various types of emulsifiers and oils to establish the manner in which they effect the moisture loss from the skin. When this is done perhaps we will be able to develop emulsions which act so as to build up moisture and soften the skin. Here, again, this study is designed as a laboratory test for accurately measuring one specific property of a cosmetic cream or lotion. A great deal of additional study and work will be needed before any clear-cut conclusions can be drawn. The work to date indicates that many humectants and hand lotions tend to increase the rate at which the skin dries out and suggests that they are not particularly effective in softening the skin

REFERENCES

(1) Goodman, L. S., and Gilman, A., "The Pharmacological Basis of Therapeutics," New York, The MacMillan Co. (1955), pp. 1017–1019.
(2) Blank, I. H., *J. Invest. Dermatol.*, **18**, 433 (1952).
(3) Peck, S. M., and Glick, A. W., *J. Soc. Cosmetic Chemists*, **7**, 530 (1956).
(4) Blank, I. H., *Proc. Sci. Sec. Toilet Goods Assoc., No* . **23**, 19 (1955).
(5) Rothman, S., "Physiology and Biochemistry of the Skin," Chicago, The University of Chicago Press (1954).
(6) Mali, J. W., *J. Invest. Dermatol.*, **27**, 451 (1956).
(7) Flesch, P., *Proc. Sci. Sec. Toilet Goods Assoc., No.* **29**, 27 (1958).
(8) Blank, I. H., and Shappirio, E. B., *J. Invest. Dermatol.*, **25**, 391 (1955).
(9) Flesch, P., and Esoda, E. C. J., *Ibid.*, **28**, 5 (1957).
(10) Gaul, E., and Underwood, G. B., *Ibid.*, **19**, 9 (1952).
(11) Powers, D. H., and Fox, C., *Proc. Sci. Sec. Toilet Goods Assoc., No.* **28**, 21 (1957).

THE ROLE OF DETERGENTS IN SHAMPOOS

By DONALD H. POWERS and CHARLES FOX*

Presented September 17, 1958, International Symposium, Copenhagen, Denmark

THE IMPORTANCE of detergents in shampoos is clearly indicated by the fact that they are used in the great majority of all important shampoos sold in the American market. It has been claimed that they alone are responsible for the growth and acceptance of shampoos to the point where their annual sales are over one hundred and twenty million dollars. It is particularly interesting to note that the formulation of these shampoos depends not only on the detergent as the active ingredient but the addition of conditioners, foam-builders, viscosity builders, delicate fragrances—all are most important in making them cosmetically acceptable.

In this paper a study of the detergents alone uncompounded is made to determine what role they play in producing a cosmetically acceptable shampoo. It must be re-emphasized that shampoos are not just cleansers;

* Warner-Lambert Research Institute, Morris Plains, N. J.

and truly cleansing and scouring the skin and hair gives an unacceptable effect.

During the past twenty years the emphasis in shampoo advertising has shifted from a preparation that thoroughly cleans the hair to a preparation that leaves the hair fragrant, soft, manageable and lustrous and, incidentally, cleans the hair and scalp mildly (1, 2). That the cosmetic industry is approaching an acceptable shampoo is evidenced by the fact that the sale of shampoos has grown to its present size in the past twenty years.

This success is not entirely due to chance or sophisticated advertising. Time and again it has been proven—that when a product fulfills a need—it will usually succeed, even if it costs more than its less acceptable predecessor. It is for this reason that aerosol shave creams have made such inroads into the sale of creams in tubes and jars; that home permanents replaced the curling iron; that aerosol hair sprays have largely replaced the bottled gum hair sets and that shampoos have replaced the bar of soap. When soft water is available, the bar of soap is ideal for a man's head of hair, but is inconvenient for a woman to use. The need was felt for a preparation that would wet the hair more readily and would lather and give a richer lather faster. Thus, the bar of soap gave way to liquid potash soap preparations. The liquid soap shampoos had a limited success but it was obvious that further product improvement was needed. Soap shampoos are fine in soft water and, when formulated with the proper ratio of C_{12} to C_{18} fatty acids, they give a rich, wet, dense, copious lather, which rinses easily and leaves the hair lustrous and manageable.

In hard water areas the latherability of the soap shampoo decreases and, what is much more serious, calcium and magnesium soaps are precipitated onto the hair, leaving a film of insoluble lime soaps. In extremely hard water areas the lime soap precipitated on the hair makes combability difficult, leaves the hair tacky and may actually lead to dirtier looking hair.

Women would not tolerate these results and corrected this condition by following the soap shampoo with a lemon or vinegar rinse. These acid rinses helped to remove the hard water soaps, leaving the hair more nearly lustrous.

It is not surprising, then, that, with the advent of synthetic detergents, the major growth and development of the shampoo market occurred. Synthetics were a group of water-soluble materials that lathered well in hard water and did not leave a heavy insoluble precipitate on the hair.

As experimentation proceeded with the synthetic detergents, it became obvious that shampoos with good consumer acceptance required something more than a colored, perfumed solution of a detergent. In many instances the synthetic detergents do not lather well in the presence of sebum—the natural oil of the hair and scalp—hair dressings, sweat, and wave set residues. They also require the addition of lather boosters to enhance the

"flash" foam. In many instances the synthetics will give a copious lather which is characterized by a loose, lacy bubble size and a "dry" feel. Such lathers do not have the rich, elegant feel of the dense, wet soap lather and, unless modified by additives, will have poor consumer acceptance.

Another class of commonly used detergents gives rise to a sensation of friction between the hands during the rinsing step. This sensation is totally different from the slippery feel one gets when using soap and must be modified if the finished product is to obtain good consumer acceptance.

Still another class of detergents gives a wonderfully rich lather but, on rinsing and drying, gives a sensation of tackiness on the skin and hair. This may be due to substantivity of the product but is not a pleasant or acceptable sensation to the consumer.

Certain synthetic detergents may do too thorough a job of cleansing, leaving the hair dry and unmanageable. This condition may be alleviated by cutting down the concentration of detergent and by the addition of fatty ingredients (3) to the shampoo.

It is of interest to note that shampoos based on synthetics have been unfairly accused of being too strong in cleansing action and, thus, presumably removing all the oil from the hair and scalp. While this may be true of the synthetic detergents when used alone (4), it certainly is not true of the successful synthetic detergent shampoos, which constitute the major portion of today's markets (5).

For example, Barnett and Powers (6) showed that most synthetic detergents were from 89 to 98 per cent efficient in removing grease from wool. In this test wool yarn, spun in the grease, was gently shaken in 0.25 per cent active solutions of the detergent at 38°C. But the same test run on successful commercial shampoos (7), which are based on some of these very same detergents, showed tremendously lower cleansing power in the order of 4 to 53 per cent (see Table 1).

TABLE 1—EVALUATION OF CLEANSING POWER OF SHAMPOOS*

Shampoo	Per cent Soil Removal†
Marrows	15.2
Breck	23.6
Hudnut	36.1
Prell	35.5
Halo	42.6
Drene	4.4
Toni	35.8
Rayve	32.2
Lustre Cream	22.5
Marlene	53.4
Helene Curtis	48.8

* Results reported by *Consumers Research*, October, 1951.
† Using Barnett-Powers Test (4).

This is further evidence that today's successful shampoos are not simply water solutions of detergents but are well-formulated mixtures, containing an acceptable balance of detergent, lather booster, foam modifier and hair conditioner. Synthetic detergents have also developed a reputation for being too harsh on the skin. Recent investigations with commonly used detergents in home laundry preparations failed to show any sensitization and nothing was found to suggest that detergents were more damaging to the skin than comparable soap products which must be quite alkaline (8).

The synthetic detergents have by no means, however, completely replaced soap in shampoos. With proper formulation one may combine soaps with synthetics which have the power to disperse lime soaps. Such combinations are usually characterized by a rich wet lather and leave the hair lustrous and manageable.

There are several excellent references available on shampoo formulation (9, 10); and a number of articles have appeared on the laboratory evaluation of detergents for shampoos (2, 4, 5, 6).

A few selected synthetic detergents suitable for use in shampoos were investigated for consumer acceptance. Aqueous solutions of the detergents were prepared, containing 12 per cent of the active anion. These were tinted and perfumed identically and adjusted to a pH value of 7.0 with hydrochloric acid.

TABLE 2—RATING OF SHAMPOO PROPERTIES BY PANEL TESTERS

	Opinion Expressed in Per cent as to														
	Latherability			Manageability			Luster			Cleanliness			Wet Combability		
Active Ingredient*	G†	F	P	G	F	P	G	F	P	G	F	P	G	F	P
Triethanolamine "lauryl" sulfate	100	0	0	59	41	0	55	27	18	91	9	0	59	33	8
Triethanolamine lauryl beta amino propionate	65	23	12	50	42	8	35	42	23	73	8	19	58	27	15
Protein fatty acid condensate	79	21	0	58	37	5	58	26	16	74	21	5	47	37	16
Triethanolamine dodecyl benzene sulfonate	86	9	5	55	36	9	46	23	31	73	27	0	55	36	9
Sodium octyl phenoxypolyoxyethylene sulfonate	50	40	10	70	20	10	60	25	15	80	5	15	60	30	10
Sodium "lauryl" polyoxyethylene sulfate	61	30	9	48	39	13	61	39	0	92	4	4	74	26	0
Sodium lauroyl sarcosinate	80	7	13	67	33	0	40	40	20	80	20	0	40	60	0
Sodium caproyl imidazoline carboxylate	81	19	0	90	5	5	67	33	0	86	14	0	95	5	0
Ammonium lauroyl isethionate	87	13	0	74	26	0	83	17	0	91	9	0	72	26	0
Sodium "coco" methyl taurate	83	17	0	58	33	9	58	33	9	100	0	0	67	25	8
Triethanolamine coconut soap	92	0	8	42	33	25	25	50	25	66	25	9	50	17	33

* Each shampoo contained 12% active anion.
† Code: G = good, F = fair, P = poor.

These preparations were coded and panel tested among a group of women office workers. The panel members were asked to shampoo their hair in their normal manner once weekly but to refrain from using any hair dressing, wave set or rinses. Each shampoo was used over a two-week period and the panel members were then checked for their opinion as to latherability, manageability, luster, cleanliness and ease of wet combing. The panel members all lived in a hard water area (approximately 150–300 p.p.m. hardness) and used unsoftened water in this test. The results obtained are presented in Table 2. For comparison, a solution of triethanolamine coconut soap at a pH of 8.5, prepared from a stripped coconut fatty acid and containing approximately 12 per cent active anion, was also included in this test.

From the data in Table 2 it is interesting to note that soap alone was the least acceptable from the standpoint of hair luster, manageability and cleanliness although quite acceptable as to latherability.

One would expect that there should be a direct correlation between hair cleanliness and luster but this apparently is not the case. For example, sodium "coco" methyl taurate was rated best for "cleanliness" yet is only intermediate in luster. Perhaps cleanliness is a combination of factors related to degree of "degreasing" as well as the amount of insoluble calcium

TABLE 3—A COMPARISON OF LABORATORY CLEANSING DATA FOR SELECTED DETERGENTS WITH PANEL TEST RESULTS

Detergent	Grease Removal, % Laboratory Tests*	Panel Test (% Voting Good Cleansing Action)
Triethanolamine "lauryl" sulfate	92	91
Protein fatty acid condensate	77	74
Triethanolamine dodecyl benzene sulfonate	73.7	73
Sodium octyl phenoxy polyoxyethylene sulfonate	81.7	80
Ammonium lauroyl isethionate	92.8	91
Sodium "coco" methyl taurate	95.0	100
Coconut soap	90.3	66

* Laboratory test data obtained from Barnett-Powers work (2, 4, 6), using 0.25% active detergent in tap water at 38°C.

and magnesium salts deposited on the hair. In Table 3, there is presented a comparison of laboratory cleansing action and panel members' opinions on a few of the detergents tested. Surprisingly good correlation was obtained between laboratory cleansing tests and use tests for most of the detergents tested except soap. In the case of soap the heavy, dulling, lime soap deposit on the hair, undoubtedly, influences opinion as to cleanliness. It should be noted that the Barnett-Powers tests cited here were conducted in New York City tap water which is very soft indeed and much softer than the 150–300 p.p.m. tap water used in these panel tests.

The solubility characteristics of the detergents studied in 350 p.p.m.

hard water are shown in Table 4. These data indicate that, while many detergents show good solubility in hard water at higher concentrations, they precipitate out on dilution or during rinsing. Undoubtedly, the heavy metal salts of many of these detergents are insoluble *per se* in water but are solubilized in an excess of the soluble detergent salt. Where detergents precipitate in hard water they will be potential hair dulling agents.

TABLE 4—SOLUBILITY CHARACTERISTICS OF SELECTED DETERGENTS IN 350 P.P.M. HARD WATER*

Detergent	Solubility as Judged by Clarity† of Solution at 0.5% level‡	0.1% level‡
Triethanolamine "lauryl" sulfate	Clear	Very cloudy
Triethanolamine lauryl beta amino propionate	Clear	Clear
Triethanolamine dodecyl benzene sulfonate	Slightly cloudy	Cloudy
Protein fatty acid condensate	Clear	Clear
Sodium octyl phenoxy polyethoxy sulfonate	Slightly cloudy§	Cloudy§
Sodium lauroyl sarcosinate	Clear	Very cloudy
Sodium lauryl polyethoxy sulfate	Clear	Clear
Sodium caproyl imidazoline carboxylate	Cloudy	Cloudy
Ammonium lauroyl isethionate	Cloudy	Cloudy
Sodium "coco" methyl taurate	Clear	Clear
Triethanolamine coconut soap	Very cloudy	Very cloudy

* Prepared by dissolving 0.259 grams of calcium chloride (anhydrous) and 0.281 grams of magnesium chloride (hexahydrate) in 1 liter of distilled water.
† Clarity was judged five minutes after solution was prepared.
‡ Percentage refers to anion.
§ This detergent is slightly cloudy at these concentrations in distilled water.

A comparison between panel opinions as to latherability and laboratory test data, using the Barnett-Powers latherometer, is presented in Table 5. The correlation is not too good when one considers the laboratory data obtained with soft or hard water. However, it is very enlightening to see what a close correlation is obtained when synthetic sebum is used as part of the laboratory test.

TABLE 5—A COMPARISON OF LABORATORY LATHERABILITY DATA* FOR SELECTED DETERGENTS WITH PANEL TEST RESULTS

Detergent	Laboratory Latherability (ml. of Lather) In Soft Water	In 175 p.p.m. Hard Water	In Soft Water Containing 2% Synthetic Sebum	Panel Test Results (% Voting Good Lather)
Alkyl sulfate	86	94	203	100
Triethanolamine dodecyl benzene sulfonate	52	70	150	86
Sodium octyl phenoxy polyoxyethylene sulfonate	57	55	92	50
Protein fatty acid condensate	73	130	100	79
Sodium caproyl imidazoline carboxylate	47	57	120	81
Soap	49	44	399	92

* These data, obtained from reference No. 2 Tables 1 and 4, are based on 3% solutions of detergent.

At the present time there are no adequate techniques published for measuring hair manageability and ease of wet combing. Mills, Ester and Henkin (11) described a technique for measuring static charge developed on hair. This technique was excellent for measuring reduction of static charge on the hair after the application of creme rinses but was inadequate for distinguishing differences in the action of detergents on the hair.

When adequate tests are developed for reliably measuring hair manageability, we will have taken a giant step forward toward being able to predict with the aid of laboratory tests the potential consumer acceptance of a new shampoo

The study of shampoos continues to show that many factors contribute to their acceptance or rejection. When synthetic detergents are formulated without additives, we discover again that cleansing action is not the whole story in a shampoo. As better and more extensive laboratory tests are available, we are coming closer to the time when we can predict a cosmetically acceptable and successful shampoo from laboratory tests.

REFERENCES

(1) Zussman, H. W., *Proc. Sci. Sec. Toilet Goods Assoc., No. 19*, 58 (1953).
(2) Barnett, G , and Powers, D. H., *Ibid., No. 24*, 24 (1955).
(3) Harris, J. C., *Am. Perf. Essent Oil Rev.*, **48**, 54 (1948).
(4) Barnett, G., and Powers, D. H., *J. Soc. Cosmetic Chemists*, **2**, 219 (1951).
(5) Ester, V. C., Henkin, H., and Longfellow, J. M., *Proc. Sci. Sec. Toilet Goods Assoc., No. 20*, 8 (1953).
(6) Barnett, G., and Powers, D. H., *Ibid., No. 15*, 16 (1951).
(7) *Consumers Research*, October (1951).
(8) "A Study of the Effect of the New Detergents on the Skin," Thomas Hedley and Co., Ltd., Newcastle Upon Tyne, Dec., 1955.
(9) Sagarin, E., "Cosmetics: Science and Technology," New York, Interscience Publishers, Inc. (1957).
(10) Harry, H. G., "The Principles and Practice of Modern Cosmetics," Vol. I in "Modern Cosmeticology," London, Leonard Hill, Ltd. (1955).
(11) Mills, E. M., Ester, V. C., and Henkin, H., *J. Soc. Cosmetic Chemists*, **7**, 466 (1956).

THE COSMETIC INDUSTRY IN DENMARK

By ERIK THOMSEN*

Summary of Paper Presented September 17, 1958, International Symposium, Copenhagen, Denmark

SINCE 1940 we have had a cosmetic tax of 25 per cent of the retail price (including tax), increased to 30 per cent in 1956. From the revenue, the total turnover is calculated (soap, toothpaste and shampoo are not taxed and therefore not included).

* Kronebakken 49, Virum, Denmark.