

Journal of the Society of Cosmetic Chemists

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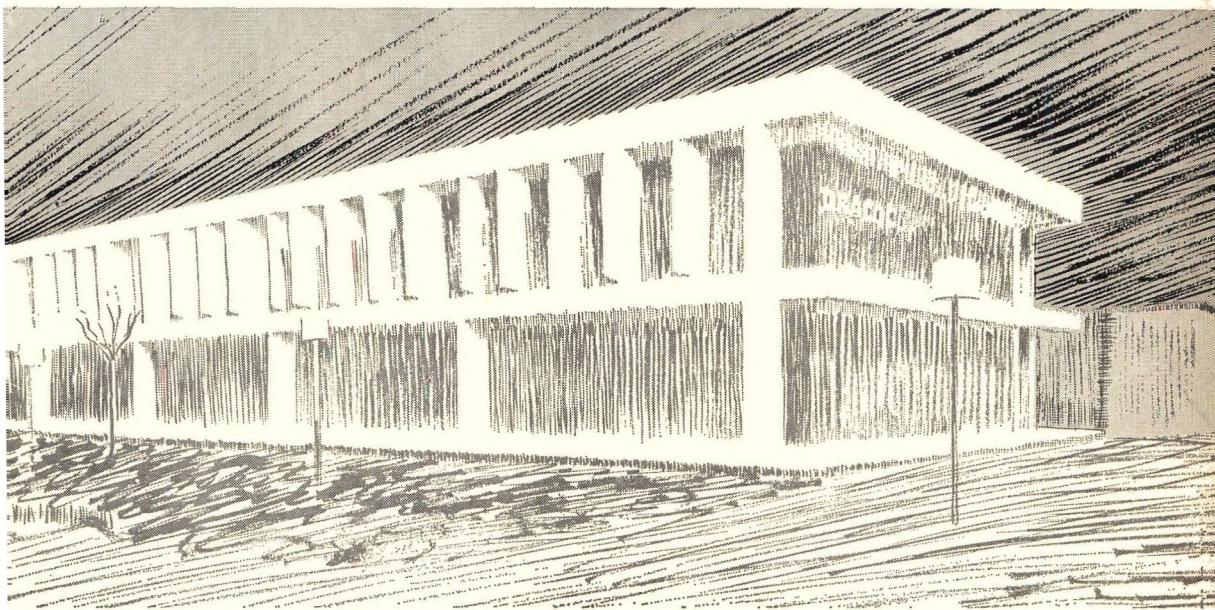
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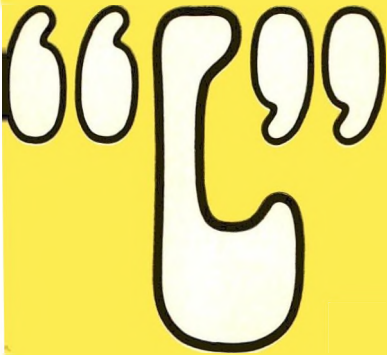
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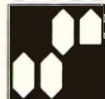
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| Carsamide SAL* (lauric myristic diethanolamide) | 4 | 3 |
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| Crotein BTA** (benzyl trimethyl ammonium hydrolyzed protein) | 1.5 | 1 |
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SYNOPSIS FOR CARD INDEXES

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The stabilization of nonionic aerosol emulsions. Propellant additives: Paul A. Sanders. *Journal of the Society of Cosmetic Chemists* 25, 581 (November 1974)

Synopsis—Previous work had shown that certain nonionic polyoxyethylene (POE) fatty ether–fatty alcohol complexes stabilized aerosol foams, but not the emulsions from which the foams were obtained. These complexes were prepared in the aqueous phase prior to addition of the propellant. In this study, aerosol emulsions containing the complexes were prepared differently. Fatty alcohols were dissolved in the propellant, and the resulting solution was added to the aqueous surfactant phase. This method formed the nonionic surfactant–fatty alcohol complex directly at the propellant–water interface during addition of the propellant.

Adding fatty alcohols with the propellant increased emulsion stability with three POE fatty ethers. Three other POE fatty ether–fatty alcohol complexes failed to stabilize emulsions regardless of how the alcohols were added. The failure of these complexes was attributed to their high water solubility.

There was no apparent relationship between the properties of the nonionic aerosol emulsions and those of the foams. Whether or not the surfactant–alcohol complex stabilized the aerosol emulsion had little effect upon foam stability.

Formulating high-foaming cosmetic products: Irving R. Schmolka. *Journal of the Society of Cosmetic Chemists* 25, 593 (November 1974)

Synopsis—Obtaining valid comparative data on the foaming properties of a multitude of surface-active agents and then using these data to prepare acceptable finished cosmetic formulations is a problem frequently encountered by the cosmetic chemist.

An apparatus designed for measuring foam in the laboratory is described. The inexpensive equipment allows flexibility of operation, is simple to clean, and offers several other important advantages for objectively developing and evaluating high-foaming cosmetic products. Foam volumes are readily determined. Comparative foam data, at 38°C, presented for dilute aqueous solutions of some leading commercially available nonionic and anionic foaming surfactants, show the latter group to be superior to the former class of compounds. The effects of varying the surfactant concentration are pointed out. Data are presented showing the influence of mixing time and mixing speed. Additional variables which alter foam heights are shown to include the presence of soil, thickeners, and other additives. Increasing the viscosity of aqueous surfactant solutions is shown to have an effect on foam. Finally, comparative foam data are given for commercial high-foaming cosmetic products, including a bubble bath preparation, dentifrices, and shampoos.

Microemulsions: Henri L. Rosano. *Journal of the Society of Cosmetic Chemists* 25, 609 (November 1974)

Synopsis—Transparent emulsions are by definition called water-in-oil or oil-in-water microemulsions. Where the average diameter of the dispersed droplets is less than one quarter of the wavelength of the incident light, no light scattering will occur and the system will be transparent. The preparation of microemulsions and the formation and stabilization of such by phase diagram, NMR, and interfacial tension measurements are reviewed. A new theory of the formation of these microemulsions based on interfacial diffusion of the surfactant or cosurfactant producing a temporary zero interfacial tension is presented.

Antiperspirants: New trends in formulation and testing technology: Eric Jungermann. *Journal of the Society of Cosmetic Chemists* 25, 621 (November 1974)

Synopsis—Aluminum chlorhydroxide has been the most widely used active ingredient in antiperspirant formulations. Recently, new chemicals, such as basic aluminum bromide, and combinations of aluminum, zirconium, and other metal salts have been introduced. In addition, new product forms are constantly being developed with different performance and cosmetic characteristics. The properties of the new active ingredients and the new formulations are discussed with respect to formulation versatility, cosmetic elegance, and efficacy. General methods used to evaluate staining potential, and deodorant and antiperspirant efficacy of these products are reviewed. A normal activity method for determining antiperspirant efficacy is compared with a method based on a thermally controlled environment, and the results obtained with these two techniques are discussed.

The Stabilization of Nonionic Aerosol Emulsions. Propellant Additives

PAUL A. SANDERS, Ph.D.*

Synopsis—Previous work had shown that certain nonionic POLYOXYETHYLENE (POE) FATTY ETHER-FATTY ALCOHOL COMPLEXES stabilized AEROSOL FOAMS, but not the EMULSIONS from which the foams were obtained. These complexes were prepared in the aqueous phase prior to addition of the PROPELLANT. In this study, aerosol emulsions containing the complexes were prepared differently. Fatty alcohols were dissolved in the propellant, and the resulting solution was added to the aqueous surfactant phase. This method formed the nonionic surfactant-fatty alcohol complex directly at the propellant-water interface during addition of the propellant.

Adding fatty alcohols with the propellant increased emulsion STABILITY with three POE fatty ethers. Three other POE fatty ether-fatty alcohol complexes failed to stabilize emulsions regardless of how the alcohols were added. The failure of these complexes was attributed to their high water solubility.

There was no apparent relationship between the properties of the nonionic aerosol emulsions and those of the foams. Whether or not the surfactant-alcohol complex stabilized the aerosol emulsion had little effect upon foam stability.

INTRODUCTION

Aerosol cosmetic and pharmaceutical foams have become increasingly popular over the past decade. Commercial foam products include shaving lathers, skin moisturizers, colognes and perfumes, hair dressings, hair setting foams, body lotions, insect repellents, sunscreens, cleansing creams, depilatories, and medicated foams containing analgesics and antiseptics.

Most aerosol foams are formulated as oil-in-water emulsions. The liquefied propellant usually constitutes the major portion of the dispersed phase. Most aerosol oil-in-water emulsions are formulated with anionic surfactants, such as the salts of the fatty acids. Adequate emulsion and foam stability can be achieved by designing the formulations so that molecular complexes are present. Molecular complexes are association compounds formed by the interaction between surfactants and long chain polar compounds (1-5). The fact that these complexes increased both emulsion and foam stability (6) suggested a relationship between the properties of the anionic aerosol emulsions and their corresponding foams.

* Freon Products Laboratory, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. 19898.

A study of anionic aerosol emulsions using photomicrographic techniques, coupled with a comparison of the physical properties of the emulsions and foams, showed that the most stable emulsions with the smallest droplet size produced the most stable foams (7, 8). From a practical standpoint, this emphasized the importance of concentrating on the properties of the emulsions as well as the foams when formulating aerosol foam products.

Nonionic surfactants, such as the polyoxyethylene ethers, are not satisfactory as a class as emulsifying agents for aerosol emulsions. Out of eight evaluated, only two were found to provide adequate aerosol emulsion and foam stability. Addition of fatty alcohols to aerosols formulated with the other six surfactants caused a marked increase in foam stability, but in many instances emulsion stability was not improved (9). The poor emulsion stability of these systems limited the use of the polyoxyethylene fatty ether surfactants in aerosols.

The fact that the POE fatty ether–fatty alcohol combinations increased foam stability but not emulsion stability indicated a lack of relationship between emulsion and foam properties. This raised the question as to whether POE fatty ether–fatty alcohol combinations formed molecular complexes similar to the anionic surfactant–long-chain polar compound complexes studied by Epstein *et al.* (2) and Goddard and Kung (3–5). Although there are no published analytical data to prove the existence of POE fatty ether–fatty alcohol complexes, there is indirect evidence. Thus, Becher and Del Vecchio (10) determined film drainage transition temperatures for several polyoxyethylene lauryl ethers in the presence of lauryl and cetyl alcohols. They regarded their curves illustrating the change in surface viscosity with temperature as being in the nature of melting point depression curves, possibly due to complex formation. Also, the stabilization of aerosol foams indicated that some type of interaction between the POE fatty ethers and fatty alcohols occurred (9). In addition, many POE fatty ether–fatty alcohol combinations were highly pearlescent in the aqueous concentrate. The pearlescence was attributed to liquid crystal formation (11). This indicated an association between the nonionic surfactants and fatty alcohols, *i.e.*, complex formation.

The failure of the nonionic pearlescent complexes to stabilize aerosol emulsions could be due both to the stability of the complexes and the method used for their preparation (11). In previous work, the complexes were formed in the aqueous phase before the addition of propellant by melting the mixture of surfactant and fatty alcohol and adding hot water. The aerosol propellant was pressure-loaded after the aqueous concentrate containing the pearlescent complex had cooled to room temperature.

If the complexes had a high molecular weight, as suggested by their pearlescence, and were highly stable, they might not break up and collect at the propellant-water interface after the propellant was added. The aerosol emulsion would then consist of a mixture of essentially unstabilized propellant drop-

lets and liquid crystalline surfactant–fatty alcohol complexes. Each would maintain its own individuality. A portion of the propellant probably would be solubilized in the interior of the complex. When the emulsion was discharged, disruption of the liquid crystal pearlescent structures could result from the turbulence created by vaporization of the propellant. This would be particularly true with solubilized propellant. The lower molecular weight fragments of the liquid crystal structure could then stabilize the foam. The fact that the foams were never pearlescent supports this explanation.

If the formation of the POE fatty ether–fatty alcohol complexes were delayed until the propellant was added, emulsion stability might be increased. This could be achieved if the fatty alcohols were dissolved in the propellant before it was loaded instead of adding the alcohols to the aqueous phase initially. Thus, when the propellant–fatty alcohol solution was added to the aqueous surfactant phase, the complex would be formed at the propellant–water interface during the addition of the propellant. If the complex were formed directly at the interface, an increase in emulsion stability might result. This approach for increasing the emulsion stability of nonionic aerosol emulsions is the subject of the present paper.

EXPERIMENTAL

Composition of the Aerosols

The aerosols had a composition of 90% aqueous phase containing a polyoxyethylene fatty ether surfactant, a fatty alcohol or alcohol blend, and 10% Propellant 12/114^o (40/60). The concentration of both the surfactant and the fatty alcohol or alcohol blend in the aerosol was 0.05 molar. This assumes that the surfactants and fatty alcohols had molecular weights corresponding to their empirical formulas. The molar ratio of surfactant to alcohol was 1:1.

Preparation of the Aerosols

The aerosols were prepared by two procedures. In the first, or standard method, the fatty alcohols and surfactant were heated to about 55°C. Water at the same temperature was added to the melted mixture with agitation. The aqueous mixture was cooled to room temperature with stirring and the propellant was pressure loaded.

In the second procedure, the fatty alcohols were dissolved in the propellant initially. The solution of fatty alcohols and propellant was then added by pressure-loading to the aqueous phase containing the nonionic surfactant. The aqueous phase was prepared by heating the mixture of surfactant and water until the surfactant melted or dissolved. The aqueous phase was then allowed to cool to room temperature with stirring.

^o Freon, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., was used as the propellant in this study.

*Active Ingredients**Nonionic Surfactants*

Seven polyoxyethylene fatty ether nonionic surfactants were used. They are listed below in Table I along with their HLB values (12) and water solubilities.

Table I
Nonionic Polyoxyethylene Fatty Ethers

| Polyoxyethylene Fatty Ether ^a | HLB Value | Solubility in Water |
|--|-----------|---------------------|
| POE (4) lauryl ether | 9.7 | Dispersible |
| POE (23) lauryl ether | 16.9 | Soluble |
| POE (2) cetyl ether | 5.3 | Insoluble |
| POE (10) cetyl ether | 12.9 | Dispersible |
| POE (20) cetyl ether | 15.7 | Soluble |
| POE (10) stearyl ether | 12.3 | Dispersible |
| POE (20) stearyl ether | 15.3 | Dispersible |

^a"Brij" surfactants, ICI America, Wilmington, Del.

Fatty Alcohols and Alcohol Blends

Lauryl alcohol alone and blends of lauryl alcohol with myristyl, cetyl, and stearyl alcohol^o were used in combination with the surfactants. A concentration of fatty alcohols in the aerosols of 0.05 molar was desired to equal that of the surfactants. This could be achieved with individual alcohols if they were placed initially in the aqueous phase. However, when the alcohols were added with the propellant, an alcohol solubility of at least 10 g alcohol/100 g propellant was needed. Only lauryl alcohol had this high a solubility, as shown by the data in Table II. Therefore, in order to include myristyl, cetyl, and stearyl alcohols in the test, it was necessary to use them in combination with lauryl alcohol. The lauryl alcohol functioned as a solubilizing agent for the other alcohols in the propellant.

Table II
Solubilities of Fatty Alcohols in Propellant 12/114 (40/60)

| Fatty Alcohol | Solubility at 21° C (g/100 g Propellant) | |
|------------------|--|-----------|
| | Soluble | Insoluble |
| Lauryl alcohol | >15 | ... |
| Myristyl alcohol | 4 | 5 |
| Cetyl alcohol | 0.1 | 0.3 |
| Stearyl alcohol | 0.1 | 0.3 |

The solubility of mixtures of lauryl alcohol with myristyl, cetyl, and stearyl alcohols in Propellant 12/114 (40/60) is shown in Table III.

^oLauryl, cetyl and stearyl alcohols were obtained from the Procter & Gamble Co., Cincinnati, Ohio. They were coded CO-12/98S, CO-16/95, and CO-18/95, respectively. The myristyl alcohol was obtained from Eastman Chemical Products, Inc., Kingsport, Tenn.

Table III
Solubility of Fatty Alcohol Blends in Propellant 12/114 (40/60)^a

| Fatty Alcohol Blend | Solubility at 21°C | |
|--------------------------|-------------------------|---------------------------|
| | Soluble Ratio (wt %) | Insoluble Ratio (wt %) |
| Lauryl/myristyl alcohols | 1/9 | 0.1/9.9 |
| Lauryl/cetyl alcohols | 6/4 | 5/5 |
| Lauryl/stearyl alcohols | 8/2 | 7.5/2.5 |

^aTested at a concentration of 10 g of blend per 100 g of propellant.

On the basis of these results, the fatty alcohol blends selected for the experimental work were lauryl/myristyl (1/9), lauryl/cetyl (6/4), and lauryl stearyl (8/2). The numbers in parentheses indicate weight per cent ratios.

Evaluation of Aerosol Emulsions and Foams

Emulsion and foam stability, foam stiffness, foam drainage, and density were measured using equipment and procedures reported previously (7, 8). Emulsion stability was determined visually by noting the time after shaking until phase separation became noticeable. The samples were shaken 20 times after preparation, allowed to stand overnight, and reshaken 20 times immediately before the measurement.

Foam stability is indicated in the tables in two ways. One is by the decrease in foam height that occurred 60 min after product discharge and the other is by the time required before first observable collapse of the foam was noted. The data were obtained by discharging the foams in front of a panel containing horizontal lines spaced at ¼-in. intervals. By noting the initial height of the foam, any change in height with time could be determined.

Foam stiffness was measured with a Cherry-Burrell curd tension meter^o (7). Foam stiffness indicates the resistance of the foam to penetration by a curd knife. The stiffness values are reported in grams.

Foam density was determined by weighing a known volume of foam 1.5 min after discharge. Foam drainage values were obtained by discharging the foam into a funnel positioned over a graduate. The quantity of liquid that drained during 60 min was measured.

RESULTS

Emulsion and Foam Stability

Forming the POE fatty ether–fatty alcohol complex at the propellant droplet interface by adding the alcohol with the propellant increased the emulsion stability with three of the surfactants—POE (2) cetyl ether, POE (10) cetyl ether, and POE (10) stearyl ether. No increase in emulsion stability was observed with POE (23) lauryl ether, POE (20) cetyl ether, or POE (20) stearyl ether. This is shown in Table IV.

^oCherry-Burrell Corp., Des Moines, Iowa.

Table IV
Effect upon Emulsion Stability of Alcohols in Aqueous Phase vs. Propellant Phase

| POE Fatty Ester | Phase Initially Containing Fatty Alcohol | Emulsion Stability ^a | | | |
|------------------|---|---------------------------------|-----------------------|--------------------|----------------------|
| | | Fatty Alcohol or Alcohol Blend | | | |
| | | Lauryl | Lauryl/Myristyl (1/9) | Lauryl/Cetyl (6/4) | Lauryl/Stearyl (8/2) |
| POE (2) cetyl | Aqueous | 30-60 min | >4 days | >4 days | >4 days |
| | Propellant | >16 hrs | >4 days | >4 days | >4 days |
| POE (10) cetyl | Aqueous | <1 min | 1-5 min | <1 min | <1 min |
| | Propellant | 1-5 min | >24 hrs | >24 hrs | >24 hrs |
| POE (10) stearyl | Aqueous | 1-5 min | 1-5 min | 1-5 min | 1-5 min |
| | Propellant | 1-5 min | >24 hrs | >24 hrs | >24 hrs |
| POE (4) lauryl | All formulations gelled in container. Stability >24 hrs | | | | |
| POE (23) lauryl | All less than 1 min | | | | |
| POE (20) cetyl | All less than 1 min | | | | |
| POE (20) stearyl | All less than 1 min | | | | |

^aEmulsion stability = time to first observable phase separation.

The increase in emulsion stability with POE (2) cetyl ether was observed only with lauryl alcohol. The other POE (2) cetyl ether emulsions were all too stable to detect any differences, regardless of how the alcohols were added. When the aqueous phase contained POE (10) cetyl or stearyl ether, a marked increase in aerosol emulsion stability resulted when the fatty alcohols were added with the propellant. However, there was little effect with lauryl alcohol alone. This is not surprising. Lauryl alcohol complexes have been shown to be less effective in improving aerosol emulsion and foam properties in anionic systems than those with myristyl, cetyl, or stearyl alcohols (6).

The lack of a direct relationship between emulsion stability and foam stability is shown in Table V. Although adding the fatty alcohol blends in the propellant increased emulsion stability with the three POE fatty ether surfactants, there was no corresponding increase in foam stability. The differences reported are not considered significant.

Foam Density

The density of the foams generally increased when the lauryl/myristyl, lauryl/cetyl, or lauryl/stearyl alcohol blends were added with the propellant. The data are given in Table VI. Again, there was essentially no effect with lauryl alcohol alone.

Other Properties

Stability, stiffness, and drainage were determined on all foams in duplicate. Variations did occur, but there was no consistent trend in any of the properties to indicate that adding the alcohols in the propellant instead of the aqueous phase had a significant effect. On the basis of the limited data available,

Table V
Relationship between Aerosol Emulsion and Foam Properties

| POE Fatty Ether | Emulsion Stability ^a | | Foam Stability ^b | |
|------------------------|------------------------------------|------------------------------|------------------------------------|------------------------------|
| | Alcohols in Aqueous Phase | Alcohols in Propellant | Alcohols in Aqueous Phase | Alcohols in Propellant |
| POE (2) cetyl ether | | | | |
| Lauryl alcohol | 30-60 min | > 16 hrs | 0 | 0 |
| Lauryl/myristyl (1/9) | > 4 days | > 4 days | 0 | 0 |
| Lauryl/cetyl (6/4) | > 4 days | > 4 days | 0 | 0 |
| Lauryl/stearyl (8/2) | > 4 days | > 4 days | 0 | 0 |
| POE (10) cetyl ether | | | | |
| Lauryl alcohol | < 1 min | 1-5 min | 29 | 33 |
| Lauryl/myristyl (1/9) | 1-5 min | > 24 hrs | 22 | 21 |
| Lauryl/cetyl (6/4) | < 1 min | > 24 hrs | 24 | 39 |
| Lauryl/stearyl (8/2) | < 1 min | > 24 hrs | 25 | 39 |
| POE (10) stearyl ether | | | | |
| Lauryl alcohol | 1-5 min | 1-5 min | 13 | 24 |
| Lauryl/myristyl (1/9) | 1-5 min | > 24 hrs | 23 | 25 |
| Lauryl/cetyl (6/4) | 1-5 min | > 24 hrs | 31 | 25 |
| Lauryl/stearyl (8/2) | 1-5 min | > 24 hrs | 31 | 31 |

^aTime to first observable phase separation.

^bPer cent decrease in height in 60 min.

Table VI
Effect upon Aerosol Foam Density of Adding Fatty Alcohols in the Propellant

| Polyoxyethylene Fatty Ether | Density (g/cc) | | | | | | | |
|--------------------------------|--------------------------------|-------|---------------------------|-------|------------------------|-------|--------------------------|-------|
| | Fatty Alcohol or Alcohol Blend | | | | | | | |
| | Lauryl | | Lauryl/ Myristyl (1/9) | | Lauryl/ Cetyl (6/4) | | Lauryl/ Stearyl (8/2) | |
| Aq. ^a | Prop. ^b | Aq. | Prop. | Aq. | Prop. | Aq. | Prop. | |
| POE (4) lauryl | 0.094 | 0.100 | 0.076 | 0.086 | 0.081 | 0.077 | 0.070 | 0.135 |
| POE (23) lauryl | 0.063 | 0.062 | 0.070 | 0.135 | 0.062 | 0.072 | 0.058 | 0.064 |
| POE (2) cetyl | 0.086 | 0.108 | 0.125 | 0.24 | 0.14 | 0.18 | 0.090 | 0.14 |
| POE (10) cetyl | 0.067 | 0.063 | 0.067 | 0.089 | 0.070 | 0.086 | 0.066 | 0.072 |
| POE (20) cetyl | 0.077 | 0.068 | 0.100 | 0.125 | 0.068 | 0.098 | 0.065 | 0.071 |
| POE (10) stearyl | 0.072 | 0.069 | 0.076 | 0.102 | 0.071 | 0.106 | 0.069 | 0.098 |
| POE (20) stearyl | 0.071 | 0.065 | 0.095 | 0.135 | 0.078 | 0.115 | 0.066 | 0.085 |

^aAlcohols initially in aqueous phase.

^bAlcohols initially in propellant.

it was concluded that any variations were the result of experimental error. It is possible that increasing the number of measurements might detect an effect not readily noticeable with duplicate determinations only.

Typical foam stability, drainage, and stiffness data obtained when the alcohols were placed initially in the aqueous phase are given in Table VII. These

Table VII
Aerosol Foam Properties
(Alcohols in Aqueous Phase)

| Foam Property | Polyoxyethylene Fatty Ether | | | | | | |
|-------------------------------------|-----------------------------|-------------|------------|-------------|-------------|-------------|-------------|
| | POE (4) | POE (23) | POE (2) | POE (10) | POE (20) | POE (10) | POE (20) |
| | Lauryl | Lauryl | Cetyl | Cetyl | Cetyl | Stearyl | Stearyl |
| Stability (% decrease in 60 min) | | | | | | | |
| Lauryl alcohol | 67 | 39 | 0 | 29 | 33 | 13 | 27 |
| Lauryl/myristyl (1/9) | 40 | 7 | 0 | 12 | 19 | 13 | 19 |
| Lauryl/cetyl (6/4) | 43 | 18 | 0 | 24 | 11 | 31 | 28 |
| Lauryl/stearyl (8/2) | 67 | 28 | 0 | 25 | 24 | 31 | 38 |
| Drainage (% in 60 min) | | | | | | | |
| Lauryl alcohol | 79 | 34 | 0 | 33 | 2 | 51 | 38 |
| Lauryl/myristyl (1/9) | 18 | 0 | 0 | 0 | 1 | 0 | 0 |
| Lauryl/cetyl (6/4) | 51 | 1 | 0 | 0 | 3 | 0 | 2 |
| Lauryl/stearyl (8/2) | 74 | 29 | 0 | 17 | 13 | 0 | 25 |
| Stiffness (g) | | | | | | | |
| Lauryl alcohol | 7 | 54 | 12 | 30 | 38 | 21 | 40 |
| Lauryl/myristyl (1/9) | 26 | 79 | 58 | 65 | 60 | 49 | 53 |
| Lauryl/cetyl (6/4) | 18 | 49 | 52 | 47 | 53 | 55 | 46 |
| Lauryl/stearyl (8/2) | 12 | 38 | 30 | 41 | 51 | 41 | 39 |

data are presented to illustrate the general magnitude of the values. The results obtained when the alcohols were added with the propellant were similar.

The lauryl/myristyl (1/9) blend gave foams with the best stability, the least drainage, and the highest stiffness in the majority of cases. This blend provides the highest concentration of fatty alcohol other than lauryl. Previous work on the effect of molecular complexes upon aerosol foam properties had shown that lauryl alcohol was the least effective of the four fatty alcohols in improving foam properties (6, 9).

DISCUSSION

Previous work had shown that when certain polyoxyethylene fatty ether-fatty alcohol complexes were preformed in the aqueous phase, they stabilized aerosol foams but not the initial emulsions. Data illustrating this, summarized from Reference 9, are given in Table VIII. The surfactants that failed to stabilize the aerosol emulsions in combination with fatty alcohols were POE (23) lauryl ether, POE (10) cetyl ether, POE (20) cetyl ether, and POE (20) stearyl ether. POE (10) stearyl ether should probably be included in this group because the increase in emulsion stability was marginal compared to the foam stability.

In the present investigation, increased emulsion stability was obtained with POE (2) cetyl ether when lauryl alcohol was added with the propellant. Since POE (2) cetyl ether by itself gives fairly stable emulsions, it is not surprising that lauryl alcohol, normally rather ineffective, would show an effect with

Table VIII
Relationship between Aerosol Emulsion and Foam Stability^a

| Emulsion Stability ^b | Polyoxyethylene Fatty Ether | | | | | |
|---------------------------------|-----------------------------|--------------------|-------------------|-------------------|---------------------|---------------------|
| | POE (4) Lauryl | POE (23) Lauryl | POE (10) Cetyl | POE (20) Cetyl | POE (10) Stearyl | POE (20) Stearyl |
| No alcohol | < 1 min | < 1 min | < 1 min | < 1 min | < 1 min | < 5 min |
| Lauryl | > 30 min | < 1 min | < 1 min | < 1 min | < 1 min | < 5 min |
| Myristyl | > 30 min | < 1 min | < 1 min | < 1 min | 15–30 min | < 5 min |
| Cetyl | > 30 min | < 1 min | < 1 min | < 1 min | 5–15 min | < 5 min |
| Stearyl | > 30 min | < 1 min | < 1 min | < 1 min | 15–30 min | < 5 min |
| Foam Stability ^c | | | | | | |
| No alcohol | < 5 min | < 5 min | < 15 min | < 5 min | < 15 min | < 5 min |
| Lauryl | 30–60 min | 15–30 min | 30–60 min | > 2 hr | 30–60 min | > 2 hr |
| Myristyl | > 2 hr | > 2 hr | > 2 hr | > 2 hr | > 2 hr | > 2 hr |
| Cetyl | > 2 hr | > 2 hr | > 2 hr | > 2 hr | > 2 hr | > 2 hr |
| Stearyl | > 2 hr | > 2 hr | > 2 hr | > 2 hr | > 2 hr | > 2 hr |

^aFrom (9); aerosols formulated with 90% aqueous concentrate and 10% Propellant 12/114 (40/60).

^bTime to first observable phase separation.

^cTime to first observable collapse.

POE (2) cetyl ether. The other emulsions with POE (2) cetyl ether were very stable, regardless of how the alcohols were added.

A major increase in emulsion stability was obtained with POE (10) cetyl ether and POE (10) stearyl ether systems by adding the alcohol blends with the propellant. The surfactant–fatty alcohol complexes were formed at the propellant–water interface and stabilized the emulsions. The general structure of the complexes formed directly at the propellant droplet interface undoubtedly differs from that of complexes preformed in the aqueous phase.

The increase in emulsion stability obtained by adding fatty alcohols with propellant occurred with the three POE fatty ethers with the lower HLB values (5.3–12.9). This indicates the complexes had a low affinity for water. They probably function at the interface as solid stabilizers. Previous work had shown that the most efficient stabilizers were insoluble in both the aqueous and propellant phases at use concentrations (13). However, it is necessary for the stabilizers to be wetted by both phases in order to be attracted to the propellant–water interface (14). The present work supports this generalization.

The fatty alcohol complexes with POE (23) lauryl ether, POE (20) cetyl ether, and POE (20) stearyl ether failed to stabilize the emulsions regardless of whether the alcohols were added with the propellant or were present initially in the aqueous phase. A reasonable explanation for this is that the surfactant–alcohol complexes were too water-soluble to act as solid stabilizers. These surfactants all have high HLB values (15.3–16.9). Thus, even when the complexes were formed directly at the propellant droplet–water interface by

addition of the alcohols with propellant, the complexes apparently left the interface and migrated to the bulk phase, leaving the propellant droplets unstabilized.

The reason surfactant–fatty alcohol complexes stabilize foams, regardless of their effect upon the emulsions, has not been clarified. Possibly, vaporization of solubilized propellant during product discharge disrupts the oriented liquid crystal complex structure. Disruption could occur even by the turbulence created when nonsolubilized propellant vaporized.

Foam stabilization could also result from the increase in viscosity of the aqueous phase caused by the complexes. This would decrease the rate of drainage. The effect of molecular complexes in increasing the viscosity of the aqueous phase is well known.

The present study has several aspects of significance to the cosmetic industry. In the first place, the results re-emphasize that the method of preparing an emulsion can profoundly affect emulsion properties. A number of cosmetic products have failed because of poor emulsion stability. Many of these might have been successful if the method of preparation of the emulsion had been examined in more detail.

The increase in emulsion stability obtained by adding fatty alcohols in the propellant provides additional evidence that complexes or association compounds are formed between the alcohols and polyoxyethylene fatty ethers. The water affinity of the surfactant, as judged by its HLB value, and the type of fatty alcohol are important factors in the ability of the surfactant-alcohol complex to stabilize an emulsion.

Although propellants containing fatty alcohols or other complexing agents are not commercially available at present, they are a future possibility. Propellants containing additives specifically designed for the preparation of cosmetic emulsion and foam products would have many attractive features. Such propellant blends might well permit the development of new cosmetic aerosol products.

CONCLUSIONS

The effectiveness of polyoxyethylene fatty ether–fatty alcohol complexes as stabilizers for aerosol emulsions depends upon their method of formation, solubility in water, and structure. Several POE fatty ether–fatty alcohol combinations that failed to stabilize aerosol emulsions when premixed in the aqueous phase prior to addition of propellant produced stable emulsions when the complex was formed directly at the propellant-water interface. The latter was achieved by adding the alcohol dissolved in the propellant to the aqueous surfactant phase. The POE fatty ethers that showed this effect had HLB values ranging from 5.3 to 12.9.

Three POE fatty ether–fatty alcohol complexes failed to stabilize emulsions regardless of how the complex was formed. The inability of these com-

plexes to stabilize the emulsions was attributed to their high water solubility. These POE fatty ethers had HLB values from 15.3 to 16.9.

Whether or not the nonionic surfactant–fatty alcohol complexes stabilized emulsions had little effect upon foam stability. This indicates a lack of relationship between the properties of the POE fatty ether emulsions and their corresponding foams. The stabilization of the aerosol foams by the complexes regardless of their effectiveness as emulsion stabilizers probably results both from an increase in the viscosity of the aqueous phase due to a surfactant-alcohol complex and disruption of the initial stable complex by the vaporizing propellant when the product is discharged.

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Formulating High-Foaming Cosmetic Products

IRVING R. SCHMOLKA, Ph. D.

Presented December 11, 1973, New York City

Synopsis—Obtaining valid comparative data on the FOAMING PROPERTIES of a multitude of SURFACE-ACTIVE AGENTS and then using these data to prepare acceptable finished COSMETIC FORMULATIONS is a problem frequently encountered by the cosmetic chemist.

An APPARATUS designed for MEASURING foam in the laboratory is described. The inexpensive equipment allows flexibility of operation, is simple to clean, and offers several other important advantages for objectively developing and evaluating high-foaming cosmetic products. Foam volumes are readily determined. Comparative foam data, at 38° C, presented for dilute aqueous solutions of some leading commercially available NONIONIC and ANIONIC foaming SURFACTANTS, show the latter group to be superior to the former class of compounds. The effects of varying the surfactant concentration are pointed out. Data are presented showing the influence of mixing time and mixing speed. Additional variables which alter foam heights are shown to include the presence of soil, thickeners, and other additives. Increasing the viscosity of aqueous surfactant solutions is shown to have an effect on foam. Finally, comparative foam data are given for commercial high-foaming cosmetic products, including a bubble bath preparation, dentifrices, and shampoos.

INTRODUCTION

The task of developing high-foaming cosmetic products is a problem often encountered by the cosmetic chemist. High-foaming products can encompass cosmetics and toiletries as diverse as shampoos, bubble baths, shave creams, dentifrices, skin cleansers, etc. The bench chemist who is given the important assignment of developing a new, improved high-foaming cosmetic formulation is faced with the formidable task of defining the term high-foaming. The formulation chemist needs objective guidelines. It should be emphasized that there are many criteria for the development of commercially successful high-foaming cosmetic products, but for the purpose of this study, attention will be focused on only one aspect, and that is “foam.”

*BASF Wyandotte Corp., Wyandotte, Mich. 48192.

The literature describes many methods and equipment for generating and measuring foam and also indicates that the well-known standard Ross-Miles (1, 2) test is still used, while other investigators have used more sophisticated apparatuses (3-5).

In order to evaluate new surfactants in comparison with well-known anionics, such as sodium lauryl sulfate, an apparatus which would meet certain requirements was needed. Such requisites include: (a) inexpensive, so that the smallest laboratory would be able to afford it; (b) simple to operate, so that a great deal of operator training would not be required; (c) easy to clean, so that downtime for cleaning would not keep the apparatus tied up excessively or require extensive dismantling; (d) mobile, so that it could be moved from the laboratory to a storage space when not needed; (e) reproducible, to be able to give data reproducible from one day to the next and from one operator to the next (this could also serve to eliminate the dependency on one particular operator); (f) flexible, to be readily adaptable for varying concentrations of active ingredients, varying types of foaming products, varying water hardnesses, varying temperatures, varying soils where needed, and varying energy input, such as one gets by varying the rpm of a mixer. This latter point cannot be overemphasized. When teeth are brushed with an electric toothbrush, for example, the amount of foam generated is greater than when the same teeth are brushed by hand. Similarly, consider the Ross-Miles foam test, where the only energy input is that of the potential energy of part of the liquid falling onto the rest of the liquid. Contrast this energy level with that developed by a Sunbeam Mixmaster, at a speed of 720 rpm, which was one laboratory method used (4) to develop foam for shampoo evaluation. Then consider the energy input which humans generate, who shampoo their own hair with their hands. No person has yet been encountered who massages his hair at 720 rpm for 1 min, much less 3 min. (g) If all these previous points are met, there is still one further criterion, and that is, the reliability of the data. The data obtained must show good correlation with actual use conditions.

EXPERIMENTAL AND RESULTS

Sorkin and coworkers mentioned the use of a glass cylinder with a device to revolve or agitate it, but gave no details as to its construction (6). It is suggested that the cosmetic industry standardize on a piece of equipment for measuring foam and possibly the apparatus described below could be the standard.

The instrument, which was used in these experiments, is referred to as the Bacon machine (7). The cost of all parts, exclusive of a stop-watch or a clock used as a timer, a standard mixing cylinder usually found in the laboratory, and exclusive of labor was about \$150, in 1974. The essential features include: accurately mounting a mixing cylinder containing the foaming solution to rotate in a vertical plane at a fixed speed; a method to stop the cylinder, by a

magnetic brake acting in the vertical position, suitable for instant reading of foam and liquid volumes; welding glass lugs to the cylinder, so that the glass stopper may be fastened to the cylinder by means of rubber bands.

One piece of auxiliary equipment needed is a water bath. Since the primary concern was with foaming products designed for use on or in the human body, a temperature of 38°C was used in obtaining all the data. Any water bath large enough to hold one or more mixing cylinders would be suitable and is a standard piece of equipment generally found in all laboratories.

One other requirement is stopcock grease,^o to provide a tight seal for the cylinder stopcock. During the course of this investigation, a high-vacuum silicone lubricant was inadvertently used. It played havoc with the foam data, as the lubricant was brushed down with a test tube brush into the cylinder in the course of cleaning out the cylinder after each run. All these data were discarded and this word of caution is made against using any silicone-containing stopcock grease for this apparatus.

The cylinder is placed in the clamp holders so that the 500-ml mark of a 1000-ml cylinder is exactly at the center of rotation, which is marked on the clamp-holder support. The equipment is flexible enough so that either a 500-ml or 1000-ml mixing cylinder can be used. However, the experiments were carried out with the larger cylinders. To minimize variations in data, cylinders of the same weight were selected since a heavier cylinder will rotate a little more slowly than a lighter cylinder, at the same voltage setting.

In the preliminary experiments, certain variables were fixed for initial screening tests. These included the concentration of active ingredient. It was decided, after conferring with a number of other cosmetic chemists, to use a 0.2% active solution, although data will be presented at other concentration levels. Whereas adjustments in speed can be made by changing line voltage with a variable transformer, all data, unless otherwise specified, are at 26 rpm. The time of rotation can be varied but this was arbitrarily fixed at 1 min, since it was thought it would most closely approximate consumer habits. As an alternative to presenting data in terms of milliliters of foam volume, it is possible to permanently record foam quantity and stability by taking Polaroid pictures of the cylinder and its contents at given time intervals. The procedure followed was to place 200 ml of solution into the cylinder, and immerse the cylinder in the water bath at 38°C for 1 hour. The water level in the water bath was maintained at a height above the height of the solution in the cylinder. The cylinder was then mounted in the set of clamps in a vertical position and the rotation started for 1 min. Foam height and liquid level were read immediately upon cessation of rotation, and liquid level was subtracted from total volume to give foam volume. The same data were recorded after 1, 2, 3, 4, and 5-min periods. However, only part of these data are presented here.

^oCelloseal, Fisher Scientific, Inc., Pittsburgh, Pa.

Table I
Foam Volumes (ml) of Anionic Surfactants, 0.2% Active, Tap Water^a

| | Initial | 2 Min | 5 Min | 2-Min % Retention |
|-----------------------------|---------|-------|-------|-------------------|
| Sodium lauryl sulfate | 975 | 765 | 705 | 78 |
| α -Olefin sulfonate | 930 | 755 | 750 | 81 |
| Sodium lauryl ether sulfate | 1030 | 830 | 800 | 81 |
| Sodium lauroyl sarcosinate | 330 | 230 | 205 | 70 |
| Sodium alkyl sulfoacetate | 870 | 680 | 650 | 78 |

^a6.5 grains per gallon hardness.

In Table I, data are presented for some commercially available anionic surfactants in 6.5 grains per gallon hardness tap water. Three sets of numbers are presented. It is believed that greater emphasis should be placed on foam data shown in the two columns on the left, since the 5-min data, while interesting in revealing foam stability, which is of interest for bubble bath applications, are not reflected in actual use conditions (for example, brushing one's teeth or in shampooing one's hair).

The foam data do show that the sodium salt of lauryl ether sulfate is slightly better, under the conditions of this test procedure, than the α -olefin sulfonate, the sodium lauryl sulfate, or the sodium alkyl sulfoacetate and all four are markedly superior to the sodium lauroyl sarcosinate. The data in the column on the right are obtained by dividing the 2-min foam volume by the initial foam volume and multiplying by 100. This value is a measure of the foam stability over the first 2 min. These data indicate that there is little difference among the foam stabilities of the top four leading foaming anionic surfactants evaluated.

In reading the foam heights, one places a fingernail at the average upper foam level immediately while reading the level of the liquid/foam interface. At times some estimation is required due to irregular levels of pockets of air developing during aging. To determine reproducibility of the data, the same solution was transferred to each of several cylinders and foam volumes were measured. The data shown in Table II indicate the reproducibility which may be obtained using this test procedure.

This equipment can also be used to measure speed of foam production. Thus, if one had set as his primary criterion the minimum time to develop a specific volume of foam, it is simple to prepare solutions, transfer equal amounts to a group of cylinders, rotate each cylinder for a different length of time, and then plot foam volume *versus* time of rotation. The data in Table III show that the effect of varying the time of rotation from 1 to 5 min is to increase the amount of foam generated. It is important to note that the percentage increase for each surfactant in extending the rotation time, as shown by the figures in the right hand column, is markedly different. This emphasizes the importance of developing a test procedure which closely approximates use conditions, so as to get valid experimental data.

Table II
Reproducibility of Foam Data
(Foam Volumes, ml, at 26 rpm)

| Compound A | | | | | | Average |
|------------|-----|-----|-----|-----|-----|----------|
| Initial | 625 | 625 | 630 | 640 | 630 | 630 ± 12 |
| 2 minutes | 460 | 460 | 470 | 490 | 470 | 470 ± 25 |
| 5 minutes | 440 | 440 | 450 | 470 | 440 | 450 ± 26 |
| Compound B | | | | | | |
| Initial | 620 | 630 | 640 | 630 | | 630 ± 14 |
| 2 minutes | 505 | 480 | 495 | 480 | | 490 ± 21 |
| 5 minutes | 450 | 450 | 475 | 450 | | 455 ± 22 |

Table III
Foam Volumes (ml), with Increasing Rotation Time

| | Time (min) | | | | | % Increase |
|------------|------------|-----|-----|-----|-----|------------|
| | 1 | 2 | 3 | 4 | 5 | |
| Compound A | | | | | | |
| Initial | 330 | 370 | 440 | 430 | 460 | 39 |
| 2 minutes | 230 | 265 | 285 | 305 | 320 | 39 |
| 5 minutes | 205 | 250 | 280 | 290 | 300 | 46 |
| Compound B | | | | | | |
| Initial | 520 | 530 | 630 | 800 | 900 | 92 |
| 2 minutes | 365 | 355 | 460 | 640 | 690 | 89 |
| 5 minutes | 305 | 320 | 440 | 600 | 640 | 110 |

If one were concerned with flash foam, the cylinder could be rotated for just a few seconds and a series of photographs taken immediately to capture the data permanently. Those questions concerned with foam texture could also be answered with a series of photographs. A group of commercially available high-foaming nonionic surfactants was then selected and foam data were measured by this procedure. The data are shown in Table IV. It is obvious that the foam volumes of the best nonionic surfactants do not approach those of the best anionic surfactants, shown previously. Again, the 2-min foam stability is shown by the value in the column on the right.

In addition, a few amphoteric surfactants were evaluated in a similar fashion, as shown in Table V. The best amphoteric give foam volumes intermediate between the best anionic and the best nonionic surfactants. Although the equipment was set to run at 30 rpm with an empty cylinder, with a load of 200 ml of solution in the cylinder, a speed of only 26 rpm developed. The effect of varying the speed, by adjusting the transformer setting, is shown in Table VI. As expected, the greater the rpm of the cylinder, the higher the foam

Table IV
Foam Volumes (ml) of
Nonionic Surfactants, 0.2% Active, Tap Water^a

| | Initial | 2 Min | 5 Min | 2-Min % Retention |
|--------------------------------|---------|-------|-------|-------------------|
| Fatty alcohol 60% EO | 570 | 465 | 390 | 82 |
| Fatty alcohol + 12 mole EO | 350 | 310 | 185 | 89 |
| Fatty alcohol 60% EO | 490 | 385 | 375 | 79 |
| Tridecyl alcohol + 15 EO | 620 | 480 | 300 | 78 |
| Secondary fatty alcohol + 9 EO | 700 | 530 | 100 | 76 |
| <i>t</i> -Octyl phenol + 9 EO | 560 | 455 | 420 | 81 |
| Polysorbate 80 | 230 | 100 | 50 | 44 |

^a6.5 grains per gallon hardness.

Table V
Foam Volumes (ml) of
Amphoteric Surfactants, 0.2% Active, Tap Water^a

| | Initial | 2 Min | 5 Min | 2-Min % Retention |
|-------------------------|---------|-------|-------|-------------------|
| Modified cycloimidine | 840 | 705 | 685 | 84 |
| Substituted imidazoline | 700 | 585 | 550 | 85 |
| Sulfonated amide | 530 | 385 | 330 | 73 |
| Oleyl betaine | 500 | 385 | 350 | 77 |
| Coco betaine | 860 | 705 | 650 | 82 |

^a6.5 grains per gallon hardness.

Table VI
Effect of rpm on Foam Volume

| | | Foam Volume (ml) | | |
|-------------|------------|------------------|-------|-------|
| | | Initial | 2 Min | 5 Min |
| A. Nonionic | 20 rpm | 500 | 400 | 295 |
| | 40 rpm | 700 | 450 | 345 |
| | % increase | 40 | 13 | 17 |
| B. Anionic | 20 rpm | 800 | 700 | 600 |
| | 40 rpm | 1000 | 855 | 795 |
| | % increase | 25 | 22 | 32 |

volume that was generated. A comparison of the per cent increase between the two surfactants studied clearly shows that not all surfactants are affected equally by an increase in speed of rotation of the cylinder. These data again emphasize the fact that foam volumes depend entirely upon the energy input.

Table VII
 Comparison of Bacon and Ross-Miles Foam Data
 (Tap Water, 0.2%, 38°C)

| | Bacon (ml) | | Ross-Miles (mm) | |
|-------------------------------|------------|-------|-----------------|-------|
| | Initial | 5 Min | Initial | 5 Min |
| Anionic | | | | |
| Sodium lauryl sulfate | 975 | 705 | 170 | 150 |
| α -Olefin sulfonate | 930 | 750 | 160 | 145 |
| Sodium lauryl ether sulfate | 1030 | 800 | 170 | 140 |
| Sodium lauryl sarcosinate | 350 | 205 | 105 | 20 |
| Nonionic | | | | |
| Tridecyl alcohol + 15 EO | 620 | 300 | 160 | 80 |
| Fatty alcohol + 12 EO | 350 | 185 | 130 | 20 |
| Fatty alcohol 60% EO | 570 | 390 | 110 | 80 |
| Polysorbate 80 | 230 | 50 | 50 | 40 |
| Poloxamer 237 | 150 | 25 | 110 | 85 |
| <i>t</i> -Octyl phenol + 9 EO | 560 | 420 | 140 | 30 |
| Fatty alcohol 60% EO | 490 | 375 | 100 | 45 |

"Tap water hardness = 6.5 grains per gallon.

The energy input of a test procedure must closely approximate actual use conditions in order to get data that are meaningful.

Because the Ross-Miles foam test is so widely used, it was decided to see what correlation, if any, would be obtained from foam data using the Ross-Miles equipment, in comparison with the Bacon apparatus. (All Ross-Miles data are an average of two test runs.) The data in Table VII show that there is only partial correlation between data obtained from the two methods, especially among the nonionics. This again indicates the importance of evaluating any foam system under laboratory conditions which most closely approximate those of actual usage.

The effect of varying the concentration of surfactant ingredient is shown in Table VIII. As expected, both surfactants show a marked increase in foam volume as their concentrations increase. When one obtains high values, such as shown for the 5% solution of Surfactant A, it is apparent that the upper limit of capacity is being reached, and figures above 1100 are not very accurate, due to limitation of the equipment. In this same table, the effect of water hardness may be clearly seen. The anionic surfactant shows a significant increase in the foam volume in distilled water, as compared to tap water, whereas the foam volumes generated by the nonionic surfactant are essentially the same in the two water hardnesses. These data are to be expected.

In developing shampoo formulations, the effects of natural sebum soil upon the hair have to be considered. With bubble bath products, skin wastes and natural soils can be expected to have an adverse effect upon foam. For tooth-

Table VIII
Foam Volumes (ml) at Varying Concentrations

| | | Tap Water | | | |
|----------|--|-----------------|---------|-------|-------|
| | | % | Initial | 2 Min | 5 Min |
| A. | | 5.0 | 1160 | 1010 | 800 |
| Anionic | | 1.0 | 820 | 655 | 550 |
| | | 0.2 | 595 | 565 | 510 |
| | | 0.1 | 550 | 405 | 400 |
| B. | | 5.0 | 860 | 660 | 500 |
| Nonionic | | 1.0 | 800 | 585 | 455 |
| | | 0.2 | 550 | 465 | 350 |
| | | 0.1 | 430 | 305 | 300 |
| | | Distilled Water | | | |
| A. | | 1.0 | 1140 | 905 | 600 |
| Anionic | | 0.2 | 920 | 760 | 550 |
| B. | | 1.0 | 780 | 605 | 450 |
| Nonionic | | 0.2 | 530 | 400 | 350 |

paste, the effects of saliva and residual food soils have to be considered. However, under normal circumstances, these adverse effects on foam are generally negligible.

Various synthetic soils have been proposed for evaluating shampoos in the laboratory, including synthetic sebum, oleic acid, mineral oil, etc. Of these, it was decided to consider the effects of the first. Using the formulation published by Barnett and Powers (8), a synthetic sebum was prepared and its effect on the foam properties of various surfactants was studied. The data, shown in Table IX, indicate the vast superiority in foam properties of anionic surfactants in the presence of this soil, compared to nonionic surfactants. One amphoteric, a cycloimidine, gave foam volumes comparable to that produced by the α -olefin sulfonate under these same conditions. Thus, if the preparation of a high-foaming shampoo is one's objective, these data indicate the inclusion of some anionic or amphoteric surfactant in the formulation would be necessary. It is suggested that these data reflect the ability of the surfactant to emulsify the synthetic sebum and thus prevent its ability to act as a defoamer. By way of comparison, data are shown in Table X, for four leading commercial shampoos at 10% and 20% dilution, showing their foam properties in the presence of 3% of sebum soil.

Many ingredients go into a finished foaming cosmetic product, other than a surfactant and water. These minor ingredients are used to impart specific properties, and are generally referred to as additives. Each of these ingredients could, and most likely does, have an effect upon the foam properties.

Table IX
Foam Volumes (ml) in Presence of 3% Sebum Soil, in Tap Water^a

| | | Surfactant Concentration (%) | | |
|-------------------------------|---------|------------------------------|-----|------|
| | | 2.0 | 5.0 | 10.0 |
| Sodium lauryl sulfate | Initial | 600 | 750 | 900 |
| | 2 min | 465 | 610 | 750 |
| | 5 min | 450 | 580 | 715 |
| α -Olefin sulfonate | Initial | 300 | ... | 650 |
| | 2 min | 175 | ... | 450 |
| | 5 min | 175 | ... | 420 |
| Sodium lauryl ether sulfate | Initial | 100 | ... | 420 |
| | 2 min | 80 | ... | 280 |
| | 5 min | 80 | ... | 270 |
| Tridecyl alcohol + 15 EO | Initial | 10 | ... | 30 |
| | 2 min | 10 | ... | 10 |
| | 5 min | 10 | ... | 10 |
| <i>t</i> -Octyl phenol + 9 EO | Initial | 10 | ... | 480 |
| | 2 min | 10 | ... | 320 |
| | 5 min | 10 | ... | 230 |
| Fatty alcohol + 12 EO | | 0 | ... | 0 |
| Modified cycloimidine | Initial | 380 | ... | 630 |
| | 2 min | 250 | ... | 520 |
| | 5 min | 235 | ... | 470 |

^a6.5 grains per gallon hardness.

It is beyond the scope of this paper to consider all possible additives in great detail and their effects upon foam. It should suffice to point out that minor adjustments such as only a change in pH, or the addition of an essential oil, without which many products would be doomed to marketing failure, could be enough to change foam volumes. Bubble baths are relatively simple to formulate, but shampoos and especially dentifrices, on the other hand, are more complex formulations, as will be described later.

A few of the more widely used cosmetic additives were selected and studied for their effects upon the foam properties of an anionic surfactant and a non-ionic surfactant. It was obviously impossible to study every commercially available additive and every surfactant. The effect of the additive upon the viscosity of the product was also of interest, since some formulators believe that one can increase the foam volume of an existing product merely by increasing its viscosity. The data, in Table XI, show the effect of 0.2% additive

Table X
Foam Volumes (ml) of Commercial Shampoos
in Presence of 3% Synthetic Sebum Soil

| | | Dilution (%) | |
|-----------|---------|--------------|-----|
| | | 20 | 10 |
| Product A | Initial | 600 | 570 |
| | 2 min | 450 | 405 |
| | 5 min | 435 | 400 |
| Product B | Initial | 640 | 570 |
| | 2 min | 485 | 430 |
| | 5 min | 460 | 410 |
| Product C | Initial | 580 | 500 |
| | 2 min | 435 | 345 |
| | 5 min | 425 | 330 |
| Product D | Initial | 625 | 510 |
| | 2 min | 470 | 330 |
| | 5 min | 450 | 310 |

Table XI
Effect of Additives on Foam and Viscosity of Surfactants
(2% Surfactant, 0.2% Additive, 100 ml)

| | Foam Volume (ml) | | | Viscosity (cps) |
|-------------------|------------------|-------|-------|-----------------|
| | Initial | 2 Min | 5 Min | |
| Anionic control | 655 | 560 | 475 | 3.1 |
| + cetyl alcohol | 600 | 535 | 505 | 3.4 |
| + CMC | 650 | 560 | 470 | 4.1 |
| + alkanolamide | 720 | 605 | 475 | 3.5 |
| + amine oxide | 690 | 580 | 550 | 3.5 |
| + sodium chloride | 650 | 565 | 450 | 3.0 |
| Nonionic control | 575 | 470 | 280 | 3.1 |
| + cetyl alcohol | 310 | 225 | 220 | 3.5 |
| + CMC | 530 | 430 | 250 | 4.5 |
| + alkanolamide | 660 | 565 | 500 | 3.1 |
| + amine oxide | 630 | 530 | 500 | 3.9 |
| + sodium chloride | 620 | 490 | 250 | 3.0 |

on a 2% surfactant solution. In these experiments a volume of only 100 ml was used. With the anionic surfactant, the addition of carboxymethylcellulose (CMC) gives the greatest increase in viscosity, but was without effect on foam. The greatest boost in foam volume is produced by the addition of the alkanolamide or the amine oxide. These data were expected. With the non-

Table XII
Foam Volumes (ml) of Commercial Shampoos

| | | Tap Water ^a | | Demineralized Water | |
|-----------|---------|------------------------|---------|---------------------|------|
| | | 10% | 1% | 10% | 1% |
| | | Product A | Initial | 1025 | 880 |
| | 2 min | 875 | 715 | 915 | 730 |
| | 5 min | 855 | 675 | 850 | 700 |
| Product B | Initial | 990 | 560 | 1050 | 825 |
| | 2 min | 815 | 405 | 860 | 660 |
| | 5 min | 800 | 400 | 775 | 625 |
| Product C | Initial | 1025 | 840 | 1100 | 1000 |
| | 2 min | 910 | 685 | 910 | 810 |
| | 5 min | 800 | 650 | 800 | 750 |
| Product D | Initial | 1025 | 870 | 1080 | 1000 |
| | 2 min | 870 | 725 | 870 | 800 |
| | 5 min | 825 | 680 | 800 | 750 |
| Product E | Initial | 1000 | 920 | 1075 | 980 |
| | 2 min | 835 | 740 | 835 | 790 |
| | 5 min | 800 | 700 | 800 | 750 |

^a6.5 grains per gallon hardness.

ionic surfactant, the CMC again gave the greatest viscosity increase, but again had no positive effect on foam. The greatest increase in foam was produced by the addition of the amide or amine oxide. Although the addition of cetyl alcohol served to increase viscosity in both cases, it had no beneficial effect upon foam volume. It is possible that by the use of other ratios of additives to surfactants, or had a study been made of other concentrations and with other surfactants, still other effects on foam and viscosity would have been observed. The data do serve to illustrate the point that an increase in the viscosity of a surfactant system by an additive can have a negative, a positive, or zero effect on foam.

Several leading commercial shampoos were evaluated for foam properties at two concentrations, 1% and 10%, in both tap water and soft (doubly demineralized) water. The foam data are shown in Table XII. There is very little difference among the five products at the 10% concentration level, but there is a noticeable difference at 1%. The same is true under soft water conditions. The data also show that the foam volumes at the 10% concentration level are about double what were obtained in the presence of 3% sebum soil, shown previously in Table X.

Table XIII
Shampoo Formulation and Foam Data

| | Formulation | | | |
|---------|-----------------------------------|------------------------|------------|-----|
| | 20.0 | Sodium lauryl sulfate | | |
| | 5.0 | Coconut diethanolamide | | |
| | 0.5 | Citric acid-hydrate | | |
| | 74.5 | Demineralized water | | |
| | Foam Volumes (ml) without Soil | | | |
| | Tap Water ^a | | Soft Water | |
| | 10% | 1% | 10% | 1% |
| Initial | 1000 | 840 | 1050 | 800 |
| 2 min | 785 | 660 | 830 | 635 |
| 5 min | 700 | 630 | 725 | 590 |
| | with 3% Sebum Soil, Tap Water | | | |
| | | 20% | 10% | |
| | Initial | 600 | 550 | |
| 2 min | 450 | 410 | | |
| 5 min | 430 | 375 | | |

^a6.5 grains per gallon hardness.

By way of comparison, a suggested starting formulation for a simple shampoo and its foam data are shown in Table XIII. The finished product has a pH of 6.5 and has a viscosity of 150 cps. The foam data are comparable to those of commercial products, both alone and in the presence of sebum soil. This is not a complete formulation. Various additives, such as a lanolin product, a fragrance, perhaps some protein fractions, etc., should be added. However, there are so many products which could be used, that it is beyond the scope of this paper to consider all possible shampoo additives.

Table XIV shows the foam data that were obtained on three leading commercial toothpastes both in tap water and in soft water. All toothpastes were run at 10% concentration at three speeds, to take into consideration the effects which might be obtained by brushing with an electric toothbrush rather than by hand. Product C appears to have a little poorer foam stability, although it is equal in foam initially.

A suggested formulation for a typical toothpaste is shown in Table XV. The foam data, shown in Table XVI, are comparable to those of the commercial products shown previously.

In Table XVII, foam data are given for a commercial bubble bath and a foaming skin cleanser. A suggested dry bubble bath formulation and its foaming properties are listed in Table XVIII. The foam data of the bubble bath

Table XIV
Foam Volumes (ml) of
Commercial Toothpaste (10% Concentration)

| | Tap Water | | | Demineralized Water | | |
|-----------|-----------|------|-----|---------------------|-----|-----|
| | rpm | | | rpm | | |
| | 44 | 26 | 18 | 44 | 26 | 18 |
| Product A | 1100 | 850 | 710 | 1100 | 750 | 560 |
| | 935 | 695 | 565 | 915 | 600 | 455 |
| | 865 | 635 | 480 | 850 | 510 | 405 |
| Product B | 1100 | 1050 | 750 | 1100 | 550 | 450 |
| | 935 | 840 | 610 | 915 | 385 | 355 |
| | 865 | 805 | 505 | 865 | 355 | 305 |
| Product C | 1075 | 775 | 750 | 1100 | 675 | 650 |
| | 810 | 620 | 505 | 820 | 510 | 510 |
| | 450 | 455 | 330 | 500 | 380 | 175 |

Table XV
Toothpaste Formulation

| | |
|-------------------------------|-------|
| Dicalcium phosphate-dihydrate | 41.0 |
| Water | 28.0 |
| Glycerine | 20.0 |
| Salt | 5.0 |
| Sodium lauryl sulfate | 2.0 |
| Dispersed silica | 1.5 |
| Carboxymethylcellulose | 1.0 |
| Saccharin | 0.5 |
| Sodium benzoate | 0.5 |
| Flavor | 0.5 |
| Total | 100.0 |

Table XVI
Foam Volume (ml) of
Experimental Toothpaste, 10% Concentration

| | Tap Water | | | Demineralized Water | | |
|---------|-----------|------|-----|---------------------|------|-----|
| | rpm | | | rpm | | |
| | 44 | 26 | 18 | 44 | 26 | 18 |
| Initial | 1100 | 1100 | 800 | 1100 | 1100 | 800 |
| 2 min | 915 | 900 | 655 | 915 | 895 | 640 |
| 5 min | 800 | 780 | 600 | 800 | 805 | 555 |

Table XVII
Foam Volumes (ml) of Two Commercial Products
(Tap Water)

| | Foaming Skin Cleanser | Powdered Bubble Bath | | |
|---------|-----------------------|----------------------|------|------|
| | 1% | 1.0% | 0.5% | 0.2% |
| Initial | 850 | 780 | 550 | 455 |
| 2 min | 660 | 640 | 410 | 280 |
| 5 min | 650 | 610 | 380 | 260 |

Table XVIII
Bubble Bath Formulation and Foam Data

| | Formulation | | |
|---------------------------------|-----------------------------|------|------|
| | Foam Volume (ml), Tap Water | | |
| | 1.0% | 0.5% | 0.2% |
| Sodium sulfate | | | 78 |
| Sodium alkyl sulfoacetate (70%) | | | 20 |
| Lauric myristic diethanolamide | | | 2 |
| Initial | 800 | 680 | 580 |
| 2 min | 640 | 540 | 435 |
| 5 min | 600 | 500 | 370 |

formulation are at least as good as those of the commercial product, shown in the previous table.

Earlier, the point had been made that one of the important requirements for an apparatus to measure foam was that the data be meaningful. It is important to note a statement in the paper by Sorkin *et al.* (6) in describing the evaluation of foam in shampoos by the glass-stoppered revolving cylinder, "It is fast, it is reproducible and it reflects the performance of the shampoo on the hair."

CONCLUSION

An apparatus for measuring foam has been described which meets several important criteria. Data have been presented which show differences in foam volumes, among different surfactants, and using different conditions. Some commercial foaming cosmetic products were evaluated and suggested starting formulations are presented for some high-foaming cosmetic products.

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Microemulsions

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Synopsis—Transparent emulsions are by definition called water-in-oil or oil-in-water MICROEMULSIONS. Where the average diameter of the dispersed droplets is less than one quarter of the wavelength of the incident light, no light scattering will occur and the system will be transparent. The PREPARATION of microemulsions and the FORMATION and STABILIZATION of such by phase diagram, NMR, and interfacial tension measurements are reviewed. A new theory of the formation of these microemulsions based on INTERFACIAL DIFFUSION of the surfactant or cosurfactant producing a temporary zero interfacial tension is presented.

INTRODUCTION

Microemulsions are transparent emulsions of high stability. Like macroemulsions, additional amphiphatic components are needed to form these emulsions. Usually, two additives, a surfactant and a cosurfactant, are required. Unlike macroemulsions, they are optically clear, the spherical droplet diameters of the dispersed phase being less than 1400 Å. This is based on the fact that if the diameter of particles in a colloidal system is less than $\frac{1}{4}$ of the wavelength of the incident light, the particles will not scatter light thereby resulting in a transparent system.

The dispersed component can be an oil and the continuous phase water or an aqueous solution, in which case the system is described as an oil-in-water (O/W) microemulsion, or the oil and water can exchange roles, in which case one speaks of a water-in-oil (W/O) microemulsion.

Since the term was first introduced by Hoar and Schulman (1), microemulsions have been studied by him and others using a wide variety of techniques. Numerous explanations of their stability have been offered (1–10) but as yet no theory explaining their formation and stability has proved completely satisfactory.

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PREPARATION OF MICROEMULSIONS

During the formation of a dispersed system the interfacial area increases markedly. The interfacial free energy equals $\Delta G_s = \gamma_i dA$ at constant temperature, volume, and number of moles constants (dA representing the increase in interfacial area). Consequently, only if γ_i is negative will ΔG_s decrease and conditions of spontaneous emulsification will be reached. When two liquids are immiscible, γ_i is always positive. It is common knowledge that in order to produce an emulsion, additives are used to reduce the interfacial tension γ_i . γ_i is equal to the work necessary to increase isothermally and reversibly the interface by 1 cm^2 . These additives are surfactants which are amphiphatic molecules adsorbed at the O/W interface. It is a known fact that the use of two surface substances in the right proportion produce better emulsions. Following these considerations, Hoar and Schulman suggested the following method to prepare microemulsions (1).

Surfactant, oil, and water are mixed together to form a lactecent emulsion and then titrated with the fourth component, the cosurfactant, until the mixture becomes clear. In the case of a W/O system, if more oil is added the system will become milky again but addition of more cosurfactant will clear the system.

The rationale behind this titration method of preparation is to obtain the optimum interfacial film combination that will produce the condition of negative interfacial tension.

*Calculation of Amount of Surfactant
in Preparation of Microemulsion*

It is assumed that all the surfactant molecules will be at the O/W interface. The total interfacial area A will be equal to

$$A = n \times \sigma = a \times 4\pi r^2$$

and the total volume of the dispersed phase will be equal to

$$V = a \times \frac{4}{3} \pi r^3$$

where

- n = number of surfactant molecules
- σ = cross-sectional area occupied by the surfactant molecule at the O/W interface
- a = total number of droplets of the dispersed phase
- r = radius of the spherical droplet

Combining the two equations gives:

$$r = \frac{3V}{n \times \sigma} \quad (1)$$

For water-in-benzene microemulsions stabilized by potassium oleate and *p*-methylcyclohexanol, the calculated droplet size agreed with those by light scattering if a $\sigma = 70 \text{ \AA}^2$ is used (6).

Using eq 1 to calculate the weight of sodium lauryl sulfate (SDS) to microemulsify 5 ml of H_2O in *n*-hexadecane, the following values were used: $r = 500 \text{ \AA}$ or $\sigma = 50 \text{ \AA}^2$ per molecule. Therefore, $n = 0.6 \times 10^{21}$ molecules which corresponds to 0.287 g of SDS

To summarize the preparation: 0.287 g of SDS is dissolved in 5 ml of H_2O ; 25 ml of *n*-hexadecane is added, then titrated while stirring with 1-pentanol until clarity is achieved. 1-Pentanol is not too soluble in oil or in water and is an efficient cosurfactant with this W/O system. Addition of more *n*-hexadecane will transform the system into a milk but addition of more 1-pentanol will clear the system again.

RESULTS

Figure 1 represents W/O microemulsions prepared by adding 40 ml of *n*-hexadecane and 0.0032 moles of carboxylic acid, 1.5 ml of 2.2*N* base solution, and titrating the mixture to clarity with 1-pentanol at 30°C. Ten or 20 ml of oil was then added, causing a transition from the clear microemulsion to a macroemulsion with a concomitant increase in turbidity. Clarity was reproduced in the sample by again titrating with alcohol. This procedure was repeated several times to get a sufficient number of points to plot. The intercept (*I*) was taken to be the number of moles of alcohol at the interface per mole of surfactant. The amount of 1-pentanol dissolved in the dispersed phase was assumed negligible. The slope (*K*) gave the solubility of the alcohol in the continuous phase (5). From the data, the free energy per mole for the absorption of alcohol into the interphase from the continuous phase was calculated using the formula:

$$\Delta G_s = - RT \ln (X_a^i / X_a^s)$$

where X_a^i and X_a^s are the mole fraction of pentanol in the interphase and the continuous phase, respectively.

The intercepts, slopes, and ΔG_s are tabulated in Tables I and II for several surfactant combinations. It was noted all ΔG_s are small negative values for these systems.

When *n*-hexadecane was used as the oil phase, the requirement for pentanol diminished and the free energy for adsorption decreased slightly as the chain length of the sulfate surfactant was increased. The same trend was shown with the carboxylates although it was less marked.

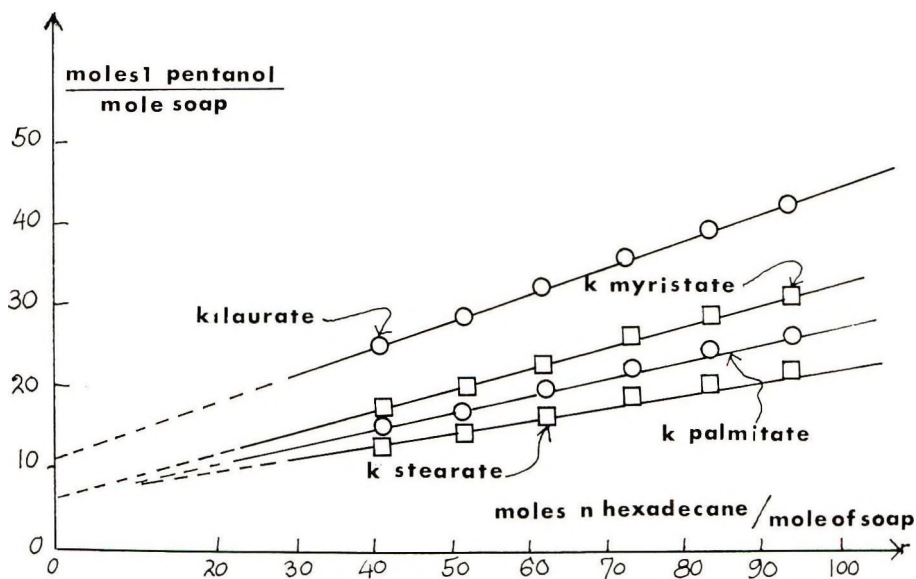
Figure 1. Microemulsions in *n*-hexadecane

Table I

Water-*n*-hexadecane Microemulsions at 30°C
(40.0 ml *n*-hexadecane; 1.44 ml water; 0.0032 moles surfactant)

| Chain Length | Long-Chain Sodium Sulfates | | | | ΔG_s kcal/mole |
|--|----------------------------|-------|---|--|---------------------------|
| | X_1 | X_2 | $\frac{k}{I}$ $\frac{\text{Moles Pentanol}}{\text{Moles Oil}}$ | $\frac{I}{k}$ $\frac{\text{Moles Pentanol}}{\text{Moles Soap}}$ | |
| C ₈ | 0.97 | 0.36 | 0.57 | 28.5 | -0.59 |
| C ₈ | 0.96 | 0.35 | 0.5 | 24.5 | -0.60 |
| C ₁₀ | 0.93 | 0.29 | 0.41 | 14.0 | -0.70 |
| C ₁₂ | 0.88 | 0.20 | 0.25 | 7.5 | -0.89 |
| C ₁₄ | 0.86 | 0.21 | 0.27 | 6.5 | -0.85 |
| Counter Ion | Dodecyl Sulfates | | | | ΔG_s kcal/mole |
| | X_1 | X_2 | $\frac{k}{I}$ $\frac{\text{Moles Pentanol}}{\text{Moles Oil}}$ | $\frac{I}{k}$ $\frac{\text{Moles Pentanol}}{\text{Moles Soap}}$ | |
| Li ⁺ | 0.78 | 0.22 | 0.29 | 3.5 | -0.75 |
| Na ⁺ | 0.88 | 0.22 | 0.28 | 7.5 | -0.84 |
| K | 0.88 | 0.22 | 0.28 | 7.5 | -0.84 |
| Rb ⁺ | 0.83 | 0.24 | 0.31 | 5.0 | -0.76 |
| Cs ⁺ | 0.78 | 0.22 | 0.29 | 3.5 | -0.75 |
| NH ₄ ⁺ | 0.78 | 0.22 | 0.29 | 3.5 | -0.75 |
| (CH ₃) ₄ N ⁺ | 0.92 | 0.28 | 0.38 | 11.5 | -0.72 |
| (C ₂ H ₅) ₂ N ⁺ | 0.93 | 0.31 | 0.45 | 13.5 | -0.66 |
| AMP | 0.90 | 0.28 | 0.40 | 8.5 | -0.69 |

Table II
Water-Benzene Microemulsions at 30° C
(40.0 ml benzene; 1.44 ml water; 0.0032 moles surfactant)

| Long-Chain Sodium Sulfates | | | | | |
|--|-------|-------|--|---|---------------------------------------|
| Chain Length | X_i | X_s | k | l | $\frac{\Delta G_s}{\text{kcal mole}}$ |
| | | | $\frac{\text{Moles Pentanol}}{\text{Moles Oil}}$ | $\frac{\text{Moles Pentanol}}{\text{Moles Soap}}$ | |
| C ₆ | 0.96 | 0.11 | 0.12 | 23.5 | -1.29 |
| C ₈ | 0.90 | 0.12 | 0.13 | 9.0 | -1.22 |
| C ₁₀ | 0.88 | 0.10 | 0.11 | 7.5 | -1.32 |
| C ₁₂ | 0.90 | 0.09 | 0.10 | 9.5 | -1.38 |
| C ₁₄ | 0.90 | 0.36 | 0.04 | 9.5 | -1.94 |
| Dodecyl Sulfates | | | | | |
| Counter Ion | X_i | X_s | k | l | $\frac{\Delta G_s}{\text{kcal mole}}$ |
| | | | $\frac{\text{Moles Pentanol}}{\text{Moles Oil}}$ | $\frac{\text{Moles Pentanol}}{\text{Moles Soap}}$ | |
| Li ⁺ | 0.86 | 0.08 | 0.09 | 6.0 | -1.39 |
| Na ⁺ | 0.90 | 0.10 | 0.11 | 9.0 | -1.32 |
| K ⁺ | 0.86 | 0.08 | 0.09 | 6.0 | -1.39 |
| Rb ⁺ | 0.80 | 0.06 | 0.07 | 4.0 | -1.53 |
| Cs ⁺ | 0.83 | 0.06 | 0.07 | 5.0 | -1.55 |
| NH ₄ ⁺ | 0.80 | 0.08 | 0.08 | 4.0 | -1.41 |
| (CH ₃) ₄ N ⁺ | 0.85 | 0.09 | 0.10 | 5.5 | -1.34 |
| AMP | 0.71 | 0.04 | 0.04 | 2.5 | -1.75 |
| Long-Chain Carboxylates ^a | | | | | |
| Chain Length | X_i | X_s | k | l | $\frac{\Delta G_s}{\text{kcal mole}}$ |
| | | | $\frac{\text{Moles Pentanol}}{\text{Moles Oil}}$ | $\frac{\text{Moles Pentanol}}{\text{Moles Soap}}$ | |
| Na carboxylate | | | | | |
| C ₁₂ | 0.91 | 0.12 | 0.14 | 10.0 | -1.22 |
| C ₁₄ | 0.90 | 0.11 | 0.12 | 9.0 | -1.29 |
| C ₁₆ | 0.85 | 0.02 | 0.02 | 5.5 | -2.26 |
| C ₁₈ | | | No microemulsification | | |
| C ₂₀ | | | No microemulsification | | |
| K carboxylate | | | | | |
| C ₁₂ | 0.95 | 0.12 | 0.13 | 18.5 | -1.27 |
| C ₁₄ | 0.94 | 0.11 | 0.12 | 15.5 | -1.30 |
| C ₁₆ | 0.92 | 0.10 | 0.11 | 12.0 | -1.33 |
| C ₁₈ | 0.90 | 0.10 | 0.11 | 9.0 | -1.34 |
| Rb carboxylate | | | | | |
| C ₁₂ | 0.94 | 0.11 | 0.13 | 15.0 | -1.28 |
| C ₁₄ | 0.91 | 0.13 | 0.14 | 10.5 | -1.19 |
| C ₁₆ | 0.89 | 0.11 | 0.13 | 8.0 | -1.24 _r |
| C ₁₈ | 0.88 | 0.10 | 0.12 | 7.0 | -1.28 |
| C ₂₀ | 0.88 | 0.09 | 0.10 | 7.0 | -1.36 |

^a Ammonium carboxylates and AMP carboxylates did not form microemulsions with benzene.

The same trends were noted when benzene was substituted for *n*-hexadecane and carboxylates were used as the surfactants. However, no leveling in the value of *I* was observed except when rubidium was the counterion and then it occurred at higher value, C₁₈. The values of *I* were significantly higher in benzene than in *n*-hexadecane in the case of the carboxylates. In all cases, the ΔG_s was lower in benzene than in *n*-hexadecane. The behavior of the long-chain sulfates in benzene was slightly different in that a minimum value was reached; C₁₀ and C₈, and C₁₂ and C₁₄ demonstrated the same requirements for cosurfactant.

The effect of changing the counterion is not as clear cut. The sterically larger counterions, such as tetramethyl and tetraethylammonium ion, required the largest amount of pentanol in the interface in hexadecane but these cations did not show any significant difference from Cs⁺, K⁺, Li⁺, Rb⁺, and NH₄⁺, in benzene when the dodecyl sulfate was the anion. The value *I* did not show any ordering in terms of the size of the counterion for the alkali cations and it is felt that this type of experiment is not sensitive enough to detect fine differences in very similar counterions.

In conclusion, these results indicate, in the systems discussed, strong interactions between the surfactant and cosurfactant molecules are not necessary for microemulsion formation.

Up to now the discussion has dealt with the case of dilute W/O microemulsions. Ternary phase diagrams of a four-component system were prepared. In the present example shown here, certain clear isotropic regions of low viscosity are observed when the K-oleate concentration was held constant (Fig. 2). On the ternary diagram there are two regions on microemulsions. It is also clear that the four components have to be mixed in the right proportions.

Association between the surfactant and cosurfactant has rarely been investigated in these systems. Interaction between the water and surfactant has been observed in water in chloroform microemulsions stabilized by decyltrimethylammonium bromide (11). Schulman and Montagne (12) investigated the conditions necessary for the formation of microemulsions in systems capable of forming strong hydrogen bonds by a film balance method, the validity of which they later doubted (13). They found that in systems capable of forming strong intermolecular hydrogen bonds, microemulsions could be formed. Those systems not capable of forming intermolecular hydrogen bonds did not form microemulsions. These results indicated that, in the systems discussed, strong interactions between the surfactant molecules and surfactant and cosurfactant molecules were necessary for microemulsion formation.

The results reported in this study conflict with this view. The work of Fowkes (14) with mixed films of sodium cetyl sulfate and cetyl alcohol at planar air-aqueous NaCl interfaces lent support to the view that strong stoichiometric complexing between the alcohol and surfactant was not necessary

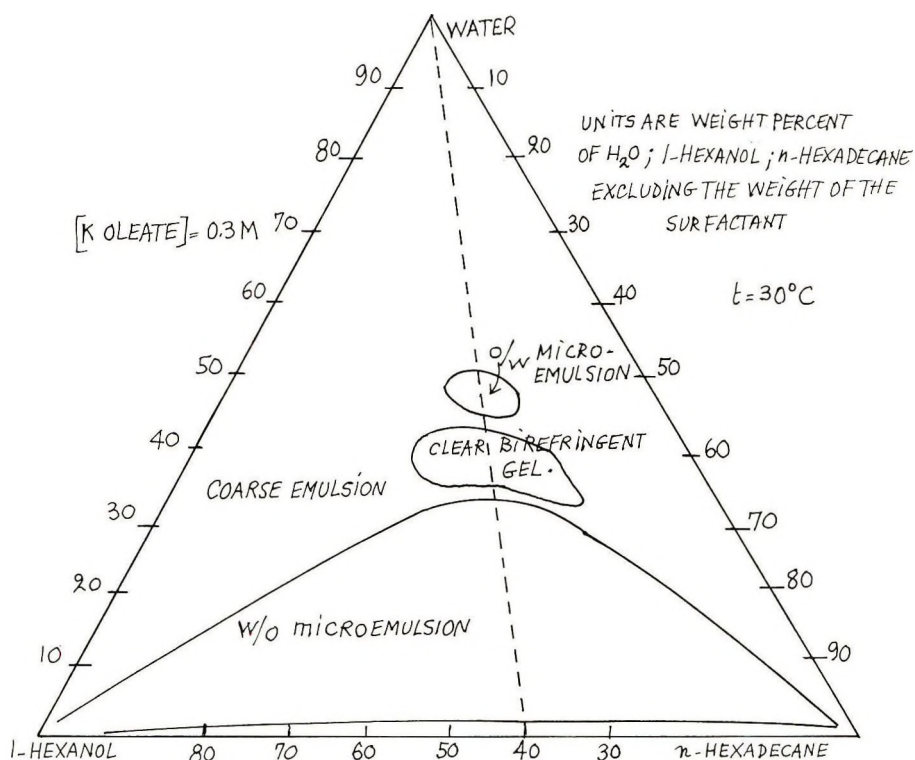


Figure 2. Water-*n*-hexadecane-1-hexanol phase diagram with K-oleate as surfactant in the concentration range of 0.4M to 0.2M

to produce a large film pressure. High film pressures at the oil/water interface would be necessary to reduce the γ_i to zero. We investigated the interaction K-oleate/1-hexanol by NMR for the systems along the dotted line on Fig. 2 and found practically no interaction. These results will be published later. We finally concluded that the Schulman theory was not adequate to explain the lack of cosurfactant/surfactant interaction, and also the fact that a spherical droplet means generally a minimum area for a given volume which in turn implies the existence of a positive interfacial tension. In addition, all the discussions offered thus far have not considered the dynamic effect of the cosurfactant in lowering γ_i by transport through the O/W interface. This aspect will be considered now.

Interfacial Tension

The interfacial tension of water against oil as a function of time monitored by using an automated Wilhelmy slide method (15). A sandblasted Pt blade pre-wet with water was attached by a thread to a microforce trans-

ducer. The signal from the transducer was amplified by a transducer amplifier.* The signal was then plotted as a function of time on a calibrated strip-chart recorder.† If the blade was drawn through an aqueous-oil interface, the signal was proportional to γ_i . No hysteresis was observed on drawing the blade through the interface from either side; therefore, it was assumed the contact angle was zero.

1-Pentanol was injected into one of the phases by using an Agla micrometer syringe‡ accurate to 0.00005 ml. Gentle stirring was maintained in the phase in which the alcohol was being injected by using a magnetic stirrer (aqueous phase) or a motorized glass stirrer (oil phase). Several injections were made into each phase so that the systems in Fig. 3 contain varying amounts of alcohol. Fifty milliliters each of the oil and aqueous phase were used.

SDS solution was introduced into the aqueous phase by injecting an appropriate amount. Sufficient time was allowed for the interface to reach equilibrium before alcohol was injected. This was judged by the stability of γ_i as a function of time.

*Transducer and amplifier manufactured by Hewlett-Packard Corp., Palo Alto, Calif.

†Sargent-Welch Corp., Skokie, Ill.

‡Burroughs-Wellcome and Co., Durham, N.C.

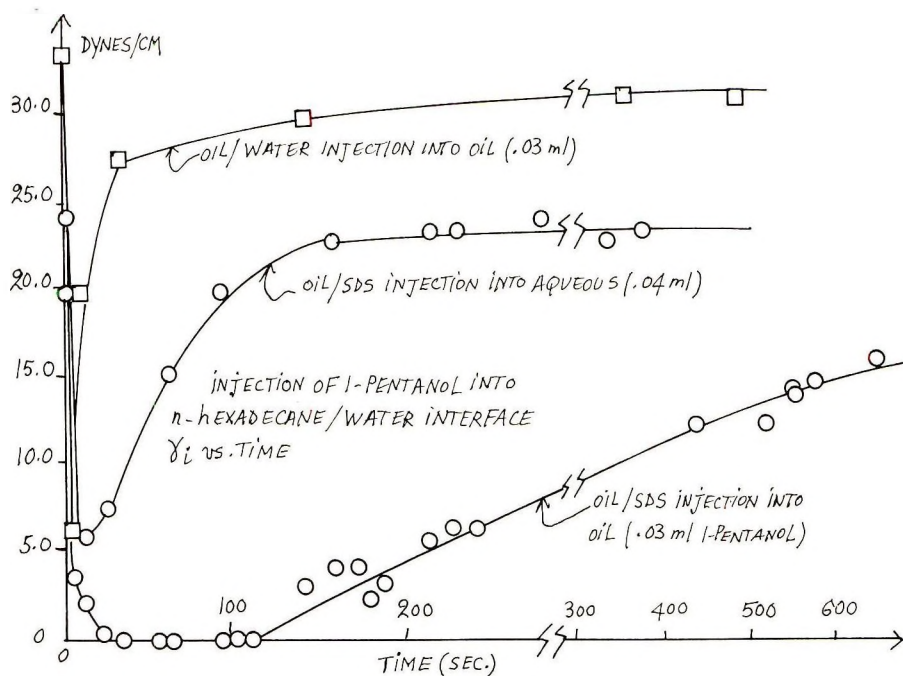


Figure 3. Injection of 1-pentanol into *n*-hexadecane/water interface (γ_i vs. time)

All systems were maintained at 30°C in a thermostated beaker 4.90 cm in diameter. The interface was cleaned initially before any injections were done by using suction through a narrow pipet.

It was observed that less alcohol was required to reduce γ_i to zero when injecting into *n*-hexadecane than when injecting into the aqueous solution. The rate of transport of pentanol across the interface was severely reduced in the presence of the absorbed monolayer of surfactant.

As mentioned previously, microemulsions are generally prepared by titrating with one of the components or by mixing all of the component parts together. Either method allows transport of the amphiphatic molecules through the interface. To determine if transport of some part is necessary for microemulsification, an aqueous solution of surfactant and pentanol was prepared. The solution contained the amount of pentanol that would be present in the final microemulsion, as determined by the distribution data given in the tables presented. Another solution of oil and its ratio of pentanol was prepared and the two solutions were mixed together for approximately 20 min but no microemulsion was formed. Microemulsions generally form almost immediately when the correct conditions are provided. The systems were not even stable with regard to phase separation upon standing for a few minutes.

DISCUSSION

It is apparent from the above experiments that it is possible for the interfacial tension of a system to drop to zero for a certain period of time due to redistribution of amphiphatic molecules while the equilibrium γ_i remains positive.

The requirement of transport across the interface in these systems was demonstrated in the experiments last described. The diffusion process has been mentioned before as a necessary condition for spontaneous emulsification (16, 17) but it is not a sufficient condition for microemulsification in these systems since 1-pentanol does not produce microemulsions in all of the dodecyl sulfate systems. It is reasonable that the surfactant must be able to stabilize the system against coagulation and coalescence after the cosurfactant has lowered γ_i sufficiently to cause dispersion. The ability of surfactant to accomplish this would depend upon the type of interfacial film it forms with the alcohol and oil present.

The larger requirement for alcohol in the systems with the bulkier counterions may be explained by the consideration that surfactants of this type would produce a more expanded interfacial film permitting faster transport of the alcohol through the interface and, therefore, the maximum film pressure would not be maintained for as long a period of time. The same reasoning would explain the effect of increasing the chain length of the surfactant. The shorter chain lengths would give a more expanded film and

permit faster transport of the alcohol. If the chain length is too long, however, transport through the interface would be too slow and the effect of the alcohol in lowering γ_i would be diminished.

It has previously been pointed out that strong association between the surfactant and cosurfactant is not necessary for microemulsification and that nonionic and ionic amphiphatic molecules, in general, adsorb independantly (17, 18). The calculated free energies for adsorption of the pentanol are small, indicating little association between the surfactant and cosurfactant—in agreement with Rosano *et al.* (5). The absence of strong interfacial complexing between the surfactant and cosurfactant was also indicated in NMR studies of W/O microemulsion in CCl_4 stabilized by long-chain sulfates (19).

It was pointed out by Adamson (6) that only a small binding energy between the surfactant and cosurfactant (100 cal/mole) is, in fact, necessary to prevent coagulation of the microemulsion droplets. The above values are well within this range. This does not exclude the possibility of strong association in the interfacial film occurring when it is feasible (12).

It seems then, that there are two parts to the process of microemulsion formation, dispersion and stabilization. The previous arguments in terms of film penetration, interfacial complexing, interfacial tension, etc., should be applied, bearing in mind the effects due to redistribution of the amphiphatic molecules amongst the phases present. It is also possible that if enough surfactant and cosurfactant are present in the right proportions, the equilibrium γ_i could be zero which would imply a spontaneous dispersion. This would be the situation assumed by Schulman.

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Antiperspirants: New Trends in Formulation and Testing Technology

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Presented December 11, 1973, New York City

Synopsis—Aluminum chlorhydroxide has been the most widely used active ingredient in ANTIPERSPIRANT FORMULATIONS. Recently, new chemicals, such as basic aluminum bromide, and combinations of aluminum, zirconium, and other metal salts have been introduced. In addition, new product forms are constantly being developed with different performance and cosmetic characteristics. The properties of the new active ingredients and the new formulations are discussed with respect to formulation VERSATILITY, COSMETIC ELEGANCE and EFFICACY. General methods used to evaluate staining potential, and deodorant and antiperspirant efficacy of these products are reviewed. A normal activity method for determining antiperspirant efficacy is compared with a method based on a thermally controlled environment, and the results obtained with these two techniques are discussed.

INTRODUCTION

Antiperspirant formulations based upon metal salts such as aluminum, zinc, or magnesium chlorides, sulfates, acetates, or sulfocarbolates as the active ingredients have been known for a long time (1, 2). The most important antiperspirant chemical used is basic aluminum chlorhydroxide (ACH) which is safer, less corrosive, and readily formulated into a variety of products (3).

The deodorant and antiperspirant market has changed dramatically over the years. Until *ca.* 1960, the most important product forms were lotions, creams, sticks, or powders, representing a 100 million dollar per year business. In 1960, aerosol deodorants, primarily alcoholic solutions containing an antimicrobial agent, came into the market, and by 1966, doubled the size of the business (4). Early attempts to develop antiperspirants in an aerosol form ran into trouble because of the acidic nature of the active ingredients. Most problems involved packaging incompatibility, valve clogging, and perfume stability. They mostly were solved by the mid-sixties (5), resulting in the introduction of a number of different types of aerosol antiperspirants.

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The early aerosol antiperspirants introduced were the so-called powder-in-oil type formulations containing 3-4% of active ingredients suspended in an oil base. There were also solution-type formulations, some in glass aerosols because of corrosion problems.

In 1971, a cosmetically different antiperspirant product was developed, an "aerosol powder"; another version, a so-called "hybrid" appeared in the marketplace one year later. The hybrid has a somewhat higher active level than the regular powder-in-oil and powder antiperspirants and lies between these products in cosmetic elegance.

The most important performance attributes of an antiperspirant are its anhydrotic and deodorant effects. In addition, the formulation must possess aesthetic and cosmetic qualities. One frequently observed drawback of these products has been their tendency to cause fabric staining. It is the purpose of this paper to discuss recent trends in the formulation of aerosol antiperspirants and some of the testing methods used to evaluate performance characteristics.

AEROSOL ANTIPERSPIRANT FORMULATIONS

Most aerosol antiperspirant formulations contain the following components: the active ingredients, usually aluminum chlorhydroxide or similar salts, a liquid system which serves either to solubilize or to suspend the active ingredient or is part of a water-in-oil emulsion, miscellaneous additives such as talc, perfume, suspending agents, and propellants. Suspension systems represent the most commercially important examples. Some products based on solution systems have been marketed, but have not been too successful. While providing somewhat greater antiperspirant efficacy, solutions are cosmetically less pleasing.

Many combinations of raw materials are available for the formulation of aerosol antiperspirants and their selection must be carefully considered, since the surface chemistry of the system can affect sedimentation and dispersion characteristics of the formula. In addition, formulations must provide maximum antiperspirant and deodorant effectiveness, maximum safety, cosmetic elegance, and minimum staining.

Active Ingredients

Aluminum chloride has been recognized for many years as an excellent antiperspirant. However, because of its low pH, it will cause fabric damage and skin irritation (6). This had led to the development of various basic aluminum compounds which are less acidic than the parent product. The most frequently used of these derivatives is basic aluminum chlorhydroxide. Other metal salts that have been formulated into antiperspirants are shown in Table I. In addition to these compounds which are considered to interfere

Table I
Active Ingredients for Antiperspirant Formulations

| |
|---|
| Aluminum chlorhydrate |
| Aluminum chloride |
| Basic aluminum bromide |
| Basic aluminum hydroxychloride–zirconyl hydroxy oxychloride |
| Aluminum hydroxychloride–zirconyl hydroxy oxychloride–glycine complex |
| Basic aluminum nitrate |
| Basic aluminum bromide–zirconyl hydroxy oxybromide |
| Magnesium aluminum zirconium gluconate chloride |
| Basic aluminum iodide |

with the sweat duct (7), other materials that have been reported include formaldehyde (8) and compounds such as anticholinergic scopolamine derivatives (9).

Amongst the metal salts which have gained some commercial importance are basic aluminum bromide (BAB) and certain zirconium complexes. Zirconium oxychloride ($ZrOCl_2$) and zirconyl hydroxychloride [$ZrO(OH)Cl$] have good antiperspirant activity, but the aqueous pH of these compounds is very low. The use of zirconium compounds as antiperspirant actives has required raising the pH without causing precipitation. Commercially, this has been achieved by buffering the zirconium salts with basic aluminum salts (10–14). While this can cause considerable gelling (14), it was found that the addition of certain amino acids such as glycine (11, 14) can control the gelation problem. There are also patents covering aluminum zirconium systems using different buffering systems in antiperspirant formulations (15, 16). A number of experimental salts have also been investigated, including basic aluminum nitrates, iodides, and mixed metal systems.

Suspending Oils

Some of the cosmetic oils used in powder-in-oil formulations are listed in Table II. They include isopropyl and propylene glycol esters of various long-

Table II
Cosmetic Oils Used in Aerosol Powder-in-oil Antiperspirants

| |
|---|
| Isopropyl myristate |
| Isopropyl palmitate |
| Mixed isopropyl esters of various fatty acids |
| Propylene glycol dicaprate |
| Propylene glycol 400 monolaurate |
| Propylene glycol dipelargonate |
| Triethyl citrate |
| Dibutyl phthalate |
| Organosilicones |

chain fatty acids, homopolymers of polypropylene oxide, dibutyl phthalate, Tween 60, and certain organosilicones. Properties of these oils include low odor, low viscosity, and good stability.

Suspending Agents

Suspending agents are frequently used in aerosol powder-in-oil systems where the active material is dispersed rather than dissolved. The suspending agents reduce the rate of settling of the dispersed materials.

An effective suspending agent commonly used is Bentone 34,[°] an organic derivative of hydrous magnesium aluminum silicate. Bentone requires batch heating and extensive homogenization. Homogenization causes the formation of hydrogen bonds between silica sites, resulting in lattice formation.

Another frequently used suspending agent is Cab-O-Sil,[†] a fire-dry fumed silica. Chains are formed *via* hydrogen bonds, and with shear mixing, an effective lattice structure can be created. Cab-O-Sil is quite sensitive to the presence and the ionic nature of other materials in the formulation. Syloid 244[‡] is another high-porosity micron-sized silica that has also been used.

The type of suspending agent used in antiperspirant powder formulations can be readily identified from X-ray diffraction determinations.

Propellants

The propellants used in aerosol antiperspirants serve several important functions: they deliver the product, serve as diluents and/or solvents, and assist in product "drying." General factors such as bounce and coldness are directly related. The colder sprays generally produce less bounce, and this is a function of the boiling points of the various propellants used. Several trade-offs are frequently necessary in optimizing an antiperspirant propellant system.

POWDER-IN-OIL FORMULATIONS

Powder-in-oil formulations represent the most important category of products presently on the market. This category contains three different types: regular powder-in-oil formulations, the so-called aerosol powders, and hybrid formulations. There are very noticeable differences from the cosmetic and aesthetic point of view between these three product forms. A typical powder-in-oil formulation is the following:

[°]NL Industries, 111 Broadway, New York, N.Y.

[†]Cabot, 125 High St., Boston, Mass.

[‡]W. R. Grace & Co., Baltimore, Md.

| Ingredient | Per Cent |
|-------------------------|----------|
| Aluminum chlorhydroxide | 3.5 |
| Isopropyl myristate | 6.0 |
| Cab-O-Sil | 0.3 |
| Perfume | 0.2 |
| Propellant | 90.0 |

Aerosol powder formulations contain about the same level of ingredients as powder-in-oils versions, but in addition also contain 1% of talc. Also, the oil level is considerably lower. A typical formula is shown below:

| Ingredient | Per Cent |
|-------------------------|----------|
| Aluminum chlorhydroxide | 3.5 |
| Talc | 1.0 |
| Suspending oil | 1.5 |
| Cab-O-Sil | 0.3 |
| Perfume | 0.2 |
| Propellant | 93.5 |

The hybrid-type formulations are similar to powder-in-oil formulations except for a higher active ingredient level (5% *vs.* 3.5%).

The differences between these three formulations are summarized in Table III. As can be seen, the ratio of active ingredient levels to the amount of oil used ranges from 0.6 for the powder-in-oil formula, to a 1.1 ratio for the hybrid product, and a ratio of 2.3 for the powder.

Table III
Formulation Differences between Aerosol Powder-in-oil,
Powder, and Hybrid Antiperspirants

| Formulation Type | % Active | % Oil | % Talc | Active: Oil Ratio |
|------------------|----------|-------|--------|-------------------|
| Powder-in-oil | 3.5 | 6.0 | ... | 0.6 |
| Hybrid | 5.0 | 4.5 | ... | 1.1 |
| Powder | 3.5 | 1.5 | 1.0 | 2.3 |

Three hybrid-type products have appeared in the marketplace. While fitting into the above general formulation system, there have been significant differences in the active ingredients and the suspending oils that were used, as shown in Table IV. All contain approximately 5% of active ingredient, but the actives differ considerably. The first contains the traditional basic aluminum chlorhydroxide powder, the second, a buffered aluminum chlorhydroxide/zirconyl hydroxy oxychloride complex, while the third uses a buffered aluminum chlorhydroxide/zirconyl hydroxy oxychloride glycine complex. The suspending oils also differ considerably.

The hybrid formulations provide somewhat higher antiperspirant efficacy than regular powder-in-oil formulations, probably because of the higher ac-

Table IV
Formulation Differences in Active Ingredients
and Suspending Oils of Three Hybrid Antiperspirants

| Product | Active Ingredients | Suspending Oil |
|---------|--|--------------------------------------|
| 1 | 5% aluminum chlorhydroxide | Mixed silicones |
| 2 | 5% basic aluminum hydroxychloride– zirconyl hydroxy oxychloride | Mixed silicones/ triethyl citrate |
| 3 | 5% aluminum hydroxychloride– zirconyl hydroxychloride– glycine complex | Dibutyl phthalate |

tive level. All three are cosmetically very acceptable. Two of the products have eliminated the staining problem often associated with aerosol antiperspirants, while one still causes considerable staining.

EVALUATION PROCEDURES

Key performance criteria for which aerosol antiperspirants are tested include the following: antiperspirant efficacy, deodorant efficacy, staining potential, and cosmetic acceptability.

Antiperspirant Efficacy Evaluation

Antiperspirant efficacy may be measured utilizing both *in vitro* and *in vivo* methods. Qualitative procedures fashioned after the work of Minor (18), who used starch-iodine indicators, involved development of so-called sweat pore patterns. Various dyes and indicators have been used in conjunction with papers, pastes, films, and lacquers (19). Zahejsky and Rovensky (20) described the use of a contact indicator spot test which was based on a color reaction between pyrogallol and ferric hydroxide in the presence of water from sweat. These procedures have value in locating and studying the activity of sweat glands.

Some *in vitro* methods are based upon the fact that aluminum salts are astringents and are capable of denaturing proteins (21), and upon the observation that permeability to sodium and iodide ions increases after treatment with aluminum salts (22).

Quantitative measures of the reduction in perspiration are usually made using gravimetric or humidity sensing techniques with human volunteers. Some attempts have been made to use animals, such as cats, mice, or rats for sweat testing purposes, but the sweat glands in these species are confined to the foot pads, and even though they have eccrine glands, they differ histologically from those of man (22–24). Recently, Lansdown evaluated the use of rat foot pads as a model for examining antiperspirants (25).

In human volunteers, gravimetric measurement of the total amount of perspiration secreted may be accomplished by the use of weighed pads or by the use of dessicant cups (26). Other types of measurement utilized resistance hygrometry, collection coils, phosphorus pentoxide cells, and electrolytic cells (27-30).

Factors Affecting Sweating Rate

Fredell and Read (31, 32) observed that there are differences in the amount of sweat produced from right to left axilla, but that the ratio of these differences is fairly consistent. They recommended that a ratio between treated and control axillae be used in judging effectiveness. Segar (27) demonstrated that sweating is a cyclical process and is not proportional to the number of total glands.

Uttley (33) recently reviewed some of the factors influencing sweating which must be considered in a test procedure. These include: relative humidity, equilibrium of sweating rate, emotional or mental stimulation, position of the body during sweating, skin area being tested, skin temperature, conditioning to environment, sex differences, and metabolic rate.

Based upon our studies, we agree with the observations of earlier workers (19, 32, 34) that a gravimetric method employing absorbent pads is an adequate procedure. Reller (19) observed that absorbent pads are more acceptable physiologically than cups.

Methods of Evaluation

We have tested two basic variations of the gravimetric method, the major difference being in the procedure used for stimulation and collection of perspiration. The first method, termed "normal activity method," utilizes normal environment conditions. The second method, termed "controlled environment method," employs thermally controlled environmental conditions. In both methods, a ratio of sweat produced by the left and right axilla is determined in a series of controlled collections. The effect of antiperspirant materials on the perspiration rate of each individual is determined by comparing the post-treatment ratio to the subjects' average control ratio. For each individual, the per cent change in sweat rate is calculated as:

$$\% \text{ change in sweat rate} = 100 \left(1 - \frac{\text{post-treatment ratio}}{\text{average control ratio}} \right)$$

These data are statistically treated by applying the Student *t* distribution to establish 85% confidence limits on the mean per cent change in sweat ratio.

Normal Activity Method

In the normal activity method, a group of panelists are recruited who remain together as a panel for at least 12 months. Prior to the start of

using the panel for test purposes, their left-to-right axillary sweating ratio is determined 12 times over a 4-week period. The average result from these determinations is used as the control ratio for each panelist for the life of the panel.

Before the start of any test, there is a 5-day period in which the panelists use no underarm products except a placebo soap. Following this are three consecutive days of antiperspirant testing. There are 15–20 people in a mixed-sex panel. Test material is applied only to the left axilla, the right axilla serving as the control. For roll-on formulations, 1 g of product is applied with a soft brush. For aerosols, a 1-sec spray from a distance of 6 in. is applied uniformly to the axillary vault. Sample application is made by a technician, using a metronome to time the spray. After 5 min, to permit evaporation of any volatile materials, a preweighed moisture collection pad is applied. These pads, measuring 2 in. x 2 in., are fashioned from sanitary napkins by stripping away several layers of cellulose filler in order to get a better axillary fit. Pads are held in place by strips of hypoallergenic tape. The exterior surface of the pad itself is covered with Saran Wrap in order to retain absorbed moisture.

The panelists are then free to pursue normal activities for 4 hours. At the end of the 4-hour period, the absorbent pads are removed and placed in tared plastic ointment jars and weight of perspiration is determined by difference.

Controlled Environment Method

In the controlled environment method, approximately the same number of panelists are used. They are asked to abstain from the use of all antiperspirant materials at least one week prior to enrollment through the completion of the test. Controlled sweat collections are made on Monday and Tuesday of the test week. Post treatment sweat collections are made on Wednesday, Thursday, and Friday. Test materials are assigned in such a way that samples are applied to the right axilla of half the panelists and to the left axilla of the remaining panelists. Axillae are rinsed with clear, warm water and dried just before each application. For aerosol products, the axillae are sprayed from the distance of 6 in. for 2 sec. Materials are applied immediately following the controlled sweat collection on Tuesday, 1 hour prior to sweat collection on Wednesday, Thursday, and Friday.

Sweating is induced by having the subject sit in a room maintained at $100^{\circ} \pm 2^{\circ}$ F and at a relative humidity of 35%. During the first 40 min of the sweat stimulation period, the panelists hold unweighed pads of Webril,* a nonwoven cotton, in their axillae. This preliminary warmup period is followed by two successive 20-min collection periods during which panelists hold pre-weighed Webril pads in the axillae. Panelists are allowed to drink ice wa-

*Kendall Co., Walpole, Mass.

ter as desired throughout the collection period. At the end of each collection period, the pads are removed and placed in tared bottles for reweighing. Antiperspirant activity is calculated as described previously.

Deodorant Efficacy Evaluation

Deodorant effectiveness is a recognized attribute of many metal salts (35–37). Efficacy is evaluated by comparison of the effect of one treatment in one axilla *versus* a second treatment in the other axilla of the individuals in panel groups (34, 38). Similar comparative methods may employ a crossover procedure. Product comparisons using a split axilla treatment without crossover in a single group suffer in reliability because odor intensity of the axillae of an individual varies. However, when the test sites in a panel are randomized by a crossover procedure, effects due to inherent differences in the axillae are minimized.

Axillary odor may be judged by the panel participants themselves, by trained judges, or both. Length of deodorant effect is usually determined at various intervals during the test, or at cessation to treatment. Evaluation may be made by estimating the degree of odor of both the axillae and the undergarment at the side of contact. Odor judgments obtained are usually based upon arbitrary numerical scales (38–40). Because these are subjective evaluations, several investigators have attempted to eliminate sources of error through the use of osmometers (41).

Utilizing a crossover method in which odor evaluations were made by trained judges, a clear deodorant effect was shown for a powder-in-oil formulation and an aerosol powder formulation, both containing 3.5% aluminum chlorhydroxide. An odor scale of 1 (little or no odor) to 5 (strong or disagreeable odor) was used. The results are shown in Table V. The data from the test and control periods were subjected to Student's *t* test and were highly significant.

A recent advance in evaluating deodorant efficacy is that developed by Dravnieks and coworkers (42, 43). Their method is based on the development of chromatographic patterns of axillary odors.

Staining Potential

Soon after the introduction of aerosol antiperspirants, it became apparent that fabric staining in the axillary area was a major problem. Initially, formulations were tested for staining propensity by applying the product directly to the fabric. It was found that this was not a satisfactory procedure since it did not reflect actual use conditions and a comparative procedure was developed.

In this procedure, a panel is used made up of 10 men and 10 women. Subjects are required to abstain from the use of all antiperspirants and deodorants or other products applied to the axillary area, and are required to use

Table V

In Vivo Deodorant Evaluation of Two Powder-In-Oil Antiperspirants
(Summary of Individual Mean Odor Scores^a)

| Subject Number | Control Period | | Test Period | |
|--------------------|----------------|---------------|-------------|---------------|
| | Dry Powder | Powder-In-Oil | Dry Powder | Powder-In-Oil |
| 1 | 4.5 | 4.7 | 2.0 | 1.9 |
| 2 | 4.0 | 4.3 | 2.8 | 2.4 |
| 3 | 4.9 | 4.7 | 1.3 | 1.5 |
| 4 | 4.1 | 4.1 | 1.8 | 1.8 |
| 5 | 5.0 | 5.0 | 1.9 | 1.8 |
| 6 | 4.8 | 4.8 | 2.8 | 2.4 |
| 8 | 2.9 | 3.0 | 2.0 | 2.2 |
| 9 | 4.0 | 4.3 | 1.5 | 1.5 |
| 10 | 3.6 | 3.8 | 1.9 | 1.7 |
| 11 | 4.4 | 4.6 | 2.9 | 2.8 |
| 12 | 4.0 | 3.7 | 2.9 | 2.7 |
| 14 | 4.4 | 3.9 | 2.3 | 1.5 |
| 15 | 4.2 | 4.5 | 2.3 | 2.5 |
| 16 | 4.5 | 4.5 | 3.6 | 3.2 |
| 17 | 3.1 | 3.2 | 2.2 | 2.1 |
| 18 | 4.3 | 4.3 | 2.1 | 1.9 |
| 19 | 3.5 | 3.5 | 2.5 | 2.6 |
| 20 | 4.6 | 3.6 | 2.4 | 2.0 |
| 21 | 4.2 | 4.4 | 3.1 | 2.9 |
| 22 | 4.3 | 3.2 | 2.0 | 1.9 |
| Mean | 4.16 | 4.11 | 2.32 | 2.16 |
| Standard Deviation | 0.5518 | 0.5862 | 0.5677 | 0.5008 |
| Standard Error | 0.1233 | 0.1310 | 0.1269 | 0.1119 |

^a A five-point scoring system was used, 1 being weak and 5 being strong and disagreeable odor.

only Ivory soap^o during the period of the test. T-shirts are supplied to the subjects at the beginning of the test period. A standard 3.5% powder-in-oil isopropyl myristate formulation is used for reference purposes. Subjects are evaluated for stain propensity in each axilla using the following schedule. On day 1, a 3-sec spray of the product is applied by a technician using a metronome for timing. The new T-shirt is then worn. Four hours later, the spraying procedure is repeated. Two hours later, the T-shirts are collected and laundered. The same routine is then followed for 2 more days. At the end of the third day, the axillary areas of each T-shirt are evaluated for intensity of stain using a photovolt reflectometer equipped with tristimulus filters. Readings are taken using each of the three filters and the staining value is calculated from the formula:

^oProcter & Gamble Co., Cincinnati, Ohio.

$$\frac{\text{amber-blue}}{\text{green}} \times 10$$

A typical value for the control formula is 0.7. A minimally visible stain yields a value of 0.3. A value of 1 or higher indicates a product which stains fabric considerably.

When evaluating test products, the procedure is the same as during the standardization except that the test product is substituted for the control. Application to the left and right axilla is randomized. Calculations are normalized to the control value of 0.7 so that results are reproducible. Some of the results obtained using this comparative method are shown in Table VI. There were considerable variations in stain potential of products, depending on product form and the type of suspending oils used.

Table VI
Staining Propensity of Aerosol Antiperspirant Formulations
(Three-Day Test Period)

| Formulation (Active/Oil) | Formulation Type | Staining Value |
|--|---------------------|----------------|
| 5% aluminum hydroxychloride— zirconyl hydroxychloride— glycine complex/dibutyl phthalate | Hybrid | 1.0 |
| 5% aluminum chlorhydrate/mixed silicones | Hybrid | 0.26 |
| 3.5% aluminum chlorhydrate/mixed silicones | Aerosol powder | 0.17 |
| 3.5% aluminum chlorhydrate/ isopropyl myristate | Powder in-oil | 0.70 |

Cosmetic Acceptability

In considering the overall properties of an antiperspirant, cosmetic and perfume qualities are a key consideration. The dispensing oils, when not runny, can create a pleasant tactile feel. The propellant, when optimized, can reduce coldness of the spray when applied to the skin. Overall, a product is cosmetically better when it goes on dry, without caking, and is gentle to both skin and clothing. The best technique for evaluating these properties and their overall effect on product acceptability is by full scale market research procedures, though some laboratory procedures for individual properties are also used.

Safety

The criteria for evaluating safety of antiperspirant formulations include a consideration of the effect of the product on the skin and its aerosolized properties. Routine safety evaluation of a new formulation comprises determination of acute oral and dermal toxicity, primary eye and skin irritation, acute and subacute inhalation studies in rabbits and monkeys, and sensitization in guinea pigs and in humans.

Aerosol antiperspirants have received considerable publicity as a result of potential inhalation hazards that may be associated with low-level, long-term exposure to propellant gases and particulate aerosols in general. Recently, Drew (44) reported that persistent lung granulomas were observed in hamsters exposed to an aerosolized liquid system based on a propylene glycol complex of ACH at 50 mg/m³ for 6 hours a day for 10, 20, and 30 days.

Antiperspirants are classified as drugs and are subject to the Food and Drug Administration's OTC review procedure. A request to provide safety and efficacy data for review by the OTC panel has been made (45) and hearings started in the early part of 1974.

ANTIPERSPIRANT TEST RESULTS

From the earlier description of the two methods for evaluating antiperspirant efficacy used in our laboratory, namely, the normal activity method and the controlled environment method, it seemed plausible to hypothesize that since methodologies were basically similar, the results too would be of the same order of magnitude, or at least provide similar directional guidelines.

Normal Activity Method

The result obtained when testing a standard powder-in-oil formulation on four different occasions spread over a period of a year and a half are shown in Table VII. The results are 3-day averages and are expressed with a confidence limit of 95%.

Table VII

Antiperspirant Efficacy of a 3.5%
Aluminum Chlorhydrate Powder-in-oil
Formulation (Normal Activity Method)

| Test Number | Mean % Sweat Reduction |
|-------------|------------------------|
| 1 | 20.6 ± 1.8 |
| 2 | 21.6 ± 2.6 |
| 3 | 21.0 ± 2.4 |
| 4 | 27.8 ± 2.7 |

Table VIII
Antiperspirant Efficacy of Different Actives
in Powder-in-oil Formulations (Normal Activity Method)

| | Per Cent Active | Mean % Sweat Reduction |
|--|--------------------|---------------------------|
| Aluminum chlorhydroxide | 3.5 | 22.8 ± 2.7 |
| Basic aluminum bromide | 3.5 | 23.6 ± 4.0 |
| Basic aluminum nitrate | 3.5 | 23.2 ± 3.9 |
| Basic aluminum bromide— zirconyl hydroxy oxy- bromide | 3.5 | 25.5 ± 4.0 |
| Basic aluminum hydroxy chloride—zirconyl hydroxy oxychloride | 3.5 | 25.1 ± 3.1 |
| Magnesium aluminum zirconium gluconate chloride | 3.5 | 22.4 ± 4.0 |
| Magnesium aluminum zirconium gluconate bromide | 3.5 | 22.7 ± 2.9 |

In a second series, different active materials were examined in a powder-in-oil formulation. The compounds tested and the efficacy results are listed in Table VIII. It was found that regardless of the active material used, the results all fell within a very narrow range.

The results obtained comparing the sweat reduction efficacy of different types of antiperspirant formulations including an aerosol powder-in-oil, an aerosol powder, a hybrid formula, a roll-on, and a 20% aluminum chlorhydroxide solution are shown in Table IX. In the solution forms (roll-on or 20% aqueous) between 35 and 40% sweat reduction was observed. The two powder versions reduced perspiration by 22%, while the hybrid formula gave a slightly higher result, namely 27%, a difference which is real from the statistical point of view, and probably due to the higher level of active ingredient (5% vs. 3.5% ACH) of the hybrid version.

Table IX
Antiperspirant Efficacy of Different
Formulation Types (Normal Activity Method)

| Product Category | Mean % Sweat Reduction |
|---------------------|------------------------|
| 3.5% powder-in-oil | 22.8 ± 2.7 |
| 3.5% dry powder | 22.1 ± 3.3 |
| 20% ACH solution | 39.9 ± 4.0 |
| Hybrid formulation | 27.0 ± 4.1 |
| Roll-on formulation | 37.5 ± 2.6 |
| Placebo | 2.8 ± 2.8 |

Table X

Sweat Reduction as a Function of Time for
3.5% Aluminum Chlorhydroxide Powder-in-oil
Formulation (Normal Activity Method)

| Time (hrs) | Mean % Sweat Reduction | | |
|------------|------------------------|------------|------------|
| | Test 1 | Test 2 | Test 3 |
| 3 | 22.4 ± 3.8 | 21.1 ± 2.9 | 24.6 ± 2.4 |
| 6 | 20.0 ± 4.3 | 20.3 ± 4.0 | 24.0 ± 2.7 |
| 9 | 18.9 ± 3.6 | 18.0 ± 3.7 | 19.2 ± 3.0 |
| 12 | 14.0 ± 4.1 | 12.4 ± 2.6 | 17.1 ± 2.5 |

Table XI

Effect of Spraying Time (Concentration)
on Sweat Reduction (Normal Activity Method)

| Duration of Spray (sec) | Mean % Sweat Reduction | |
|----------------------------|------------------------|------------|
| | Formula A | Formula B |
| 0.5 | 8.5 ± 2.5 | 10.7 ± 2.5 |
| 1 | 22.8 ± 2.9 | 25.1 ± 4.5 |
| 2 | 28.0 ± 3.2 | 30.3 ± 3.7 |
| 4 | 34.9 ± 3.8 | 35.7 ± 3.7 |

Since the various powder-in-oil formulations gave results in a very narrow efficacy range, regardless of active ingredient, it was decided to test the sensitivity of the method. A series of sweat reduction determinations were carried out as a function of time. Four collections were made following one application, at 3, 6, 9, and 12 hours on 3 successive days. The data obtained in three separate tests with a 3.5% powder-in-oil formulation are shown in Table X. Each test, conducted independently, produced essentially the same per cent decreases in sweat reduction over time. The method was able to distinguish quite successfully and distinctly between relatively small variations in sweat reduction.

In a second series of tests in which different spraying times were used, data were similarly obtained after one application in 3 consecutive days. The data are in Table XI. As the spraying time increased, the per cent sweat reduction also increased.

The effect of the aluminum chlorhydroxide particle size on efficacy was also evaluated. Three different grades were used: Chlorhydrol Ultrafine,^o one grade with a smaller particle size (56% retained on 10- μ screen), and one with a larger particle size (96% retained on 10- μ screen). No significant differences were found between the grades, as shown in Table XII.

^oReheis Chemical Co., Phoenix, Ariz.

Table XII
Effect of Particle Size
on Sweat Reduction (Normal Activity Method)

| | Mean % Sweat Reduction |
|---|------------------------|
| Regular (UltraFine ACH) | 22.8 ± 2.9 |
| Smaller particle size than UltraFine ACH (96% retained on 10- μ screen) | 24.9 ± 3.3 |
| Larger particle size than UltraFine ACH (56% retained on 10- μ screen) | 23.9 ± 3.1 |

Table XIII
Antiperspirant Efficacy of a 3.5% Aluminum Chlorhydrate
Powder-in-oil Formulation (Controlled Environment Method)

| Test | Mean % Sweat Reduction |
|------|------------------------|
| 1 | 12.6 ± 3.6 |
| 2 | 33.6 ± 5.2 |
| 3 | 16.0 ± 4.1 |
| 4 | 22.3 ± 9.8 |

Table XIV
Antiperspirant Efficacy of a 3.5% Basic Aluminum Bromide
Powder-in-oil Formulation (Controlled Environment Method)

| Test | Mean % Sweat Reduction |
|------|------------------------|
| 1 | 35.0 ± 4.2 |
| 2 | 6.7 ± 6.0 |
| 3 | 21.2 ± 4.2 |

Controlled Environment Method

The same 3.5% powder-in-oil formulation used in the normal method was evaluated under the controlled environmental conditions. The results obtained are summarized in Table XIII. Results ranged from 12.6% to 33.6% sweat reduction. In another series, a 3.5% basic aluminum bromide powder-in-oil formulation was tested. The results are shown in Table XIV and again showed little reproducibility.

DISCUSSION OF RESULTS

In general, it was found that in our hands when using the controlled environment method, there was a wide spread of results when the same formu-

lations and the same active ingredients were tested. Because of these difficulties, we have fewer results to report, and are continuing to investigate this technique.

On the other hand, the normal activity method gave reproducible results under a variety of conditions. It did not show any real differences between the effectiveness of different active ingredients under the same formulation conditions. That did not mean that the normal activity method was insensitive, since it very effectively distinguished between powder-in-oil formulations and roll-ons, and clearly indicated variations of antiperspirant efficacy as a function of time or concentration.

The controlled environment method differs from the normal activity method in several ways. The controlled method employs a 2-sec spray, whereas the normal method utilizes a 1-sec spray. Treatment and collection times are different; in particular, the time periods for collection between the normal and controlled methods differ in length (4 hours vs. 40 min) and conditioning i.e., the controlled method utilizes a conditioning period before the pads are applied for collection purposes.

Another reason for the differences observed between the normal and the controlled testing techniques is possibly due to the conditions used in the controlled test. Going into a 100°F sweat chamber at 35% humidity can be a challenging stimulus to the body. Consequently, not only is perspiration elicited as a function of temperature, but also due to the challenge to the central nervous system (19)

CONCLUSIONS

We have concluded that the normal activity method is a more useful tool for providing guidance on the relative efficacy of different formulations and different active ingredients. The method also closely approximates what the consumer experiences in actual use and we have been able to correlate efficacy data with observations reported in large-scale, carefully designed consumer tests.

Certain additional considerations must be kept in mind when considering gravimetric procedures for the determination of antiperspirant efficacy. Bakiewicz (46) has shown that when thermal stimulation is used to induce perspiration, results can vary with body position. Results can also be influenced by drinking cold liquids, variations in the relative humidity of the room, or even by selecting panelists who are "high sweaters" or "low sweaters." For example, Tronnier and Rentschler (47) reported that the same product under controlled environmental conditions gave a 20% sweat reduction when applied to a low sweater, while there was a 50% reduction with a group of people classified as high sweaters.

To summarize our views on antiperspirant test methodology: regardless of the methods used by us or reported in the literature, most of our results for

sweat reduction efficacies for aerosol powder-in-oil and hybrid formulas fall between 20% to 30%. These figures can be restated by saying that a subject was sweating with a 70% to 80% efficiency rather than his normal 100% efficiency. Thus, even if laboratory procedures know how to measure these differences, it is debatable whether the consumer can distinguish between them. While not negating the use of these gravimetric methods to provide data to use as a guide to optimize formulations, or to compare new active ingredients, or to evaluate interaction of materials, care must be taken when these numbers are used for promotional purposes. Small differences, even though statistically significant, should not be magnified out of proportion. It is important that management understands and appreciates the differences in testing methods, and recognizes the limitations and specialized meaning of the data derived from these techniques.

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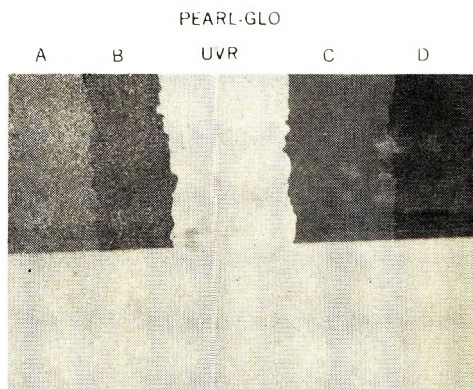
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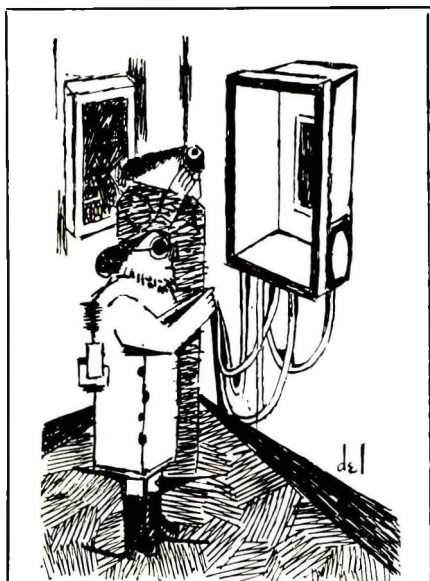
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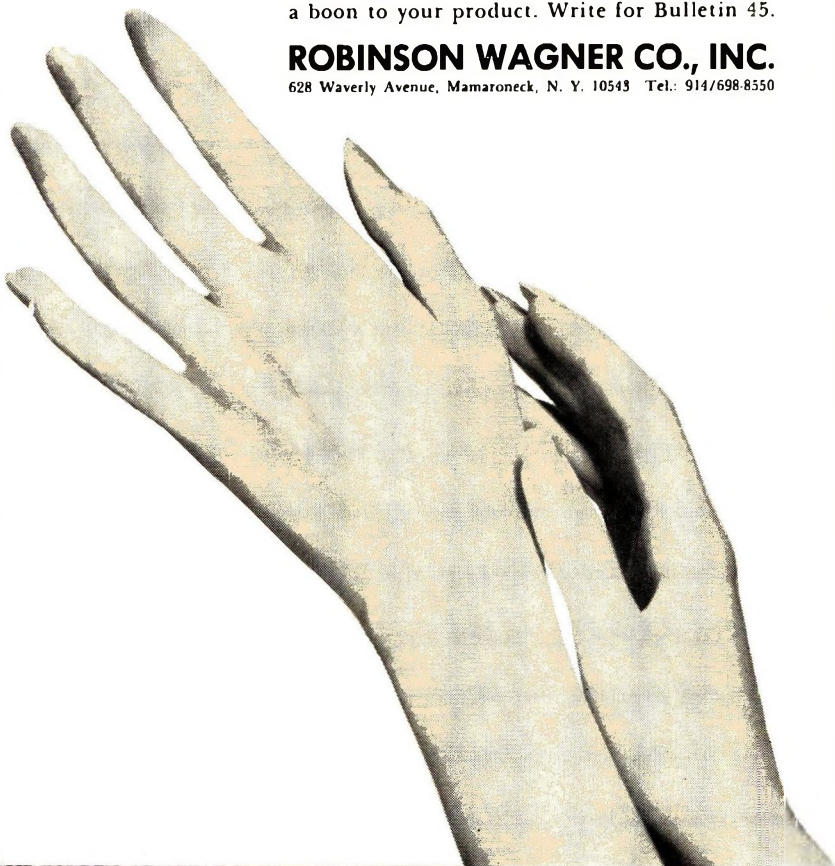
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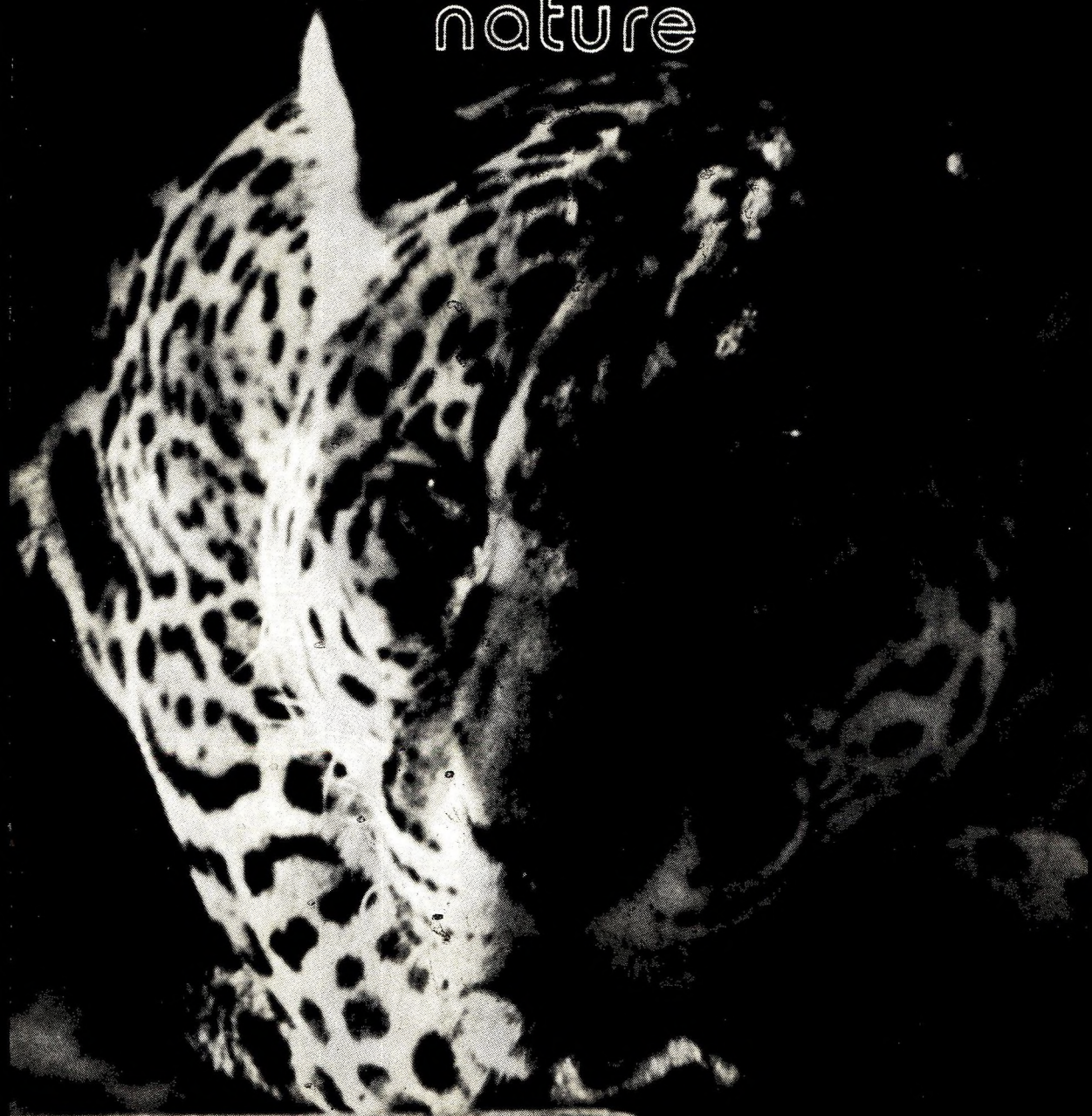
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