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3,839,571 MICROBICIDAL HAIRDRESSING Teresa R. Ciccone, Green Brook, and William J. Gangwisch, Highland Park, N.J., assignors to Colgate-Palmolive Company, New York, N.Y. No Drawing, Filed June 17, 1971, Ser. No. 154,186 Int. Cl. A61k 7/06, 27/00

U.S. Cl. 424--2706 Claims

#### ABSTRACT OF THE DISCLOSURE

Microbicidal hairdressing compositions which are effective against bacteria and fungi, such as those normally present on the human hair and scalp, comprise an alkyl di-lower alkyl arylalkyl ammonium saccharinate, such 15 as a higher alkyl di-methyl benzyl ammonium saccharinate, a hydrophilic oil and a hydrophobic oil, both of which are ethers of poly-lower alkylene glycol(s) and lower alcohol(s), and an aqueous or aqueous alcoholic

The described hairdressings are useful in mentioned proportions to make clear liquid or gel preparations. They groom the hair, giving a desirable lustre and facilitating the restyling or combing thereof. They also counteract the growth of bacteria, fungi, yeasts and other microor- 25 ganisms, such as Pityrosporum ovale, without objectionably depositing opaque coatings on the hair.

## SUBJECT OF THE INVENTION

The present invention relates to transparent hairdressings possessing hair conditioning properties as well as the ability to inhibit the growth of Pityrosporum ovale. These preparations, when applied to the hair and scalp, make the hair more readily controllable and easily combed 35 into place. The products are especially useful as men's clear hairdressings but may also find applications in clear preparations for the treatment of women's hair.

## BACKGROUND OF THE INVENTION

For years extensive research has been conducted in efforts to produce cosmetic preparations that also possess microbicidal properties. Many cosmetics, toiletries and washing agents have been formulated to contain a wide variety of bactericides and fungicides. Preparations for 45 the skin have been made which include bactericides that are effective against Staphylococcus aureus and compositions for the hair have been made, incorporating antimicrobial compounds which are effective against Staphylococcus aureus and Pityrosporum ovale, the latter of 50 which has been considered as a causative agent for the development of dandruff and excessive scaling of the human scalp. Such compositions however, have heretofore not been made in clear or transparent form since the incorporation of the antimicrobial compounds has made the 55 composition opaque.

## DESCRIPTION OF THE INVENTION

It has now been found that an effective antimicrobial hairdressing can be made as a transparent or clear prod- 60uct. The importance of the present discovery becomes evident when it is realized that microbicides which have been found to be clinically effective against dandruff, such as zinc omadine and selenium disulfide, are incapable of forming clear hairdressings in the normal media which 65 may be employed for such compositions. Thus, the present products are unobvious because they are truly effective antimicrobial hairdressings and may be produced in

Surprisingly, tests indicate that the higher alkyl di- 70 methyl benzyl ammonium saccharinates and equivalent compounds of similar structure, when combined with the

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polyalkylene glycol ethers described herein result in effective microbicidal compositions. It could have been expected that a diminution of the antimicrobial effectiveness of the saccharinate compound would occur because of the combination of the germicide with the nonionic oils. The desired properties of the present compositions are obtainable when the product is a liquid or gel, and the composition can be incorporated in an aerosol spray product.

In accordance with the present invention a hairdressing comprises minor proportions of antimicrobial higher alkyl di-lower alkyl arylalkyl ammonium saccharinate and hydrophobic and lipophilic lower alkyl monoethers of poly-lower alkylene glycols, in an aqueous or aqueous alcoholic carrier medium. Specifically, such hairdressing compositions are clear liquid or gel preparations and preferably comprise higher alkyl (C12-C16) di-methyl benzyl ammonium saccharinate, a hydrophilic polyethylene-polypropylene glycol monoether of butanol which is of molecular weight from about 1,400 to 1,600 and is derived from equal parts by weight of propylene oxide and ethylene oxide and a lipophilic polypropylene glycol monoether of butanol which has a molecular weight of about 2,000-2,500, in a carrier medium which is aqueous ethanolic. Also within the invention are antimicrobial uses of the composition of higher alkyl di-lower alkyl arylalkyl ammonium saccharinate and the mixed polyalkylene glycol ethers.

The antimicrobial saccharinates employed are those of 30 the formula

$$\begin{bmatrix} R_1 \\ R-N-(CH_2)_n \\ R_2 \end{bmatrix}^{\bullet} \begin{bmatrix} O^- \\ N \\ SO_2 \end{bmatrix}$$

wherein R is higher alkyl, A<sub>1</sub> and R<sub>2</sub> are lower alkyls, and n is from 1 to 4. Among the R groups which may be employed are the higher alkyls of 8 to 20 carbon atoms, preferably the straight chain alkyls of 10 to 18 carbon atoms, e.g., myristyl, lauryl, decyl, palmityl and stearyl. Of these, the tetradecyl (myristyl) and dodecyl (lauryl) are most preferred. Usually, such higher alkyls are obtained from mixtures comprising also minor proportions of other higher alkyls, such as palmityl. Most preferred alkyl distribution includes about 40%  $C_{12}$ , 50%  $C_{14}$  and 10% C<sub>16</sub>. The lower alkyls, R<sub>1</sub> and R<sub>2</sub>, are of 1 to 4 carbon atoms, preferably of 1 to 2 carbon atoms and most preferably are both methyl. However, it is not required that R<sub>1</sub> and R<sub>2</sub> be of the same carbon content. The alkylene group, the number of carbon atoms of which is designated by n, is lower alkylene of 1 to 4 carbon atoms, preferably of 1 to 2 carbon atoms and most preferably, is a methylene carbon atom. The aryl group, although it may include other aromatic rings, such as naphthyl or substituted phenyl, is most preferably phenyl. Thus, the arylalkyl group is most preferably benzyl. Nevertheless, equivalent compounds may be employed wherein the aromatic ring, the alkyls, the alkylene and the saccharinate ring are suitably substituted with non-interfering substituents, such as lower alkyl, halogen, nitro, amino or hydroxy groups. If such substitution is present, it will usually be on the aromatic ring or the higher alkyl, R.

An important consideration in selecting the antimicrobial saccharinate is that it should be strongly microbicidal, especially effective against Pityrosporum ovale, and it should be compatible with the other constituents of the hairdressing compositions, especially with the polyalkylene glycol ethers, alcohol, water and gelling agent, if present to form clear solutions or gels. Thus, the saccharinate should be substantially soluble in the carrier or

solvent medium. It must not cause clouding or creaming of the hairdressing.

The mixed polyethylene-polypropylene glycol ether hydrophilic oil component of the present preparations is one in which the proportions of polyoxyethylene and polyoxypropylene are such that the hydrophilic properties of the product predominate, making it water soluble, while still giving it the thickness and lubricity of an oil. Because the polyethylene glycol or polyethylene oxide component employed to produce the polyoxyethylene portion of the 10 hydrophilic oil is that component which usually favors hydrophilic characteristics, to increase such properties an increase in polyethylene glycol or polyethylene oxide monomer may be effected. Correspondingly, to increase the lipophilic properties, the proportion of polyoxy- 15 propylene or, in some cases, polyoxybutylene, can be increased, with greater lipophilic effects being obtained from using the higher polyoxyalkylene, such as polyoxybutylene, due to its increased carbon/oxygen ratio. The lipophilic or hydrophilic properties of the polyalkylene 20 glycol and its solubilites are also related to chain lengths or molecular weights and these factors, with ethylene oxide-propylene oxide ratios and etherifying monohydric alcohol carbon contents, are chosen to botain the desired hydrophile-lipophile balance and water solubility for the 25 hydrophilic oil. The various polypropylene glycol or polyoxypropylene alkyl ethers are mixtures of polymers of various chain lengths, as are the hydrophilic polymers previously discussed. The chain lengths and the chain terminating compound are chosen so that the product 30 will be desirable lipophilic, oily and clear. The polymers should be soluble in the alcohol or aqueous alcoholic media employed. Solubility in water itself may be very small, often being less than 2%. In preferred embodiments of the invention, mixtures of polyoxypropylene 35 butyl monoethers are used. The described compounds are known and methods for their manufacture are given in U.S. Pat. 2,448,664 at columns 5-8 and in the working examples. This patent describes the useful class of the lipophilic polymers and a similar description, with re-  $^{40}$ spect to the hydrophilic polymers, is found in U.S. Pat. 2,425,755, previously cited.

Preferred blends of glycols or lower alkylene oxides to make the present hydrophilic oils are blends of polyethylene oxide and polypropylene oxide or the equivalent 45 glycols, which contain from 25 to 75% of the polyethylene glycol and 75 to 25%, of the polypropylene glycol or equivalent oxides, preferably 40 to 60% and 60 to 40%, respectively, exclusive of the etherifying chain terminating radicals. The polymers made are preferably termi- 50 nated with hydroxyl or alkyl groups of 1 to 8 carbon atoms, preferably a lower alkyl of from 3 to 5 carbon atoms. Usually the polymers will be terminated at one end with an OH and at the other with a normal alkyl. To obtain the desired hydrophilic oils the molecular weights 55 should be regulated to average in the range of about 400 to 4,000, preferably from 1,000 to 2,000 and most preferably from 1,400 to 1,600. In a similar manner, with respect to the lipophilic oils, the chain terminating monohydric alcohol is usually of 1 to 8 carbon atoms and is 60 linear. Preferably, it is of 3 to 5 carbon atoms. The molecular weight of the lipophilic oil is normally within the range of 400 to 4,000, preferably from 1,500 to 3,000. The water solubility of such compounds will generally be from 0.2 to 1% at room temperature. It has been found 65 that mixtures of the lipophilic oils are useful and in such cases, preferred mixtures are of such compounds of molecular weights between 1,800 to 2,200, with those of such weights of 2,300-2,700. In such instances, the etherifying monohydric alcohol is preferably butanol. In 70 the mixtures described, it will generally be preferable to include, as the major constituent of the mixed lipophilic polyalkylene glycol ether, that of the higher molecular weight, and often it will constitute from 70 to 90% of the mixture.

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Both the hydrophilic and lipophilic oils may, in appropriate cases, be replaced, usually only in part, by similar oils or slight modifications. Thus, instead of employing monohydric alcohol chain terminators, in some cases glycols or glycerol may be used for this purpose. Polyoxylower alkylene glycols of the "Carbitol" and "Pluronic" types may be used, as may similar compounds of equivalent properties. Generally, however, these will constitute only a minor proportion of the "oil" content of the clear, microbicidal hairdressing.

The aqueous carrier or solvent employed for the microbicidal saccharinates and the hydrophilic and lipophilic oils and adjuvants is usually water, alcohol, or a solution of lower alcohol in water. It will usually be desirable to maintain the hardness of the water under 150 parts per million and waters having hardness equivalents, in terms of calcium carbonate, below 50 p.p.m. and preferably below 20 p.p.m., are most desirably employed. Of course, the solvent system should be clear and free of suspended matter or other impurities which might undesirably affect the clarity or color of the product. The lower alcohols used will normally be either ethanol, which is preferred, or isopropanol, although minor proportions of n-propanol, n-butanol, isobutanol or tertiary butanol can be present. Generally, when aqueous-alcoholic solvents are being employed they will comprise from 30 to 80% ethyl alcohol and 70 to 20% water, with the preferred embodiments having 50 to 70% alcohol and 50 to 30%

In the manufacture of gelled hairdressings, a gelling agent is employed to thicken and set the dressing into gel form. Many such thickening agents are known in the cosmetic arts, including both organic and inorganic thickeners. Useful gelling agents form hairdressings that are clear and generally organic gums or thickeners will be employed. Useful colloidal organic thickeners include the carboxyalkyl celluloses, the hydroxyalkyl celluloses, carboxypolymethylenes, ("Carbopols") and the various natural gums. Also useful are the polyvinyl pyrrolidones, vegetable proteins, starch derivatives, gelatins, polyacrylates, polyvinyl alcohols, and dextrans. Among the natural gums are karaya, tragacanth, gum acacia, algins, agar, pectin, carrageenan, guar, locust bean gum, Irish moss extractives and various derivatives thereof.

Specific cellulose compounds that can be used include ethers or esters such as methyl cellulose, methyl ethyl cellulose, sodium carboxymethyl cellulose, sodium carboxymethyl hydroxyethyl cellulose, hydroxyethyl cellulose, and hydroxyethyl starch, alkali metal starch phosphates, and carboxymethyl starch. The synthetic materials include ethylene maleic anhydride copolymers, polyvinyl alcohol, polyvinyl pyrrolidone, vinyl pyrrolidine copolymers and the carboxyvinyl polymers, e.g., "Carbopol" 934. The various synthetic and natural organic gums, hydrocolloid thickeners and gelling agents are described at length in *The Chemistry and Manufacture of Cosmetics*, Vol. II, Second Edition, by Maison G. DeNavarre (D. Van Nostrand Company, Inc., 1962), at pages 109–154.

Especially useful thickening agents which yield clear gels are carrageenan gum, polyvinyl alcohol, polyvinyl pyrrolidone and the ethylene maleic anhydride copolymers, such as "Copolymer No. 11" (Monsanto Corp.).

Often it will be desirable to employ mixtures of the various thickening agents, so as to modify the thickening or gelling effects to obtain best results for a particular application. Generally, no more than two or three gums will be mixed and usually a significant proportion of each will be present. Thus, for example, in a preferred hydrocolloid mixture for gelling purposes, there will be present from 5 to 25% of hydroxypropyl methyl cellulose capable of producing an aqueous solution of 4,000 centipoises viscosity at standard conditions and from 75 to 95% of ethylene maletic anhydride copolymer, such as "Copolymer No. 11"

75 mer No. 11."

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Various adjuvants may be present in the hairdressings. Included among such adjuvants are colorants, perfumes, buffers or pH regulating chemicals, antioxidants, ultraviolet ray absorbers, stabilizers and supplementary microbicides. The coloring agents and perfumes which are used are standard water or alcohol soluble materials which do not cloud or form films in the present compositions. Ultraviolet light absorbers, e.g., 2,2',4,4'-tetrahydroxy-benzophenone, may also be employed to stabilize color and perfume both in the product and during use.

The proportions of the various constituents of the hair-dressings are maintained within desired ranges to produce the best product. The antimicrobial higher alkyl di-lower alkyl ammonium saccharinate generally comprises at least 0.1% of the final product while more than 5% is usually unnecessary. Within the 0.1 to 5% range, a preferred con-

centration is 0.3 to 1%.

The water insoluble polyethylene-polypropylene glycols are used to increase the conditioning properties of the hairdressing, and, because their structure is so similar to that of the hydrophilic oil present, this can be done readily without creating unstable products, emulsions or hairdressings which tend to separate. Normally, for best results, the proportions of hydrophilic and lipophilic glycol ethers will be such that from 40 to 95% of the polyalkylene glycol content will be of the hydrophilic oil 25 type. For liquid preparations it is preferred that the hydrophilic oil should constitute a major proportion, usually from 80 to 100% and preferably from 90 to 95% of the mixture. When gels are made, from 40 to 60%, preferably about 50% of hydrophilic glycol will be used. Exemplary of the lipophilic alkylene oxide random copolymers which may be employed in suitable compositions are "Ucons' manufactured by Union Carbide Corp. and identified as LB-65, LB-1145, LB-1715, LB-3000, LB-70-X, LB-400-X and LB-1800-X. The characteristics of these products, including specific gravities, viscosity indexes, viscosities at 100° F., pour points and flash points are given in Table IV-22 at page 232 of the text Polyethers. Part I, edited by N. Gaylord and published in 1963 by 40 Interscience Publishers. Also in Table IV-22 are description of the properties of water soluble oils of this type, identified as "Uncors" 50-HB-55, 50-HB-660, 50-HB-5100, 75-H-450, 75-H-1400, 75-H-90,000, and Dow Chemical Co. Polyglycols 15-100, 15-200, 15-1000. 45 The Dow compounds are terminated by glycerol.

The water soluble hydrophilic oil is present in minor proportion, generally from 0.5 to 30% and preferably from 5 to 25% of the product. The water insoluble polyalkylene glycol may comprise from 0.5 to 15% of the 50 preferably from 1 to 8% thereof. From 1 to 4% is preferably present in liquids and from 4 to 8% in the gels.

The carrier or solvent medium of the hairdressing may constitute the balance of the product if no thickeners and/or other adjuvants are present. The water or aqueous 55 alcoholic medium which is often used instead will constitute a significant proportion of the hairdressing, usually being from 40 to 98.9% thereof, with a major proportion, 50.1 to 90% being preferred.

When a gel hairdressing is made, it will normally contain from 0.3 to 5% of an organic gelling agent to thicken the composition. Small proportions, from 0.1 to 0.4% of such products may be employed to increase the viscosity of a liquid hairdressing. Of course, the thickening effect is dependent on the particular gelling agent being used 65

and the composition being thickened.

By utilizing the proportions of various ingredients given, clear hairdressings having exceptionally good antimicrobial properties are obtained. This is surprising because the nonionic hydrophilic oil and the related lipophilic oils contain polyoxyalkylene groups and may also contain free hydroxyls which would lead one to expect that they would behave similarly to surface active materials of related structures. In the past it has been observed that such surface active compounds have had 75

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detrimental effects upon the microbicidal properties of various compounds. Yet, in the present case, the hydrophilic oils of these hairdressings do not have such detrimental effects and indeed have been shown to aid in maintaining or improving the activities of the particular higher alkyl di-lower alkyl ammonium saccharinate microbicides of this invention. At the same time, such oils help to condition the hair and give it a satisfactory lustre. Even after application of the hairdressing to the hair and evaporation of carrier components, including the water or aqueous alcoholic carrier, the use of a damp comb is enough to revitalize the hair because of the combination of the moisture with the hydrophilic oil and the combined action of both on the hair. The hydrophilic oils and the microbicides of this invention are compatible with the other constituents which may be employed to thicken liquid preparations or to make gels. They are also compatible with the usual adjuvants employed for hairdressings. The hydrophilic oil gives body to the liquid hairdressings, compensating for the thinning effects of alcohol and water. The alcohol helps to solubilize the various contituents, as does the water, and improves the evaporation rate of the product so that the hair returns to a dry, lustrous state soon after application of the hairdressing. Thus, it is seen that the various components of the present products co-act to produce a hairdressing preparation of superior qualities. Although a hairdressing can be intentionally made opaque or can be formed into an emulsion or cream, according to known techniques, it is most frequently desired that modern hairdressings leave no creamy or greasy deposit on the hair and it is usually important that the product, as applied, should appear to be transparent. Most of the various effective microbicides, useful against fungi and bacteria found on the hair, are insoluble in conventional hairdressing compositions and in the present oils. Accordingly, their use is limited to opaque lotions or creams.

The combinations of hydrophilic and lipophilic polyethylene-polypropylene glycol oils or monoether derivatives thereof with the described saccharinate microbicides result in improved hair conditioning properties, while still maintaining the microbicide's effects. This is somewhat unexpected because the hydrophilic oils appear to possess no antimicrobial activity and the lipophilic oils, alone or in mixture with each other don't inhibit microbial growths. Yet, with the saccharinate microbicides, the disclosed oils appear to increase the effectiveness against Pityrosporum ovale, possibly by enlarging the area over which the microbicide may work. Thus, it is highly desirable for antimicrobial activity, as well as for conditioning effects, that the present compositions contain both hydrophilic and lipophilic oils and preferably include a mixture of the lipophilic oils, such as was previously mentioned herein with one or more of the hydrophilic polyoxyethylene-polyoxy-

propylene polymers.

The following examples illustrate some preferred embodiments of the invention. Unless otherwise indicated, all parts percents given are by weight and temperatures are in degrees centigrade.

## EXAMPLE 1

EXAMPLE	
	Parts
Ethanol	63.05
Lipophilic polypropylene glycol butyl monoether ("Ucon" LB-1715, Union Carbide Corp., cos-	
metic grade)	1.75
Lipophilic polypropylene glycol butyl monoether	
("Ucon" LB-1145, Union Carbide Corp.)	0.50
Polyethylene-polypropylene glycol butyl monoether	
(hydrophilic oil, "Ucon" 50-HB-660, Union	
Carbide Corp., cosmetic grade)	15.75
Perfume	0.50
Higher alkyl (40% C <sub>12</sub> , 50% C <sub>14</sub> , 10% C <sub>16</sub> ) di-	0.50
methyl benzyl ammonium saccharinate ("Onyx-	
ide" 3300, 95% active, Onyx Chemical Co.)	0.52
Deionized water	17.62

Colorant, F. D. and C. Blue Dye No. 1 (1% aque-0.10 50, ultraviolet absorber, GAF Corp.) \_\_\_\_\_

A liquid hairdressing of the above formulation is made by sequentially adding to a mixing vessel, with stirring, the formula amounts of ethanol, "Ucon" LB-1715, "Ucon" LB-1145, "Ucon" 50-HB-660, perfume, higher alkyl dimethyl benzyl ammonium saccharinate, water, colorant and "Uvinul" D-50. No difficulties in formulation are encountered and a clear liquid product results.

After preparation, all of which takes place at room temperature, the product is packed and stored, ready for shipment. It is of good stability on storage and the higher alkyl dimethyl benzyl ammonium saccharinate is effective against Pityrosporum ovale when used, despite lengthy

When applied to the hair in usual quantities, about two to five cubic centimeters per application of 2 to 5 grams per day, the product has a microbicidal action against Pityrosporum ovale, due to the presence of the alkyl dialkyl arylalkyl ammonium saccharinate, in combination 25 with the hydrophilic oil ("Ucon" 50-HB-660). Such action is also observed when the product is applied to other sites of microbial growths. This is verified by standard agar plate "halo" tests, against Staphylococcus aureus and Pityrosporum ovale, wherein improved indications of 30 germicidal actions are noted when the hydrophilic polyethylene-polypropylene glycol is present with the saccharinate microbicide in aqueous media. The hairdressing also acts to condition the hair, making it easy to comb and giving it a lustre during and after application. It also im- 35 prove manageability of the hair on remoistening hours after application of the hairdressing.

Other clear liquid hairdressing preparations utilizing similar hydrophilic oils or mixtures thereof, preferably in combination with mixed lipophilic oils and with other of 40 the described higher alkyl lower dialkyl arylalkyl ammonium saccharinates, which may be unsubstituted or substituted, in water or aqueous alcoholic meduim bases, as described in the foregoing specification, when used in the proportions therein given, produce similarly useful 45 and acceptable products. Such products are notable for being clear liquid hairdressings, while containing an effective microbicide. Even after several restylings of the hair with a damp comb after a single application of such a product, the hair can still be readily restyled and main- 50 tains its lustre and softness. The conditioning effect of the composition is still obtained and the hair is not dulled by a coating on the hair of a layer of the composition, which stays transparent on the hair. Conditioning effects are further improved by thep resence of the lipophilic 55 type oils in the products, in addition to the effects obtained from the hydrophilic oils.

### **COMPARATIVE EXAMPLE 2**

Taits
Ethanol (SD No. 40) 53.3
Ultravoilet light absorber ("Uvinul" N-35, GAF) 0.1
Myristyl dimethyl benzyl ammonium saccharinate 0.5
Lipophilic oil, "Ucon" LB-1715 (Union Carbide) 11.0
Lipophilic oil, "Ucon" LB-3000 (Union Carbide) 11.0
Surface active agent, "Tween" 20 (Atlas Chemical
Corp.) 1.2
Perfume 0.4
Deionized water 22.3
F. D. & C. dyes, 0.1% agueous solution 0.2

A liquid hairdressing of the above formula is made by substantially following the method of Example 1, sequentially mixing, with stirring, the formula amounts of ethanol, ultraviolet ray absorber, saccharinate, Ucons, per8

ature. The product produced is a clear liquid having a specific gravity of about 0.9, a pH of about 6, an alcohol content of 50% by weight and a content of microbicidal saccharinate of 0.5%. If necessary, pH adjustment may be effected by addition of 50% aqueous citric acid solution or a 19.1% Na<sub>2</sub>O caustic soda solution.

The product made has bactericidal and fungicidal properties but is inferior to the hairdressings of this invention containing a hydrophilic "Ucon" or equivalent hydrophilic polyoxyalkylated oil because of a tendency buildup of oil and a development of stickiness on the hair with continued applications. When, in accordance with the present invention, hydrophilic "Ucon" oils, such as "Ucon" 50-HB-660, "Ucon" 50-HB-55, "Ucon" 75-H-1400 are added, in amounts from 2 to 8%, e.g., 5%, alone or in mixture, the applied hairdressing becomes more hydrophilic in nature and is more readily distributed over the hair when the hair is wetted and combed, and undesirable buildup and stickness are decreased. Such results are also obtainable when the combinations of hydrophilic and lipophilic oils are employed at lower total proportions, with totals of about 1 to 45%, preferably about 5-15% being preferred, and with a major proportion of the oil content preferably being hydrophilic.

The presence of a hydrophilic oil such as "Ucon" also aids in maintaining the product clear in the bottle as well as after application to the hair. The conditioning effects obtained are surprising, considering that the hydrophilic "Ucons" are much less hygroscopic than other water soluble "poly" carriers, such as polyethylene glycol, polypropylene glycol, glycerol and sorbitol.

#### EXAMPLE 3

EAAMFLE 3	
Part I	<b>Parts</b>
Deionized water	30.77
Hydroxypropyl methyl cellulose ("Methocel"	
60 HG 4000, Dow Chemical Company)	0.25
Ethylene maleic anhydride copolymer "Co-	
polymer No. 91," Monsanto Corp.)	2.00
Colorant, F. D. and C. Blue Dye No. 1 (1%	
aqueous solution)	0.05
Part II	
Ethanol (SD 40, 190 proof)	49.23
Polyethylene-polypropylene glycol, viscosity of	
660 Saybolt Universal Seconds at 100° F.	
(hydrophilic oil, "Ucon" 50-HB-660, Union	
Carbide Corp., cosmetic grade)	7.50
Lipophilic polyalkylene glycol ("Ucon" LB-	,,,,
1145, Union Carbide Corp.)	7.50
Perfume	0.20
Mixed higher alkyl (C <sub>12, 14, 26</sub> ) dimethyl ben-	0.20
zyl ammonium saccharinate, 95% active	0.50
Part III	0.50
Aminomethylpropanol, 50% alcoholic solu-	
tion (Commercial Solvents Corp.)	2.00
tion (Commercial Bolvents Corp.)	2.00

A gel hairdressing of the above formula is made by admixing the various constituents of Part I, II and III, respectively and then blending them together at room temperature. Part I is made by heating the water to about 100° C. and stirring in the hydroxypropyl methyl cellulose until it is sufficiently dispersed, after which that mixture of thickener and water is cooled to about 70° C. and the ethylene maleic anhydride copolymer is admixed with it and dispersed or dissolved therein. Next, the 65 thickened solution is cooled to room temperature, about 25° C., and the colorant is added, completing the making of Part I.

Part II is made by admixing, at about room temperature, the alcohol, "Ucon" 50-HB-660, "Ucon" LB-1145, perfume and microbicidal saccharinate. Parts I and II are admixed and then a neutralizing quantity of aminomethylpropanol, Part III, is added.

The product is poured into jars and is allowed to set to a gel. It is an excellent transparent antimicrobial hairfume, water and colorants at approximately room temper- 75 dressing and may be used on the hair in a manner similar

to that in which other such hair preparations are employed. It is microbicidal, being effective against *Staphylococcus aureus* as well as *Pityrosporum ovale*. Except for its different physical form the product exhibits all of the properties described for the liquid preparation of Example 1.

When, in place of the hydrophilic or lipophilic oils, the carrier or the gelling agent, other such materials within the scope of the invention are employed within the mentioned proportions, other useful gel hairdressings of exceptional microbicidal effects are produced. For example, the saccharinate may be replaced with another higher alkyl di-lower alkyl arylalkyl ammonium saccharinate, e.g., stearyl diethyl phenylethyl ammonium saccharinate, the lipophilic oil may be changed to a mixture of "Ucons," e.g., LB-1145, LB-1715, and LB-3000, the hydrophilic oil may be replaced with "Ucon" 75-H-450, and the solvent proportions may be varied. The products so made will be effective transparent hairdressings with microbicidal action against *Pityrosporum ovale*.

## EXAMPLE 4

Part 1	Parts
Deionized water	31.6
Ethylene maleic anhydride copolymer resin No.	
91, Lot D-627, Monsanto	1.2
"Ucon" 50-HB-660	
Part II	0.5
Hydroxypropyl methyl cellulose ("Methocel"	
60 HG 4,000, Dow)	0.3
"Ucon" 50-HB-660	7.0
Part III	
Lipophilic polyalkylene glycol butyl ether,	
	75
"Ucon" LB-1145, Union Carbide)	7.5
Perfume	0.4
Ethanol (SD 40)	49.2
Ultraviolet ray absorber ("Cyasorb UV 284,	
American Cyanamid)	0.1
Manistral Issued diseased by a serious and a serious and	0.1
Myristyl-lauryl dimethyl benzyl ammonium sac-	
charinate	0.5
Stearyl dimethyl benzyl ammonium chloride	0.2
Part IV	
Aminomethyl propanol	0.8
Ethanol, SD 40	0.7
•	0.7
Part V	
Deionized water (make-up for losses)	1.0

A clear gel hairdressing of the above formula is made by heating the Part I ingredients to 93° C. while stirring with a homogenizing mixer, adding the Part II materials, in combination, cooling to about 30° C., while continuing mixing, and adding the Part III ingredients, after which Parts IV and V are blended in with the mixing gel. The product has a viscosity of about 15,000 centipoises at 25° C. and is a useful, clear gel hairdressing which diminishes the growth of *Pityrosporum ovale*.

In a variation of this formula, when the EMA gelling agent is changed to Lot D-1256, a viscosity of about 7,000 centipoises results. Again, this product is a useful, clear, microbicidal gel hairdressing.

When, in the above formulas, the higher straight chain higher alkyl di-lower alkyl arylalkyl ammonium saccharinate is replaced by other such compounds, e.g., lauryl dimethyl benzyl ammonium saccharinate, cetyl diethyl phenyl propyl ammonium saccharinate, stearyl dimethyl p-chloro or p-methyl benzyl ammonium saccharinate, or equivalent microbicidal saccharinates of such type, and the proportions are varied ±20% from the example amounts, within the given ranges, useful microbicidal clear hairdressings are produced. Similarly, when 75

the "Ucons" are varied within the limits disclosed herein, the products produced are clear, substantially non-hygroscopic and aid in conditioning and controlling the hair in use. The proportions of lipophilic "Ucon" or equivalent material may be diminished so that the essential or sole "Ucon" component is the hydrophilic material, which is found to aid in producing an acceptable microbicidal product. Yet, for the best balanced hairdressings, combinations of lipophilic and hydrophilic oils are used and in such products mixed lipophilic oils of the types described are preferred. In a similar manner, variations may be made in the alcohol-water contents within the ranges described, to obtain products of different viscosities and utilities. The hairdressings may be produced as gels, solids and liquids, and may be incorporated in "aerosol" sprays together with a propellant.

The invention has been described with respect to illustrations and working examples. It is not to be considered as limited to the compositions described because it is clear that one of skill in the art can substitute equivalents for elements of the invented compositions and processes without departing from the spirit of the invention.

What is claimed is:

1. A transparent liquid hairdressing which comprises from 0.1 to 5 % of a microbicide of the formula

$$\begin{bmatrix} R_1 \\ R-N-(CH_2)_n \\ R_2 \end{bmatrix}^{+} \begin{bmatrix} O \\ C \\ N \end{bmatrix} - \begin{bmatrix} O \\ C \\ S \end{bmatrix} O_2$$

wherein R is higher alkyl of 8 to 20 carbon atoms, R<sub>1</sub> and R<sub>2</sub> are lower alkyls of 1 to 4 carbon atoms, and n is from 1 to 4; 0.5 to 30% of a hydrophilic polyethylene-polypropylene glycol ether containing 25-75% of the polyethylene glycol and 75 to 25% of the polypropylene glycol, said ether having hydroxyls and alkyls of 1-8 carbon atoms as chain terminating radicals, and said ether having a molecular weight from about 400 to 4,000; 0.5 to 15% of a lipophilic poly-lower alkylene glycol ether having a molecular weight from about 400 to 4,000; and 40-98.9% of an aqueous or aqueous-alcoholic carrier medium.

2. A hairdressing according to Claim 1 wherein the higher alkyl is selected from the group consisting of about 40% C<sub>12</sub>, about 50% C<sub>14</sub>, and about 10% C<sub>16</sub> alkyls and mixtures thereof.

3. A clear hairdressing according to claim 1 comprising from 0.3 to 1% of higher alkyl ( $C_{12}$ – $C_{16}$ ) dimethyl benzyl ammonium saccharinate, 5 to 25% of hydrophilic oil of molecular weight in the range of 400 to 4,000, 1 to 8% of lipophilic oil of molecular weight in the range of 400 to 4,000 and 50.1 to 90% of aqueous-ethanolic me-

**4.** A clear hairdressing according to claim **3** wherein the hydrophilic oil is an  $C_1$  to  $C_8$  alkyl ether of molecular weight of 1,000 to 2,000 and the lipophilic oil is an alkyl ether of molecular weight of 1,500 to 3,000.

5. A clear hairdressing according to Claim 4 wherein the hydrophilic oil is a butyl ether of molecular weight of 1,400 to 1,600 and comprises approximately equal proportions of ethylene oxide and propylene oxide and the lipophilic oil is a mixture of polypropylene glycol butyl ethers of molecular weights in the ranges of 1,500 to 2,200 and 2,300 to 2,700, those butyl ethers having a molecular weight of 2,300 to 2,700 comprising 70% to 90% of the mixture.

example amounts, within the given ranges, useful microbicidal clear hairdressings are produced. Similarly, when 75 from 0.5 to 5% of an organic gelling agent, selected from

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the group consisting of natural gums, natural thickeners, synthetic gums, synthetic thickeners and mixtures thereof.  3,427,382 2/1969 Haefele  3,536,810 10/1970 Moculiski							
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