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New Lanolin Acid Quaternary Salts for use in Hair Treatment Preparations

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Synopsis: The action of QUATERNARY AMMONIUM SURFACTANTS on HAIR has been studied for many years. Several of the characteristics, which are important in formulating with these SALTS, are dependent upon their molecular configuration. In this paper, lanolin compounds which essentially comprise QUATERNARY DERIVATIVES (QUATS) of LANOLIN ACIDS are described. The preparation of a derivative of lanolin consisting essentially of the reaction product of a lanolin acid and a specific diamine followed by quaternization is outlined. The chemical and physical properties of quats are briefly reviewed and compared with emphasis on these new lanolin acid derivatives, and their chemistry and processing is highlighted. Each of these quaternary salts was incorporated into hair conditioning preparations and evaluated on human hair.

Introduction

It has been known for a long time that quaternary ammonium surfactants display many unusual and desirous properties and functions (1). Much work has been done demonstrating germicidal activity (5), softening effects (2, 3), antistatic properties (4), substantive qualities, and other uses of these materials. Many of these properties find applications in cosmetics, where quaternary ammonium compounds are useful as preservatives (5), hair conditioning agents (6), emulsifiers (7), etc. However, it has long been known that these materials possess a relatively high level of toxicity both to the skin and eyes (8). Also, they have a low compatability level with other commonly used cosmetic materials—specifically anionic emulsifiers and surfactants (9).

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It was our goal in this study to develop a quaternary ammonium derivative, which would be less irritating, and yet, as chemically active as other common quaternaries presently used for hair treatment in the cosmetic industry.

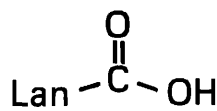
In this paper, we will chemically describe some new quaternary ammonium compounds, which are derived from a well established nonirritating (10) highly emollient material—lanolin acids. We will discuss some of their properties, specifically eye irritation, germicidal activity, and solubilities. Also, studies comparing two lanolin acid quaternaries with some other commercially used quaternary ammonium compounds in a shampoo and a cream rinse formulation involving salon testing of human hair will be presented.

Chemical Description

Lanolin, which is extensively used in cosmetic compositions, is generally considered to consist of a mixture of naturally formed esters derived from higher alcohols and higher fatty acids. By saponifying the lanolin esters with alcoholic alkali, one can separate the alkaline soaps of lanolin acids from the unsaponifiable portion containing lanolin alcohols. By acidification of the alkaline soaps, crude lanolin acids of the composition shown in Table I are obtained. These acids are refined through a distillation and deodorization process described in a U.S. patent.* The acids are then bleached or decolorized.

Table I

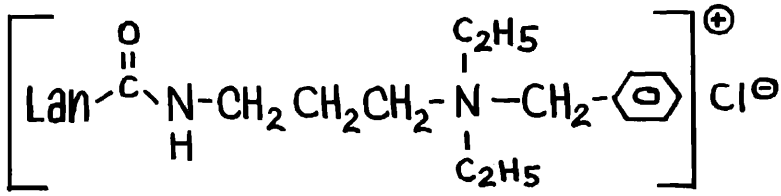
LANOLIN ACIDS:



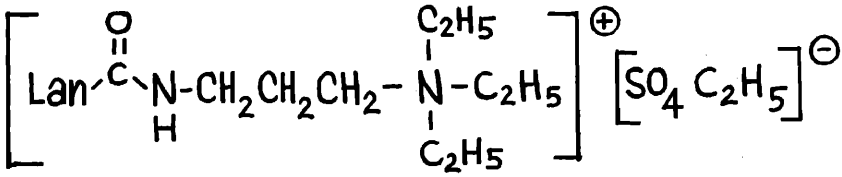
where 'Lan' represents:

	%
n-alkanoic acids	7
iso-alkanoic acids	23
anti-iso-alkanoic acids	30
hydroxy-alkanoic acids	28
unidentified	12
	100%

*Richey, *et al.*, Pat. #3, 272, 850.

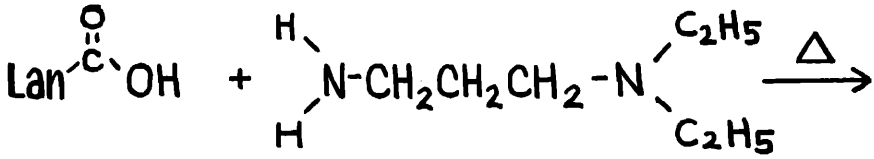


DIETHYL-AMINOPROPYL LANOLIC ACID-BENZYL-AMMONIUM CHLORIDE

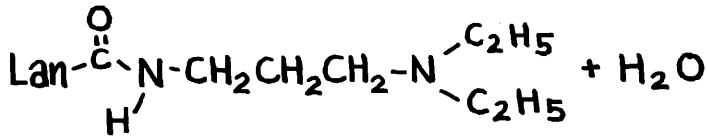


TRIETHYL-AMINOPROPYL LANOLIC ACID-ETHOSULFATE

Figure 1. Structures of lanolin quaterniums



LANOLIN ACIDS DIETHYL-AMINO-PROPYL-AMINE



AMIDOAMINE INTERMEDIATE

Figure 2. Preparation of intermediate

Apparently, the refining procedure eliminates a number of the more than 40 acids, which compose the crude lanolin acids. At any rate, the thus refined lanolin acids react with the amines described below and are then converted to the quaternary ammonium derivatives, which are also discussed below.

The general structural formulas of the lanolic acid quaternary ammonium derivatives are shown in Fig. 1. The quaternary compounds were prepared from a common amido amine intermediate. This intermediate was prepared by combining equimolar quantities of lanolin fatty acid and diethylaminopropylamine (as shown in Fig. 2.) Conditions for the reaction simply required heating to 150-160°C at first at atmospheric pressure for 2h, and finally under reduced pressure (0.1 mm Hg) for a period of about 3-4 h. The extent of reaction was followed by measuring evolved water and by a combination of acid and amine values.

The diamine required for reaction with the lanolin acid to form the intermediate must be a diamine having one of its nitrogen atoms bearing two substitutes (as shown in Fig. 3). In other words, one of the nitrogens of the diamine is a tertiary amine with no site available for reaction. The other nitrogen of the diamine is either a primary or a secondary amine and thus it becomes available, via one of its hydrogens, for reactions with a lanolin acid (11).

The quaternization of the amidoamine was carried out by combining equimolar quantities of the intermediate with a suitable quaternizing agent and heating to 110-120°C at atmospheric pressure for a period of about 4 h. The extent of reaction was measured by the decrease in amine value (reactions are shown in Fig. 4).

The choice of benzyl chloride as a quaternizing agent was based on the fact that analogous types of quaternaries are among the most common and comparisons to existing products could be made easily, without the fear of another variable. The choice of diethyl sulfate as the other quaternizing agent was more or less arbitrary, and any other suitable materials such as aliphatic hal-

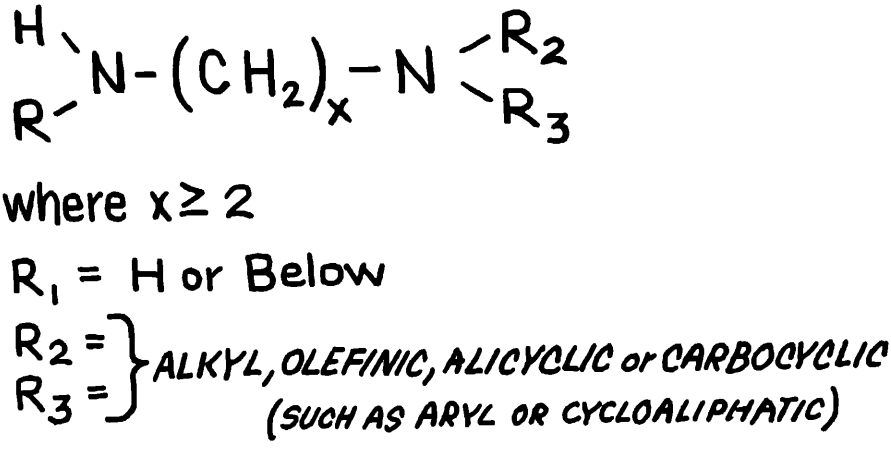


Figure 3. Required diamine

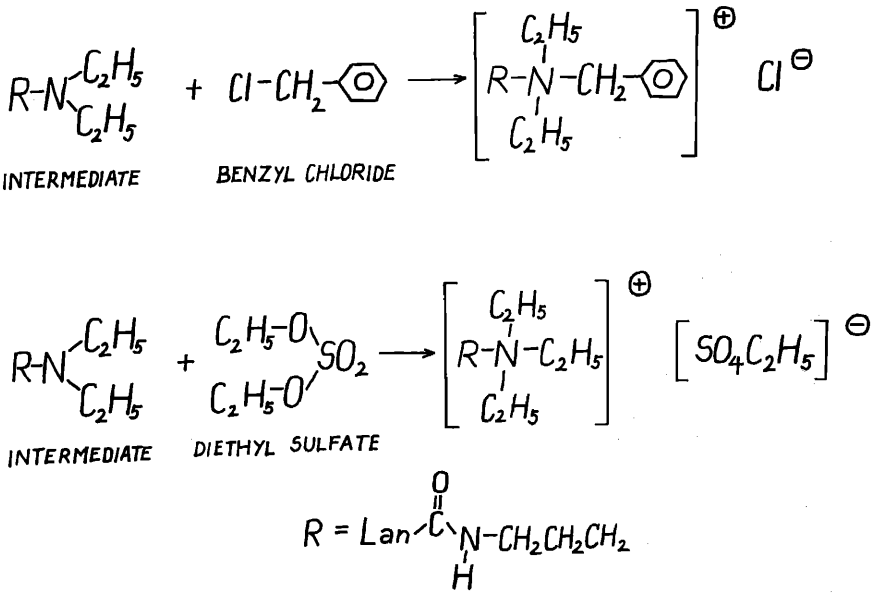


Figure 4. Quaternization

TABLE II
Typical Properties of Quats

	LanBAC	Stearalkonium Chloride	LanES	Quarternium 7
Form	Amber Semisolid	Creamy White Dispersion	Amber Very Viscous Liquid	Cream Colored Dispersion
Active content	81.9%	16.0%	76.3%	79.7%
Total chloride content	5.8%	—	N/A	7.8%
pH (1% aqueous sol'n)	6.2	3.0-4.0	5.0	3.4
Surface tension (1% aqueous sol'n (@ 25°C)	41.4 dynes/cm	34 dynes/cm	40.3 dynes/cm	—
Ross Miles Foam Data–				
Initial:	100 mm	50 mm	150 mm	150 mm
After 5 min:	80 mm	40 mm	110 mm	130 mm

ides, aromatic halides, or other aliphatic alkylating agents, such as ethylene chlorohydrin, could have been used. Among such halides and esters which may be used are methyl chloride, methyl bromide, butyl bromide, di-methyl sulfate, and the like (11).

The resulting experimental lanolin quaternaries are dark amber materials ranging in viscosity from a thick liquid for the ethosulfate derivatives, to a hard brittle solid for the benzyl chloride derivative. Since these quaternium

salts are soluble in water, aqueous solutions ranging in activity of 10 to 25 per cent offer an easier means of handling these materials.

Typical specifications of these lanolin quaternaries are compared to two other commercial quaternary ammonium compounds (Quaternium 7 and Stearalkonium Chloride) in Table II.

Analytical Procedures

Various procedures were used to support evidence of our reactions. The structure of the lanolin acid amidoamine intermediate was confirmed by infrared analysis. The acid carboxyl absorbance was absent and was replaced by absorbition in the region 1640 cm^{-1}, which is indicative of amides. Also, the so-called Amide II band appearing near 1550 cm^{-1} was observed. The absence of unreacted primary amine was determined titrametrically (12). Quaternary activity was determined via a titration with tetraphenyl boron (13).

Physical Properties

I. Compatability with Anionic Surfactants

Experimental—10 per cent active solutions of Triethanolamine (TEA) Lauryl Sulfate. Sodium Laureth Sulfate (3 moles of ethylene oxide (ETO)), Quaternium 7, Stearalkonium Chloride, the experimental lanolin benzyl chloride quat (LanBAC) and the experimental lanolin ethosulfate quat (LanES) were prepared. The pH of these solutions were adjusted to 4 with citric acid. (The pH of the Quaternium 7 and the Stearalkonium Chloride solutions were under 4, so that these were not adjusted.) Blends were then prepared by adding 1, 5, 10, 15, and 20 g of cationic solution to 99, 95, 90, 85, and 80 g of an anionic solution. The solutions were warmed on a steam bath when necessary to obtain clarity. The resulting 40 solutions were then set aside for 2 weeks.

Results—Formation of either a cloud, haziness, or a precipitate in the solutions was taken as an indication of incompatability (14). Those solutions, which remained clear were taken to be compatible. The results are summarized in Fig. 5.

It was found that upon mixing, both lanolin acid quaternary ammonium derivatives formed clear solutions without warming. Also, the lanolin quaternary salt solutions showed superior compatability in an anionic medium to the other two cationic ammonium compounds tested.

Blends of the 10 per cent active cationic solutions and 10 per cent active anionic solutions were prepared by adding 5 parts of the cationic solution to 95 parts of the anionic solutions. These blends were further diluted to yield a total 1 per cent active solution of surfactant. Ross-Miles foam tests were run on the anionic solutions alone and the various blends of the cationic-anionic blends. Foam height measurements were taken initially and after 5 min. The resulting data demonstrated tht the lanolin derived quaterniums interfered

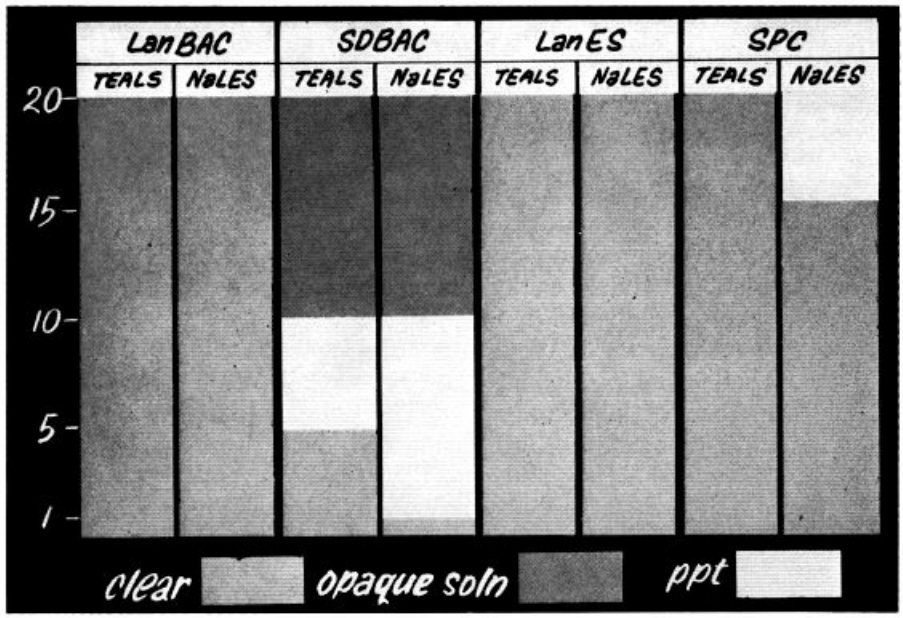


Figure 5. Compatability with anionics

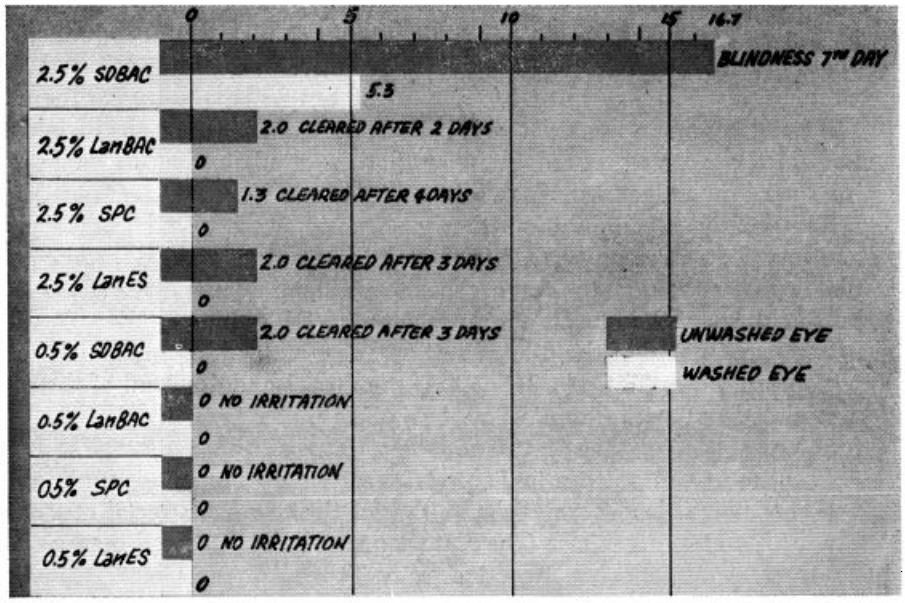


Figure 6. Draize eye irritation scores

with the foaming power of the anionics less than the Quaternium 7 and the Stearalkonium Chloride. This again demonstrated higher compatability between the cations of the lanolin quaterniums in solution with the anions of the detergent salts.

II. Eye Irritation

Experimental—0.5 and 2.5 per cent active solutions were prepared for the Quaternium 7, Stearalkonium Chloride, LanBAC, and LanES. The resulting 8 solutions were submitted to an outside laboratory for Draize Rabbit Eye Irritation tests. Six normal healthy albino rabbits were used in this experiment. The animals were divided into 2 groups of 3 animals each. Group 1 had 0.1 ml of the test solution instilled into the right eye with no further treatment. Group 2 had 0.1 ml instilled into the right eye followed 4 sec later by washing out with 20 ml of lukewarm water. The untreated left eye of each animal served as its own control. Both the treated and control eyes were examined every 24 hours for 4 days and then again on the seventh day. The scores recorded were made according to the Draize scale for scoring occular lesions (15).

Results—As can be seen in Fig. 6, the lanolin quaternaries proved to be less irritating than the other two cationic salts used in the test. The LanBAC was shown to be less irritating than Stearalkonium Chloride at 5 times the concentration of Stearalkonium Chloride.

III. Germicidal Activity

Experimental—In this experiment, 2 aspects of a germicidal activity were studied—namely, the zones of inhibition and the plate count reduction. Five per cent active Quaternium 7, Stearalkonium Chloride, LanBAC, and LanES were prepared and submitted to an outside testing laboratory for these tests. The solutions were diluted 1:5 for both determining the zones of inhibition and for the plate count reduction, so that the results shown in Table III are for 1 per cent active quaternary solutions.

For the zones of inhibition, the quaternaries were tested against two organisms: Staph aureus ATCC* 6538 and Strep pyogenes ATCC* 8668. In the plate count reduction, the test organism was Staph aureus ATCC 6538. A 24-h broth culture of the test organism was diluted 1-10 with sterile distilled water before use. One ml of the diluted test organism was added to 9ml of the sample and stored at 37°C. At 2, 5, 10, 15 minutes, 1 and 4 h 1 ml of the sample was plated out with Tryptic Soy Agar. The plates were incubated at 35°C for 48 h.

Results—As can be seen in Table III, the two experimental lanolin quaternaries exhibited larger zones than either of the two commercial quaternaries against both test organisms. The plate count reduction showed the two lanolin quaternium salts to be as effective as the Stearalkonium Chloride, and more

*American Type Culture Collection, Washington, D.C.

Table III

GERMICIDAL ACTIVITY

ZONES OF INHIBITION:

QUAT (1% ACTIVITY)	ORGANISM	
	S. Aureus	S. Pyogenes
STEARALKONIUM CHLORIDE	3.4 mm	3.9 mm
Lan BAC	4.8 mm	5.5 mm
QUATERNIUM 7	2.7 mm	4.4 mm
Lan ES	6.4 mm	5.2 mm

PLATE COUNT REDUCTION: (% Reduction)

	TIME (MIN)					
QUAT (1% activity)	2	5	10	15	1hr.	4hrs.
STEARALKONIUM CHLORIDE	99.99+	99.99+	99.99+	99.99+	99.99+	99.99+
Lan BAC	99.99+	99.99+	99.99+	99.99+	99.99+	99.99+
QUATERNIUM 7	80.00	95.67	99.98	99.99+	99.99+	99.99+
Lan ES	99.99+	99.99+	99.99+	99.99+	99.99+	99.99+

effective than Quaternium 7. Stearalkonium Chloride, along with the 2 lanolin quats, achieved a 99.99+ per cent reduction in plate count in under 2 min, while Quaternium 7 required 15 min to achieve this plate count reduction.

IV. Applications

Shampoo Study—In developing a shampoo for a study of this type, we wanted a low pH clear simple formula with as few ingredients as possible so as not to interfere with the conditioning properties of the quaternaries during their evaluation. We desired though, a formula which would foam well, clean well, and be acceptable to the consumer (panelist) An amphoteric was used for the bulk of the detergent action. A small amount of TEA lauryl sulfate was added to boost the foaming. An amide level of 5 per cent was used to provide a suitable viscosity and add to foam stability. A total 3–per cent active quaternary was used (see Table IV). This formula provided a clear liquid shampoo of moderate viscosity.

Table IV

Low pH Quaternary Shampoo

	WT. %
Amphoteric-10	30.00
TEA — Lauryl Sulfate (40%)	8.00
Quaternary (10% active Solution)	30.00
Lauramide DEA	5.00
Propylene Glycol	6.50
Deionized Water	20.20
Perfume	0.30
	100.00

PROCEDURE:
Heat and mix the first four ingredients to 70°C until clear and homogeneous. Let cool and adjust the pH to 5.0 with lactic acid. Add perfume — the mass is now cloudy. Add the propylene glycol and mix until clear. Add the rest of the water.

Two shampoos were prepared. The first contained the LanES quaternium and the other contained Quaternium 7. Half-head studies involving 6 subjects were employed to evaluate the shampoos. The right side was reserved for the LanES shampoo and the left side for the Quaternium 7 shampoo. The subjects were all females in their mid-teens with shoulder length or longer virgin hair. Experiments were performed in the beauty salon of a well known testing agency.

In the procedure used, the hair of the subject was first examined for color, texture, condition, and length. The hair was parted in the middle and combed out. One side was wetted, then washed with a measured amount of one of the shampoos. The other side was also wetted and washed with a measured amount of the other shampoo. At this point, foam quality and quantity were observed. Then the head was rinsed and washed again in the same manner. After the final rinse, the hair was evaluated with a wet comb. The tangles were combed out with the large teeth of a comb and then with the small teeth. Ease of combing, hair conditioning effects, and slip were then evaluated by the subject, operator, and observer. The hair was set with rollers and the subject was placed under the dryer until the hair was thoroughly dry. After completion of the drying, the rollers were removed and the hair was combed out. The hair was again evaluated by the subject, operator, and observer for conditioning, sheen, manageability, softness, degree of static charge, curl retention, and any other properties which appeared to be either exceptional or poor.

Table V

Quaternary Creme Rinse

	WT. %
Quaternary (10% active solution)	30.00
Glycerol Stearate, SE, acid stable	1.50
Hydroxypropyl Methylcellulose (1% solution)	40.00
Deionized Water	28.00
Perfume	0.50
	100.00

PROCEDURE:
Heat the GMS and water together to 75°C and let cool to 30°C with slow continual stirring. Add the other ingredients and package.

pH was adjusted to 5.5 with Lactic Acid.

Results—In all 6 cases, the 2 shampoos used were very similar as far as foam quality and quantity are concerned. If anything, the right (LanES) side produced a tighter bubble, which gave the appearance and feel of a thicker creamier lather. Both shampoos rinsed equally well. During the wet comb evaluation, the left side (Quaternium 7) excelled. In 4 cases out of 6, the left side combed out easier with less tangles and had more slip, which allowed the comb to glide through the hair easier. After comb out, the right (LanES) side generally felt as if it had a slightly greasy film remaining.

After setting and drying, the right (LanES) side was preferred for sheen, manageability, and body. Both shampoos controlled fly away well; in only one case, the subject preferred her right over her left side in the fly away evaluation.

In general, marked distinctions between the two shampoos did not exist. Differences were very small in most cases, thus showing the LanES to be as effective as the Quaternium 7.

Creme Rinse—The formula employed for this study was simple but effective in pointing out the differences between the LanBAC and the Stearalkonium Chloride. The formula is shown in Table V. The small percentage of gum was added to provide a viscosity sufficient to improve the formula's stability.

Experimental—Half-head tests were employed to evaluate the two products. Six females in their mid-teens, with long virgin hair were used. The hair was washed twice with a commercial bland shampoo, then parted in the middle of the head. The Stearalkonium Chloride creme rinse was used on the left side and the LanBAC creme rinse was used on the right side. The rinses were diluted 10 to 100 ml at the salon and applied to the hair. The full 100 ml was

used on each side. This was followed by a thorough rub in for approximately 3 min and then a thorough rinse. A wet comb evaluation was followed by a set and drying. The curlers were removed and a final evaluation of the hair was carried out.

Results—Both rinses applied equally well and rinsed out well. The left (Stearalkonium Chloride) side was preferred by all in the wet evaluation for ease of combing and amount of slip on the hair. In some cases, the right (LanBAC) side yielded a lesser amount of tangles.

After setting and drying, the right (LanBAC) side was preferred by 5 out of the 6 females for sheen, fluffiness of the hair, manageability, feel, and body. As in the shampoo study, the lanolin quaternary was preferred in the final evaluation, although it suffered somewhat in the wet comb evaluation.

Summary

In this paper, we presented two new quaternary compounds derived from lanolin acids. We discussed their method of preparation and described other derivatives that could be prepared. It was demonstrated that their use in shampoo and creme rinse formulas compared with commercially available compounds of this type. Lower eye irritation scores and higher germicidal activity were presented along with an experiment demonstrating greater compatibility with anionic surfactants. (Received July 15, 1975)

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