MERCAPTANS IN COSMETICS*

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AT FIRST glance the title of this paper strikes one as a paradox, because the word *cosmetics* connotes a pleasant-smelling preparation, while the unpleasant odor of mercaptans is proverbial. In fact, they have been described by such terms as *evil, provoking, ferocious, revolting, unbearable,* and *nauseating.*

The odor of mercaptans is most persistent even in extreme dilution. Emil Fischer(1) commented on the fact that ethyl mercaptan can be detected by smell in amounts as small as 2×10^{-12} of one gram. Note that this is less than $^1/_{200}$ of the smallest amount of sodium that can be detected with the spectroscope. The revolting odor of the defensive secretion of the skunk is due to butyl mercaptan(2). The malodor of feces (3) and urine (4) after asparagus has been eaten is at least in part due to the presence of methyl mercaptan.

Meaning literally *seizing mercury*—the name *mercaptan* is derived from the Latin *mercurium captans*, and it originated in the fact that mercaptans react very readily with mercuric oxide to form crystalline compounds. Although the first synthesis of a mercaptan was reported as early as 1834 by Zeise(5), the mercaptans as a group of compounds have been so little explored that no standard nomenclature has been adopted for them. There are at least five systems of nomenclature for mercaptan compounds and the need for systematizing the nomenclature was the subject of a recent article(6).

Undoubtedly mercaptans have been used in the synthesis of many other compounds, but these uses have never been publicized. In general their presence is not desired. In the petroleum industry alone, millions of dollars have been spent on research for methods of removing mercaptans from petroleum. During the first world war, *n*-butyl mercaptan was under consideration as a camouflage gas and a small plant did produce some. The second world war brought forth two uses; *lauryl mercaptan* as a modifier in the manufacture of Buna S synthetic rubber; and *dithioglycerol* as an antidote or protective agent against Lewisite gas. The name "Bal" for British Anti-Lewisite is commonly applied to this latter compound since it was developed by the British. This compound is finding peace-time use as an antidote for

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arsenic and mercury poisoning.

It has always appealed to me that the cosmetic industry has been the first user of many materials. Here again, the cosmetic industry can truthfully boast that it was first to commercialize for peace-time use a material from a new group of compounds—the mercaptans.

Of the two discoveries which have led to the use of mercaptans in cosmetics, one has revived a dying market; the other has revived a field which had already been pronounced dead, and this mercaptan cosmetic has grown to be the single biggest income-producer in our entire industry. The former reference is to the cosmetic product, the cream depilatory; the latter, to a product, the cold waving lotion, and the new methods of cold waving growing from it.

Mercaptans in Depilatories

Cosmetic depilatories containing sulfides have been known and used for centuries. *The Arabian Nights* and many other ancient records mention them, yet the same problems which were so picturesquely described by Koeune(7) in 1937 have existed unsolved for centuries. In Koeune's own words

> The use of sulphides in depilatories brings in its train a number of vexed problems which have, and probably can be, only partially solved. For example, we have, first and foremost, the problem of minimising and disguising the distinctly insalubrious odour. Then, of scarcely less importance, we have to consider the serious caustic action on the skin. And in case by some mysterious alchemy we should dissipate the smell of the sulphide, a malign fate draws across the track some very red herrings in the form of drying out of the depilatory in the tube, deterioration of the active ingredients, discoloration of the paste, while the good perfume which one has reluctantly sacrificed to the God of Sulphide turns in its grave and rises up in horrible forms which stink of the very pit itself.

Like so many problems crying for solution, "the mysterious alchemy" called for by Koeune was forthcoming independently and almost at the same time from two research groups. In Holland a Dutchman, Karel Bohemen, found that thioglycolic acid and other mercapto-carboxylic acids could be used in certain alkaline media. His discovery resulted in the issuance of patents in certain foreign countries to him or his agent—Fletcher. In America, Evans and McDonough discovered that mercaptans could be used in cosmetic cream depilatories, and after a priority contest with Bohemen, a U. S. Patent was issued only to them. In foreign countries because the conflict with Bohemen patents was governed by different laws, the patents issued to Evans and McDonough cover the use of mercaptans other than mercapto-carboxylic acid in depilatories.

Briefly summarized, Evans and McDonough found that:

1. All mercaptans in an alkaline solution, preferably at a pH greater than 9.0 and less than 12.5

will remove hair without irritating the skin. To illustrate this Table I has been prepared.

TABLE I—EFFECT OF pH ON RATE OF DEPILATION BY MERCAPTAN

pH	Hair Removal in	Time to Irritate
8.0	Not in 30 min.	None in 30 min.
8.5	Not in 30 min.	None in 30 min.
9.0	30 min.	None in 30 min.
9.5	24 min.	None in 30 min.
10.0	19 min.	None in 30 min.
10.5	15 min.	None in 30 min.
11.0	12 min.	None in 30 min.
11.5	9 min.	None in 30 min.
12.0	7 min.	None in 30 min.
12.5	5 min.	Slight in 30 min.
13.0	3 min.	Severe in 15 min.

Thioglycolic acid (0.5 molar) was used in this experiment because we had found that substituted mercaptans were not only better because of their odor but also more effective and less irritating. Of the substituted groups we had found the ionizing groups, particularly the acidic groups such as —COOH, to be preferred over the non-ionizing groups such as the ether groups.

2. The concentration of the mercaptan should be greater than 0.1 mole per liter of solution and need not be greater than 1.5 moles per liter. To illustrate this Table II has been prepared.

3. Any non-volatile alkaline material can be used provided that a) its dissociation constant is greater than 2×10^{-5} and b) it does not form an insoluble salt with the particular mercaptan. For example, monoethanolamine alone even when used in sufficient amount to give a pH of 11 will not make a satisfactory depilatory; and barium hydroxide is not usable with thioglycolic acid because it forms an insoluble salt.

4. Although it is preferable to have the concentration of the alkaline material slightly greater than the total acidic equivalency of the mercaptan, it should never be greater than twice.

5. The filler or cream-forming materials serve an important function in mercaptan depilatories other than just the ease of localizing the depilatory in application. As mercaptans in an alkaline medium oxi-

TABLE II—EFFECT OF CONCENTRATION OF MERCAPTAN (THIOGLYCOLIC ACID) ON RATE OF DEPILATION

Molar Concentration of Thioglycolic Acid	pH by Excess $Ca(OH)_2$	Time to Remove	Irritation in 30 Min.
0.05	12.35	None in 30 min.	None
0.10	12.30	Partial in 20 min. Complete in 30 min.	None
0.20	12.28	Partial in 10 min. Complete in 15 min.	None
0.50	12.29	Partial in 6 min. Complete in 9 min.	None
0.80	12.26	Partial in 6 min. Complete in 9 min.	None
1.50	12.26	Partial in 8 min. Complete in 10 min.	None
2.00	12.28	Partial in 8 min. Complete in 10 min.	None

dize rapidly, the thicker application serves as a protection from oxidation by the air while the mercaptan is acting at the level of the skin. Also, because the free liquid content of the cream is low, the danger of irritating the follicle is obviated. The choice of fillers or cream-forming materials is much wider with mercaptans than with sulfide depilatories.

6. Because the substituted mercaptans produce depilatories that are substantially non-odorous, one is likely to overlook that they have solved one of the most troublesome problems associated with sulfide depilatories, namely, that of perfuming the product. As stated by Koeune, this is not merely a matter of covering the odor of the depilatory but of finding aromatic materials which will not be destroyed or changed into foul-smelling compounds by the ingredients of the depilatory. With the mercaptan depilatories we have found that a much wider choice of perfume materials is possible not only because lighter fragrant types may be used but also because many perfume materials destroyed or changed by sulfide depilatories remain unchanged in mercaptan depilatories.

7. The mercaptan depilatories are less irritating than the sulfide depilatories. On this point our original findings have been confirmed by others. For example, Consumers Union reported(8) that thioglycolate depilatories "are somewhat milder in their action than the sulfide depilatories and medical authorities believe that they are less likely to cause dermatitis than the sulfides."

During an epidemic of ringworm in Hagerstown, Maryland, when a commercial thioglycolate depilatory was applied to even the infected areas on a large group of school children for the removal of hair, there were no unfavorable results.

The thioglycolate depilatories were first offered to the American public in June, 1939, and although the war has hampered their exploitation, nevertheless, it is estimated that this year the sales of cosmetic depilatories will be approximately three times the sales of any previous year, and more than ten times the amount sold in 1938. The mercaptan depilatories will be the reason for that advance.

Mercaptans in Cold Waving

The depilatory market, though, cannot even approach that of cold waving, because the income from this source is derived not only from sales of the product for use at home but also from the huge amounts of the product used in the beauty shop.

Within the short period of five years cold permanent waving has become the preferred method of permanent waving of the women of America. Today over 50% of all permanent waving is done by the cold process, and it has been estimated that between 25,000,000 and 30,000,000 permanent waves will be given professionally by the cold waving process during 1946.

Permanent waving accounts for approximately 60% of the income

of a beauty shop, and cold waving alone accounts for over 30% of the shop's income. As the total yearly income of the beauty shops of America is estimated to be one billion dollars, cold waving not only becomes the most significant source of income for the 300,000 beauty operators but also plays an important role in our national economic structure.

All of this commercial revolution has happened since the spring of 1941. After the unfortunate death of an Atlanta matron who had just had a cold wave, the Federal Government effectively halted all cold waving by the seizure of the cold wave lotions. These, however, contained *ammonium hydrogen sulfide*, which was the only chemical agent then used commercially to wave hair at low temperature in a short period of time.

One large chain of beauty salons which had spent a small fortune in ventilating equipment to dispose of the toxic and malodorous hydrogen sulfide gas was the first to utilize commercially a cold wave lotion containing mercaptan as the successful displacement for the noxious sulfide lotions. Thus at one stroke the poison, bad odor, and cumbersome equipment associated with the use of the sulfide lotions were displaced by the mercaptan lotions which are superior in every respect.

The cold wave product introduced by this group of salons was an earlier discovery made as a result of extensive research and development in our laboratory. The principle is that mercaptans, particularly in an alkaline medium, were effective waving agents and could be used for waving at low temperature. Without going into the details of these experiments, some of the conclusions reached were as follows:

The substituted mercaptans were not only more effective but also preferable because in the proper medium they gave less odor. The concentration of the mercaptan was less than 15% and preferably was in the range of 2% to 10%.

In cold waving with mercaptans the range of pH is very important. Although below pH 7 cold permanent waving is possible, the time required is very long. No critical difference in time is noted below pH 7. At this pH there is a break, for at this point the time to wave sharply decreases with even a slight increase in pH.

The critical upper limit for pH is 10, because at this pH and above, the hair is seriously damaged before it can be waved satisfactorily.

A particularly critical range of pH is from 9.2 to 9.5. Within this range the hair can be waved quickly without being damaged; therefore, this range is to be preferred for commercial use especially in beauty shops.

Although many alkaline compounds may be used, the bases having a dissociation constant less than 5×10^{-3} give the best results. The volatile bases are particularly effective; for example, ammonia and ethylamine are preferable to the non-volatile monoethanolamine.

and this, in turn, is preferred to the stronger alkalies such as sodium hydroxide. Waving with mercaptan is remarkably kind to the hair. Despite recent publicity, waving with thioglycolic or other mercaptans can be done with complete safety. As a matter of fact, it is a testimonial to cold waving with thioglycolic acid that only two adverse articles have been published, and both of these are open to considerable criticism.

Answers have been made and are being made to these two articles elsewhere. It is sufficient to say here that statistics prove the safety of mercaptans in cosmetics. With both depilatories and cold waving there are tremendous expanding markets; yet the insurance rates on both products have been constantly decreased.

In conclusion, it should be pointed out that these two commercial uses of mercaptans in cosmetics will undoubtedly serve not only to stimulate interest in the use of them in other cosmetics; but also—more important—to remove the barrier of prejudice against many other chemical substances which we in the cosmetic industry may have thought of no value because they of themselves displeased our aesthetic senses.

It was as a result of the two discoveries discussed here that research brought thioglycolic acid (and other mercaptans) from the status of laboratory curiosities to full scale commercial production. New uses for these products are now being evaluated; and thus the cosmetic industry once again indirectly affects the well-being of other industries.

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