

[54] **THIOGLYCEROL-NITROGEN BASE
MOLECULAR COMPLEX**
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Related U.S. Application Data

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R, 260/583 EE, 260/584 R
[51] **Int. Cl.**.....**C07c 149/24**, C07c 149/14

[58] **Field of Search**.....260/583 EE, 309,
260/309.6, 584 R, 609

[56] **References Cited**

UNITED STATES PATENTS

3,686,296 9/1972 Yablonsky.....260/583 EE

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[57] **ABSTRACT**

A thioglycerol-nitrogen base molecular complex use-
ful as a depilatory; complexes are unimolecular or
hemimolecular.

8 Claims, No Drawings

THIOGLYCEROL-NITROGEN BASE MOLECULAR COMPLEX

This is a division of application Ser. No. 812,903, filed Apr. 2, 1969 now U.S. Pat. No. 3,686,296.

This invention relates to depilatory compositions. More particularly, it concerns depilatory compositions wherein the active depilating agent is a molecular complex of thioglycerol and a nitrogen base.

A variety of organomercurio compounds have been suggested for use in the prior art as depilatories. These, however, leave much to be desired with regard to the speed with which they remove hair at pH's which are tolerable to the skin, e.g., pH 8.5 to 10.5. Thus, for example British Pat. No. 636,181 proposes, as depilatories, mercapto carboxylic acids in conjunction with enough free organic base to make the solution alkaline. This composition lacks much with respect to the rate at which the hair may be safely removed from the skin.

British Pat. No. 693,438 concerns a depilatory composition which comprises a combination of thioglycerol with certain inorganic bases, such as the hydroxides of the alkali metal or the alkaline earth metals. Again, the inorganic base is merely added in sufficient quantity to establish a certain alkaline pH. This too leaves much to be desired regarding the rate at which the hair may be safely removed.

It has now been found that molecular complexes formed between nitrogen bases and thioglycerol in which the molar ratio of nitrogen base to thioglycerol or thioglycerol to nitrogen base is 1:1 or 1:0.5 are highly efficient depilatory agents. These are particularly effective in aqueous compositions which have a pH in the range of 8.5 to 10.5.

It is, accordingly, an object of the present invention to provide depilatory compositions which are highly efficient in rapidly removing hair from skin, said compositions being most effective in the pH range of about 8.5 to 10.5.

It is also an object of the present invention to provide depilatory compositions of the type mentioned in the above object in which the active depilatory agent is a molecular complex of a nitrogen base and thioglycerol.

Other and more detailed objects of this invention will be apparent from the following description and claims.

As noted above, the active depilatories of the present invention are nitrogen base-thioglycerol molecular complexes. These complexes may be expressed generically by the formulas selected from the group consisting of:



and



in which A is a nitrogen base and the ratio a/b , i.e., the molar of nitrogen base to thioglycerol or thioglycerol to nitrogen base is 1 or 0.5.

The stoichiometry of these complexes vary with the nitrogen base selected. It has been determined in a manner known in the prior art, through studies of the fluidities of aqueous solutions containing the materials as a function of mole fractions of the nitrogen base. See the following authorities:

Dunstan and Thole, *VISCOSITY OF LIQUIDS*, Page 44 (London, 1917).

Faust, O., *ZEIT. PHYSIK. CHEM.*, 79 (97) 1912.

Hatschek, Emil, *THE VISCOSITY OF LIQUIDS*, Page 142, G. Bell and Sons, London, 1928.

Kurnakow, N., and Shemtechushni, S., *ZEIT. PHYSIK. CHEM.*, 83, 481, 1913.

Kurnakow, N., *ZEIT. ANORG. CHEM.*, 135, 81 (1924).

The fluidities of the solutions were determined at 30°C using both the Ostwald viscosimeter and the falling sphere method, the latter being more convenient due to the high viscosity of the solutions.

The stoichiometry of the present complexes determined in this manner was shown to be either equi or hemi molar. The alkyl amine complexes are examples of the former, whereas the alkanol amine complexes are examples of the latter. This stoichiometry is also reflected in the activity of compositions containing thioglycerol and employing varying amounts of nitrogen base. It has been found that the presence of the nitrogen base generally enhances the depilatory activity of the particular thio compound. However, nitrogen base concentration in excess of that necessary for complete complex formation does not increase the depilation activity above the completely complexed thio mixture. On the other hand, when the concentration of the nitrogen base is below that necessary for complete complexing of the thio compound, the depilation activity is appreciably diminished.

A screening method has been developed for quantitatively evaluating the depilatory activity of a composition. This is based on the observation that human hair undergoes a characteristic form of swelling in many depilating solutions. This swelling may be reduced to two sequential events: pp a. cross sectional swelling and

b. longitudinal swelling.

Both of these swellings when plotted against time produce a sigmoid curve. The sigmoid character is, however, more clearly defined in the case of the longitudinal. This has, Thihas, accordingly, been adopted for measurement of the depilatory activity.

The measurement T_L , the time period at which the maximum rate of longitudinal swelling is initiated, is taken as a quantitative indication of the effectiveness of a depilating solution. A preparation possessing a T_L value of 3 minutes is capable of completely depilating a rabbit's belly in less than a minute. A number of well-known commercial depilatory preparations for human skin have T_L values in the range of about 25 minutes. It has been found that while the hair remains intact, the T_L value may for all intents and purposes be considered independent of the cuticle conditions.

The fact that the nitrogen bases of this invention do not merely serve to render the final compositions alkaline, is shown by the following observation:

Two aqueous solutions were prepared, one utilizing merely sufficient nitrogen base (i.e., methylamine to bring the hydrogen ion concentration to the desired low level (pH 10). A second aqueous solution was prepared with sufficient of said nitrogen base to completely complex the compound employed, i.e., thioglycerol in the molar ratio of 1M:1M. Hydrochloric acid was then added to the latter solution to increase its hydrogen ion concentration and bring it to the same level as the first solution. The depilating activity of each of the solutions were determined as measured by the T_L value. The first solution had a value of 6-7,

whereas the second solution had a value of 1.5–2; showing an appreciably greater depilatory activity in solution two containing a complex of the present invention.

Any of a large number of nitrogen bases and mixtures thereof may be employed in preparing the complexes of this invention. However, the ease of complex formation increases with the increase of the K_b of the nitrogen base. This is also correlated with the increase in depilatory activity of the product if the evaluation is carried out in the desired pH range, i.e., 8.5 to 10.5. Generally, it may be stated that nitrogen bases having a K_b in the range of about 10^{-10} to $10^{-1.6}$ are quite suitable for the present purposes.

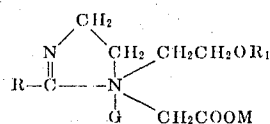
The nitrogen bases which have been found to be advantageous in this invention vary quite widely structurally and include such lower alkyl amine (one to six carbon atoms) AS methylamine, dimethylamine, ethylamine, isopropyl amine, di-isopropyl amine, di-n-propyl amine, methyl isopropyl amine, dimethyl isopropyl amine, acetamidine, cyclohexyl methyl amine, isobutyl amine, tert. butyl amino cyclohexane; and such lower alkanol amines one to six carbon atoms) as monoethanolamine, triethanolamines, 6 hydroxy-n hexylamine, 4 hydroxy-n butylamine, 5 hydroxy-1-pentylamine; urea, heterocyclic nitrogen bases such as imidazole, 1,2 dimethyl-2 pyrroline, piperidine, quinuclidine, pyrrolidine, 2 cyclohexyl pyrrolidine, pyrroline guanidine and guanidine hydrochloride, etc.

Another class of nitrogen bases that are especially useful for the present invention is sold under the trade designation DERIPHAT. These are described by the formulas:



wherein M is a salt-forming cation (e.g., Na or H) and R is the hydrocarbon moiety of the long-chain fatty acid RCOOH, e.g., (C_7 to C_{35} and preferably C_7 to C_{18}) fatty acid. These include sodium N-coco- β -aminopropionate (DERIPHAT 151); N-coco- β -amino propionic acid (DERIPHAT 151C); N-lauryl, myristyl- β -amino propionic acid (DERIPHAT 170C); disodium N-tallow- β -iminopropionate (DERIPHAT 154); disodium N-lauryl- β -iminopropionate (DERIPHAT 160) and the partial sodium salt of N-lauryl- β -iminopropionic acid. These are particularly suitable because of the extremely low order of mercaptan odor exhibited by complexes made from these bases, an odor which is a drawback in many commercial products.

Still another class of nitrogen bases that is suitable for the present purposes is sold under the trade designation MIRANOL. These are defined by the general formula:



in which:

- a. R is the hydrocarbon moiety of the long-chain fatty acid RCOOH, (e.g., C_7 to C_{35} preferably C_7 to C_{18} fatty acids);

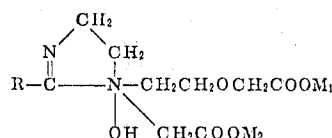
b. R_1 is H, Na or $-\text{CH}_2\text{COOM}$;

c. M is Na, H or an organic base and

d. G is OH, an acid salt or the salt of an anionic surface active sulfate or sulfonate.

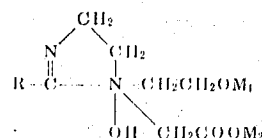
These are described in U.S. Pat. No. 2,528,378, 2,773,068 and 2,781,354. Specific compounds of this character that can be employed in this invention are set out in Tables II and III below.

TABLE II



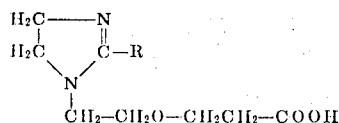
R	RCOOH which serves as source for R	M ₁	M ₂	Trade Designation
C ₁₁ H ₂₃	coconut oil acids	Na	Na	MIRANOL C2M CONC
C ₁₁ H ₂₃	coconut oil acids	H	H	MIRANOL C2M-SF CONC
-----	½ caprylic and ½ ethylhexoic caprylic	Na	Na	MIRANOL JEM CONC
C ₇ H ₁₅	linoleic	Na	Na	MIRANOL J2M CONC
C ₁₇ H ₃₁	linoleic	Na	Na	MIRANOL L2M-SF CONC

TABLE III



R	RCOOH which serves as source for R	M ₁	M ₂	Trade Designation
C ₁₁ H ₂₃	lauric	Na	Na	MIRANOL HM CONC
C ₁₇ H ₃₃	oleic	H	Na	MIRANOL OM-SF CONC
C ₉ H ₁₉	capric	H	Na	MIRANOL SM CONC
C ₁₇ H ₃₃	stearic	H	Na	MIRANOL DM

A further class of nitrogen bases that has been found to be useful in preparing the complexes of the present invention is marketed under the trade designation MONATERICS. These are substituted imidazoles of formula:



wherein R is a long-chain hydrocarbon moiety (e.g., C_7 – C_{35} and preferably C_7 – C_{18}) derived the fatty acid RCOOH. Particular compounds of this character that are employed herein are given in Table IV below.

TABLE IV

R in Formula VIII	Origin of R	Mol Weight
Monateric C-A	C_7 – C_{17} coconut fatty acids	360
Monateric L-A	C_{11} lauric acid	340
Monateric O-A	C_{17} oleic acid	417
Monateric S-A	C_{15} – C_{17} stearic acid	410

In using the molecular complexes of the present invention as depilatories it is highly desirable to incorporate them in an aqueous base. The amount of water contained in these aqueous composition can vary. In general, the water will constitute between about 20 to 80 percent by weight of the total finished product.

The natural pH of the complexes formed between the nitrogen bases and the thioglycerol will vary depending upon the nitrogen base selected or the relative amounts of the respective components of the complex. The most effective pH range for depilating with the present complexes is pH 8.5 to 10.5. Where the natural pH is too low, it may be increased by using any suitable base. Methylamine has been found to be especially suitable for this purpose although other bases, e.g., NaOH may also be employed. Similarly, where the natural pH of the complex is too high, e.g., above 10.5, it may be brought into the proper range with an acid. Hydrochloric acid has been used to advantage for this purpose.

The amount of the thioglycerol-nitrogen base complex contained in a composition relative to the total weight of the composition will vary depending on the particular nitrogen base selected and the results desired. In general, however, it will constitute between 20 to 80 percent by weight of the total composition.

The thioglycerol-nitrogen base complexes of this invention may be incorporated in a variety of carriers and may be employed for a variety of purposes. Thus, for example, they can be employed in simple aqueous solutions or be incorporated in cream base or a gel. These may be employed for a variety of purposes, some of which are mentioned below:

- fast acting depilatory (wipe on, wipe off);
- self-neutralizing permanent waving solution;
- hair straightener (anti-kinking solution);
- non-gum, non-grease men's hair groom;
- shaving cream which will appreciably condition hair and facilitate shaving;
- men's pre-shave lotion.

In using the compositions of the present invention as depilatories, procedures well known to those skilled in the art are employed. The compositions are applied to areas of skin from which the hair is to be removed. This is allowed to remain in contact with the hair for no more than about 4 minutes after which it is wiped off taking off the hair.

The following examples are further illustrative of the present invention. It is to be understood, however, that the invention is not limited thereto.

EXAMPLE 1

An aqueous solution was prepared containing 1.0 M thioglycerol and 1.0 M methylamine. The pH of this composition was adjusted to 10 with NaOH solution. This composition when applied to a hair penetrated the cuticle of the hair in one-half of a minute. It had a T_L value of 1.8 and when applied to the skin removed the hair in under 4 minutes.

The following Examples are given in tabular form. These are also aqueous solutions comparable to that prepared in Example 1. The corresponding data is given for each composition

TABLE IV

Ex. No.	Concen. of Thioglycerol	Nitrogen Base and Concentration	pH and agent used to adjust the pH	T_L
2	0.75 M	imidazole	10.0	2.0
3	1.0 M	1.5 M imidazole	(methylamine) 9.5	3.0
4	1.0 M	0.5 M imidazole	(NaOH) 10.0	4.5-
5	1.0 M	0.5 imidazole	methylamine) 9.0	5.0
6	2.0 M	2.0 M imidazole	(methylamine) 8.75	5-6
7	1.0	4.0 imidazole		6-7
8	1.0 M	methylamine	10.0	2-
9	1.0 M	2.0 M imidazole		2.5
10	1.0 M	0.5 M ethylamine	10.0	4.0
11	1.0 M	1.0 M Na-N-coco-aminopropionate (DERIPHAT 151C)	(NaOH) 9.5	3.75
12	1.0 M	1.0 M N-coco-amino-propionic acid (DERIPHAT 151C)	10.0	2.50
13	1.0 M	0.5 M DERIPHAT 151C	(methylamine) 10.0	3-4
14	1.0 M	1.0 M DERIPHAT 151C	(methylamine) 9.5	2-3
15	1.0 M	2.0 M DERIPHAT 151C	(methylamine) 10.0	4-
16	1.0 M	0.5 M MONATERIC	(methylamine) 9.5	4.5
17	1.0 M	1.0 M MONATERIC LA	9.5	3.70
18	1.0 M	2.0 M MONATERIC LA	(methylamine) 9.5	6-7
19	1.0 M	2.0 M MIRANOL C2M	(methylamine) 9.5	3-
20	1.0 M	0.5 M MIRANOL C2M	(methylamine) 9.5	3.5
21	1.0 M	0.5 M SF	(methylamine) 10.0	4-
22	1.0 M	1.0 M MIRANOL C2M	(methylamine) 10.0	4.5
23	1.0 M	0.5 M SF	(methylamine) 9.5	3.5-
24	1.0 M	1.0 M urea	(methylamine) 10.0	4.0
25	1.0 M	2.0 M urea	(methylamine) 9.5	6-7
26	1.0 M	2.0 M urea	(methylamine) 10.0	4-5
27	1.0 M	2.0 M urea	(methylamine) 9.0	12-
28	1.0 M	2.0 M urea	(NaOH) 10.0	14
29	1.0 M	2.0 M dimethylamine	(NaOH) 11.5	4-5
30	1.0 M	1.0 M dimethylamine	9.5	8-9
31	1.0 M	2.0 M dimethylamine	(HCl) 11.5	10-
32	1.0 M	4.0 M dimethylamine	11.5	12
33	1.0 M	0.5 M methylamine	11.5	5-6
34	1.0 M	1.0 M methylamine	10.0	1.5-
35	1.0 M	1.0 M methylamine	10.0	2
36	1.0 M	2.0 M methylamine	(HCl) 10.0	2.5-
37	1.0 M	2.0 M methylamine	(HCl) 9.5	3.5
38	1.0 M	2.0 M monoethanolamine	(HCl) 10.0	3.5-
39	1.0 M	1.0 M monoethanolamine	10.0	4.0
40	1.0 M	1.0 M monoethanolamine	9.75	6-7
41	1.0 M	2.0 M monoethanolamine	10.0	6-7
42	1.0 M	4.0 M monoethanolamine	9.25	4.5-
43	1.0 M	2.0 M monoethanolamine	9.25	5
44	1.0 M	4.0 M monoethanolamine	9.25	5-6

In Example 1 through 33 above, water is used as the vehicle. However, in each case aqueous alcoholic solutions may be used as the solvent for the complex. Methanol-water mixtures containing up to 50 percent by volume of methanol may be used in place of the water. When ethanol is employed it may constitute up to about 25 percent by volume of the aqueous alcoholic vehicle.

The following examples illustrate compositions of the present invention employing gels or cream bases as the vehicle for the thioglycerol-nitrogen base complex.

EXAMPLE 34

thioglycerol	1.0M
Na-N-coco-β-aminopropionate	1.0M

lauryldimethylamine oxide	10% by wt.
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This product has a natural pH of 9.5 and is in the form of a gel. It had a T_L value of from about 2.0 – 2.5.

EXAMPLE 35

A cream base was prepared containing the following ingredients in percent weight:

Cream Base	
isopropyl palmitate	4.0
hexachlorophene	0.5
hexachlorophene	3.0
merthiolate	.005
water	to 100%

Using this base as a solvent, a composition was prepared containing thioglycerol and MIRANOL C2M-SF (See Table II above) in concentrations of 1M respectively. The pH of this composition was adjusted to 9.5 with NaOH. The composition had a T_L value of 4.0 – 4.4.

EXAMPLE 36

Using the base described in EXAMPLE 35 as solvent, a composition was prepared containing thioglycerol and methyl amine in concentrations of 1M respectively. This material had a natural pH of 10 and a T_L value of about 2.0 – 2.5.

EXAMPLE 37

A slurry was prepared from hydroxypropyl methyl-cellulose (4,000 CPS) and water containing said cellulose derivative and water in the ratio of 1:4 by volume. Using this slurry as a solvent, a composition was prepared containing thioglycerol and methyl amine in concentrations of 1M respectively. This had a natural pH of about 10 and a T_L value of 2 – 2.5.

Although the invention has been described with reference to specific forms thereof, it will be understood that many changes and modifications may be

made without departing from the spirit of this invention.

What is claimed is:

1. A nitrogen base-thioglycerol molecular complex having a formula selected by the group consisting of:

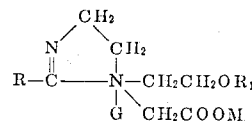


and



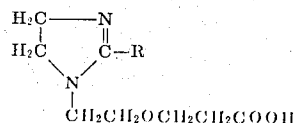
in which A is a nitrogen base and the molar ratio a/b is 1 or 0.5.

2. A complex according to claim 1 wherein the nitrogen base has a K_b value in the range of from 10^{-10} to $10^{-1.6}$.
3. A complex according to claim 1 wherein the nitrogen base is a lower alkyl amine.
4. A complex according to claim 1 wherein the nitrogen base is a lower alkanolamine.
5. A complex according to claim 1 wherein the nitrogen base is imidazole.
6. A complex according to claim 1 wherein the nitrogen base is of the formula:



in which:

- a. R is a hydrocarbon moiety of the long-chain fatty acid RCOOH;
- b. R_1 is H, Na or $-CH_2COOM$;
- c. M is Na, H OR A salt-forming organic base;
- d. G is OH, an acid salt or the salt of an anionic surface active sulfate or sulfonate.
- 7 A complex according to claim 1 wherein the nitrogen base is of the formula:



in which R is the long-chain hydrocarbon moiety derived from the fatty acid RCOOH.

8. A complex according to claim 3 in which the lower alkyl amine is methylamine.

* * * * *