parts of soap or about 0.6% to yield an effective germicidal soap. For practical reasons, however, we prefer, as above stated, to use somewhat larger amounts of the added germicidal agent.

Our germicidal soaps, which are indistinguishable in appearance from ordinary toilet soaps, may be used as ordinary detergent soaps and are especially recommended for uses in which both detergent and degerming characteristics are desired. Soaps containing 2% of 2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane have already been used daily by a considerable number of persons over a period of months, with excellent results. In addition, it has been noted that soap containing 2% of 2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane is particularly valuable for routine surgical and hospital use and generally helpful as a prophylactic agent in the prevention of infections caused by pathogenic bacteria on the skin. Also, results indicate that such a soap, used routinely for a period of a week, materially reduces the bacterial population of the skin and that a surgeon would be able to maintain at all times under normal conditions as low a bacterial population on his skin as the surgeon might expect to have after he has prepared himself for an operation by means of the standard hospital "scrub-up"

technique. Such results have not been reported for any other soaps thus far tested.

The term "soap" as used herein is employed in its popular or ordinary meaning. The term refers to cleansing agents, made usually by the action of alkali on fat or fatty acids and consisting essentially of sodium or potassium salts of fatty acids, both saturated and unsaturated.

The term "germicidal soap" for the purposes of this patent application refers to those soaps which are effective against *Staphylococcus aureus*. For example, if a soap is effective against *Staphylococcus aureus*, the soap is considered to be germicidal, whether or not it is effective against any other types of bacteria.

The condensation products used in this invention may be prepared by condensing certain phenols with formaldehyde or formaldehyde-yielding substances in the presence of sulfuric acid at temperatures between about 0° C. and 20° C., the reaction occurring, advantageously, in the presence of a liquid which is inert under the conditions of the reaction and which is further characterized by being a solvent for the phenol employed and also by being miscible with sulfuric acid. The resulting 2,2'-dihydroxy halogenated diphenyl methane may be isolated in known manner. An example of a known way to isolate the desired condensation product is that wherein the products of reaction are quenched in ice or ice water and the resulting precipitate is washed acid-free; the washed precipitate is then dried and recrystallized from a solvent such as benzene or toluene; and finally, the recrystallized product is dried to remove substantially all of the solvent therefrom.

The alkali metal salts of the condensation products may be prepared by treating a solution of the condensation products used in this invention with an aqueous alkali hydroxide solution and filtering the resulting alkali metal salt.

In the claims the recitation of the halogenated dihydroxy diphenyl methanes is intended also to include the corresponding mono-alkali metal salts.

The foregoing illustrates the practice of our invention which, however, is not to be limited thereby but is to be construed as broadly as permissible in view of the prior art and limited solely by the appended claims.

We claim:

1. A germicidal detergent soap comprising soap and a minor proportion of 2,2'-dihydroxy halogenated diphenyl methane.
2. A germicidal detergent soap comprising soap and 1 to 3% of a 2,2'-dihydroxy-halogenated diphenyl methane.
3. A germicidal detergent soap comprising soap and minor proportion of 2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane.
4. A germicidal detergent soap comprising soap and 1 to 3% of 2,2'-dihydroxy-3,5,6-3',5',6'-hexachloro diphenyl methane.
5. A germicidal detergent soap comprising soap and minor proportion of 2,2'-dihydroxy-3,5-3',5'-tetrachloro diphenyl methane.
6. A germicidal detergent soap comprising soap and 1 to 3% of 2,2'-dihydroxy-3,5-3',5'-tetrachlorodiphenyl methane.
7. A germicidal detergent soap comprising soap and minor proportion of 2,2'-dihydroxy-3,5-3',5'-tetrabromo diphenyl methane.
8. A germicidal detergent soap comprising soap and 1 to 3% of 2,2'-dihydroxy-3,5-3',5'-tetrabromo diphenyl methane.

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9. A germicidal detergent soap comprising soap and a minor proportion of 2,2'-dihydroxy chlorinated diphenyl methane.

10. A germicidal detergent soap comprising soap and 1 to 3% of 2,2'-dihydroxy chlorinated diphenyl methane. 5

11. A germicidal detergent soap comprising soap and a minor proportion of 2,2'-dihydroxy brominated diphenyl methane.

12. A germicidal detergent soap comprising soap and 1 to 3% of 2,2'-dihydroxy brominated diphenyl methane. 10

13. A germicidal detergent soap comprising soap and a minor proportion of 2,2'-dihydroxy-3,6-3',6'-tetrachloro-5,5'-dibromo diphenyl methane. 15

14. A germicidal detergent soap comprising soap and a minor proportion of 2,2'-dihydroxy-3,5,6-3',5',6'-hexabromo diphenyl methane.

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