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GERMICIDAL CLEANSING COMPOSITION

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This invention relates to novel cleansing compositions having improved antibacterial properties and pertains more specifically to germicidal compositions containing a fatty acid soap matrix, a germicidal agent and an anionic potentiating agent, the anionic potentiator being present in proportions which enhance the effective antibacterial properties of the germicidal agent.

To thoroughly cleanse the surface of the human body it is necessary to reduce the bacteria population residing on the surfaces of the skin. This reduction of the skin surface bacteria sanitizes the skin. It also helps to reduce axillary odors caused by microorganisms remaining on the skin after washing has been completed.

Mild or bland soaps are generally good physical cleaning agents for the skin but are ineffective against microorganisms which are part of the permanent or resident flora. Most soaps only attack bacteria on direct application and will not affect microorganisms which contact the skin shortly after washing has been completed. These shortcomings of pure soap compositions have been overcome in certain instances by adding a germicidal agent to the soap. In these binary mixtures of soap and germicidal agent, the germicide deposits on the surfaces of the skin during the washing process and remains active on the skin surface for a sufficient length of time to work its cidal action on the resident bacteria. While remaining active, the germicidal agent also attacks later depositing bacteria. The lingering antibacterial action of the germicidal agent increases the deodorant properties of the binary mixture.

Antibacterial effectiveness alone is not sufficient to render soap-germicidal compound formulations commercially attractive. Many soap-germicidal mixtures have little commercial utility because of inherent limitations in the physical characteristics of the binary mixture. For example, the incorporation of about 2% of bis-(2-hydroxy-3,5,6-trichlorophenyl)methane in a soap bar formulation provides a very effective germicidal composition. However, bis-(2-hydroxy-3,5,6-trichlorophenyl)methane will not permit the production of an esthetically pleasing bar formulation as the bar tends to discolor, particularly in sunlight. By reducing the content of the bis-(2-hydroxy-3,5,6-trichlorophenyl)methane to about 0.5% this commercial deficiency is avoided but the bar formulation no longer has an acceptable germicidal activity for sanitizing the surfaces of the skin.

Other germicidal agents are commercially objectionable at effective levels because of cost, odor and/or toxicity. To overcome these disadvantages it has been deemed eminently desirable to have a means for potentiating the activity of germicidal agents such that they can be used in relatively low concentrations in the formulation of commercial cleansing compositions, particularly those compositions compounded in bar form.

One of the objects of the present invention is to provide a deodorant soap-germicidal-compound-containing formulation which is capable of providing highly effective antibacterial activity on human skin through the use of very low concentrations of germicidal agent. Another object is to provide a composition which not only is an effective physical cleaning agent but which also enhances the skin retention of the antibacterials contained therein. A further object is to provide a commercially attractive deodorant soap containing a germicidal agent having potentiated germicidal activity. Still further and other objects will be apparent from the description which follows.

It has been found that an unexpectedly high level of germicidal agent can be deposited on the skin when an aqueous solution containing a relatively small percentage of the germicidal compound and an anionic potentiator of the class hereinafter defined is applied to the skin. The amount of the germicidal agent which deposits on the skin from these potentialized compositions is much greater than that from a pure soap composition containing the same amount of germicidal agent. The degree of enhanced deposition of the germicidal agent on the skin varies with the potentiator and the germicidal agent employed. Particular combinations have been discovered which give results that are far superior to the degree of effective germicidal deposition on the skin heretofore known to be obtainable.

Unfortunately, the anionic potentiators of the instant invention are not well suited as the sole basis of a skin cleansing preparation. The degree of mildness of the potentiating agents is not as high as is ordinarily desirable and their hygroscopic properties and physical characteristics make it difficult to formulate attractive bar formulations.

Surprisingly, however, the unusual potentiating property of the instant potentiators can be utilized in combination with soap to produce an ideal ternary germicidal formulation which is mild to the skin and free from the inherent commercial disadvantages of the mixtures composed only of an anionic potentiator and a germicidal compound. It has been found that these new and novel ternary compositions are most effective when composed of a fatty acid soap matrix, a potentiating agent of the class hereinafter enumerated and germicidal agent of the class hereinafter enumerated in which the ratio of fatty acid soap to potentiating agent is from about 1:1 to about 10:1 and the ratio of the germicidal content is below about 1:50 but above about 1:500 of the combined content of the soap and potentiating agent.

Tallow:coconut fatty acid soaps are employed in the compositions of the instant invention. Fatty acid sodium and/or potassium soaps having a 80:20 tallow:coconut content provide the best results. Other ratios of tallow:coconut fatty acid soap can be used, although the coconut fatty acid soap content should be maintained above about 10% as the coconut component both assists in solubilizing the tallow fatty acid soap and contributes

beneficially to the antibacterial effectiveness of the instant compositions. However, no more than 90% of the soap matrix component should be coconut in order to insure desirable mildness. Satisfactory results are achieved with a fatty acid soap matrix consisting of tallow and coconut fatty acid soap wherein the ratio of tallow to coconut fatty acid soap is from about 90:10 to about 10:90. The importance of the coconut component is illustrated in Example IV below.

The anionic potentiating agent which is employed in the present invention is tetrapropylene benzene sulfonate, pentapropylene benzene sulfonate or C_{15}-branched chain soap having the formula $MOOCHCCH_3C_{12}H_{25}$ wherein M is sodium or potassium. The carboxylic acid starting materials for making C_{15}-branched chain soap can be produced from olefins as taught in U.S. Patents 2,831,877 and 2,876,241. Sodium and potassium are the preferred hydrophilic components of these potentiators. The polypropylene benzene sulfonates useful in the present invention have average chain lengths of nine and twelve carbon atoms respectively with three methyl branches attached to the chain. If desired, mixtures of two or more of these anionic potentiators can be used. Certain other potentiators such as coconut alkyl sulfate can be used but potentializers of this type having unbranched hydrophobic groups surprisingly are less effective in potentiating the deposition of the germicidal compound on the skin than are the anionic potentiators of the preferred type which have branched chain hydrophobic groups.

Not all germicidal agents perform equally well in the instant ternary compositions. The germicidal activity of the bisphenols, particularly bis-(2-hydroxy-3,5,6-trichlorophenyl)methane, bis-(2-hydroxy-5-chlorophenyl) methane and 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenyl sulfide and the salts and derivatives of neomycin, especially neomycin palmitate and neomycin benzylidine, are improved most notably by the present potentiating mixture. Mixtures of these specific germicidal agents can also be used, such as a mixture of bis-(2-hydroxy-3,5,6 - trichlorophenyl)methane and (2,2' - dihydroxy-3,3',5,5'-tetrachlorodiphenyl sulfide. Other germicidal agents, including the halogen substituted salicylanalides such as 5,3-dichlorosalicylanalide, 5,2',4'-trichlorosalicylanalide and 3,5,3',4'-tetrachlorosalicylanilide, show some improved performance activity but are less spectacularly potentiated than the bisphenols and the neomycin compounds. Some known germicidal agents such as trichlorocarbinilide exhibit no observable potentiated activity.

In formulating the compositions of this invention in bar form the best results are achieved by employing a mixture composed of from about 10% to about 50% of an anionic potentiator having a branched chain hydrophobic group and from about 50% to 90% of a fatty acid soap matrix, preferably 80:20 tallow:coconut sodium or potassium soap, and adding thereto a sufficient amount of a bisphenol or neomycin compound to give the desired antibacterial activity. Care should be exercised to use only so much of the germicidal agent necessary to give the desired effect. If excessive amounts of germicide are used, one of the principal benefits to be derived from the present invention is lost. In general, sufficiently active compositions can be obtained by employing from about 0.01%–1% of bisphenol and even smaller quantities, preferably 0.001–0.5%, of a neomycin salt or derivative based on active neomycin content. Enhanced germicidal deposition on the skin is evident even in the use of about 2% of a bisphenol and such combinations are within the scope of this invention even though discoloration may occur.

It is believed that the soap matrix and anionic potentiator of the ternary mixture combine during the washing process to form mixed micelles. The branched chain on the hydrophobic group of the potentiating agent appears to contribute beneficially to this micelle formation. The mixed micelle formation increases the concentration of the germicidal agent at the skin-soap matrix/potentiating agent interface thus depositing a greater amount of germicidal agent on the skin than is deposited by the soap alone. Since the potentiators of this invention are anionic surface active agents, they can be used in the quantities which are necessary to form the mixed micelles without constituting a load in the composition and thereby decreasing the general surface active properties of the composition. Satisfactory performance results are achieved when the compositions of the instant invention compose from 0.2% to 5.0% of an aqueous solution used to wash the surfaces of the skin. The skin is preferably contacted with the solution for at least about one-half minute and then thoroughly rinsed off the skin with clear water.

The antibacterial compositions of this invention are particularly well suited for solid bar formulations. However, if desired, they can be provided in the form of a solution in a suitable solvent. Conventional additives such as coloring agents, preservatives, perfumes, thickeners, etc., may be included as is the practice in the art in compounding acceptable formulations without materially affecting the enhanced germicidal activity of the compositions.

The following specific examples are intended to illustrate the nature of the present invention. References to parts or percentages are intended to mean values by weight unless otherwise indicated.

EXAMPLE I

Various aqueous solutions were first prepared containing 80:20 tallow-coconut sodium soap and a germicidal agent. A bactericidal test consisting of counting and recounting bacteria population before and after exposure was used to measure the percent reduction in bacteria on the skin after exposing the skin to the various solutions containing the hereinafter named germicides for 10 minutes. Actual counting was performed 24 hours after the test was completed to insure adequate incubation of the bacteria for reliable counting. Radio-tagged bis-(2-hydroxy-3,5,6-trichlorophenyl)methane was employed in one test to determine the amount of germicidal agent retained on the skin in a typical test in order to correlate deposition and germicidal activity. Solutions were then prepared containing in addition to the 80:20 tallow:coconut sodium soap and germicidal agent an anionic potentiator having a sodium or potassium hydrophilic group. Similar testing of these solutions was then carried out. The outstanding potentiating effect of the potentiating agent is evident from the comparative results set forth in Table I. Approximately 10 observations were averaged in arriving at each of the reported figures. The figure given for "average percent of potentiation" is the average positive difference in "percent reduction in bacteria population" before and after the addition of the potentiator.

It is readily apparent that a small concentration of either bis-(2-hydroxy-3,5,6-trichlorophenyl)methane or neomycin palmitate can be easily potentiated to a high (excellent) degree of cidal effectiveness. The potentiation of the bisphenols in general is more notable than that of neomycin palmitate since neomycin and the salts and derivatives thereof are generally more effective in small quantities than are equivalent quantities of other germicidal agents. The "average percent of potentiation" shown in Table I for neomycin palmitate is given as a range since the actual potentiation is primarily a function of the amount of neomycin palmitate employed. Table I also illustrates the less pronounced potentiation of the halogen substituted salicylanilides. As hereinbefore stated, no potentiation is evident with the carbanilides such as 3,4,4'-trichlorocarbanilide.

Table I

	[a] Soap matrix or soap matrix + potentiator	Percent conc. of *a*	[b] Germicidal agent	Percent conc. of *b*	Ratio of *a*:*b*	μg. of germicidal agent/sq. in. of skin	Percent reduction in bacteria population	Average percent of potentiation	Comparative overall degree of bactericidal effectiveness
(1)	80:20 TCS	4.0	Bis-(2-hydroxy-3,5,6 trichlorophenyl) methane.	.08	50:1		45		
	80:20 TCS	0.5	do	.01	50:1	6.1	52	79	Excellent.
	1:1 TCS+C_{12}ABS	1.0	do	.01	100:1	10.1	94		
	1:1 TCS+C_{15}ABS	1.0	do	.01	100:1	11.0	93		
	1:1 TCS+C_{15}BCS	1.0	do	.01	100:1	14.9	91		
(2)	80:20 TCS	0.5	Bis-(2-hydroxy-5 chlorophenyl)methane.	.01	50:1		28		
	1:1 TCS+C_{15}BCS	1.0	do	.01	100:1		67	140	Good.
(3)	80:20 TCS	0.5	2,2'-dihydroxy-3,3'5,5'-tetrachlorodiphenyl sulfide.	.01	50:1		28		
	1:1 TCS+C_{15}ABS	1.0	do	.01	100:1		60	115	Fair.
(4)	80:20 TCS	0.5	3,5,3'4'-tetrachlorosalicylanilide.	.01	50:1		42		
	1:1 TCS+C_{12}ABS	1.0	do	.01	100:1		60	43	Do.
(5)	80:20 TCS	4.0	Neomycin palmitate (20% neomycin).	.08	50:1 (250:1 as base)		97		
	80:20 TCS	0.5	do	.01	50:1 (250:1 as base)		80		
	80:20 TCS	0.5	do	.005	100:1 (500:1 as base)		57	25-70	Excellent.
	1:1 TCS+C_{12}ABS	1.0	do	.01	100:1 (500:1 as base)		99		
	1:1 TCS+C_{15}BCS	1.0	do	.01	100:1 (500:1 as base)		97		
	1:1 TCS+C_{15}ABS	1.0	do	.001	1000:1 (5,000:1 as base)		85		

Key: TCS—Tallow:coconut sodium soap; C_{12}ABS—sodium tetrapropylene benzene sulfonate; C_{15}ABS—sodium pentapropylene benzene sulfonate; C_{15}BCS—$NaOOCHCCH_3C_{12}H_{25}$. Similar results are obtained by substituting potassium for the sodium hydrophilic group.

EXAMPLE II

An aqueous solution was prepared containing 0.5% by weight of 80:20 tallow:coconut potassium soap and 0.5% by weight of sodium pentapropylene benzene sulfonate. To this solution, 0.001% by weight (based on total weight of solution) of neomycin benzylidine was added. The solution showed an 86% reduction in bacteria population when tested on the skin in the manner described in Example I. A solution containing 0.5% of 80:20 tallow:coconut potassium soap and 0.001% of neomycin benzylidine reduced the skin surface bacteria population by 38%. The apparant potentiation of the neomycin salt attributable to the potentiating ability of sodium pentapropylene sulfonate is about 120%.

EXAMPLE III

Aqueous solutions similar to those shown in Table I were prepared, varying the ratio of the 80:20 tallow:coconut sodium soap:potentiating agent while retaining the same content of germicidal agent. Typical results set forth in Table II show that a reduction in the content of the anionic potentiator reduces the antibacterial activity of the solution. The antibacterial activity of the solutions was tested as described in Example I. Approximately 10 observations were averaged in arriving at the reported figures for "percent reduction in bacteria population."

Table II

	[a] Germicidal Agent	Percent conc. of *a*	[b] Percent conc. of 80:20 tallow:coconut sodium soap	[c] Percent conc. of C_{15}BCS	[c] Percent conc. of C_{12}ABS	Ratio of *b*:*c*	Percent reduction in bacteria population
(1)	Neomycin palmitate	0.001	.5	.5		1:1	85
		0.001	.5	.1		5:1	50
		0.001	.5	.05		10:1	28
(2)	Bis-(2-hydroxy-3,5,6 trichlorophenyl) methane.	0.01	.5		.5	1:1	90
		0.01	.5		.3	5:3	81
		0.01	.5		.05	10:1	54

C_{12}ABS—Sodium tetrapropylene benzene sulfonate.
C_{15}BCS—$NaOOCHCCH_3C_{12}H_{25}$.

EXAMPLE IV

Two aqueous solutions were prepared, the first containing only 0.5% of 80:20 tallow:coconut potassium soap, and the second 10:90 tallow:coconut potassium soap. A bactericidal test similar to the bactericidal test described in Example I was used to test the antibacterial effectiveness of these solutions on the skin. When tested on the skin, the respective solutions showed an 18% and 25% reduction in bacteria population. A third aqueous solution containing only 0.5% of tallow potassium soap was prepared and similarly tested on the skin. This tallow soap solution reduced the bacteria population on the skin by less than 10%. The results of these tests indicate that coconut fatty acid soap is more effective against bacteria than tallow fatty acid soap and that the addition of a small amount of coconut fatty acid soap to form a tallow:coconut soap matrix greatly increases the antibacterial activity of soap.

To each of the three solutions prepared above, a germicidal agent, namely, bis-(2-hydroxy-3,5,6-trichlorophenyl)methane, was added. In addition to the germicidal agent, potassium pentapropylene benzene sulfonate was added to each solution. The resulting solutions had the following composition:

	Percent
Soap or soap matrix	0.5
Potentiator	0.5
Germicidal agent	0.01

These solutions were then tested on the skin for bactericidal activity in the manner described in Example I. The following average reduction in skin surface

bacteria population was measured for the solutions having the indicated soap or soap matrix component:

	Percent
(1) 80:20 tallow:coconut potassium soap	91
(2) 10:90 tallow:coconut potassium soap	99
(3) Tallow potassium soap	35

These results clearly show the importance of the coconut fatty acid soap component in the tallow:coconut fatty acid soap matrix in the instant ternary composition. In addition to helping solubilize the tallow portion of the soap matrix, the presence of the coconut fatty acid soap is necessary to achieve a high (excellent) degree of overall effectiveness in antibacterial activity. A high degree of antibacterial effectiveness cannot be achieved by using tallow fatty acid soap alone.

EXAMPLE V

An exceedingly useful and commercially satisfactory deodorant bar having potentiated antibacterial activity was prepared by adding 150 gm. of sodium tetrapropylene benzene sulfonate, 150 gm. of 80:20 tallow:coconut sodium soap and 3 gm. of bis-(2-hydroxy-3,5,6-trichlorophenyl)methane to a stainless steel beaker. These ingredients were heated to 250° F. accompanied by rapid stirring for 15 minutes and then poured into a bar mold while still hot. After being sufficiently cooled, the bar was removed from the mold. Similar compositions were prepared varying the quantities of sodium tetrapropylene benzene sulfonate to bis-(2-hydroxy-3,5,6-trichlorophenyl)methane within the range of 50:1 to 100:1.

Ohter bars were prepared in a similar manner by using 150 gm. of 10:90 tallow:coconut potassium soap, 150 gm. of sodium pentapropylene benzene sulfonate or 150 gm. of $NaOOCHCCH_3C_{12}H_{25}$ and either 3 gm. of bis-(2-hydroxy-5-chlorophenyl)methane or 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenyl sulfide. Still further bars were prepared using 1 gm. of neomycin palmitate or neomycin benzylidine as the germicidal agent with 150 gm. of 80:20 tallow:coconut sodium soap and 150 gm. of either tetra- or pentapropylene benzene sulfonate. The quality of the finished bars was further varied by the addition of ingredients, such as perfumes, coloring agents, and thickeners well known in the bar formulation art.

Bars prepared in the above manner were used for general personal bathing requirements and were found to be particularly advantageous in reducing axillary odors.

It is to be understood that the instant invention is not limited to any particular type of bar composition or to the specific examples herein described, but may be embodied in other forms without departure from its spirit.

What is claimed is:

1. A germicidal cleansing composition having improved antibacterial properties due to a potentiating effect by a C_{15}-branched chain soap anionic potentiator upon a soap matrix and a germicidal agent, said composition consisting essentially of:

(1) from about 50% to about 90% of a fatty acid soap matrix consisting of tallow and coconut fatty acid soap wherein the ratio of tallow to coconut fatty acid soap is from about 90:10 to about 10:90, the cation of said soap being selected from the group consisting of sodium and potassium;

(2) from about 10 to about 50% of an anionic potentiator consisting of C_{15}-branched chain soap having the formula $MOOCHCCH_3C_{12}H_{25}$ wherein M is selected from the group consisting of sodium and potassium, the ratio of said fatty acid soap matrix to said anionic potentiator being from about 1:1 to about 10:1; and

(3) a germicidal agent selected from the group consisting of bis-(2-hydroxy-3,5,6-trichlorophenyl)methane, bis-(2-hydroxy-5-chlorophenyl)methane, 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenyl sulfide, neomycin palmitate, neomycin benzylidine, and mixtures thereof,

the ratio of said fatty acid soap matrix plus said anionic potentiator to said germicidal agent being from about 50:1 to about 500:1.

2. The germicidal cleansing composition of claim 1 wherein the fatty acid soap matrix is 80:20 tallow:coconut fatty acid sodium soap and the germicidal agent is neomycin palmitate.

3. The germicidal cleansing composition of claim 1 wherein the fatty acid soap matrix is 80:20 tallow:coconut fatty acid sodium soap and the germicidal agent is bis-(2-hydroxy-3,5,6-trichlorophenyl)methane.

4. The germicidal cleansing composition of claim 1 wherein the fatty acid soap matrix is 80:20 tallow:coconut fatty acid sodium soap and the germicidal agent is neomycin benzylidine.

5. The germicidal cleansing composition of claim 1 wherein the fatty acid soap matrix is 80:20 tallow:coconut fatty acid sodium soap and the germicidal agent is bis-(2-hydroxy-5-chlorophenyl)methane.

References Cited by the Examiner

UNITED STATES PATENTS

2,338,689	1/1944	Parker et al.	252—142 XR
2,831,877	4/1958	Koch	260—413
2,876,241	3/1959	Koch	252—432 XR
2,898,264	8/1959	Weber	252—107 XR
3,013,007	12/1961	Dale	252—106 XR
3,022,286	2/1962	Griendt	167—63 XR

FOREIGN PATENTS

564,948	3/1958	Belgium.
761,269	11/1956	Great Britain.

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