United States Patent

Berenson et al.

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[54] **GERMICIDAL DETERGENT COMPOSITIONS IN CONTROLLING DANDRUFF**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 783,123, Dec. 11, 1968, abandoned.

[52] **U.S. Cl.** **424/204,** 424/316, 424/319

[51] **Int. Cl.** **A61k 27/00**

[58] **Field of Search**.....424/204, 319, 316

[56] **References Cited**

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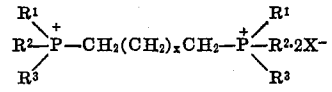
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Primary Examiner—Stanley J. Friedman

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[57] **ABSTRACT**

Compositions, generally useful for germicidal detergent applications, comprising a mixture of (a) an amphoteric surfactant such as N-coco β-amino propionic acid or a fatty (coco) amido alkyl betaine and (b) an organophosphorus salt of the formula:



wherein R^1, R^2 and R^3 independently are alkyl (C_1—C_{12}), phenyl, or hydroxyalkyl (C_1—C_4); x is 6–14 and X is an anion. Compound (b) is also useful, in aqueous or alcoholic solution, or with other cosmetically acceptable ingredients, in the control of dandruff.

6 Claims, No Drawings

GERMICIDAL DETERGENT COMPOSITIONS IN CONTROLLING DANDRUFF

This application is a continuation-in-part of Ser. No. 783,123, filed Dec. 11, 1968 now abandoned.

This invention relates (1) to germicidal detergent compositions useful generally in the treatment of the skin and hair, (2) to methods of controlling dandruff, and (3) to antidandruff compositions.

BACKGROUND

A. Germicidal Detergent Compositions

While certain compounds such as quaternary ammonium salts are known to be surface active as well as germicidal, the surface activity falls short, at use concentrations which are economical, of promoting the detergency required in products for treatment of the hair and skin such as shampoos, rinses, surgical scrub compositions, cosmetic creams, anti-perspirants, and other cosmetic and grooming compositions where detergency coupled with germicidal activity is important. The improved detergency therefore is generally provided by combining a known detergent with a known germicide.

The selection of a detergent and germicide for combination in compositions effective for the intended purpose is not a simple matter, however. Thus, the numerous properties required in a germicide intended for contact with the skin and hair drastically limit the field of choice. Among these properties may be included inherent microbial effectiveness (broad spectrum antimicrobial activity particularly against bacteria, yeasts and molds or fungi known to thrive on the mammalian body); substantivity (sorbability) or tendency to be deposited on the skin and hair (including the scalp); microbiological availability (elution rate) while on the skin and hair including the scalp; activity at economical use concentrations; substantially no harmful effect to the skin or hair or disagreeable odor; stability (no substantial loss of activity or tendency to separate from other ingredients of formulations while in storage); no substantial reactivity with the metal linings of vessels used in preparation or packaging; and compatibility with the detergent as well as other cosmetic ingredients normally included in germicidal detergent compositions.

Likewise, the choice of detergent is critically limited not only by the requirements of the environment being treated but also by the germicide selected for the compositions. Thus, in addition to the requirements of no harmful effect on skin or hair at use concentrations, no disagreeable odor, and effective detergency particularly as accompanied by foamability, the detergent must not substantially inactivate the germicide and must be compatible with the germicide such that the combination, in the conventional cosmetic vehicles, and over the pH range desirable for cosmetic use, remains stable during a storage period. To the foregoing may be added the further important requirement that the germicidal agent not lose its activity by reason of drying out on the skin or hair. While certain germicides are known to be effective in combination with detergents for use on the skin and hair, it has been observed that these germicides rapidly dry out, thereby losing their germicidal activity.

Given all the foregoing properties in the detergent and germicide as well as in the combination, the consumer has preference for a composition which is clear or transparent over a composition which is opaque. The reason for this resides not only in the high degree of quality ascribed to clear or transparent compositions but also in the technical advantage that the residue on the skin or hair of a clear or transparent composition is substantially non-detectable whereas the residue of an opaque composition is undesirably apparent, in some instances even to the extent of modifying the color and texture of the hair.

B. Antidrandruff Compositions

When it is proposed to use a known germicide for the control of dandruff whether on the animal or human scalp, but particularly the latter, certain of the foregoing requirements as well as others become especially critical as compared with germicidal-detergent uses generally. The reason for this concerns the nature of "dandruff" and the state of the dandruff control art. At the present time it is believed that a dandruff condition involves not a simple, identifiable disease but several factors in which a diseased state may or may not be important. For example, although some investigators have noted the presence of *Staphylococcus aureus* and *Pityrosporum ovale* skin bacteria along with the oily, dead scale usually called "dandruff", absolute statements that these particular organisms are the sole cause of dandruff have been disproved since these bacteria have been found on the majority of scalps, whether dandruff scale is present or not. See "Antidandruff Preparations", H. J. Spoor, in Cosmetics, Science and Technology, Interscience, New York, 1957, pp. 641—650. Consequently, the knowledge that a certain compound (such as that described in U.S. Pat. No. 3,364,107) controls broad classes of microbes specifically including *S. aureus* and *P. ovale*, is wholly insufficient to lead one to conclude that the compound would be effective in combatting a dandruff condition.

"Dandruff" is therefore a complex condition, involving the accumulation of sloughed off epidermal scale, oily secretion and acquired soil. It is known that this accumulation offers an ideal nutrient medium for many types of microorganisms, including those already mentioned, giving rise to infections such as seborrhea. It is believed that growth of these microbes promotes or is accompanied by itching, hair loss and the unpleasant appearance associated with increased desquamation of epidermal cells. Acceptable dandruff control therefore requires at least the following properties in a material chosen for this use in addition to those properties set forth above for general germicidal-detergent use: antimicrobial effect at least against the microorganisms commonly associated with dandruff; ability to reduce scaling and to relieve itching; and water solubility and cosmetic vehicle compability sufficient to permit preparation of aqueous formulations and cosmetic formulations in which a major portion of the vehicle is non-aqueous.

SUMMARY OF THE INVENTION

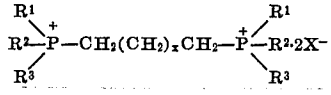
An object of this invention is to provide a germicidal detergent composition or mixture having the foregoing properties, especially the properties of substantivity to the skin and hair, resistance of the germicidal ingredient to drying out when the composition is applied

in conventional cosmetic vehicles, and clarity. A further object is to provide a method of combatting and controlling dandruff conditions in animal and human hair, and compositions for this purpose. These and other objects, features and advantages are further detailed in the following description.

Accordingly, the composition of the present invention which is useful for general germicidal-detergent applications contains as essential ingredients (a) certain amphoteric surfactants and (b) a certain organo phosphorus salt having germicidal properties. Ingredient (a) provides the required detergency in the composition. For dandruff control, ingredient (b) may be employed with a non-aqueous cosmetically acceptable vehicle without ingredient (a) and without water, if desired; however, the preferred composition even for antidandruff use is the composition comprising (a) and (b) in an aqueous medium.

DETAILED DESCRIPTION

The organo phosphorus salt germicidal agents are known compounds and may be represented by formula (I):



wherein R^1, R^2 and R^3 independently are alkyl (C_1–C_{12}), phenyl, or hydroxyalkyl (C_1–C_4); x is 6–14 and X is an anion.

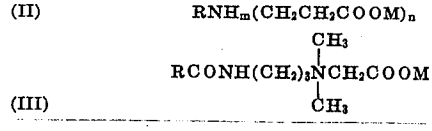
The anion represented by X includes halides such as chloride, bromide, and iodide; and perchlorate, nitrate, sulfate, R^4OSO_3—, R^4OSO–, R^4SO_3— where R^4 is alkyl or aryl such as methyl, ethyl, propyl or butyl, and phenyl. Those salts are preferred which enhance the water solubility of the compounds and of these the halides are preferred. Hydroxyalkyl includes both straight and branch chain alkyl such as 3-hydroxypropyl, 3-hydroxybutyl, and the like.

Illustrative of the salts are the following:

1,10-decamethylenebis [diphenylethylphosphonium bromide];
1,10-decamethylenebis[tributylphosphonium bromide];
1,10-decamethylenebis[diethylphenylphosphonium bromide];
1,10-decamethylenebis[di(3-hydroxypropyl)phenylphosphonium bromide];
1,10-decamethylenebis[trioctylphosphonium bromide];
1,10-decamethylenebis[tris(3-hydroxypropyl)phosphonium bromide];
1,10-decamethylenebis[dilaurylphenylphosphonium bromide];
1,10-decamethylenebis[diphenyllaurylphosphonium bromide];
1,8-octamethylenebis[triphenylphosphonium chloride];
1,16-hexadecamethylenebis[triphenylphosphonium bromide];
1,12-dodecamethylenebis[triphenylphosphonium bromide];
1,8-octamethylenebis[triphenylphosphonium ethyl sulfate];
1,12-dodecamethylenebis[triphenylphosphonium propyl sulfate];
1,16-hexadecamethylenebis[triphenylphosphonium acetate];
1,12-dodecamethylenebis[triphenylphosphonium toluene sulfonate];
1,8-octamethylenebis[triphenylphosphonium nitrate];
1,10-decamethylenebis[triphenylphosphonium nitrate];
1,10-decamethylenebis[triphenylphosphonium perchlorate];
1,8-octamethylenebis[triphenylphosphonium perchlorate];
1,10-decamethylenebis[triphenylphosphonium sulfate];
1,8-octamethylenebis[triphenylphosphonium sulfate];
1,10-decamethylenebis[triphenylphosphonium bromide];
1,16-hexadecamethylenebis[triphenylphosphonium chloride].

The last two compounds in the foregoing list are preferred.

The amphoteric surfactants are selected from compounds of formulas (II) and (III):



In formulas II and III, R is alkyl of at least 8 carbon atoms and M is hydrogen or a cation. In formula II, m is 0 or 1, n is 1 or 2, and the sum of n and m is 2. Alkyl in the definition of R is the fatty residue of a fatty acid (or mixture of fatty acids) employed in preparing the primary amine reactant which, in turn, is reacted with acrylic monomers in forming the amphoteric product. While the carbon content of R may vary up to about 22 carbon atoms, the preferred range is about 12 to 14 carbon atoms since this range provides better surface active properties particularly with respect to foamability. Typical cations include the water solubilizing alkali and alkaline earth metals and amines such as sodium potassium, barium, ammonia, and triethylamine.

Typical of amphoteric surfactants of formula II, useful singly or in admixture, are the following:

Sodium N-coco B-aminopropionate
N-coco β-amino propionic acid
N-lauryl/myristyl β-amino propionic acid
Disodium N-tallow β-iminodipropionate
Disodium N-lauryl β-iminodipropionate
Partial sodium salt of N-lauryl β-iminodipropionic acid

The amphoteric surfactants of formulas II and III above are known compounds as described, for example, in U.S. Pat. Nos. 2,619,467, 2,816,920 and 2,993,071. The formula III compounds are also known as fatty (coco) amido alkyl betaines. Of the foregoing sufactants, N-lauryl/myristyl β-amino propionic acid and the fatty (coco) amido alkyl betaines provide the best results and therefore are the preferred surfactants, alone or in admixture.

Although U.S. Pat. No. 3,364,107 discloses combinations of the above organo phosphorus salts with commercial anionic synthetic detergents, the use therein is in the laundering of fabrics where the problem of compatibility and stability of the compositions is not pronounced. In contrast, the present environment of use on skin or hair as well as acceptability of the liquid formulation to the consumer, require close attention to compatibility and stability of formulations prepared with the germicide and detergent. Thus, it has been found that the commercial anionic synthetic detergents generally are incompatible with the organo phosphorus salts, presumably due to the cationic character of the organo phosphorus salt. The use of nonionic surfactants alone, although compatible with the organo phosphorus salt, is excluded by reason of their poor lathering quality and tendency to reduce the substantivity of the organo phosphorus germicide to the skin and hair. However, for some specialized uses, minor amounts of cationic surfactants or nonionic surfactants, each alone or in admixture, may be employed with the amphoteric surfactants provided they do not substantially reduce the essential characteristics of the composition. While cationic surfactants are compatible with the organo phosphorus germicide, such surfactants tend to be irritating to the skin and are not as substantive. However, cationic surfactants may be included in the compositions of the present invention in minor amounts provided they do not seriously detract from the essential characteristics of the compositions.

The amphoteric surfactants of the formulas II and III above have been selected over other well known amphoteric surfactants, such as the amine oxides, other betaines, and cycloimidates, since it has been observed that these other amphoteric surfactants tend to reduce antibacterial activity with the germicide at the pH range of use, tend to reduce the activity of the germicide, or provide inadequate lathering. The pH range desirable for cosmetic formulation is about 6.5 to about 8.0. It is a surprising result that, although the amphoteric surfactants of the invention become anionic above their isolectric points (which in the case of the formula II compounds range from about pH 2.1 to pH 4.7), no substantial incompatibility with the cationic organo phosphorus salt is observed over the pH range for cosmetic applications.

The organo phosphorus salt germicides of the present invention may be employed in amounts of from about 0.05 to about 25%, based on the weight of the amphoteric surfactant, and in amounts of from about 0.01 to about 20%, based on the weight of the total composition, including diluents and other additives. The preferred ranges are from about from 2.5 to about 15%, based on the weight of the amphoteric surfactant and from about 0.5 to about 2.0%, based on the weight of the total composition, including diluents and other additives. The amphoteric surfactant is employed in amounts of from about 0.1 to about 25%, based on the total weight of the composition, preferably from about 0.5 to about 15%, same basis. When the surfactant comprises a mixture of the N-coco-B-amino propionic acid (or propionate) of formula II and the betaine of formula III, these surfactants may vary in relative proportions from 1—99% to 99—1%, but preferably are employed in the range of 10—40% by weight of the formula II compounds to 90—60% by weight of the formula III compounds.

To the essential combination of amphoteric surfactant and germicidal compound may be added a wide variety of ingredients conventional in the skin and hair cosmetic arts. For example, it is common to employ a diluent or cosmetically acceptable carrier such as water, a water miscible alcohol such as ethyl alcohol or isopropyl alcohol, and the like. Other well known ingredients include preservatives, such as formalin; dyes such as those listed by the Food and Drug Administration; perfumes; buffering agents for pH control; and various conditioning and grooming agents such as lanolin and lanolin derivatives, fatty alcohols or fatty esters, ethoxylated polyhydroxy esters, cholesterol, coconut oil, mineral oil and the like.

The compositions of the invention are formed in the conventional manner by mixing the amphoteric surfactant and organo phosphorus germicide alone or in the presence of a diluent which is cosmetically acceptable, or also with other cosmetic ingredients such as described above. When antidandruff effect is intended, the germicidal ingredient (b) may be dissolved in water to the extent of about 0.01 to 5.0% and applied as a rinse to the affected area. Preferably, however, the germicidal ingredient is used in admixture with surfactant (a), particularly in combination with cosmetic ingredients conventionally employed in shampoos, lotions, and the like.

The following examples are intended as further illustration of the invention but are not necessarily limitative except as set forth in the claims. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

The formulations shown in Table I below are prepared and subjected to a hair protection test with the results shown in Table I. The surfactants of the formulations are identified as follows:

Surfactant	Name
1	Alkyl (C_{12} coco fatty) ammonium sulfonic acid betaine
2	Alkyl (C_{12} coco fatty) carboxylic betaine
3	N-coco β-amino propionic acid
4	70/30 lauric/myristic diethanolamide
5	1:1 mixture of alkyl dimethyl benzyl ammonium chloride (50%) and alkyl isoquinolinium bromide (75%)
6	Nonylphenol/ethylene oxide condensate, mol ratio 1:9.5

The germicide in Table I is 1,10-decamethylenebix[triphenyl-phosphonium bromide] and the sequestrant is ethylene diamine tetraacetic acid, tetrasodium salt.

The hair protection test measures germicidal activity and substantivity of the compositions to the hair and is conducted as follows:

Hair Protection Test

Human hair swatches (20 strands, 2 inches long, knotted together at one end) are immersed in a 1:1 dilution of the composition containing the germicidal ingredient for at least two minutes. The treated hair is

rinsed twice in 100 ml. aliquots of sterile tap water. The hair swatches are then dried for two minutes under an Oster hair blower drier. The swatches are placed on the appropriate agar and overlayed with 5 ml. of the same agar containing one loopful (4 mm. OD) of the appropriate test organism per 10 ml. of agar. Plates are incubated at 37° C. until growth appears and zones of inhibition can be read. The compositions are rated as active (+) or inactive (−) according to whether growth zones are not or are observed in substantial quantity, respectively. Inconclusive activity is (±).

TABLE I

Formulations

Ingredients, % by weight	A	B	C	D	E	F
Surfactant 1	44.4					
Surfactant 2		44.4				44.4
Surfactant 3			44.4	44.4	44.4	
Sequestrant	1.0	1.0	1.0	1.0	1.0	1.0
Ethanol SD–40	8.0	8.0	8.0	8.0	8.0	8.0
Surfactant 4	5.0	5.0	5.0		5.0	5.0
Germicide		1.0	1.0	2.0	2.0	2.0
Surfactant 5	1.0					
Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100

Hair Protection Test

Test Organism	A	B	C	D	E	F
S. aureus	−	+	+	+	+	+
S. epidermis	−	+	+	+	+	+
C. parapsilosis	−	−		+	+	−
C. mycoderma				+	+	+
P. ovale	−	−	−	+	+	−
R. mucilaginosa	−	+	+	+	+	

Compositions, C, D and E, representative of the invention, exhibit not only superior germicidal activity but also superior lathering and substantivity to the hair as compared with the other compoistions which contain different amphoteric surfactants. Substantivity is proved by reason of the germicidal activity persisting through repeated rinsings and drying.

EXAMPLE 2

Substantially as described in Example 1, the formulations shown in Table II below are prepared and tested, with the results shown in Table II. The surfactants and germicide are the same as in Example 1. TEA—L—SO_4 is triethanolamine lauryl sulfate and the thickener is hydroxy propyl methyl cellulose (1%).

TABLE II

Formulations

Ingredients (Wt. %)	A	B	C	D	E
Surfactant 5 (50%)	1.0			1.0	
Germicide		0.5	0.5		0.5
Thickener	40.0	40.0	40.0	40.0	40.0
Surfactant 3	40.0	40.0			
TEA–L–SO_4			40.0		40.0
Surfactant 6				40.0	
Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100

Hair Protection Test

Test Organism	A	B	C	D	E
S. aureus	+	+	−	+	+
P. ovale	−	+	−	−	±
C. parapsilosis	±	+	−	−	+

It will be seen from Table II that only composition B, representative of the invention, provided activity against all three microbial species. Composition B was also superior to the others in substantivity and detergency (lathering).

EXAMPLE 3

Substantially as described in the foregoing examples, the formulations shown below in Table III are prepared and tested, with the results also shown in Table III. The surfactants, sequestrant and germicide are the same as in Example 1. Composition C represents a formulation with increased viscosity and in Composition D and pH has been lowered by addition of an acid. These results show that Composition A, representative of the invention, is superior to the others in that it controlled all four test organisms including *P. ovale*, a species generally found in the same environment with dandruff.

TABLE III

Formulations

Ingredients (Wt. %)	A	B	C	D
Surfactant 3	44.4	—	—	—
Surfactant 2	—	44.4	44.4	44.4
Sequestrant	1.0	1.0	1.0	1.0
Ethanol SD—40	8.0	8.0	8.0	8.0
Surfactant 4	5.0	5.0	10.0	5.0
Germicide	1.0	1.0	1.0	1.0
NaCl	—	—	2.0	—
Citric Acid	—	—	—	0.8
Water	qs	qs	qs	qs

Hair Protection Test

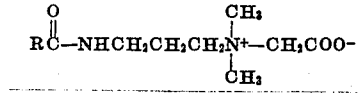
Test Organism	A	B	C	D
R. Mucilaginosa	+	+	−	+
C. Mycoderma	+	+	+	+
P. Ovale	+	−	−	−
S. Aureus	+	+	+	+

EXAMPLE 4

Table IV below illustrates other formulations in which the surfactants, sequestrant and germicide are the same as in Example 1 except the following:

Surfactant 7: alkyl sulfate salt of lauroylcycloimidinium-1-ethoxy ethionic acid-2 ethionic acid, disodium salt.

Surfactant 8:



where R is C_{12} derived from coco fatty acids. Available from Goldschmidt Chemical Company.

All of the formulations contain 20% active amphoteric and formulation E is representative of the invention. Table IV also shows results of hair protection tests conducted substantially as described in Example 1. It will be noted that only formulation E is active against both organisms although all the formulations contain an amphoteric surfactant and the same germicide. The germicidal activity is therefore the cooperative effect of both the germicide and the specific amphoteric surfactant.

TABLE IV

Formulations

Ingredients (Wt. %)	A	B	C	D	E
Surfactant 7	52.7				
Surfactant 1		40.0			
Surfactant 2			57.2		
Surfactant 8				66.7	
Surfactant 3					44.4
Sequestrant	1.0	1.0	1.0	1.0	1.0
Ethanol SD-40	8.0	8.0	8.0	8.0	8.0
Surfactant 4	5.0	5.0	5.0	5.0	5.0
Germicide	1.0	1.0	1.0	1.0	1.0
Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100

Hair Protection Test

Test Organism	A	B	C	D	E
S. Aureus	−	+	+	+	+
P. Ovale	−	−	−	−	+

EXAMPLE 5

Table V below demonstrates that other surfactants (the cationic surfactant 9 of formulation A and the amine oxide amphoteric Surfactant 10 of formulation C) may be added to the basic combination of germicide and amphoteric surfactant without adversely affecting the hair protection afforded by the basic combination. It will be noted that formulations B and D, lacking the germicide, give negative results. The hair protection test, the germicide and Surfactant 3 are the same as in Example 1 and the other ingredients are as follows:

Surfactant 10: Alkyl (50% C_{14}, 40% C_{12}, 10% C_{16}) dimethyl benzyl ammonium saccharinate

These results are significant since it is often desirable to add such other materials (representative of conditioners, softeners, preservatives, germistats, and the like) when formulating hair treating compositions which incorporate the basic composition of the invention. Compatibility and germicidal-detergent efficacy is not thereby sacrificed.

TABLE V

Formulations

Ingredients (Wt. %)	A	B	C	D
Surfactant 3	44.4	44.4	44.4	44.4
Surfactant 9	3.0	3.0	3.0	3.0
Surfactant 10	0.5	0.5	—	—
Germicide	1.0	—	1.0	—
Water	qs to 100	qs to 100	qs to 100	qs to 100

Hair Protection Test

Test Organism	A	B	C	D
S. Aureus	+	−	+	−
P. Ovale	+	−	+	−
C. Albicans	+	−	+	−

The compatibility of the germicides and amphoteric surfactants of the invention (formulas I, II, and III above) over the range of pH useful in the treatment of the hair and skin (pH 6.5 – 8.0) is a highly surprising and beneficial result. Thus, although these amphoteric surfactants become anionic above pH 3.5–4.7 (upper limit of isolectric range), they nevertheless remain compatible with the organo phosphorus germicide, which is cationic. The formulations thus remain substantive, germicidally active, and stable despite pH conditions under which incompatibility would normally be expected. Formulations of the foregoing examples illustrative of this anomalous result are formulation C of Table I, formulation A of Table III, formulation E of Table IV (each pH 7.5–7.6) and formulation B of Table II (pH 6-8)

EXAMPLE 6

Substantially as described in the foregoing Examples, the following preferred formulation of Table VI is prepared (in which the germicide is the same as in Example 1) and tested, the results also being indicated in the Table.

TABLE VI

Formulation		Hair Protection Test	
Ingredients	Wt. %	Test Organism	
Germicide	2.0	*S. aureus*	+
Surfactant 8	60.0	*C. parapsilosis*	+
N-lauryl/myristyl β-amino propionic acid	5.0	*P. ovale*	+
Surfactant 4	8.0	*R. mucilaginosa*	+
NaCl	4.0	*C. albicans*	+
Sequestrant	1.0		
Propylene glycol	5.0		
Citric to pH 7.5–8.0	0.4		
Water	qs to 100		

EXAMPLES 7–13

The following formulations illustrate various products incorporating the germicidal detergent composition of the invention. The germicide is that of Example 1.

7.	HAND & BODY LOTION	
	Germicide	0.5
	Surfactant 3	10.0
	Glyceryl Monostearate	3.0
	Isopropyl Palmitate-Myristate	5.0
	Lanolin	2.0
	Propylene Glycol	5.0
	Water	74.5
8.	MEDICATED CREME RINSE	
	Germicide	1.0
	Surfactant 3	5.0
	Stearyl-Dimethyl Benzyl Ammonium Chloride	5.0
	Polyoxyethylene Glycol 400 Disterate	3.0
	Water	84.0
9.	HAIR DRESSING	
	Germicide	0.25
	Ethyl Alcohol SD-40	40.00

	Surfactant 3	2.50
	Water	57.25
10.	GERMICIDAL CLEANER	
	Germicide	0.5
	Surfactant 3	5.0
	Ethoxylated Iso-Octyl Phenol	5.0
	Coconut Diethanolamide	5.0
	Propylene Glycol	10.0
	Tetrapotassium Pyrophosphate	10.0
	Water	64.5
11.	DIAPER DEODORANT	
	Germicide	1.0
	Surfactant 3	5.0
	Propylene Glycol	5.0
	Water	89.0
12.	ATHLETES' FOOT LOTION	
	Germicide	0.25
	Surfactant 3	3.00
	Boric Acid	0.10
	Alcohol SD–40	15.0
	Acetone	10.0
	Water	71.65
13.	SURGICAL SCRUB	
	Germicide	1.0
	Ethoxylated Nonyl Phenol	10.0
	Surfactant 3	25.0
	Coconut Diethanolamide	5.0
	Alcohol SD–40	10.0
	Water	49.0

EXAMPLE 14

By substituting 1,16-hexadecamethylenebis[triphenylphosphon-ium chloride] for 1,10-decamethylenebis[triphenylphosphonium bromide] in Examples 1–13, substantially equivalent formulations are obtained.

EXAMPLE 15

This example demonstrates the antidandruff utility of the organophosphorus salts of the invention.

A total of 258 adult humans arranged in five groups of approximately 50 each were formed. Each subject in an initial qualifying examination had been judged by a professional dermatologist to have severe dandruff as defined by a score of 6, 7 or 8 determined by totalling the values from the following scale where the values resulted from two inspections of the scalp, the first for loose dandruff (dandruff on or in the hair) and the second for adherent dandruff (dandruff still attached to the scalp):

4 — very severe dandruff
3 — severe dandruff
2 — **moderate dandruff**
1 — **mild dandruff**
0 — absent dandruff

The total value of 6, 7 or 8 excluded only those subjects whose total resulted from a combination of 4 (loose dandruff inspection) and 2 (adherent dandruff inspection. Also excluded were subjects having identifiable dermatological conditions, such as psoriasis. The five groups were so constituted as to equalize all variables, statistically.

The subjects were instructed to shampoo once weekly, always on the same day of the week, with an assigned test product. The five test products (A–F) are described below. Test products B through E are applied by the subjects without prior treatment of the hair but application of test products A (a rinse) was preceded by shampooing with a commercial shampoo not containing an antidandruff agent. The subjects then were required to report for examination 5 days after the shampooing, 2, 4, 6 and 8 weeks after the initial, qualifying examination. At each examination the dermatologist graded both loose and adherent dandruff, the condition of each subject's scalp (dry, oily or normal), and the degree of itching. In addition, at least 25 subjects from each of the groups using test products C and D were examined for safety of the product at the qualifying examination and then after the eight weeks of use of the test products. The safety tests were designed to measure adverse reactions and were based on a complete blood count, including: Red Blood Cell count, White Blood Cell Count, Hemoglobin, Hematocrit, Differential White Blood Cell Count, Appearance of red blood cells, Erythrocyte Sedimentation Rate, Serum Glutamic Oxalacetic Transaminase, Blood Urea Nitrogen, Serum Bilirubin, Thymol Turbidity and Routine and Microscopic Urinalysis.

The test products, a different one of which was assigned to each of the five groups of subjects, were as follows:

TABLE VII

Test Products (parts by weight)	A	B	C	D	E[1]
1,10-Decamethylenebis [triphenylphosphonium bromide]	1.0	1.0	2.0	0.5	
Ethyl alcohol, SD–40, 190 proof	5.0	5.0	5.0	5.0	
N-coco-β-amino propionic acid, 45% active			44.5	44.5	
Ethylene diamine tetraacetic acid, sodium salt, 40% active		1.0	1.0	1.0	
70/30 Lauric/myristic diethanolamide, 95% active		5.0	5.0	5.0	
Propylene glycol		3.0	3.0	3.0	
Perfume		0.5	0.5	0.5	
Demineralized water		qs to 100			

[1]Test Product E: a commercially available lotion shampoo containing 2% by weight of zinc pyridinethione as the anti-dandruff ingredient.

Table VIII below establishes the magnitude of effectiveness of the five test products in terms of an approximation of the quantity of dandruff at the start and at the end of the study. The Table also shows the percent reduction in dandruff throughout the eight weeks of the test. From a statistical standpoint, the results establish that all of the test products were highly effective in combatting dandruff.

TABLE VIII

Test Group	Product	No. of Subjects	Start	End	% Reduction, start to week: 2	4	6	8
1	A	50	6.6	4.5	18	21	33	31
2	B	54	6.6	4.3	14	18	32	35
3	C	54	6.7	4.1	18	22	36	39
4	D	53	6.6	4.6	16	27	33	31
5	E	47	6.6	3.6	11	18	39	45

Table IX below shows that hair and scalp condition, in terms of dryness, normalcy or oiliness, was improved by each test product, test products C and D being the most effective.

TABLE IX

Condition of Scalp and Hair

Group	Product	Start % Dry	Start % Normal	Start % Oily	Finish % Dry	Finish % Normal	Finish % Oily
1	A	10.0	48.0	42.0	10.0	60.0	30.0
2	B	7.4	53.7	38.9	14.8	57.4	27.8
3	C	11.1	42.6	46.3	9.3	57.4	33.3
4	D	11.3	34.0	54.7	7.5	47.2	45.3
5	E	19.1	48.9	31.9	17.0	55.3	27.7

Table X below shows that itching was relieved in most cases by each test product, those products containing at least 1% of the germicide being the most effective.

TABLE X

Degree of Itching

Group	Product	Start	Average End of week 8	% Reduction Weeks 0–8
1	A	.9	.6	30.4
2	B	1.1	.7	37.9
3	C	1.1	.7	35.1
4	D	.9	.7	27.1
5	E	1.0	.6	44.7

With respect to the safety tests, which were conducted on subjects in the groups using test products C and D, no adverse reactions were noted.

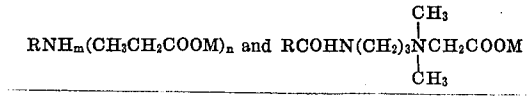
Although the clinical studies reported above relate to use of the compositions of the invention for the control of dandruff on the scalp and hair of humans, many of the hair- or fur-bearing lower animals such as dogs, cats and other domesticated or wild animals are subject to the same conditions of excessive scaling and accumulation of scales and oily debris on the skin or hide generally described as "dandruff". Accordingly, the invention is not limited to the treatment of human dandruff but includes treatment of such conditions in the hair- or fur-bearing lower animals as well.

It should be apparent from the foregoing description that although it is preferred to employ the specified amphoteric surfactants with the organophosphorus salts when treating dandruff conditions, as in shampoos or lotions, these surfactants are not critical for dandruff control. Accordingly, for this specific use the organophosphorus salts may be dispersed in any cosmetically acceptable vehicle, including water alone, ethyl or isopropyl alcohol alone, alcohol-water mixtures, oil-in-water or water-in-oil emulsions and the like, and applied in the conventional manner as shampoos, lotions, creams, pastes, gels, ointments, and the like. Moreover, while certain relative proportions and amounts based on total compositions have been described, such proportions and amounts may vary widely, depending on the viscosity or cosmetic effects desired as well as level of germicidal activity.

We claim:

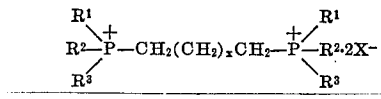
1. A method of controlling dandruff which comprises applying to a region afflicted with dandruff an effective amount of a composition which comprises effective amounts

a. an amphoteric compound selected from the group consisting of



wherein R is alkyl of at least eight carbon atoms, M is hydrogen or a cation selected from the group consisting of water solubilizing alkali and alkaline earth metals and amines, *m* is 0 or 1, *n* is 1 or 2, and the sum of *n* and *m* is 2, and

b. an organophosphorus compound of the formula



wherein R^1, R^2 and R^3 independently are alkyl (C_1–C_{12}), phenyl or hydroxyalkyl (C_1–C_{14}); *x* is 6–14 and X is an anion selected from the group consisting of halides, perchlorates, nitrates, sulfates, R^4OSO_3, R^4OSO, and R^4SO_3 where R^4 is alkyl or aryl.

2. The method of claim 1 wherein said organophosphorus compound is applied as an aqueous mixture in which (a) is N-coco-β-amino propionic acid, N-lauryl/myristyl β-amino propionic acid, or fatty (coco) amido alkyl betaine.

3. The method of claim 1 wherein said organophosphorus compound is 1,10-decamethylenebis[triphenylphosphonium bromide].

4. The method of claim 1 wherein said organophosphorus compound is applied as an aqueous-alcoholic mixture.

5. The method of claim 3 wherein said organophosphorus is applied as an aqueous mixture in which (a) is a mixture of N-lauryl/myristyl β-amino propionic acid and fatty (coco) amido alkyl betaine.

6. The method of claim 5 wherein said organophosphorus compound is 1,10-decamethylenebis[triphenyl phosphonium].

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