

STABILIZED GERMICIDAL SOAPS AND PROCESS OF MAKING THE SAME

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This invention relates to a process for the preparation of germicidal detergents and to germicidal detergents obtained by this process and more particularly to detergent compositions which combine the detergent properties of ordinary soaps and nonsoap detergents with the germicidal properties of N-substituted thiuram sulfides, and to a process of preparing such detergents.

It is for this reason that germicidal soaps which have recently been placed on the market have found a wide application. Such soaps contain a small amount of a germicidal agent and the use of the soap in daily washings provides sufficient germicide to keep the bacterial count at a practical minimum. In fact, the bacterial count can be lowered to a point at which it equals or is even lower than that produced by the surgeon through the application of the standard hospital scrub-up technique. Hexachlorophene (2,2'-dihydroxy-3,5,6-3',5',6'-hexachlorodiphenyl methane) has been proposed for use in soap. This substance, however, in common with other 2,2'-dihydroxy halogenated diphenyl methanes, has a low potency at low concentrations. It is not very effective against gram-negative organisms such as *Escherichia coli*. Soaps containing hexachlorophene tend to darken in daylight, and may have or develop an objectionable odor which lessens the attractiveness of such soaps to the consumer. Moreover, 2,2'-dihydroxy halogenated diphenyl methanes are expensive chemicals, and since fairly large amounts (1 to 3% basis soap weight) are needed for effective germicidal action, hexachlorophene germicidal soaps have to be marketed at a price differential compared to ordinary soaps.

In addition to the 2,2'-dihydroxy halogenated diphenyl methanes, various phenolic materials have been combined with soap, but because of the generally recognized depressing action of soap upon the bactericidal properties of germicidal agents, germicidal soaps have not been obtained. This point has been effectively demonstrated by Kunz and Gump and is reviewed in some detail at columns 3 and 4 of their U.S. Patent No. 2,535,077, dated December 26, 1950. Although the 2,2'-dihydroxy halogenated diphenyl methanes are wanting in some respects, they have been recorded as unique in that their germicidal potency is relatively unaffected by soap. In

view of the very considerable research which led to the development of these compounds, the discovery of another germicide which could be combined effectively with soap would be quite unexpected.

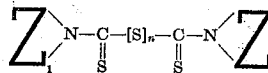
5 In accordance with the instant invention, a germicidal detergent soap is provided comprising as a germicidal agent a thiuram sulfide having each thiuram nitrogen atom fully substituted with aliphatic groups, and a peroxide which acts as a stabilizer for the thiuram sulfide.

10 At concentrations appreciably less than would be used in the case of hexachlorophene (2,2'-dihydroxy-3,5,6,3',5',6'-hexachloro diphenyl methane), such thiuram sulfides are capable of producing germicidally potent soap compositions.

15 The compositions of the invention are more active
against gram-negative organisms such as *Escherichia coli*
than hexachlorophene soaps and are more substantive to
the skin than hexachlorophene soaps. The soaps of the
invention lack offensive odors. The low cost and avail-
20 ability of these thiuram sulfides favorably distinguish
them from other germicides.

The term "thiuram sulfide" is inclusive of thiuram monosulfides, disulfides, trisulfides, tetrasulfides and hexasulfides.

25 The aliphatic thiuram sulfides used as a germicidal agent in the soap compositions of the invention have the following formula:

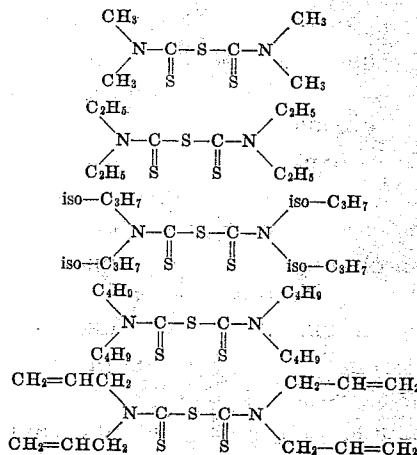


³⁵ *n* has the value of one to six, and Z₁ and Z₂ each are selected from the group consisting of a single bivalent cycloaliphatic radical and two monovalent aliphatic radicals. The number of carbon atoms is not critical, but the antibacterial activity tends to decrease as the number of carbon atoms increases, and therefore Z₁ and Z₂ preferably have from two to eight carbon atoms.

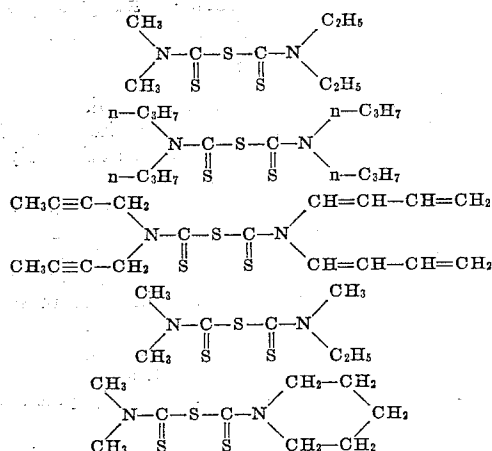
When Z_1 and/or Z_2 are bivalent, taken with the thiuram 40 nitrogen atom they form a saturated or unsaturated heterocyclic ring in which the thiuram nitrogen atom is one of the ring atoms. A typical heterocyclic radical of this type is piperidine.

When Z_1 and/or Z_2 are monovalent, they can be selected from the group consisting of saturated and unsaturated straight and branched chain aliphatic radicals, preferably having from one to four carbon atoms. Among those which can be employed are ethyl, methyl, propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, sec.-butyl, butadiene, butylene and propylene. Alkyl radicals having from one to two carbon atoms are preferred.

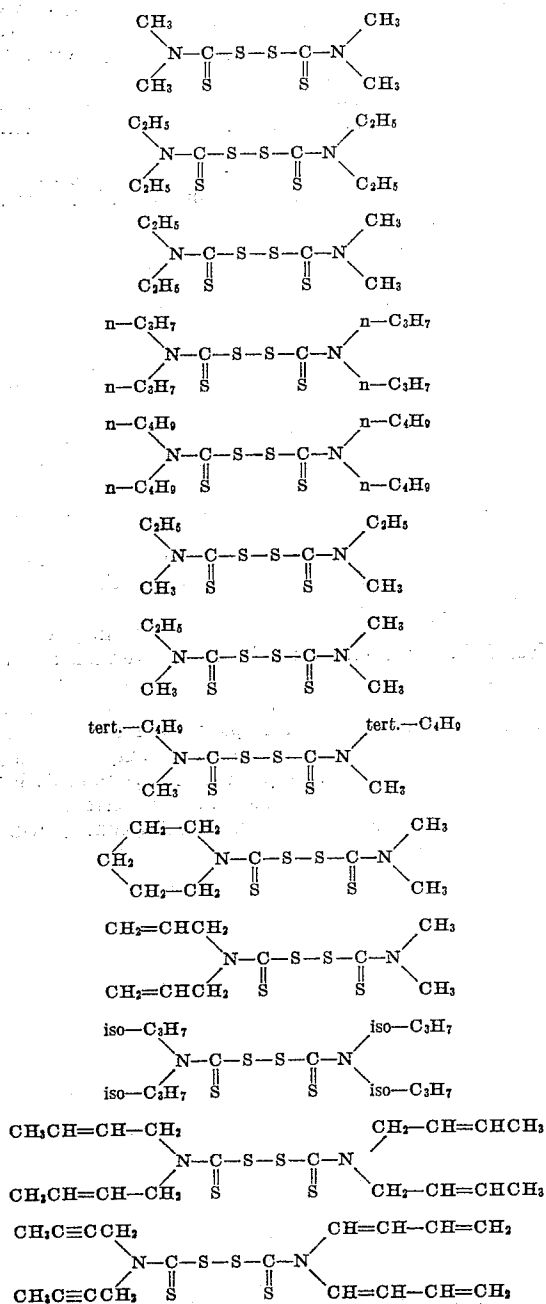
Typical aliphatic thiuram monosulfides coming within the invention are:



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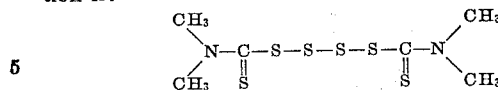


Typical aliphatic thiuram disulfides coming within the invention are:

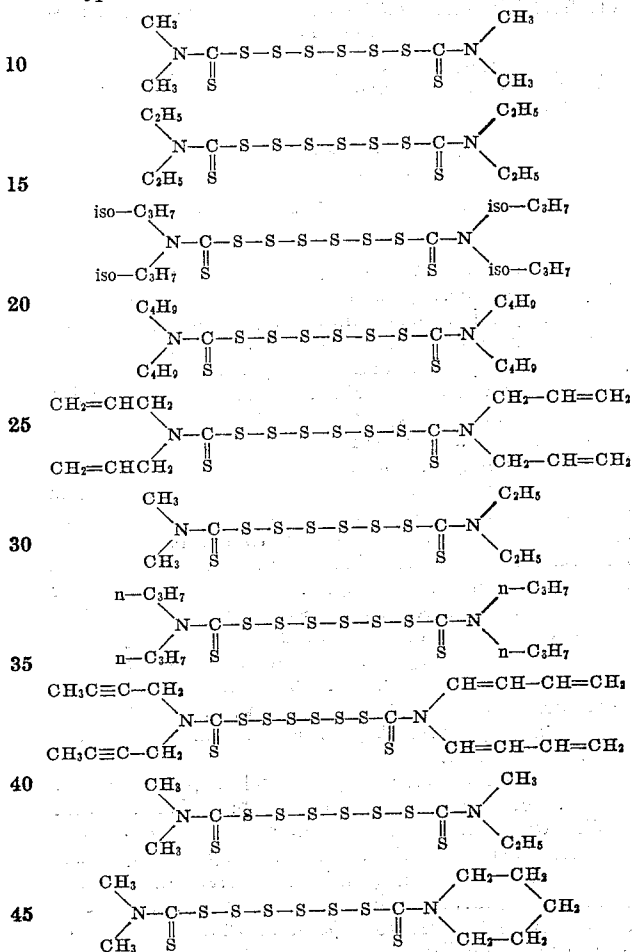


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A typical thiuram tetrasulfide coming within the invention is:



Typical thiuram hexasulfides are:



The aliphatic thiuram sulfides are known classes of materials, and their preparation is set forth in the literature. For the most part they are insoluble in water, soluble in alcohol, acetone and benzene, and very soluble in chloroform and carbon disulfide. In the quantities in which they are employed in soaps, they do not produce skin irritation, are not toxic, and are compatible with the usual soap components, including neutral salts, perfume, opacifiers and small amounts of carbonates.

The term "soap" as used herein refers to alkali metal soaps of the saturated and unsaturated higher fatty acids having from about eight to about twenty-six carbon atoms, such as capric, caprylic, lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic, arachidic, behenic, margaric, tridechoic, and cerotic acids and the mixtures of such acids naturally occurring in fats, oils, waxes, and rosins, such as the soaps of coconut oil fatty acids, tallow fatty acids, pig fat, fish oil fatty acids, beeswax, palm oil fatty acids, sesame oil fatty acids, peanut oil fatty acids, olive oil fatty acids, palm kernel oil fatty acids, cottonseed oil fatty acids, soyabean oil fatty acids, corn oil fatty acids, babassu oil fatty acids, rosin acids, abietic acid, and greases.

Only small amounts of thiuram sulfide are required to render soap germicidal. An amount as low as 0.01% based on the weight of the soap produces a soap composition having excellent antibacterial potency. As much as 5% has been used to advantage. There is no need to

employ more than is required to give the desired germicidal effect, and in general for this reason from 0.2 to 2.0% would be preferred. Increasing the concentration of thiuram sulfide beyond 5% further increases the cost of the soap and might tend to reduce the detergent properties of the composition. At unnecessarily high concentrations there is a possibility of skin irritation due to the thiuram sulfide. It will readily be seen that the thiuram sulfide concentration is not critical but would be determined from a consideration of these factors, as long as enough is used to give the desired antibacterial effect.

When exposed to high temperatures for long periods of time or over long periods of storage even at ordinary temperatures thiuram sulfide in a soap composition shows a tendency to decompose. The decomposition products are unknown but appear to include complex sulfur compounds, amines, carbon disulfide, and mercaptans. These materials lead to the development of an undesirable and in some cases an exceedingly unpleasant odor. Reactive sulfur-bearing compounds appear also to be available, because if a soap containing the decomposition products of thiuram disulfide comes into contact with copper ion a dark colored sulfur compound of copper is formed, insoluble in water, resulting in a dark colored stain which can be removed by customary cleaning methods or by treatment with acid but which it is desirable to avoid if possible. In accordance with the invention, therefore, there is incorporated in the thiuram sulfide soap composition a peroxide which acts as an inhibitor against the decomposition of the thiuram sulfide.

The term "peroxide" is inclusive of any organic or inorganic compound which forms hydrogen peroxide in alkaline solution, for example, sodium perboate, sodium pyrophosphate peroxide, lauroyl peroxide, benzoyl peroxide, and sodium persulfate. The organic peroxides are preferred because they leave no salt residue upon decomposition.

In general, it can be said that any amount of the peroxide will improve the stability of the thiuram sulfide soap against odor and staining, and the amount which would be employed therefore will depend upon the storage stability which is required. It may be observed that in the cases where the soap, because of prior processing methods, contains reducing agents, for example, hydro-sulfite added in the kettle to bleach the soap, it is necessary to employ a supplemental amount of the peroxide to function as an oxidizing agent to destroy such reducing agents.

There is no upper limit to the amount of peroxide which can be used. Amounts within the range of 0.05 to 2% have been found to give adequate inhibition of odor formation and staining, but as much as 5% is not disadvantageous, although usually unnecessary and therefore not economical. Even more than 5% can be used.

It has been found that free alkali must be eliminated from the thiuram sulfide-peroxide-soap composition. This may be accomplished, if the peroxide is acidic, by addition of a sufficient additional amount of the peroxide where necessary to take up all of the free alkali. If the peroxide is not acidic, then free acid is added in the amount required to take up all of the free alkali. As the acid, there can be used an inorganic acid, such as boric acid, or an acidic inorganic salt, such as sodium bicarbonate, or an organic acid, including the long and short chain aliphatic acids, especially the free soap acids of which the soap is formed, e.g., stearic, myristic, and palmitic acids, or mixtures of any of these.

When a peroxide is incorporated in these soap compositions, it is important that all of the ingredients be added before the thiuram sulfide, and that the thiuram sulfide be thoroughly dispersed in the soap mixture. Mixing of the batch should not be continued beyond the point at which the thiuram sulfide is thoroughly dispersed.

While several mixing procedures will be apparent to

those skilled in the art in order to achieve this result, the following procedure is recommended: The soap chips are weighed into the mixer and followed immediately by addition of the peroxide. The peroxide can be added in the form of a solution or dispersion in water, in which the concentration of the peroxide is not critical. Mixing is continued for a sufficient time to insure thorough dispersion of the peroxide in the soap. The remaining components of the mix, for example, perfume and dye, are added, in the form of a solution if desired, as quickly as possible and mixing is continued again for a long enough period to insure a thorough dispersion. Thereafter the thiuram sulfide is added with complete and adequate mixing only for the time to insure uniformity of dispersion. The final mix then can be treated in the conventional ways to produce the desired soap. To form a bar, for example, the mix can be plodded and extruded using conventional equipment.

The thiuram sulfide soaps in accordance with the invention can be formed as bar soaps, powered soaps, chip soaps, flake soaps, bead soaps, bar and cake soaps and soap compositions intended for toilet, washing and disinfectant purposes in addition to their use as detergents. The compositions can be dried in any desired way; spray drying is convenient in many instances. It is desirable to hold the temperature to which the mix is subjected during conversion into its final form below the temperature at which the thiuram sulfide would be decomposed. Soap mixtures in accordance with the invention have been subjected to temperatures up to 125° F. for periods of up to one hour without disadvantage.

The germicidal effectiveness of the soap compositions of the invention has been measured by the Serial Basin Handwashing Test (a modification of the Price Test described by Arthur R. Cade, Soap and Sanitary Chemicals, June 1950, pages 37 and 38), the Zone Reduction Test and the Skin Disc Test (a modification of the Zone Reduction Test). Details of these tests follow:

(1) *The Serial Basin Handwashing Test.*—This test determines the skin bacterial flora at various time intervals as brought about by the continuous use of germicidal soap over a two week period or more. At least six individual subjects are used as a panel in each test. Two types of soap are used in the test, the germicidal soap employed daily for the two week test period and the plain soap used where the wash water is collected in various basins for determining the counts of bacteria removed.

The subject exposes the arms up to the elbow, and 2000 cc. of lukewarm tap water are run into the sterilized first basin, the bacterial count of the water being determined by removing two 1 cc. samples which are added to 15 to 18 cc. of nutrient agar. The subject moistens the hands up to the wristline, then applies plain soap for fifteen seconds followed by thorough lathering for sixty seconds. The hands are rinsed thoroughly for fifteen seconds into the basin.

Two more similar washings are carried out successively under the tap, the area covered extending almost to the elbows, and the water is discarded.

The subject then moves to the second basin containing 2000 cc. of lukewarm tap water and carries out the washing procedure exactly as in the first basin.

The subject then moves to the third basin and repeats the washing procedure of Basins 1 and 2.

Two 1 cc. of samples of 2000 cc. wash water in each basin are removed using a sterile pipette and added to 15 cc. of nutrient agar in sterile Petri dishes. This is agitated, allowed to cool and harden and incubated at 37° C. for forty-eight hours. At the end of this time the number of colonies present are counted and the counts multiplied by 2000.

The above test is repeated at intervals over the two weeks test period. The percent reduction in bacterial count is computed on the basis of the reduction in count of the 2nd and 3rd basin wash waters.

(2) *The Zone Reduction Test.*—This test measures the inhibitory effect of an 8%¹ solution within the zone of direct contact of the solution with the bacteria-seeded agar. A range of dilutions is investigated to determine the minimum concentration of germicide in the soap solution required to effect a strong reduction in the bacterial count in the agar in direct contact therewith. An 8%¹ solution of the soap is used since this is approximately the concentration of soap found in lather.

For use in the test, cultures of *Staphylococcus aureus* and *Escherichia coli* are maintained on nutrient broth with transfers made daily. In preparing the agar plates, 0.1 ml. of a twenty-four hour nutrient broth culture of the test organism is mixed thoroughly into 15 ml. of melted nutrient agar, which is then poured into a Petri plate and permitted to harden.

Filter paper discs (0.5 inch in diameter) prepared from Whatman Filter Paper No. 2 are placed on the hardened agar circularly (about 0.75 inch from the periphery).

Each disc is wetted carefully with one measured drop of the 8% solution of a test soap, using a syringe (25 gauge needle). Six or seven discs can be arranged on each seeded agar plate, including the control plain soap. Duplicate plates are prepared and are incubated for twenty-four to forty-eight hours at 37° C.

In counting the plates, the filter discs are carefully removed with forceps and the zones of disc contact are examined microscopically (100×) with replicate counts made of fields selected at random. To facilitate counting, a Howard Micrometer Disc (No. 823) can be inserted into the ocular piece (10×); five fields of three adjacent squares are counted and the average field count determined.

The antibacterial potency of a test soap solution is expressed in terms of a "Bacteriostatic Index" which is computed from the average zone readings as follows:

Bacteriostatic index

$$= \frac{\text{Av. zone count of test soap}}{\text{Av. zone count of control soap}} \times 100$$

Index:

>85—no antibacterial activity
60–85—slight
30–60—moderate
<30—strong
0—very strong

The test is a simple, convenient and direct method of determining bactericidal activity, and compositions which show strong activity at low concentrations under the conditions of the test have proved to be effective in actual handwashing tests with human subjects.

(3) *The Skin Disc Test (a modification of the Zone Reduction Test).*—Dehydrated calf skin discs are used instead of filter paper discs. These are rehydrated in sterile water for fifteen minutes and then placed in test tubes with 25 cc. of the 8%¹ test solutions and shaken

¹ Basis soap weight.

for fifteen minutes. At the end of this time, the soap solutions are drained from the discs and sterile water added. The discs in the sterile water are shaken for fifteen minutes with a frequent change of water and then placed on the inoculated agar as in the Zone Reduction Test.

The compositions prepared in accordance with the invention have shown excellent germicidal effectiveness when subjected to these tests.

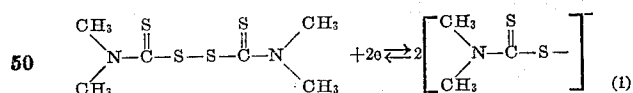
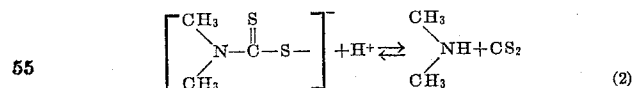
The following example illustrates the invention:

Soap chips (750 lbs.), formed from a charge of 80% tallow and 20% coconut oil, bleached by the addition of sodium hydrosulfite Na₂S₂O₄, and containing 0.05% free alkali, were weighed into the mixer, following which 1 lb. 8 oz. of lauroyl peroxide was added at once. Mixing was continued for five minutes after which 5 lbs. 13 oz. of perfume and dye were added over a period of one minute and mixing continued for three minutes. Tetramethyl thiuram disulfide (7 lbs. 11 oz.) was added by spreading it over the surface of the mix and mixing was continued for not more than four minutes. At the end of this time the tetramethyl thiuram disulfide was found to be thoroughly dispersed in the soap. The mix was transferred to a refiner where it was extruded through screens into another extruder and then into a plodder and formed into bars, all at temperatures between 100 and 115° F.

Any of the above-mentioned thiuram sulfides and/or peroxides can be substituted for the tetramethyl thiuram disulfide and lauroyl peroxide with satisfactory results.

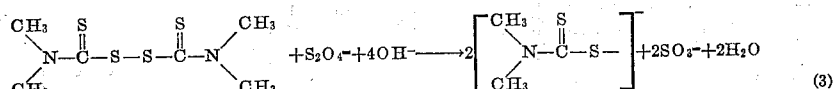
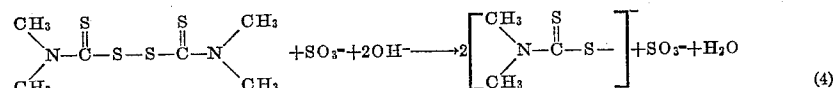
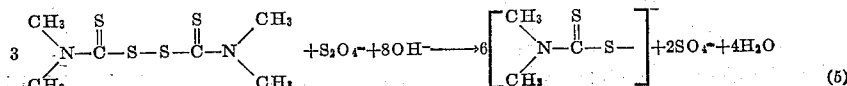
The soap bars obtained were packed in an inner wrap of glassine paper and an outer carton of white patent coated board and subjected to storage at ordinary room temperatures for nine months. No change in the product was noted, whereas in the case of a soap containing thiuram sulfide but no lauroyl peroxide prepared exactly as set forth, yellowing of both the glassine and the board was observed, due probably to sulfur compounds formed by decomposition of the tetramethyl thiuram disulfide. The aged product containing the lauroyl peroxide had no odor and did not produce stains in the presence of copper ion, whereas the product which did not contain the lauroyl peroxide did produce such stains and had a strong odor.

It has been postulated that the decomposition of the thiuram sulfide which leads to the difficulties noted above follows the following course:



The carbon disulfide, dimethylamine and other decomposition products of dithiocarbamate, would be responsible for an "off" odor in the product.

A reducing agent such as hydrosulfite or sulfite might react in a similar fashion:



From Equation 5 it can be seen that one molecule of hydrosulfite can be responsible for the decomposition to the dithiocarbamate state of three molecules of tetramethyl thiuram disulfide and that the decomposition is very sensitive to hydroxyl ion.

It is thought that the stabilizing compound inhibits decomposition of the thiuram sulfide by serving as an electron acceptor and by destroying $S_2O_4^{2-}$ and SO_3^{2-} ions. The role of free acid is to take up hydroxyl ion and thus inhibit Reactions 3, 4 and 5.

It is known that thiuram sulfide forms the dithiocarbamate in alkaline aqueous solution by hydrolysis or in any aqueous solution in the presence of a reducing agent. (Germs or bacteria may act as reducing agents.) In use it is not clear whether the germicidal properties of the soap are due to the thiuram sulfide or to the dithiocarbamate, but it is not important to establish this since both are present in soap solutions. Dithiocarbamate has been found to enjoy but a transitory existence in soap compositions, and therefore in order to preserve its activity in soap solutions which are subsequently prepared from the compositions, should it be the germicidal agent in the soap solution as used, the thiuram sulfide is kept from forming the dithiocarbamate in the soap, but not in the solution, by the peroxide of the invention.

The free alkali is determined in accordance with the following procedure: The soap, before addition of dye, thiuram sulfide and stabilizing agent, is weighed out in a 250 ml. extraction flask on a triple beam or torsion balance, 12.4 gms. in the case of soap chips or fine soap, i.e., soaps of higher fatty acids, 31 gms. in the case of framed soaps and pan samples, i.e., soaps of about 63% fatty acids. To the soap is added approximately 100 ml. of neutralized alcohol and several glass beads and the soap is dissolved completely in the alcohol by boiling gently on a hot plate under a reflux air condenser. One ml. of phenolphthalein indicator is added and the solution titrated while hot to the disappearance of the phenolphthalein color. N/4 solutions are used for framed soaps and pan samples, and N/10 solutions for soap chips and fine soaps. The color change is not very definite for the latter and is recognized in a change of color rather than a disappearance. A blank determination is made on 100 ml. of the neutralized alcohol for each batch when N/10 solutions are used, and the volumes of acid or alkali required for neutralization are noted. The calculation then is carried out according to the following equations:

For soap chips and fine soaps:

$$\frac{\text{Ml. N/10 acid (corrected)} \times 0.0031 \times 100}{12.4}$$

$$= \text{percent Na}_2\text{O Ml. N/10 acid} \times 0.025 = \text{percent Na}_2\text{O}$$

For framed soaps and pan samples:

$$\frac{\text{Ml. N/4 acid} \times 0.00775 \times 100}{31}$$

$$= \text{percent Na}_2\text{O Ml. N/4 acid} \times 0.025 = \text{percent Na}_2\text{O}$$

The compositions of the invention meet all of the requirements for germicidal soaps, as is evident from tests which have been carried out on them, and are indistinguishable in appearance from ordinary soaps. They can be used as ordinary detergent soaps and are especially recommended for uses in which both detergent and degerming characteristics are desired. The test results show that the compositions used routinely for a period of from one to two weeks lower the bacterial flora of the skin to a very low level, equivalent to that obtainable by means of the standard hospital scrub-up operation. The compositions are particularly valuable for routine surgical and hospital use and generally useful in the prevention of infections arising from skin bacteria.

Those skilled in the art will perceive many variations in the compositions of the invention. For example, the aliphatic thiuram sulfide need not be the only germicidal

agent; other germicides, such as 2,2'-dihydroxy halogenated diphenyl methanes, can be included, for example, if desired.

The soap compositions, in addition to the soap and germicide, will also usually contain fillers, coloring materials and perfumes, as desired, as is familiar to those skilled in the art.

The compositions containing the thiuram sulfide may contain mixtures of detergents, such as soap and an anionic nonsoap, or soap and a nonionic nonsoap. Typical satisfactory anionic nonsoaps are the alkyl sulfates, typified by sodium lauryl sulfate, known in the trade as Duponol C, the alkyl aryl sulfonates, typified by the sodium polypropylene benzene or toluene sulfonates, and the sodium keryl benzene or toluene sulfonates, the sulfated ethoxynated phenols, typified by the ammonium salt of sulfated ethoxynated nonyl phenol, prepared by condensation of nonyl phenol with five moles of ethylene oxide, and the sodium fatty acid esters of taurine, typified by sodium palmitic or oleic methyl tauride or mixtures thereof, and the esters of higher fatty acids and hydroxy ethane sulfonates such as oleic acid ester of hydroxy ethane sodium sulfonate. Also useful are non-ionic nonsoaps, such as the polyethylene glycol esters of the higher fatty acids, typified by polyoxyethylene ethylene and propylene glycol stearates, the polyethylene glycol ethers of alkyl phenols, typified by the condensation product of octyl and nonyl phenol with five to twelve moles of ethylene oxide, and the higher fatty acid esters of sorbitan-ethylene oxide condensates, such as sorbitan monostearate ester of polyoxyethylene glycol. They may be in any of the forms described heretofore, including cakes or powders, and may include various fillers, sudsing agents and ingredients conventionally employed in detergent formulations. They may be compounded for various purposes, such as for shampoo, dishwashing, textile laundering, toilet soaps and similar preparations.

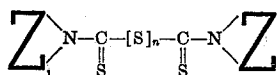
The thiuram sulfide may be included in compositions which contain soap or other surface active agents not intended primarily for detergent use, such as various powdered cosmetics.

All percentages in the specification and claims are by weight of the soap.

This application is a continuation-in-part of application Serial No. 397,001, filed December 8, 1953, now abandoned.

I claim:

1. A germicidal detergent composition substantially free from free alkali comprising soap, a germicidal amount of a thiuram sulfide having the formula:



where n is an integer from one to six and Z_1 and Z_2 are hydrocarbon radicals having from two to eight carbon atoms and are selected from the group consisting of a single bivalent cycloaliphatic radical and two monovalent aliphatic radicals, and a peroxide characterized by forming hydrogen peroxide in alkaline aqueous solution, said peroxide being in an amount to stabilize the detergent composition against decomposition of thiuram sulfide as evidenced by the development of odor and staining characteristics.

2. A germicidal detergent soap comprising soap substantially free from free alkali, a peroxide characterized by forming hydrogen peroxide in alkaline aqueous solution, and a germicidal amount of an N-tetramethyl thiuram sulfide said peroxide being in an amount to stabilize the detergent composition against decomposition of thiuram sulfide as evidenced by the development of odor and staining characteristics.

3. A germicidal detergent soap comprising soap substantially free from free alkali, a peroxide characterized

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by forming hydrogen peroxide in alkaline aqueous solution, and a germicidal amount of N-tetramethyl thiuram monosulfide said peroxide being in an amount to stabilize the detergent composition against decomposition of thiuram sulfide as evidenced by the development of odor and staining characteristics.

4. A germicidal detergent soap comprising soap substantially free from free alkali, a peroxide characterized by forming hydrogen peroxide in alkaline aqueous solution, and a germicidal amount of N-tetramethyl thiuram disulfide said peroxide being in an amount to stabilize the detergent composition against decomposition of thiuram sulfide as evidenced by the development of odor and staining characteristics.

5. A germicidal detergent composition in accordance with claim 1 in which the thiuram sulfide is present in an amount within the range from 0.01 to about 5%.

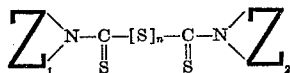
6. A germicidal detergent composition in accordance with claim 1 in which n has the value of one.

7. A germicidal detergent composition in accordance with claim 1 in which n has the value of two.

8. A germicidal detergent composition in accordance with claim 1 in which the peroxide is lauroyl peroxide.

9. A germicidal detergent composition in accordance with claim 1 in which the peroxide is benzoyl peroxide.

10. A process of forming a germicidal detergent composition comprising dispersing in soap a peroxide characterized by forming hydrogen peroxide in alkaline aqueous solution, said peroxide being in an amount to stabilize the detergent composition against decomposition of thiuram sulfide as evidenced by the development of odor and staining characteristics, and then dispersing therein a germicidal amount of a thiuram sulfide having a formula:



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where n is an integer from one to six and Z_1 and Z_2 are hydrocarbon radicals having from two to eight carbon atoms and are selected from the group consisting of a single bivalent cycloaliphatic radical and two monovalent aliphatic radicals, including adding an acidic compound if necessary to eliminate free alkali and form a composition substantially free from free alkali.

11. A process in accordance with claim 10 in which the peroxide is acid-reacting, and is added in an amount to eliminate free alkali in the final composition.

12. A process in accordance with claim 10 in which the acid-reacting compound is an inorganic acid.

13. A process in accordance with claim 10 in which the acid-reacting compound is an inorganic acid-reacting salt.

14. A process in accordance with claim 10 in which the acid-reacting compound is an organic acid.

15. A process in accordance with claim 10 in which the peroxide is lauroyl peroxide.

16. A process in accordance with claim 10 in which the peroxide is benzoyl peroxide.

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