

THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS

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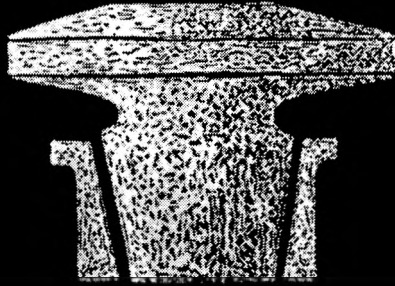
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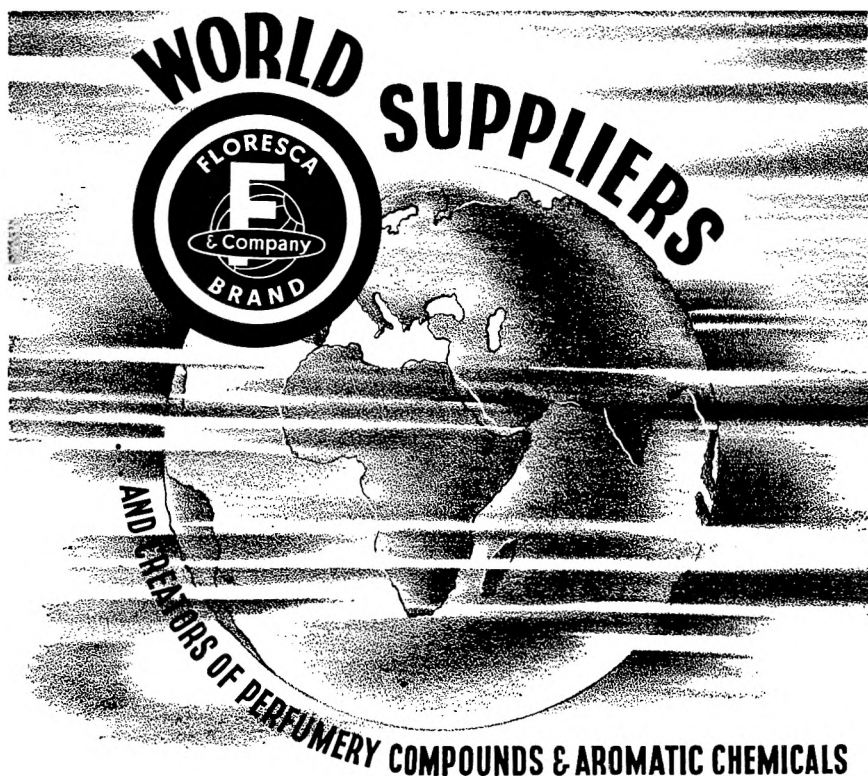


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Stanley J. Bush, F.R.I.C.

President 1963-64

SOME ECONOMIC ASPECTS OF PERFUMERY

G. J. E. HACKFORTH-JONES, M.A.*

Presented at the Symposium on "Perfumery", organised by the Society, at Cheltenham, Glos., on 14th November 1962.

Classical fragrances are often too dear owing to their dependence on a small number of very expensive natural products. Substitutes for these may be sought in both the natural and the synthetic field, but in both cases results may prove disappointing. Progress may result from the use of new chemical bodies, and it is to be hoped that manufacturers will offer more such materials for general sale.

CLASSICAL PERFUMERY is essentially the perfumery of natural products, initially achieved without the use of synthetic materials and, in recent times, by the use of a limited range of synthetics to give specific character and to bring out the depth and richness of expensive naturals. Classic perfume types are known and admired throughout the world, and there would be little need to consider altering them if it were not for difficulties of raw material supply and steadily increasing cost.

To illustrate this I have set out the following skeleton formulae, the first of which is of an Eau de Cologne, and the second of an aldehydic perfume containing important quantities of Rose Otto and Jasmin Absolute. When properly executed these are triumphs of the perfumer's art.

FORMULA A

Eau de Cologne compound

| <i>Quantity</i> | | <i>Cost in shillings per kilo</i> | <i>Cost of quantity used</i> |
|-----------------|----------------------|---------------------------------------|----------------------------------|
| 325 | Bergamot | 180 | 54.0 |
| 250 | Lemon | 100 | 25.0 |
| 150 | Mandarin | 100 | 15.0 |
| 50 | Lavender oil, French | 80 | 4.0 |
| 40 | Rosemary | 15 | 0.6 |
| 5 | Clary sage | 300 | 1.5 |
| 45 | Neroli, French | 9,000 | 405.0 |
| 100 | Petitgrain, French | 500 | 50.0 |
| 10 | Rose base | 120 | 1.2 |
| 5 | Ethyl acetate | 7 | — |
| 5 | Musk ketone | 60 | 0.3 |
| 15 | Benzoin resin | 150 | 2.2 |
| <hr/> | | | <hr/> |
| 1,000 | | | 558.8 |
| <hr/> | | | <hr/> |

*Yardley & Co. Ltd., London, W.1.

FORMULA B

Aldehydic perfume compound

| <i>Quantity</i> | | <i>Cost in shillings per kilo</i> | <i>Cost of quantity used</i> |
|-----------------|--------------------------------|---------------------------------------|----------------------------------|
| 5 | Aldehyde C.9 1/10 | 20 | 0.1 |
| 10 | Aldehyde C.10 1/10 | 20 | 0.2 |
| 20 | Aldehyde C.11 1/10 | 30 | 0.6 |
| 5 | Aldehyde C.12 1/10 | 20 | 0.1 |
| 10 | Methyl nonyl acetaldehyde 1/10 | 30 | 0.3 |
| 25 | Bergamot | 180 | 4.5 |
| 10 | Bergamot, terpeneless | 400 | 4.0 |
| 50 | Ylang-ylang extra | 350 | 17.5 |
| 50 | Methyl ionone | 150 | 7.5 |
| 20 | Hydroxycitronellal | 100 | 2.0 |
| 20 | Alpha ionone | 300 | 6.0 |
| 15 | Linalol, ex Coriander | 200 | 3.0 |
| 10 | Dianthus base | 400 | 4.0 |
| 50 | Muguet base | 300 | 15.0 |
| 15 | Lilac base | 150 | 2.2 |
| 50 | Jasmin base | 300 | 15.0 |
| 40 | Rose Otto, Bulgarian | 11,000 | 440.0 |
| 50 | Jasmin absolute, French | 14,000 | 700.0 |
| 20 | Rose absolute, French | 7,000 | 140.0 |
| 5 | Orris concrete | 5,000 | 25.0 |
| 40 | Cinnamic alcohol, ex Styrax | 200 | 8.0 |
| 10 | Styrax resin | 150 | 1.5 |
| 5 | Patchouly extra | 400 | 2.0 |
| 7 | Vetyver Bourbon | 250 | 1.8 |
| 2 | Oakmoss absolute | 800 | 1.6 |
| 5 | Civet absolute | 5,000 | 25.0 |
| 100 | Ambergris tincture 3% | 80 | 8.0 |
| 200 | Musk 3% | 1,000 | 200.0 |
| 10 | Vanillin, ex clove | 100 | 1.0 |
| 60 | Musk ambrette | 60 | 3.6 |
| 30 | Musk ketone | 60 | 1.8 |
| 50 | Coumarin extra | 100 | 5.0 |
| <hr/> | | | |
| | 1,000 | | 1,646.3 |
| <hr/> | | | |

On the right side of each of the formulae I have set out cost information, the first column being the approximate cost in shillings per kilo of the materials utilized, and the second column giving the calculated cost for the quantity used. It will be seen that in the Eau de Cologne more than half of the cost is made up of Oil of French Neroli, while in the aldehydic perfume three-quarters of the total cost consists of Rose and Jasmin. In both cases, the net compound cost is high and if dilutions are made at the conventional strengths, i.e. 5% for cologne, and 18% for perfume, the net product cost will be so great that only a small percentage of the public will be prepared to buy them.

Forty years ago this may not have been a serious problem since perfumery houses did not seek to sell their products other than in small volume

to wealthy people. Moreover, even allowing for the diminishing purchasing power of modern currency, natural floral products were cheaper in the past than they are nowadays. Now, however, there is a need to put classical products of high quality before a wide public at a price they can afford to pay. How can this be done?

ALTERNATIVES

If economies are to be made in formulae of this type it is obviously necessary to find substitutes for the constituents which make up the bulk of the cost. This can be done either by finding alternative natural products of approximately the same odour but substantially reduced cost, or by completely abandoning the expensive naturals in favour of compounded bases composed principally of cheaper materials. But this proves difficult to achieve. After intensive study one gains great respect and admiration for perfumers of the past who, in the first place, selected the qualities of raw material on which finished perfumes were based. It seemed to me, when I began to study perfumery fifteen years ago, that the obvious practical answer to high cost raw materials would lie in the cultivation of the plants concerned in territories where labour was plentiful and cheap—for it goes without saying that the cost of a natural raw material is made up very largely of the cost of the labour which goes into its cultivation and harvesting. Taking the case of Neroli, for example, it seemed reasonable that if its cost of cultivation in France became prohibitively high owing to the rising standards of living of the local peasantry, one needed only to look to the southern shore of the Mediterranean, taking care to graft onto local stock the desired variety of Bitter Orange tree and one would obtain an oil which, if it differed slightly in tonality, would be comparable in value with that obtained in France. I had heard, of course, that experiments of this nature had been tried already with Orange Flower, Rose, Jasmin, Bergamot, Orris, Tuberose, Cassie and, returning to the present day, Clary Sage, Tarragon, even Lavender. Surely amongst so many experiments a certain proportion of successes would be inevitable, that is to say, while no oil would remain exactly as it had been, a few at least would be improved. For how could the perfumers of old have established in every case, optimum growing areas for their natural products? Looking back on this problem in the light of recent experience, I wonder whether nineteenth century producers did not do exactly that. We have perhaps underrated the small scale experiments repeatedly carried out at a time when formal publication was less fashionable, but the results of which became, by word of mouth, quite widely known. May it not have been that at that time, when synthetic chemicals were either not available or available only in crude quality, that a thorough investigation was made of the potentialities for essential oil production of most, if not of

all, countries of the world? The nineteenth century had its successes. Have there been any in the twentieth?

Success is, of course, a relative term, and if oils produced in non-traditional areas are seldom as good as those from normal sources, they nevertheless have a substantial value. Moreover, in some cases transplantation not only coarsens but also strengthens an oil, thereby conferring on it potentialities which the parent oil did not possess. Geranium Bourbon, for example, has so much more power than Geranium de Grasse that, even without the large cost differential, it would inevitably be preferred for many uses.

The present position regarding the quality of some of the oils obtainable from alternative sources is, in my opinion, as follows :

| | | |
|---|--|--|
| <i>Jasmin</i> | French | Pre-eminent. |
| | Italian | Best qualities floral, but lacking in odour strength. |
| | Algerian | Having good strength, but heavy and indoloid in character. |
| | Egyptian | Best qualities good, but of somewhat individual odour. |
| | Moroccan | Of improving quality but seemingly lacking in richness. |
| | | Other sources of Jasmin yield products markedly different from those listed above. |
| <i>Rose by extraction</i> | French | Pre-eminent. |
| | Moroccan | Good but lacking in richness. |
| | Bulgarian | Good but lacking in top note character. |
| | Turkish | Good but lacking in top note character. |
| | Russian | Hors de concours. |
| <i>Rose by distillation</i> | Bulgarian | Pre-eminent. |
| | Turkish | Excellent, but of differing tonality. |
| | Moroccan | Excellent, but of lesser strength. |
| | Other sources give oils of variable quality. | |
| | <i>Geranium (by distillation)</i> | French |
| Bourbon | | Of outstanding character and strength. |
| Algerian | | Toward French in character but less fragrant. |
| Moroccan | | Good, but without the special characteristics of Bourbon and Algerian. |
| Other important sources exist concerning which I do not feel qualified to express an opinion. | | |

These lists may be continued and, in each case, the old established source shows up as pre-eminent.

These opinions are based on experiments in which finished products of classical types have been made up employing each of the oils in turn.

It turns out that the costs of the oils offered on the open market often approximate closely to the values which may be set upon them in actual use. In other words, returning to the problem of making available to a wider public the classical creations of perfumery it will be seen that while one can reduce the cost by substituting dear natural constituents with similar products obtained by cultivation in lower cost areas, the degree of economy

obtained corresponds with the degree of difference noticeable in the finished perfume.

PLANT SELECTION

If one accepts that cultivation of the desired essential oil-producing plants in differing geographical locations gives broadly unrewarding results, there remains the possibility that one may select a strain of plant giving a higher yield of oil and so obtain a lower cost price without the necessity of undertaking capital investment in underdeveloped and most likely, politically unstable, foreign countries.

The lavender family has proved particularly suitable for the exercise of plant selection, but results have not always been in accord with expectation. Lavender oil is notorious for the ease with which it can be adulterated, and lavender "to a price" has been, and still is, offered for sale by many companies. Some buyers have been quite satisfied to accept these oils providing that they comply with the relevant standard set by the Pharmacopoeia. But to others it has come as a surprise to discover, often following the use of the new analytical techniques, that the oils they had been in the habit of accepting contained little or no true lavender. Consumers' desires to buy nothing but pure oil made it all the more necessary for the producers to select lavender plants giving high yields. Odour evaluation was largely ignored since it was believed that the ester content of the oil was an index of odour quality. The results are, of course, well known. Two selected plants were widely cultivated—these have come to be known as Matherone and Maillette. Both give oils of highly satisfactory physical and chemical constants, coupled with yields per unit area of land two or three times greater than those normally associated with true lavender. Unfortunately, it has since been found that from the purely olfactive standpoint these oils have very limited value and, at the time of writing, individual lots are offered for sale at prices similar to those quoted for Lavandin. Thus in this case, selection has undoubtedly proved a failure.

On the other hand, one important French company has studied lavender selection over a long period. Paying due regard to the perfumer's opinion that company has isolated strains of lavender giving superior yields (though not as good, of course, as Matherone and Maillette), and at the same time oils comparable in quality with normal true lavender.

One cannot turn from plant selection without mentioning the one outstanding commercial success which has been achieved, i.e. the invention of Abrialis Lavandin. This plant was originally intended to meet the requirement for a high ester and therefore (it was supposed) a high quality Lavandin giving a larger yield per unit of land cultivated. When offered originally at a price higher than that asked for normal Lavandin it enjoyed little

success, as indeed might have been expected in view of its coarse borneol-like character. But it was soon found that it gave such a good yield to the farmer that it could be economically sold at a price much lower than that previously associated with normal Lavandin and it quickly became, by virtue of its strength and freshness of character, an ideal substance with which to perfume all manner of household products. The present production of Lavandin, in the vicinity of 800 tons per annum, consisting almost exclusively of the Abrialis variety, testifies to the success of this particular selection.

COST REDUCTION BY MEANS OF CHEMICAL SUBSTITUTION

We have seen that development in the agricultural field, whether by cultivation of plants in low cost countries or by cultivation of selected strains, is likely to yield oils of inferior olfactive characteristics. There remains the possibility of reproducing the desired odour by chemical means.

Broadly there are two ways of achieving this :

(a) *The exact reproduction of the desired essential oil*

It is theoretically possible to analyse any oil down to its ultimate constituents, and given sufficient time and money to synthesize each constituent, and blend these in the known proportions. Refinements of analytical technique have made possible the identification of many constituents of essential oils which could not be identified twenty years ago. Unfortunately, the same methods have indicated the presence of an even larger number of minor constituents present in trace quantities which undoubtedly have an important effect on the odour of the natural oil. It would be splendid, of course, if one could decide which of the constituents of the essential oil are vital in determining its odour, and which can be ignored, but this decision has proved very difficult to make. In practical terms the problem has become one of synthesis, with the manufacturer making as many as possible of the identified constituents, and hoping that blends of these will be virtually identical with the parent oil. The results obtained have been disappointing to some extent, and I know of no compounded product which reproduces nature so closely that one would have a moment's doubt that it might really be a natural oil.

(b) *Reproduction of the olfactive effect produced by an essential oil*

This is the field in which most progress has been made. It is really an extension of (a), but being less ambitious can more easily be deemed successful. The principle behind it is that only a small part of an essential oil can be performing an effective function in the end product. All essential oils contain a proportion of inodorous terpenes which can be completely ignored. Other constituents include some which are unstable in conditions

of actual use—thus Bergamot oil, for example, is adversely affected by most grades of soap particularly as regards its top note character. Great progress has been made on the chemical side by concentrating on a few newly identified constituents of important essential oils, and synthesizing these and their close chemical analogues. With these chemical materials it is frequently possible to reproduce natural effects, and then to go beyond nature by using large amounts of chemical bodies which are present only in traces in natural oils.

A list of such items must necessarily be incomplete, and some materials may be not so much new as newly available at realistic cost. The following have proved of interest :

Leaf alcohol and related hexenols and hexenals.

Isomers of octenol.

Isomers of nonenol.

*cis*Jasmone and related jasmones.

Geranyl tiglate and other esters of tiglic acid.

Nerolidol and its derivatives.

Ethyl linalol and its derivatives.

*laevo*Citronellol.

Proprietary materials related to Ambergris.

Publication of details of other important materials is awaited. It must be recognized that a manufacturer faces a dilemma concerning the publication of the results of his own research. Research expenses are high and may be expected to rise still higher in the future, as techniques become more refined. The market for new chemicals is narrow and, even if really satisfactory patent protection is obtained, the loading of cost to cover research expenses renders the chemicals difficult to sell in any quantity. If publication is postponed, bases may be prepared which by virtue of their specific character may receive rapid acceptance.

On the other hand, if a manufacturer relies on the secrecy of the formula of a base rather than on patent protection for an individual chemical, he runs the risk that the latest analytical techniques may be used to break down his product. Chemistry is now so far advanced that the characterisation of a single chemical body, once it has been isolated, may be rapidly achieved and a convenient synthesis is likely to be worked out without much difficulty. It could well occur, therefore, that another organization would market the special chemical material quite soon after the appearance of the special base.

There are two points which appear to favour the publication of details of new chemicals at an early stage assuming patent protection to be feasible. One is, that this will tend to discourage, to some extent, the application of

analytical techniques to finished bases and perfumes, and the second, that it will enable progress in perfumery to be discussed in an open and free atmosphere. It is our united aim that the public should receive the best possible finished product. In so far as we achieve this the market for perfumery products will become larger, to the advantage of all.

(Received : 27th September 1962)

Introduction by the lecturer

The formulae were put into the paper to illustrate that in certain classes of product you have a very high-cost element in a very small number of constituents. One has constantly to look for ways of avoiding steadily increasing costs, but when you look to other natural sources for raw material you get a situation where the diminished cost of the natural product from the low cost area is offset by the diminished value that one finds in practice. It turns out that the costs of the oils offered on the open market often approximate closely to the values which may be set upon them in actual use. So one looks further to see if one cannot find a means of employing bases, either completely natural, or chemical, or combinations thereof, and there again one finds the results to some extent disappointing up to now, although theoretically they could be very good. As far as I am aware, up to now no one has succeeded in producing really satisfactory substitutes for these particular expensive naturals, and indeed for any of the naturals which I personally use—so long as they are being used in their proper manner. I am thinking of the use of Bergamot in soap, which is probably an improper way of using Bergamot anyway, because it is not fully stable.

I dealt rather sketchily with some materials which seem to me to help in avoiding the use of such large quantities of very expensive materials, and I rather deliberately left out two or three such materials because they are treated in rather a confidential way.

DISCUSSION

DR. G. B. PICKERING : At the Tropical Products Institute we have a section which deals with essential oils and spices, and one of its functions is to help overseas producers who are interested in these materials. In view of the lecturer's remarks, it might be constructive to outline some of the difficulties which overseas growers encounter when trying to produce perfumery materials.

Firstly, the production of expensive oils and floral extracts requires considerable skill, so that until recently it would be the European farmer in the tropics and not the local inhabitants who would have to undertake work of this kind. Such farmers, with great areas of land to manage, and

only unskilled labour available, tend to concentrate on a few large-scale crops, such as coffee, pyrethrum, sisal or tobacco, for which much larger markets are available. They have little time for the small-scale experiments which are so necessary in the development of essential oil plants, and frequently only turn to these when other crops are over-produced. Attracted by the high price per pound of floral products, they make a few desultory experiments, meet with difficulties, and abandon the attempt once the market for the staple crops returns to normal.

Before condemning them, we should remember that the difficulties are formidable. Not only is there the tropical climate, with its short periods of violent rains, followed by long periods of drought, but the plant metabolism may be changed or even fail to survive in the new environment. Many plants yield very different oils when transplanted into a new habitat, and some temperate plants—peppermint is one—will not mature properly in the 12-hour period of daylight found near the equator. Again, distillation is an art unknown to the ordinary farmer and only a few manufacturers of chemical plant know of the essential oil still. These remarks apply with greater force to solvent extraction.

Finally, the new producer is faced with a market where prices fluctuate widely, and sometimes violently, and although his product can, to an increasing extent, be assessed scientifically, the final test—that of the perfumer—is subjective and, he suspects, sometimes influenced by the state of the market. The manufacturer is, naturally, unwilling to incorporate an oil with new properties into his formulation without an assured supply, whilst the producer does not care to risk a large expenditure on what appears to him to be a difficult product for a fickle market, and so a vicious circle is formed. In spite of these difficulties, there are many perfumery materials that could be produced in new territories and some, I suspect, may ultimately be produced there for local consumption whether the European manufacturer buys them or not. Before turning in despair to synthetics, both users and growers might try to co-operate once more to produce the natural perfume materials.

THE LECTURER : I have much sympathy with your remarks, and would like to reassure you that there will always be a very substantial demand for natural products whatever may happen in the field of synthetics. Perfumery seeks diversity above all else, and in some astonishing way natural oils seem to have greater differentiation than one would suppose from a study of the chemical bodies of which they are composed. Of course, where we are considering established oils the difficulties of setting up production in new territories are immense. The French nation as a whole are much more perfumery conscious than any other and this may account for

their pioneering activities in establishing essential oil production in all parts of the world. I have suggested that a lot of unreported trials must have taken place in the nineteenth century, and it is correspondingly difficult to establish satisfactory alternative sources in the twentieth century. You mention local consumption. This is greatly to be desired since it implies a certain degree of protection to a nascent industry. One has the feeling that production for local consumption in such countries as India and Turkey may one day result in the emergence of important new essential oil industries. It is greatly to be desired that the former British colonies should also foster their local production. Apart from the well known essential oils I foresee a greatly increased consumption of Galbanum, Cascarilla, Khas, etc.

DR. Y.-R. NAVES : Should you not emphasise the larger variation in price of raw materials of vegetable origin in particular florals, concretes and absolutes ? These major variations are determined only in part by the hazards of cultivation.

THE LECTURER : I think Dr. Naves has in mind that I ought to have pointed out the advantages which ensue if one can once establish formulae relying, so far as the main part of their cost is concerned, on synthetics. A great part of my own work is devoted to this end. I think it only right to point out, however, that in so far as the major oils are concerned, no precisely identical chemical substitutes exist. One may, of course, get excellent results with chemical blends, but these results are never quite the same as with the natural and to that extent one has changed the terms of reference of the problem.

DR. Y.-R. NAVES : It is certainly clear that the distribution of production amongst several distinct geographical and political areas is favourable to the consumer. The latter must envisage the conjoint use in his formulae of products obtained from these different geographical and political centres in order to be in a position to counteract the economic consequences of price increases due to local conditions or scarcity of one of these products. In the same way, the consumer must accept the use of suitable substitutes alongside the natural products.

THE LECTURER : I agree with Dr. Naves that it is important to use oils from a number of disconnected sources, and that one should use chemical bases also if possible. The advantages of the price stability resulting from this policy are extremely important. On the other hand, on a cost for cost basis the quality of the end product is seldom improved and not infrequently spoiled to some extent.

DR. Y.-R. NAVES : Doubtless it is well to remember that the large

increase in the culture of varieties of high yielding lavender (Matheronne and Maillette) was due to the peasants' faulty assessment of the reception which could be given by consumers of essential oils to the products of new plantations. I recall the position described in *Soap, Perfumery and Cosmetics*, 1,110 (1959).

Dr. Tullen and I showed [*Bull. Soc. Chim. France* 2,124 (1960)] that Materon lavender oil is characterised by a content of terpinene-1-ol-4 almost double (3-3.5% compared with approx. 1.5%) that of a good lavender oil. That is one of the causes of its depreciation, and the analyst must pay particular attention to it.

THE LECTURER: I have regarded the production of Materon lavender as an example of what can happen when an effort is made to increase yield without any attempt to assess the effect on the finished odour. You draw my attention to the observations by Robertet in 1959 that Materon lavender was sold during the first three years of its production at the same price as the fine oils. This surprises me since even at the outset Materon was never offered to me at more than about half the price of good lavender, the thesis being that the trade should find room for an oil of acknowledged lower quality which could be used in less expensive products such as soaps and bath salts. As I see it, the producers thought that an oil would certainly be accepted if it had the right analytical characteristics regardless of its odour. They were proved wrong.

It is interesting to compare this experience with the much more deliberate and careful introduction of the high ester or Super Lavandin—a plant which has been known I believe at least as long as Materon. With the Lavandin the perfumer's opinion was sought from the outset and the oil is coming into use very much as was foreseen.

We are indebted to you for indicating the cause of the disagreeable character of Materon lavender.

DR. Y.-R. NAVES: Long experience of producing new synthetic perfumery materials makes us rather cautious with respect to your desire that their nature should be divulged under the protection of patents, instead of using them secretly in bases.

It is almost always very difficult to foretell which of these products will achieve large production. A general protection of a product, even if it is possible in all cases, is extremely costly. The protection of rights thus acquired is almost always very long and also costly; it is moreover often uncertain because of gaps, inadequacies or errors in the law. Finally, in certain countries and not least for the consumption of synthetic perfumes, it is possible to introduce the product made elsewhere. It is not only sea transport which is acquainted with "pavillons de complaisance".

It is therefore necessary to understand that, considering the costs of research and of production development of a truly original product and the legal possibility of continuing its production in spite of patent demands by third parties, the industry is not obliged to divulge the nature of such products by way of patents.

It is clear that analytical facilities are constantly improving but it is well to reflect that there is often a great deal of work and expense between identifying a new substance and being able to produce it economically and consistently.

It is not possible to establish a general rule for or against the disclosure of a new product. Each case must be considered on its own merits.

THE LECTURER: I accept your observation unreservedly. I am sure if I were in your position I would have very similar feelings. Nevertheless, it is a pity that so much has to remain concealed and one wonders whether some kind of agreement could be reached between leading manufacturers which might enable the pooling of a certain amount of the less vital information with a consequent rationalisation of production. Seeing the matter from my side of the fence I have often suspected that several different concerns were manufacturing the same secret chemicals unknown to each other.

DR. M. H. KLOUWEN: I agree completely with you that the olfactive judgement should be of primary importance. But in many cases support for this opinion can be found in chemical or physical analysis. Experiments carried out by the Institute of Horticultural Plant Breeding (I.V.T., Wageningen, Netherlands) showed that the yield of oil of *Angelica archangelica* roots could be significantly improved by way of selection [De Bruyn, J. W., Elzenga, G., and Keuls, M., *Euphytica* 3 147 (1954)]. The content of pentadecanolide, olfactively the most important constituent of the oil, was at the same time correspondingly decreased.

THE LECTURER: I think your question illustrates a problem which very frequently arises in plant selection. If one seeks to improve one factor, in this case the yield, one almost invariably finds that another factor is adversely affected. I am not myself a large user of *Angelica* and do not know what precise characteristics are most sought after in this oil. The pentadecanolide content must be of importance since it is indeed a very beautiful substance; but since it may be purchased at quite an economically acceptable price it seems to me that the other constituents of oil of *Angelica* are probably, in aggregate, more important. One would have to examine the oils obtained by plant selection to see whether some other characteristics

besides the pentadecanolid content had been adversely affected. If this were not so, then plant selection would have achieved the desired object.

MR. J. G. J. KOK: As far as we know geranyl tiglate has never been identified as such in geranium oil [Gildemeister, E. and Hoffmann, F. *Die ätherischen Öle* V 374 (1959)]. In our opinion the olfactive qualities of the ester are not such that its presence in geranium oil would be of decisive influence on the total odour of the oil.

THE LECTURER: I listed a number of materials the use of which might be responsible for progress within the industry. Let me say at once that if I had been aware of the work on 11-oxahexadecanolide I would certainly have included it, since it appears to be one of the most interesting developments with musk odours which has yet been produced.

I do not think the identification of geranyl tiglate in natural geranium oil is fundamental to the point I am making, which is the broad one that success in the use of new chemicals is most easily achieved if these bear a close relation to materials already present in natural oils. I think this entitles me to include ethyl linalol, for example. As to the olfactive qualities of the material, I am much in the hands of the suppliers. Of two samples of geranyl tiglate which we examined, one, from an American source, appeared to us to be very much the finer, and we have established, on an experimental basis, a small number of applications for it.

SOME ASPECTS OF CONTACT SENSITIZATION DUE TO PERFUMERY RAW MATERIALS

P. H. WITJENS, Dr. ir.*

Presented at the Symposium on "Perfumery", organised by the Society at Cheltenham, Glos., on 14th November 1962.

Different factors which might influence the occurrence of contact sensitization due to perfumery chemicals are discussed.

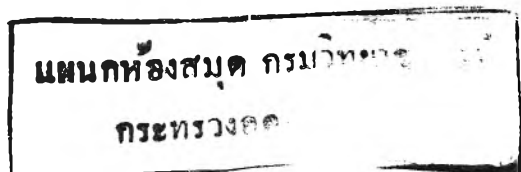
SENSITIZATION OF MAN by contact of the skin with perfumery chemicals is fortunately a phenomenon of relatively rare occurrence. It is for this reason that older publications only occasionally report cases of dermatitis caused by allergic reactions due to specific odoriferous chemicals or essential oils. The increase in the use of cosmetics, and particularly of synthetic detergents and similar products, is reflected in an increasing number of published case histories, reaching a peak during, and shortly after, the period 1940-1945, when impurities in the raw materials as a result of their prevailing scarcity have been in part responsible for the occurrence of dermatitis¹. While these publications on the whole helped to augment the number of recorded cases, there is a distinct tendency in a number of recent studies, in which odoriferous chemicals were also partly considered as eczematogene noxes, to study incidental sensitization reactions against a more general background, both in relation to the medico-biological, and to the chemical, aspects of the sensitization process.

It is particularly when studying the theoretical backgrounds that the rarity of the occurrence of contact sensitization in human beings renders the experimental treatment difficult to a degree. Nevertheless, the ever-increasing degree in which man is brought into contact with organic compounds possessing, in most cases, completely new structural constellations, makes it imperative to study the possibility of contact sensitization, in addition to other toxicological data, from a point of general hygiene.

The field of synthetic perfumery chemicals is no exception, and in fact it may be more desirable for this study since these products are functionally predisposed to an intensive contact with the skin, with a duration of application which can extend over the better part of a man's lifetime.

The study of the phenomenon of sensitization from a chemical point of view will in the first instance be centred around the investigation of the molecular structures which are a condition for eliciting contact sensitization.

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The medico-biological approach of the problem which will not be dealt with has recently been referred to by Calnan², where methods of biological determination were discussed.

Experimental evidence clearly shows the necessity for the low molecular sensitizing agent to form a high molecular compound with proteins, or protein derivatives of the organism, before sensitization takes place³. For the time being, however, this part of the mechanism of sensitization does not give much of a clue with regard to the structural condition with which the sensitizer must comply, for chemical reactions with proteins can be brought about by numerous organic compounds which have never been known to cause sensitization. There is no doubt that apart from the presence of specific reactive functional groups, other structural requirements will have to be met. An important part, for instance, will be played by such factors as steric hindrance and spacial structure, a part which, however, can only be made understandable in its relation to the molecular structure of the proteins involved. For the time being too little is known about the changes in properties which a protein has to undergo before it can act as an antigen for contact sensitization. Only when this knowledge has been extended can conclusions be drawn with respect to the requirements for the structure of organic sensitizers³.

It is true, though, that certain indications of a limited scope have been obtained about this aspect by the study of the phenomenon of cross-sensitization or group-reactions. Whilst sensitization reactions are in general brought about only by specific contact with the product with which the organism has been sensitized, this reaction can in certain cases also be brought about by contact with compounds which are chemically allied to the sensitizing agent. The structural problem can be approached by the study of this relationship which can easily be carried out experimentally, although it has already been clearly established that in human beings individual differences in reactions in cross-sensitization occur.

In several recent investigations the relationship between the sensitizing action, and the chemical structure, by means of cross-sensitization has been the subject of a study by Fregert⁴ on sensitization of a group of products allied with stilbestrol, and by Hjorth⁵ concerning balsam of Peru, and constituents thereof. In tests carried out on persons who showed a distinct sensitization for these products, the reaction capacity in respect of products which showed a specific structural relationship, was investigated. In judging the results of this type of experiment, a clear distinction should be made between compounds which are converted into the original sensitizing agent either by means of a chemical reaction or as a result of enzymatic processes in the skin, and products which possess a structural analogy with the allergene⁶.

Investigations carried out by Schulz⁷ have shown that cross-sensitization can cause over-sensitiveness to a specific product, e.g. ammonium thioglycolate, in persons who have been in prolonged contact with this material, without spontaneous sensitization taking place. Under the influence of sensitization for the related thioglycolic hydrazide Voss⁸ was able to prove these phenomena both on test persons and in guinea pigs for the same type of compounds. Inasmuch as the number of human test objects who are sensitized for a specific compound is nearly always limited, the more or less identical reaction in guinea pigs in cross-sensitization constitutes a very valuable addition to the test material. This is all the more true as cross-sensitization can be highly individual, and a group of test persons sensitized by a primary allergene can react very differently among themselves to a series of secondary allergenes, i.e. allergenes which produce cross-sensitization reactions. When a larger group of secondary allergenes is tested, one will observe distinctly individual reaction patterns. The occurrence of this individual pattern is explained by Sulzberger⁹, who assumes that different functional groups of one sensitizing agent may give rise to different allergenes of which only homologous secondary allergenes may lead to cross-sensitization, whereas no reaction will occur in the absence of this related allergene.

On the one hand there exists a group allergy whereby many facts can be concealed from experimental observation as a result of a very individual reaction pattern. On the other hand, there is the possibility of the formation of over-sensitiveness for already known low, or non-sensitizing, products by primary sensitization due to new structurally related chemicals. This leaves the perfumery chemist with a problem which will continue to claim his attention in research, because structures from practically the entire field of organic chemistry play an important part in perfumery. With our limited, and frequently fragmentary, knowledge of the relationship between chemical structures and sensitizing capacity, it is almost impossible to draw correlations between them in prospective odoriferous chemicals.

The biological experiment will therefore always have to supply the necessary data and such an experiment is greatly complicated by the phenomena discussed above.

The formation of an allergene from a low-molecular organic chemical takes place by the reaction of the organism of the test object with a protein or a derivative thereof. As a result, this protein acquires specific properties which distinguishes it from the body protein and against which the organism builds up its anti-bodies. There are indications that the proteins from which the allergenes are formed, are in a removed position from the epidermic surface, so that the synthesis of the allergene must be preceded by a process of transport in or through the epidermis³.

The extent in which this penetration, and this transport of the sensitizing

agent, can take place will be determined by its chemical configuration. The great differences between the sensitizing action of related compounds, such as those found by Sulzberger⁹ for sulfadiazine and sodium sulfadiazine, could possibly be accounted for in this manner.

It is also to be expected that the carrier in which the sensitizing agent has been incorporated, and in which the contact with the skin takes place, will play a part in the speed of transport to the protein components of the allergene. This can be of considerable importance because of the possibility of a sensitizing potential produced by some perfumery chemicals, as the contact of the skin with these chemicals frequently takes place in the presence of products which are highly surface-active. This statement is justified on the grounds that perfumery chemicals largely make contact with the skin in the presence of soaps, detergents and cosmetics which, in general, contain surface-active agents.

This influence of the vehicle can be demonstrated by the results of human patch tests with 2-cuminyI-propanal, where on changing the type of emulsion of the carrier from an o/w to a w/o emulsion, an impressive change in dermatological response was observed. The positive reactions obtained with the o/w emulsion base almost completely disappeared when similar tests were made in a w/o base¹⁰. In the above tests, the problem is clearly one of transportation of the product in question, brought about by differences in contact, solubility, etc. The change of the reactivity of the skin under the influence of a previous (or simultaneous) contact with detergents or soap^{11,12} becomes, however, a more complicated matter. While certain detergents themselves may cause skin irritation previous treatment of the skin with less aggressive surface-active agents may also lead to a considerable lowering of the threshold value for sensitization with other chemicals. Thus, it might well be possible that unexpected allergic reactions will occur, if, in the dermatological examination, insufficient attention is paid to changes in the properties of the epidermis, which may result from continued contact with highly surface-active material. This may also apply with respect to perfumery raw materials and only a properly conducted test programme with the completed product will give evidence for the safety of use.

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Introduction by the lecturer

I would like to stress that skin sensitization with man due to perfumery is a phenomenon of rare occurrence. Nevertheless a careful observation of these phenomena is fully warranted. The quantities of perfume being used in some form or other are rising steadily. This is especially applicable to perfume compounds incorporated in end-products based on highly surface active materials, which will naturally promote an intensive contact with the skin.

It is a happy coincidence that the study of contact sensitization, especially due to simple organic chemicals, is starting to emerge from a purely empirical one and has recently been treated more and more by a more fundamental approach. In these theoretical considerations, especially with regard to the chemical aspects, the experience in perfumery, with its raw materials, covering nearly the entire field of organic chemistry, will no doubt be of much value.

Likewise, knowledge obtained in this way may serve the perfumery chemist as a guiding principle and as an additional source of reference in the study of the dermatological properties of new perfumery chemicals. In particular, the tendency in perfumery chemistry to replace natural products, where the dermatological behaviour is traditionally known, by synthetic chemicals may introduce the necessity of careful evaluation of the possibility of an adverse effect in contact with the skin.

The experimental approach to the phenomenon of skin sensitization is rather difficult owing to the fact that contact sensitization is not a general response of the human organism, but a rather exceptional and individually abnormal reaction on a normally harmless contact of foreign materials with the skin. In order to study the physiological and chemical backgrounds of contact sensitization in man, the investigator has, in general, to confine himself to a very limited group of test subjects.

On the other hand, there is the possibility of studying sensitization effects on animals (rabbits and guinea pigs) but we have to realize that the effects produced in those animals are probably different from those to be expected with man.

DISCUSSION

MR. G. L. GARDEL : May I assume that your research was carried out on single products, and that you did not use them in combination with other materials? I have found, from experience, that this sort of behaviour can be expected with single products, but when they are mixed with other components in a perfume compound, there is no effect whatsoever.

THE LECTURER : I agree with that experience, and there are several possible reasons for this. In the first place, the concentration of the product is appreciably lowered in this way. Another reason is that the process is not finished when the material is applied to the skin, is in fact just commencing. The product has to penetrate the skin to a certain extent and has to react with other organic structures. All these processes may be influenced or interrupted by the presence of, say, 99% of other materials. Even the way in which the material is applied, e.g. in a cream base, an alcoholic solution, etc., may have an influence on the dermatological response.

MR. B. H. KINGSTON : Is it not possible that the presence of alcohols, normally present in perfume blends, will render innocuous the aldehyde and ketone sensitizers, due to the formation of acetals and ketals?

THE LECTURER : Yes.

MR. D. BASS : Do you have any experience of perfumes irritating the eyes? I think it is common practice to perfume eye lotions. There are certain detergents available for baby shampoos, that do not irritate the eyes or sting them. Is there a perfume that does not irritate the eyes?

THE LECTURER : I think this is quite another problem. You are dealing here with primary irritation, and this is essentially different to sensitization. Primary irritation is a more direct reaction on nerve endings and an effect which is reproducible by all humans. Sensitization is just an effect that occurs after repeated application of much lower concentrations that are not irritant as such, and only affect a small proportion of people—it is not the normal reaction. As far as the eye irritation is concerned, one experiences a feeling of pain in the eyes due to a difference in osmotic pressure and this will safeguard the eyes against prolonged contacts with foreign materials. Even plain distilled water stings the eyes, because it is not isotonic. As far as the shampoos are concerned, I consider it better to have a shampoo that stings, rather than one that gives no pain but which might be harmful; one is not warned in the second case and that may be much more dangerous.

DR. J. H. MERZ : Do you find that a whole group of sensitized people are sensitive to the same sort of materials, or is it a question of idiosyncrasy—one person may be sensitive to one thing and someone else to another.

THE LECTURER : The reactions are completely individual.

MR. J. M. BLAKEWAY : Do you have to screen guinea pigs for particular sensitivities, in the same way that you do human beings? Are they more sensitive than humans, less, or do they have the same peculiarities?

THE LECTURER : In the case of guinea pigs and rabbits we use special strains which are pre-disposed for sensitization. The reactions of the individual animals of these strains are almost identical. In general, animals are less sensitive.

MR. P. J. L. BONGARD : Has sensitization any connection with the pH of the skin?

THE LECTURER : It would lead me too far into medicine to answer this question. The pH can certainly be correlated with the occurrence of eczematous reactions, but deviations from the normal pH of the skin belong to medicine.

MR. G. M. HOWARD : Am I to understand that for your tests you select a specific number of people who are prone to sensitization?

THE LECTURER : Not in our tests, but there are investigators who are working in this way.

MR. G. M. HOWARD : Is it correct to select a section of the community who are subject to allergic effects, for specific tests on sensitization?

THE LECTURER : In experimental work to study the theoretical backgrounds of contact sensitization the chance of achieving results is much higher in these pre-selected groups of test-people. In a group of normal people these studies are almost impossible from a practical point of view.

DR. V. KLEIN : I assume that the normal method of determining sensitization is a patch test.

THE LECTURER : Yes.

DR. V. KLEIN : In carrying out the patch test, where do you determine the concentration to differentiate between a primary irritation and sensitization? Some years ago one of our men, who developed a serious dermatitis, was sent to a specialist who carried out some 30 patch tests on his back with concentrated materials including aldehydes, alcohols, etc. As a result, almost all of the tests were positive but the man was certainly not sensitive to so many of the materials. Where do you determine the threshold?

THE LECTURER : By lowering the concentration. When we have positive reactions we reduce the dose and try to find a threshold. If this is 50 times or 100 times the normal use value in perfume compounds, then it may still be possible to use the product involved.

CORROSION IN ALUMINIUM CONTAINERS

E. K. CLARKE, B.Sc., M.Inst.Pkg.*

Presented at the Symposium on "Aerosols", organised by the Society, at Southport, Lancs., on 25th April 1963.

An investigation of a method to predict corrosion was made with cells constructed with electrodes of nickel, and aluminium taken from pressure containers. The electrolytes were a series of different hair sprays. The current flowing was plotted automatically as the cells were discharged over 24 hours. No general correlation was found between these results, and the results of storage tests except for formulations containing highly corrosive ingredients.

INTRODUCTION

THE AEROSOL industry is still technically very much in its infancy. A kind of folklore is often found behind very firmly bound beliefs about the behaviour of aerosol systems. An opinion once stated, and then quoted, becomes "fact". The effect of this is to make predictions about the behaviour of such systems (particularly with regard to stability and corrosiveness) very uncertain. The most experienced workers, like the earlier workers in the aircraft industry, still have to say, "Let's try it and see!".

Probably the most worrying problem is the prediction of corrosion. Apart from damage to the product, the container can be attacked, and especially in the case of aluminium, perforated with disastrous effect. Various tests have been suggested which might rapidly show up corrosion. Thus it has been suggested that the increase in dissolved metals, or the increase in aldehydes be measured. Bower¹ has recently shown that pH measurements whilst related to corrosion do not enable *predictions* to be made about complete formulations, whilst Root² has shown the value of pH in assessing batches of propellant.

This paper discusses a preliminary examination of a method which has been used, or considered, by many people concerned with aluminium containers, particularly non-pressurized ones. The method is a modification of the Denison Cell described elsewhere^{3,4}. A cell is constructed having one electrode of aluminium and the other of nickel, using the product under test as the electrolyte. The cell is allowed to discharge under its own potential force and the current which is of the order of microamps is measured over a period of time. The type of polarisation curve produced is said to be characteristic of the type of corrosion that may be expected.

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It has been thought that there are three types of curve which can be related to the kind of corrosion found in practice, and these are shown in *Fig. 1*. Curve *A* is said to be given by non-corrosive formulations, curve *B* by formulations which cause general surface etching with evolution of hydrogen, and curve *C* by formulations which cause the pitting-type of corrosion.

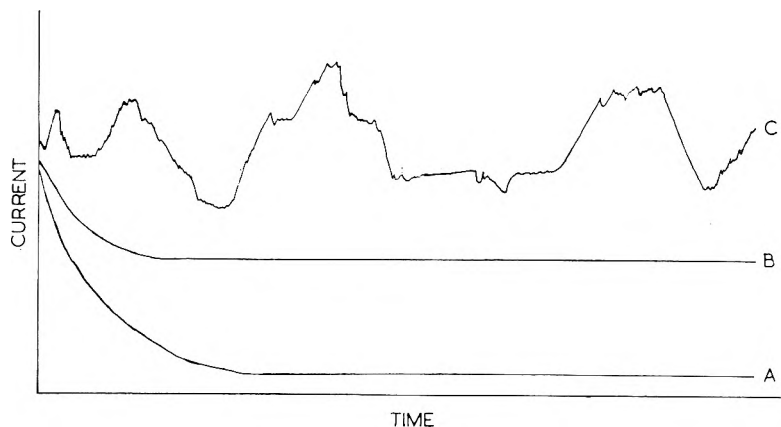


Figure 1

Three types of corrosion curve

This type of cell has enabled a sensible choice to be made between various formulations over a range of non-pressurized products packed in collapsible aluminium tubes. For example, in my experience this method has helped to choose inhibitors for a new type of toothpaste. The method has not, however, been foolproof, and formulations have been found which pass this test and yet give trouble on storage. The reasons for this are discussed later. On the other hand, formulations which failed the test were certainly unsuitable.

A simple cell can be constructed for products to be packed into collapsible tubes. Pressurized products obviously require a different type of cell. The containers used for pressure packing also vary widely, including tinsplate containers with soldered or welded seams, drawn blackplate, aluminium with tinsplate ends, two-piece aluminium with aluminium ends, and one-piece aluminium containers. Valve cups also may be in tinsplate or aluminium, and various lacquer systems are available for the various components.

For simplicity in this preliminary investigation it was decided to concentrate mainly on one formulation type (hairsprays), and to use the most

simple container system—the unlacquered aluminium one-piece, sealed with a valve in an unlacquered aluminium cup.

CONSTRUCTION OF CELLS AND STANDARDISATION OF ELECTRODES

The cells used were constructed by modifying glass compatibility testers. As can be seen from *Fig. 2* these consist of tough glass vessels closed at the top with metal plates, and carrying means for mounting valves having the standard one inch cup. The valves are secured, not by swaging, but by small plates screwed to the assembly.

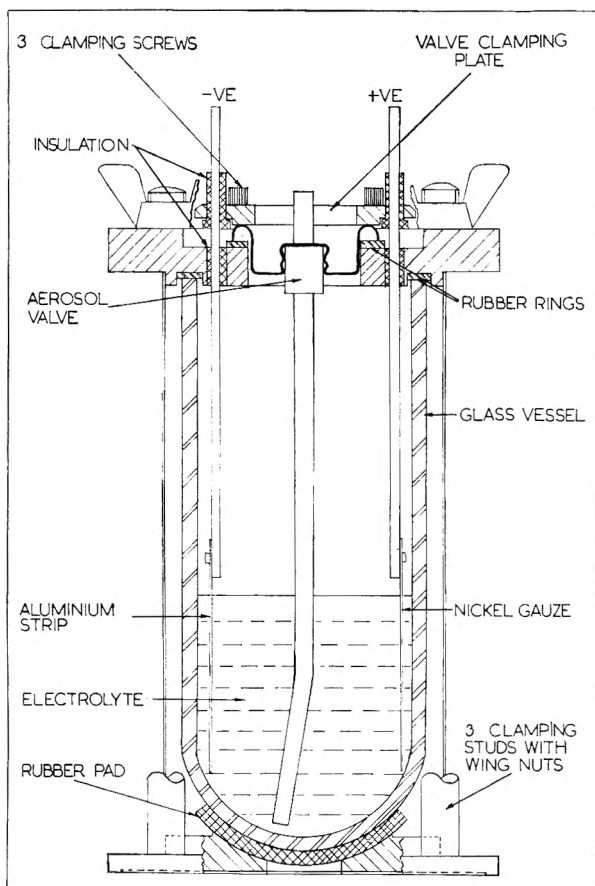


Figure 2
Corrosion cell

The top plates were drilled with holes 1.5" apart and brass rods passed through, being secured and insulated with an epoxy resin. In these particular

cells the rods were of such a length that they ended with a mounting screw about $\frac{1}{4}$ " above the level of 80 ml of liquid in the vessels. The electrodes were $2" \times \frac{3}{4}"$, with a small hole drilled about $\frac{1}{4}"$ from one end to take the mounting screw. Thus when mounted in the cell, $1\frac{1}{2}"$ of electrode dipped below the surface of an 80 ml fill.

The cathodes were constructed of nickel gauze, and degreased in benzene as described for the anodes.

The anodes were made by cutting open aluminium one-piece containers and removing the top and bottom ends. The sides were flattened and abraded on both sides with wet, fine emery paper to remove scratches. They were then polished successively with carborundum powders 2F, and 500, suspended in glycerin. Pieces $2" \times \frac{3}{4}"$ were cut from the prepared sheets using a guillotine, and holes drilled $\frac{1}{4}"$ from one end of each. The cut edges were smoothed with wet emery paper. The cut pieces were degreased in a Soxhlet extractor over benzene, for one hour. After this the electrodes were not touched by hand and were stored in a desiccator until required. The anodes were then etched for two minutes in boiling nitric acid (10%), rinsed thoroughly in distilled water, dried between filter papers and placed in a desiccator for a maximum of 30 minutes before use.

After the electrodes had been fitted in the cells, the latter were filled without delay with a total of 80 ml of concentrate and propellant. The experiment was also started without delay.

It was thought best that the aluminium be standardised to eliminate any variation in the amount of scratching or surface treatment which the metal had received.

The current flowing when the cells were discharged was found by discharging through a 10,000 ohm resistor and measuring the potential across the resistor with a *Cambridge* recording galvanometer.

The internal resistance of these cells when filled with normal anhydrous hairsprays was about 10^5 — 10^6 ohms. The 10^4 ohm resistor mentioned above therefore approximates to a short circuit of the cell. The potential of many of the cells was measured on open circuit with a potentiometer, and found to average about 0.5v.

STORAGE TESTS

Every formulation which was tested on the corrosion cell was also put on storage test. The storage tests were carried out in unlacquered one-piece containers which were closed with valves mounted in unlacquered aluminium valve cups and also in internally lacquered one piece containers closed with valves in lacquered tinsplate cups. The method of filling was to place the concentrate into the container, then displace the air by blowing

in about 3 cc (measured as liquid) of the propellant to be used, and immediately sealing the valves onto the containers. The propellant was pressure-filled through the valves.

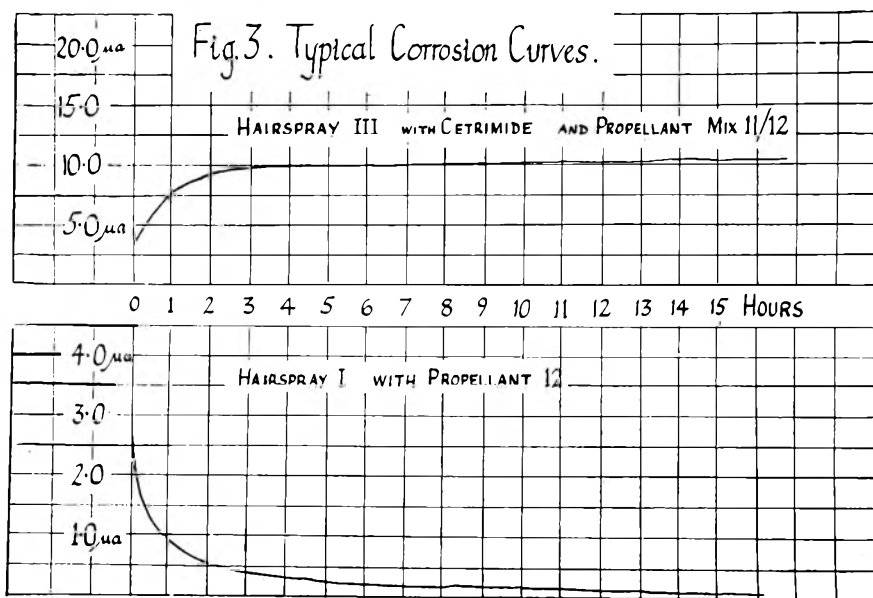
Twelve containers were stored, on their sides, at each of the conditions— 1° ; 20° ; and 40°C . One container from 40° was examined after one week, and one container from each condition after one, three, and nine months. Further examinations up to two years will be carried out in due course.

FORMULATIONS

The formulations were all hairsprays, except for one test with Industrial Methylated Spirits alone, and varied in type of resin, perfume, and denaturant. All were made up in such a manner that when the propellant was added, the water content of the system was less than 0.5%, except where added deliberately as indicated in the tabulated results.

RESULTS

As mentioned above, each cell was allowed to discharge for 24 hours while the current was measured. The graphs generally were very similar in shape, the current falling fairly quickly to a lower value than at the start, except with one or two very corrosive formulations (*Fig. 3*) where an increase was found. In all cases, however, the current became fairly steady



after about 15 hours, and for that reason the reading obtained after this time was selected for comparison with the storage test results. The results of the corrosion cells and the storage tests are summarized in *Table 1*, and compared.

Table 1

| Formula | Pro-pellant | Cell Reading* | Prediction of suitability & rank in order of corrosion found on storage tests. Highest number is most corrosive. | | |
|-----------------|-------------|---------------|---|---|---|
| | | | 3 months at 40° in UNLACQUERED containers | 9 months at 20° in UNLACQUERED containers | 9 months at 20° in LACQUERED containers |
| I | 11s | 0.0 | N 4 | D 2 | S 3 |
| I | 12 | 0.1 | N 4 | D 1 | S 3 |
| IMS | 11/12 | 0.1 | S 2 | test stopped | not tested |
| II | 11/12 | 0.1 | S 1 | N 3 | S 1 |
| I | 11 | 0.2 | D 3 | N 4 | N 6 |
| I | 11/12 | 0.2 | D 3 | N 4 | S 4 |
| III | 11/12 | 0.2 | D 3 | N 4 | S 2 |
| IV | 11/12 | 0.1—0.4 | S 2 | D 1 | N 5 |
| IV + Cetrimide | 11/12 | 1.5 | N 6 | stopped at 3 months | N 7 |
| IV + Cetrimide | 12 | 2.6 | N 6 | stopped at 3 months | N 7 |
| I + 5% water | 12 | 1.0—4.0 | N 5 | N 5 | S 1 |
| III + Cetrimide | 11/12 | 20.0 | N 6 | stopped at 3 months | N 8 |

* 15 hour reading in MICROAMPERES from graphs.

N—not suitable.

D—doubtful.

S—suitable.

It can be seen that the graphs fall into two main groups, those with 15 hour readings up to 0.4 microamps, and those with readings over 1.0 microamps. The formulations can also be divided into two groups, those considered suitable for use in the containers used, and those unsuitable. A formulation was judged unsuitable if the container exhibited any pits.

It can be seen that the two groups found by each method do not coincide. Neither do the order, in which the formations could be ranked by either method, correlate with one another.

DISCUSSION

This method will pick out formulations which contain actively corrosive ingredients, such as Cetrimide. This can be done in about 24 hours, compared with about one week, if strips of aluminium were merely immersed in the product in a compatibility tester and then examined visually.

Formulations which become corrosive slowly because of a gradual interaction between ingredients (such as between ethanol and trichlorofluoromethane) are not actively corrosive when packed and should not be expected to give different graphs to stable formulations at that time. This, it is suggested, is the reason why failures with the method are found, as with the toothpaste mentioned in the introduction. It is considered that if the containers are stored long enough for the contents to become corrosive, and thus yield an appropriate graph on the corrosion cell, the corrosion inside the dispensers would already be visible to the eye.

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Introduction by the lecturer

The reason for the work described in this paper was a desire to find a method of prediction. It was hoped that it would be possible to decide which formulations would or would not corrode the containers for pressure packs, without time and labour-consuming storage trials.

The simplest possible practical system was chosen: The all aluminium container and valve cup without lacquer, and one kind of formula—the alcoholic hair spray. If success was achieved with this the method could be extended to more complex systems.

The results show that certain predictions were made after three months. If all the "Not Suitable" and "Doubtful" formulations had been rejected after three months the whole series would have come to an end. However, after nine months storage three of the combinations in unlacquered aluminium were found not to have perforated. They are the ones packed in unlacquered containers which have been marked as "Doubtful". If any of these three were in other respects outstanding formulae, they might merit further and larger scale testing to make a conclusion possible.

All the containers from the unlacquered sets which had not perforated had some patches of etching corrosion. Some of the containers holding other formulations which had perforated were completely clean inside except for the perforation! In some instances the same formulation produced some containers with only slight etching, and some with perforations.

It therefore seems likely that the three formulations which did not perforate were probably a chance occurrence. A larger number would be needed to settle this point.

The safest conclusion is that all the formulae are unsuitable in the unlacquered aluminium pack. Slow perforation is as serious as fast. In fact the cell reading taken when fresh may hide an accelerating reaction.

From this series of experiments, I draw the general conclusions that the corrosion cell is not relevant in trying to predict whether or not a formula will corrode. It will probably pick out the highly corrosive combinations which would show up quickly anyway. Three months' storage at 40°C is an inefficient method of prediction unless one is willing to use it only as a screening test; successful formulae remaining on test much longer before being passed.

My recommendation would be to test lacquered and unlacquered containers at least at 20°C and at 40°C. If there are any traces of corrosion after three months I would reject the formula. If after nine months there were no blemishes at all at 20°C, and only very minor ones at 40°C, I would be prepared to pass the formula. If one was very anxious to use a formula which failed this test, the only solution is to pack at least 250, and preferably more than 500 containers and store them for nine months at 20°C. The formula would then be passed if no containers are perforated or badly pitted.

DISCUSSION

MR. A. HERZKA: Your findings appear to confirm that for pressurized packs there is no real substitute for long term storage tests.

How do you account for the difference between curve C, Figure 1 and the curve for Hairspray III, Figure 3?

THE LECTURER: I too believe that there is no more sensible way of testing pressurized packs than long term storage. As I have indicated, short term tests can serve as screening tests to remove extremely corrosive products, although there is a risk that successful formulae will also be rejected occasionally. No product-pack combination should ever be released unless it has successfully passed at least nine months' storage at the normal service temperature.

I do not know enough about the basic processes underlying the reactions in the cell to give a reason for the difference between curve C and the curve

for Hairspray III. However, curve C is typical of the results obtained when testing products, such as shampoos, which are designed for aluminium collapsible tubes, and which gave corrosion of the pitting type. Such systems are, of course, aqueous in comparison with the pressure packs we have been testing which are almost anhydrous.

MR. A. HERZKA: Have you carried out any tests with this method on hair lacquers in internally plain and lacquered tinfoil containers, shaving cream formulations, and antiperspirants?

THE LECTURER: Although some of the formulations have been tested in tinfoil containers, I have not systematically covered the same ground or attempted to relate those results I have in tinfoil with the aluminium containers. As I mentioned above I was confining myself to as simple a system as possible. Aluminium containers, whether lacquered or not, presumably exhibit the same sort of corrosion reactions. The tinfoil container is a much more complex affair.

I have tried to use this method on shaving cream formulations without success and have not pursued it very far. I did get very high readings from the corrosion cells, probably because of the high water content. On the limited numbers tried it was not possible to distinguish between corrosive and non-corrosive formulations. I have not tried antiperspirants.

DR. P. H. WITJENS: May I ask if anodised aluminium containers have been included in the experiments?

THE LECTURER: No. I would like to emphasise that in using these cells I was trying to find a method which would predict whether the product/aluminium combination was inherently corrosive. The question of what treatment or lacquer will best protect the aluminium is another matter.

MR. K. DIXON: Has this method been considered as a screening test to eliminate variables from storage tests?

THE LECTURER: This method will certainly remove highly corrosive combinations from test. It must be remembered, however, that the difference between highly corrosive and slightly corrosive can be slightly academic. A formulation which eats through 10% of the containers after one year, is just as commercially a disaster as one which eats through 50% in three months!

On the whole I am inclined to think that the best screening test is short term storage in the chosen pack, lacquered and unlacquered, and examination with a microscope after three months. Containers showing the slightest blemish would condemn the formulation. There is then the risk that a usable formulation is in fact being rejected, but this is probably unavoidable.

LANOLIN DERIVATIVES FOR PRESSURIZED FORMULATIONS

A. HERZKA, B.Sc., F.R.I.C.*

Presented at the Symposium on "Aerosols", organised by the Society, at Southport, Lancs., on 24th April 1963.

The solubility of ten lanolin derivatives in nine different propellant and propellant/alcohol systems is described. The results indicate that most of the materials exhibit satisfactory solubility at 0° C.

INTRODUCTION

THE SOLUBILITY of ten lanolin derivatives in propellant and propellant/alcohol systems was investigated in order to establish their likely usefulness in formulations intended for pressurized packing. As the propellant may be added to a formulation either at ambient (room) temperature or at a low temperature, i.e. during cold filling, the tests were carried out at 20° C and at 0° C.

The following products were tested :

i. *Anhydrous lanolin, B.P.*

The physical and chemical properties of anhydrous lanolin (refined wool fat), even amongst samples all complying with the British Pharmacopoeia or the Toilet Preparations Federation specification, can vary to an appreciable extent according to the source of the raw wool fat and the refining methods employed. Since it is conceivable that solubility in propellants could be one of the variables involved, it should be put on record that the lanolin used in the present work was refined from wool fat centrifugally-recovered from wool washed with soap, not detergents. Refining processes included chemical as opposed to absorptive deodorisation and bleaching. The lanolin used was a pale, superfine quality, complying with both of the specifications mentioned above. The substance is used in a very wide range of cosmetic products not only because of its outstanding emollience on the skin, but also by virtue of its powerful w/o emulsifying properties, plasticising and hair-conditioning properties, etc.

ii. *Wool alcohols, B.P.*

This official pharmaceutical description is essentially a misnomer, the product being more accurately described as wool wax alcohols, lanolin

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alcohols, etc. The so-called wool alcohols represent the unsaponifiable fraction of wool fat, the theoretical yield being about 50% from refined lanolin but varying according to the raw material used and the methods used for saponification, extraction and refining. The physical properties of this refined product also vary according to its previous history, examples of properties affected being—emulsifying power, cholesterol content, hydroxyl value, and to a certain extent, solubility. The product used was produced from anhydrous lanolin of pharmaceutical quality and extracted with trichloroethylene, subsequent refining operations including vacuum—deodorisation and chemical bleaching.

The uses of wool alcohols in cosmetics are basically similar to those of lanolin, but the product is much harder, having a brittle waxy consistency as compared to an unctuous grease. Its w/o emulsifying properties are much more powerful than those of the original lanolin.

It may be used in pressurized emulsions, or, for example, as a plasticiser or film-modifier in hair sprays. Like lanolin, wool alcohols are insoluble in water, and thus can only be utilised in pressure packs in the form of emulsions or as solutions in organic solvents or in a suitable propellant system.

iii. *Liquid lanolin "A.C.E."*

This is a chemically modified lanolin derivative, consisting of an almost fully acetylated fraction of wool alcohols. It is a clear, moderately viscous fluid, very readily taken up by the skin without any residual stickiness. The product has virtually no emulsifying properties by reason of the blocked hydrophilic groups, but is very emollient, conditions the hair and imparts gloss, and is soluble in, and compatible with, a wide range of products used in cosmetics and pharmacy.

iv. *Alcohol soluble lanolin*

Prepared from B.P. quality wool alcohols, and not chemically modified in any way, the physical characteristics of this material are those of a soft, easily melted, orange coloured wax with a faint, characteristic odour. It has a high content of free cholesterol, and is thus a ready means of achieving an alcoholic solution of cholesterol (which itself has limited solubility in cold alcohol) for scalp treatments. Alcohol soluble lanolin still retains some of the powerful w/o emulsifying characteristics of its parent wool alcohols, but is much less efficient and gives less stable emulsions.

It is ideal for the preparation of alcoholic hair sprays. The product is stabilised during manufacture to be resistant to oxidation, and its films, even when freely exposed to the air, never become brittle or powdery, and

are always easily removed from the hair, if desired, by washing or shampooing.

v. *Liquid lanolin "50 Super"*

This is a chemically unmodified fluid fraction of the lanolin esters obtained by physical segregation, similar to the conventional solid lanolin chemically and dermatologically, but in the form of a clear fluid which is more easily applied to, and absorbed by, the skin, and which has better general solubility in organic solvents.

vi. *Liquid lanolin I.S.O.*

A blended and oil-solubilised lanolin, it consists of a mixture of 40% unreacted lanolin with free alcohols and *isopropyl* esters. It is a clear, very mobile, pale yellow liquid soluble in anhydrous ethanol, *isopropanol*, acetone, mineral oil and many other organic substances, and is valuable in brillian-tines, hair sprays, hand lotions, etc., where the minimum viscosity and the absence of stickiness are important.

vii. *Liquid lanolin "R.I.C.2"*

Another blended and oil-solubilised lanolin, it contains 25% of unreacted lanolin together with 25% of ricinoleic esters and free alcohols. It combines the properties of lanolin and castor oil, and is so formulated as to have a wide range of compatibilities with cosmetic ingredients. The product is a clear liquid of low viscosity, is emollient to the skin and gives a good gloss to the hair.

viii. *Liquid lanolin "L.I.N."*

This product belongs to the same class as (vi) and (vii) above, and contains 40% of chemically unreacted lanolin with linoleic esters and free alcohols. In physical characteristics it is similar to the I.S.O. grade (vi), but the unsaturated components are valuable for the skin and impart an outstanding gloss to the hair. The odour is faint, the unsaturated note being hardly detectable, and the product is stabilised against auto-oxidation.

Products (vi), (vii) and (viii) are characterised by low cloud and pour points.

ix. *Water soluble lanolin "75"*

Water soluble lanolin consists of ester/ether compounds resulting from the reaction between the natural esters of which lanolin is composed and

ethylene oxide. The latter condenses to form long chains joined by ether linkages which become hydrated when dissolved in water and enable the product to form transparent solutions which are of an essentially colloidal nature. The hydration may be reversibly disrupted by heating a solution, temporary cloudiness or insolubility then being manifested.

Most of the cholesterol contained in the original lanolin (approximately 20%) reacts with the ethylene oxide, and thus the products no longer conform to identity tests such as the Liebermann-Burchard reaction. The product is fairly hard, and is no longer soluble in mineral oil, but emollient and readily absorbed by the skin without residual stickiness. In addition it possesses wetting, foaming, emulsifying, gelling and solubilising properties, and this surface activity enables it to be used in soaps or shampoos, for example without any significant deleterious effect on lathering power such as results from any but a small addition of pharmaceutical anhydrous lanolin. Emulsions are, of course, no longer of the w/o but of the o/w type.

x. *Water soluble wool alcohols "20"*

This consists of pharmaceutical wool alcohols B.P. of the highest quality ethoxylated to a sufficient extent for full solubility in water, and therefore comprises the polyglycol ethers of the natural, complex fatty alcohols derived from lanolin. These include alcohols of steroid, triterpene and aliphatic types and, on the basis of their mean molecular weight, the molar ratio of alcohols to ethylene oxide in the ethoxylated product is approximately 1:20. At this degree of ethoxylation most of the original, high free-cholesterol content has undergone condensation, the product now yielding only a small amount of digitonide complex and giving only a weak reaction in the colorimetric Liebermann-Burchard test. Ethoxylation also greatly reduces the acetyl value and melting point, and the product is rather softer in consistency than wool alcohols B.P., and becomes plastic when warmed in the hand.

Although a greater degree of ethoxylation will yield a product which has a rather higher solubility in water, the solubilising action exerted on non-water soluble substances is at an optimum when the molar ethoxylation ratio is between 1:15 and 1:20. A minimum ratio of 1:20 is necessary for aqueous solutions to be reasonably clear, and water soluble wool alcohols "20" thus provides the most satisfactory compromise between solubility and solubilising power, and hence represents an extremely versatile and useful product.

Its use in pressurized formulations may be summarized as—water soluble emollient, o/w emulsifier, solubiliser for liquid lanolin or perfume oil, etc., hair conditioner, plasticiser or film former in hair sprays.

Table 1 summarises the analyses of these ten products.

Table 1

| | Anhydrous lanolin B.P. | Wool alcohols B.P. | Alcohol soluble lanolin | Liquid lanolin 50 Super | Liquid lanolin ISO | Liquid lanolin LIN | Liquid lanolin RIC 2 | Liquid lanolin ACE | Water soluble lanolin 75 | Water soluble wool alcohols 20 |
|---|------------------------|--------------------|-------------------------|-------------------------|--------------------|--------------------|----------------------|--------------------|--------------------------|--------------------------------|
| Ash (%) | 0.02 | 0.05 | 0.04 | 0.01 | 0.01 | 0.01 | 0.02 | 0.04 | 0.13 | 0.20 |
| Volatiles (1 hr. at 105° C.) (%) | 0.10 | 0.35 | 0.40 | 0.17 | 2.00 | 1.20 | 3.00 | 0.20 | 0.20 | 0.30 |
| Free cholesterol (%) | 1.5 | 34.0 | 25.9 | 3.3 | 1.2 | 1.2 | 0.8 | 0.8 | trace | trace |
| Total cholesterol (%) | 20.0 | 34.6 | 27.6 | 13.8 | 5.6 | 5.6 | 3.5 | 25.0 | 0.3 | 1.1 |
| Unsaponifiables (%) | 52.0 | 96.3 | 93.0 | 54.0 | 31.8 | 41.3 | 23.6 | 84.8 | — | — |
| Acid value | 0.4 | 1.4 | 2.9 | 1.0 | 0.4 | 0.6 | 0.7 | 1.4 | 0.2 | 2.0 |
| Saponification value | 95.0 | 6.0 | 14.0 | 100.0 | 140.0 | 114.0 | 146.0 | 155.0 | 16.0 | 9.0 |
| Iodine value (Wij) | 27.0 | 35.0 | 35.3 | 27.5 | 23.0 | 77.0 | 35.1 | 48.4 | 23.0 | 22.0 |
| Acetyl value | 29.0 | 140.0 | 160.0 | 38.2 | 46.0 | 64.9 | 79.6 | 8.0 | 34.4 | 60.0 |
| Melting point (°C) | 40.0 | 60.0 | 43.0 | 18.3 | — | — | — | 15.0 | 49.2 | 47.5 |
| Flash point (open) (°F) | 400 | 340 | 290 | 400 | 305 | 335 | 306 | 425 | 530 | 500 |
| Cloud point (°F) | — | — | — | 55 | 48 | 36 | 30 | 56 | — | — |
| Pour point (°F) | — | — | — | 55 | 35 | 25 | 25 | 50 | — | — |
| Specific gravity at 20° C | 0.94 | 0.96 | 0.98 | 0.95 | 0.89 | 0.89 | 0.90 | 0.98 | 1.14 | 1.11 |
| Viscosity (Redwood No. 1) at 60° C (secs) | 730 | — | 977 | 738 | 51 | 57 | 64 | 392 | 3453 | 60 |
| Solubility in water | nil | nil | nil | nil | nil | nil | nil | nil | complete o/w | complete o/w |
| Emulsifying tendency | w/o | w/o | nil | w/o | w/o | w/o | w/o | w/o | complete o/w | complete o/w |

EXPERIMENTAL

The following systems were tested :

- A — propellant 12
- B — propellant 11
- C — propellant 114
- D — propellant 12/IMS, DM7 grade, 74 o.p. (2:1 w/w)
- E — propellant 11/IMS, DM7 grade, 74 o.p. (2:1 w/w)
- F — propellant 114/IMS, DM7 grade, 74 o.p. (2:1 w/w)
- G — propellants 11/12 (1:1 w/w)
- H — propellants 11/12/IMS, DM7 grade, 74 o.p. (1:1:1 w/w)
- I — propellants 11/12/isopropanol 99% (1:1:1 w/w)

5% by weight of each product was mixed with the propellant, or pre-dissolved in the alcohol prior to the addition of the propellants. With anhydrous lanolin B.P. (i) and liquid lanolin "50 Super" (v) it was, however, necessary to introduce the product directly into the test bottle, and each material was warmed therein together with the requisite amount of alcohol in order to achieve maximum solution prior to the addition of the propellant. Whenever a particular material was found to be insoluble in a system

containing either propellant 11 or 114, the dispenser was warmed and kept at 50° C for 15 minutes, amidst constant shaking, to obtain maximum solution. No warming took place with System A (propellant 12), but where necessary, the dispensers were shaken intermittently for 1 hour. All filled dispensers were allowed to stand for 1 hour at 20° C before being examined for solubility. The results obtained are detailed in *Table 2*.

Dispensers filled with each variable were re-examined after 6 weeks' storage at both 20° C and 0° C, in the following manner.

Dispensers stored at 20° C

- (1) Visible assessment of solubility
- (2) Assessment of sprayability, and observation of valve blockage, if any.

Dispensers stored at 0° C

- (1) Visible assessment of solubility at 0° C, and after being allowed to stand for 24 hours at 20° C.
- (2) Assessment of sprayability, and observation of possible valve blockage, at 0° C, and after being allowed to stand for 24 hours at 20° C.

Containers and valves

Plastic coated glass containers were utilised for all tests. For systems *A-H*, Aerosol Research valves AR74 with SF64 (0.02") actuators were employed, and for system *I*, Precision valves [J18 stem, standard housing (0.08")] with reverse taper break-up spray actuators. There was no definite preference for the Aerosol Research valve, but Precision valves suitable for glass containers were not available to us at the time when these experiments were started.

RESULTS

Table 2. Solubility of 10 lanolin products after 1 hour at 20° C

| Lanolin products | Propellant systems | | | | | | | | | Total |
|------------------|--------------------|----|----|----|----|----|----|----|----|-------|
| | A | B | C | D | E | F | G | H | I | |
| i | 4 | 3 | 6 | 4 | 3 | 4 | 3 | 3 | 4 | 34 |
| ii | 5 | 3 | 6 | 3 | 3 | 3 | 3 | 2 | 2 | 30 |
| iii | 4 | 1 | 6 | 1 | 1 | 3 | 2 | 1 | 3 | 22 |
| iv | 5 | 2 | 6 | 2 | 1 | 2 | 4 | 2 | 2 | 26 |
| v | 4 | 1 | 6 | 2 | 1 | 3 | 2 | 1 | 2 | 22 |
| vi | 2 | 2 | 6 | 1 | 2 | 2 | 2 | 1 | 1 | 19 |
| vii | 6 | 2 | 6 | 2 | 1 | 1 | 2 | 1 | 1 | 22 |
| viii | 1 | 2 | 6 | 1 | 2 | 2 | 1 | 1 | 1 | 17 |
| ix | 4 | 4 | 6 | 2 | 2 | 4 | 4 | 2 | 4 | 32 |
| x | 6 | 4 | 6 | 2 | 2 | 3 | 4 | 4 | 4 | 35 |
| Total | 41 | 24 | 60 | 20 | 19 | 27 | 27 | 18 | 24 | |

Key

- 1 = soluble—no precipitate
- 2 = soluble, with negligible precipitate (visible only on close scrutiny)
- 3 = soluble, with slight precipitate (readily seen on inverting bottle)
- 4 = partially soluble, with either a dense precipitate or an insoluble liquid layer floating on the surface
- 5 = partially soluble with dense precipitate and insoluble waxes
- 6 = totally insoluble
- a = agglomeration of precipitate

Table 4. Spray results after 6 weeks

| Lanolin products | Propellant systems | | | | | | | | | | | | | | | | | | | | | | | | | | |
|------------------|--------------------|-----|---|---|---|-----|---|---|---|---|---|---|------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 20° C | | | | | | | | | | | | 0° C | | | | | | | | | | | | | | |
| | A | B | C | D | E | F | G | H | I | A | B | C | D | E | F | G | H | I | A | B | C | D | E | F | G | H | I |
| i | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| ii | U | S | S | S | S | U/S | S | S | S | U | S | S | S | S | U | S | S | S | U | S | S | S | S | S | U | S | S |
| iii | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| iv | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| v | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| vi | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| vii | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| viii | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |
| ix | S | S | S | S | U | S | S | S | S | S | S | U | S | S | U | S | S | S | S | S | S | S | S | S | S | S | S |
| x | S | U/S | S | S | S | S | S | S | S | S | U | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S |

Key:

S = Valve and actuator satisfactory

U = Actuator blocked (where blockage occurred at 0° C a new actuator was fitted for the second test after 24 hours at 20° C)

U/S = Actuator blocked, then released itself

Summary

(1) After 1 hour at 20° C

Propellant 12 (dichlorodifluoromethane)

The solubility of the lanolin products is poor in Propellant 12, with the exception of liquid lanolin I.S.O. (vi) and liquid lanolin "L.I.N." (viii). The addition of IMS effects complete, or nearly complete, solubility of all products, with the exception of anhydrous lanolin, B.P. (i).

Propellant 11 (trichlorofluoromethane)

The solubility of the lanolin products is good or excellent, with the exception of water soluble lanolin "75" (ix) and water soluble wool alcohols "20" (x). The addition of the IMS effects virtually complete solubility of products (ix) and (x).

Propellant 114 (dichlorotetrafluoroethane)

The solubility of the lanolin products in Propellant 114 is negligible. The addition of IMS effects complete, or nearly complete, solubility of all products except anhydrous lanolin, B.P. (i), and water soluble lanolin "75" (ix).

Propellants 11/12 mixture

The solubility of the lanolin products is good or excellent, with the exception of alcohol soluble lanolin (iv), water soluble lanolin "75" (ix), and water soluble wool alcohols "20" (x). The addition of the IMS effects virtually complete solubility of the first two products, but has no effect on the last named. The addition of the *isopropanol* does not have so marked an effect, although it improves the solubility of the alcohol soluble lanolin (iv).

(2) Storage for 6 weeks at 20° C

In general there have been only minor changes in solubility during the test period. The exceptions are alcohol soluble lanolin (iv) in Propellant 11 (B), and water soluble lanolin "75" (ix) in propellants 11/12/IMS (H) where partial precipitation has occurred, accompanied by agglomeration in the latter. There has also been a tendency for some of the other precipitates to agglomerate which could be a potential cause of valve blockage.

(3) Storage for 6 weeks at 0° C

There is a slight decrease in solubility of some of the products, and also a tendency for some of the precipitates to agglomerate, but this phenomenon is not restricted to those products which form agglomerates during storage at 20° C.

(4) Storage for 6 weeks at 0° C, followed by storage for 24 hours at 20° C

In general the solubilities are similar to those noted after storage for

6 weeks at 20° C, with the exception of wool alcohols, B.P. (ii) in Propellant 11 B), which retains a heavy precipitate.

(5) Spray results after 6 weeks

In all instances of valve failure, blockage occurred in the actuator and not in the valve body. There were seven instances of complete blockage, and one of partial blockage. Insoluble waxes were the most frequent cause and agglomerated precipitates were responsible for two occurrences. Fine particulate precipitates did not cause any actuator blockage, even when present in large amounts. Anhydrous lanolin, B.P. (i), liquid lanolin "A.C.E." (iii), alcohol soluble lanolin (iv), liquid lanolin "50 Super" (v), liquid lanolin I.S.O. (vi), liquid lanolin "R.I.C.2" (vii), and liquid lanolin "L.I.N." (viii) did not cause valve blockage in any of the propellant systems tested.

CONCLUSIONS

By adding the numbers in *Tables 2* and *3* both horizontally and vertically, a total for each individual lanolin product in all propellant systems is obtained, together with a total for each individual propellant system containing all lanolin products. The lower the total, the better the solubility or solvent power.

Liquid lanolin I.S.O. (vi) was found to be the most soluble product, and water soluble wool alcohols "20" (x) the least soluble one.

Propellant 11/propellant 12/IMS (H) was found to be the best propellant system in respect of solvent power, immediately after filling. After 6 weeks' storage, however, the propellant 11/IMS system (E) exhibited the best solvent power, with the propellants 11/12/*isopropanol* system (I) as second best. Propellant 114 (C) was the worst solvent system at all times.

It is worth noting that most of the lanolin derivatives exhibit satisfactory solubility characteristics at 0° C.

ACKNOWLEDGEMENT

Westbrook Lanolin Company, which sponsored this work, is thanked for permission to publish these findings.

(Received : 8th March 1963)

DISCUSSION

MR. R. E. ECKTON : May I ask if in conducting these tests any changes in odour resulting from the exposure of these materials to aerosol conditions were noticed ?

THE LECTURER : None.

MR. S. J. BUSH : Did you carry out any experiments in which other materials which one would expect to find in aerosol formulations were used, in addition to lanolin derivatives ?

THE LECTURER : No.

PHYSIOLOGICAL PROPERTIES OF PROPELLANTS

H. KÜBLER, Dr. rer. nat.*

Presented at the Symposium on "Aerosols", organised by the Society, at Southport, Lancs., on 25th April 1963.

The properties, MAC and LD 50 values of the various propellants, all of which belong to the less toxic Groups 5-6, are referred to.

Inhalation tests indicate that up to 5% by volume of propellants 11, 12, 113, 114 and vinyl chloride is tolerated. The quantity of halogenated acids formed during the thermal decomposition of the propellants between 100°C and 1000°C is so great, that their irritation prevents the inhalation of carbon monoxide and phosgene.

The results obtained by various workers confirm the absence of skin irritation.

THERE EXIST about forty chemical compounds which are in a gaseous state at room temperature, and which can easily be liquefied. From these, the propellants for aerosol packs are chosen, and the essential features are vapour pressure, boiling point, solubility, chemical resistance, flammability and low toxicity. Only a few of the gases fulfil the greater part of these requirements. The most important property of a propellant is the low order of toxicity, especially by inhalation.

Only a few substances can be tolerated by human individuals in any quantity, whereas other substances which are of decisive importance for metabolism, have a pronounced toxic action in higher concentrations. For instance, carbon dioxide can cause weakness or even suffocation of humans. We must therefore determine the toxic threshold or the concentration at which injuries to health occur. The only gases suitable as propellants are those where this concentration is far below the amount likely to be used in the most extreme circumstances. Complete non-toxicity in any concentration cannot be demanded for this purpose.

The MAC-value characterises the compatibility of a substance, while the LD 50 limit indicates the toxicity. These values differ in so far that by exceeding the MAC-value one does not necessarily cause any harmful effects, but a substance can be lethal even before the LD 50 value is reached. One must differentiate between the toxicity due to the differing intake of a substance, i.e., by mouth, subcutaneous, percutaneous, intravenous, and

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by inhalation. In practice only inhalation tests can be performed with gaseous substances. The concentration, by volume, of the gas in the atmosphere which after a definite inhalation period has a lethal effect or causes injuries to health, takes the place of the LD 50 value. A very high propellant concentration could be harmful, because it results in a reduction of the oxygen content of the atmosphere. The so-called "interference level" is of the order of about 12.5 volume % oxygen. We do not know such a case; it cannot occur during shipment or during the storage of pressurized dispensers, but it could happen due to a sudden leakage from large propellant cylinders, or during cleaning of the latter.

Undoubtedly, the MAC-value does not give a definite indication for the physiological suitability of a gas, but the propellants commonly used have an identical value of at least 500 ppm. While the MAC-value indicates the concentration by volume (cc), which is tolerated in 1 m³ of air daily for inhalation in 8 hours, e.g., in a filling plant, an individual is exposed only temporarily to a certain concentration of vapour while a pressure pack is used. As a result, the use of a solvent with a MAC-value below 500 ppm may be permissible, particularly as there are often very good technical reasons for doing so. In the event that one is faced with two equivalent substances having different MAC-values, one or both of which are below 500 ppm, then one would select the substance with the higher value.

Toxicity Groups

- Group 1 : Gases at a concentration in air from 0.5–1.0% by volume have a lethal effect by inhalation after 5 minutes, or cause serious, irreversible damage,
e.g., phosgene, sulphur dioxide.
- Group 2 : Gases at a concentration in air from 0.5–1.0% by volume have a lethal effect by inhalation after 30 minutes or cause serious, irreversible damage,
e.g., ammonia, methyl bromide.
- Group 3 : Gases at a concentration in air of 2–2.5% by volume have a lethal effect by inhalation after 1 hour, or cause serious, irreversible damage,
e.g., carbon tetrachloride, chloroform, methyl formate.
- Group 4 : Gases at a concentration in air of 2–2.5% by volume have a lethal effect by inhalation after 2 hours, or cause serious, irreversible damage,
e.g., dichloroethylene, methyl chloride, ethyl bromide.

- Group 4-5 : Less toxic than 4, but more than 5,
e.g., methylene chloride, ethyl chloride, propellant 113.
- Group 5a : Considerably less toxic than 4, but more than 6,
e.g., propellants 11, 22, carbon dioxide.
- Group 5b : Less toxic than 5a, but more than 6,
e.g., dimethyl ether, propane, butane, vinyl chloride.
- Group 6 : Gases at a concentration in air of 20% by volume seem to
produce no harm after inhalation for 2 hours,
e.g., propellants 12, 114.

This classification^{1,2} should be defined somewhat more precisely in such a manner, that constant intervals can be adopted for Groups 4-6. This would mean :

- Group 4-5 : The inhalation of a concentration of 6.5% by volume, for a period of 2 hours has a toxic or harmful effect.
- Group 5a : The inhalation of a concentration of 11% by volume for a period of 2 hours has a toxic or harmful effect.
- Group 5b : The inhalation of a concentration of 16.5% by volume for a period of 2 hours has a toxic or harmful effect.

According to Reed¹, propellants with a MAC value smaller than 100 ppm should not be used. I fully agree with Reed insofar but would like to extend the MAC value, indicated by him, to the solvents commonly used in aerosol packs. Reed has published a list in which the MAC values are compared with the toxic class values for many propellants. *Table 1* lists those values, together with values for other propellant blends, which I have added.

The propellants and propellant diluents* belong to toxicity Groups 5a, 5b and 6, with the exception of methylene chloride. Group 5a refers to 11% by volume, corresponding to 677 g propellant 11/m³. Group 5b refers to 16.5% by volume, corresponding to 460 g vinyl chloride/m³. Such a propellant concentration is inconceivable during the use of pressurized dispensers. In the most extreme case this propellant quantity would be equivalent to the content of 1½ × 18 oz dispensers. Thus 7½ dispensers would have to be sprayed in a very small room of 176.5 c. ft. For this operation at least 75 minutes are necessary, but during that time air has been partly replaced. Another example : In a very narrow hairdresser's room of 105.9 c. ft., which, of course, is not closed towards all sides, a hairspray is used. 3 × 460 g vinyl chloride correspond to 6 × 18 oz dispensers which are sufficient for the

Table 1

| Designation : | Chemical symbol | Propellant | Toxicity group | MAC | LD 50 | Boiling point °C |
|---|---|------------|----------------|----------|-------|------------------|
| Trichlorofluoromethane | C Cl ₃ F | * 11 | 5a | 1000 | — | + 23.7 |
| Dichlorodifluoromethane | CCl ₂ F ₂ | * 12 | 6 | 1000 | — | - 29.8 |
| Dichlorofluoromethane | CHCl ₂ F | 21 | 5a | 1000 | — | + 8.9 |
| Chlorodifluoromethane | CHClF ₂ | 22 | 5a | 1000 | — | - 41.0 |
| Methylene chloride | C H ₂ Cl ₂ | * 30 | 4-5 | 500 | 0.27 | + 40.8 |
| 1, 2, 2-Trichloro-1, 1, 2-trifluoroethane | CClF ₂ .CCl ₂ F | 113 | 4-5 | (1000) | — | + 47.6 |
| sym. Dichloro-tetrafluoroethane | CClF ₂ .C Cl F ₂ | * 114 | 6 | 1000 | — | + 3-5 |
| asym. Dichloro-tetrafluoroethane | C Cl ₂ F.CF ₃ | 114a | 6 | — | — | + 3.2 |
| 2, 2-Difluoroethane | CH ₃ .CH F ₂ | 152a | 6 | — | — | - 24.0 |
| Ethyl chloride | CH ₃ CH ₂ Cl | 160 | 4-5 | 1000 | — | + 12.2 |
| Vinyl chloride | CH ₂ :CHCl | * 1140 | 5b | 500-1000 | — | - 13.9 |
| 1, 1, 1-Trichloroethane | C Cl ₃ .C H ₃ | 140a | 5a | 500 | 12.9 | + 74.4 |
| Octafluorocyclobutane | (CF ₂) ₄ | * C 318 | 6 | (1000) | — | + 6.0 |
| Carbon dioxide | CO ₂ | * — | 5a | 5000 | — | subl. |
| Nitrous oxide | N ₂ O | * — | — | — | — | - 89.5 |
| Nitrogen | N ₂ | * — | 6 | — | — | -195.8 |
| Air | — | — | 6 | — | — | — |
| Propane | CH ₃ .CH ₂ .CH ₃ | * — | 5b | (1000) | — | - 42.2 |
| nButane | CH ₃ CH ₂ CH ₂ CH ₃ | * — | 5b | (1000) | — | - 0.5 |
| isoButane | (CH ₃) ₂ CHCH ₃ | * — | 5b | (1000) | — | - 11.7 |
| Sulphur dioxide | SO ₂ | — | 1 | 10 | — | - 10.0 |
| Phosgene | CO Cl ₂ | — | 1 | 1 | — | + 7.6 |
| Ammonia | NH ₃ | — | 2 | 100 | — | - 33.5 |
| Carbon tetrachloride | C Cl ₄ | 10 | 3 | 25 | 7.0 | + 76.7 |
| Methyl chloride | C H ₃ Cl | 40 | 4 | 50 | — | - 23.7 |
| Chloroform | C H Cl ₃ | 20 | 3 | — | — | + 66.2 |

treatment of at least 300 customers. But it is not possible to treat more than 20 persons in 8 hours.

The following figures were obtained in answer to the question: What concentration, by volume, of vinyl chloride can be achieved during spraying?

Insecticide or roomspray :

Spray duration : 10 sec in a room of 706.3 c. ft. capacity :
0.001% by volume.

Hairspray :

Duration of spray : 30 sec in a room of 282.5 c. ft. capacity :
0.025% by volume.

Fixative :

Duration of spray : 3 min in a room of 706.3 c. ft. capacity :
0.140% by volume.

The MAC value is equivalent to 0.05 % by volume.

Ullmann³ mentions that 0.5% by volume may be inhaled for many hours without danger, and that 5% by volume causes a slight numbness. These data have been confirmed by tests on animals for a period of 100 days, performed at the Battelle Institute, in Frankfurt/M. The tests included mice, rats and guineapigs, and the three propellants vinyl chloride, mixtures of propellant 11/12 50 : 50 and 10 : 90, and the three concentrations 0.5, 1.5 and 5.0% by volume. Including the controls, 120 animals of each type, in groups of 10 (5 male, 5 female), were exposed 2 hours daily for 100 days to an open inhalation system. Care was taken to ensure a constant air flow (physiological oxygen importation) in the cylindrical inhalation chambers. During the test period, the animals were fed with normal food, and they were weighed weekly. The tests indicated the following results :

- (a) The test animals showed no reactions to the inhalation of the propellant 11/12 blend. No deviations from the normal conditions appeared up to 1.5% by volume of vinyl chloride. An inhalation of 5% by volume of vinyl chloride first of all increased the mobility of the animals, and then reduced it as the tests progressed. The reactions were reversible.
- (b) The growth function was not influenced at all.
- (c) The blood pattern of all animals was normal.
- (d) There was no disturbance of the liver.
- (e) The autopsy of all test animals, and the histopathological examination of parts of them, showed no morphological determinable changes in the examined organs.

Schade⁴ confirmed these results in his experiments with 0.5—5.0% by volume of vinyl chloride. Hence 5% by volume is below the concentration which causes disturbances to the sense of balance (equilibrium), a state which precedes anaesthesia.

These results do not agree with the findings of Torkelson⁵. The obvious assumption is that the liver injuries which have been detected on animals, are due to impurities in vinyl chloride.

The vinyl chloride, tested by us, was of the highest chemical purity. Another test carried out with a shellac-based hairspray utilising the propellant vinyl chloride⁶ gave the same results as that with propellants 11 and 12. Three groups of white mice beneath a plastic cover were sprayed for 30 seconds daily, for 5 weeks, from a distance of 20—25 cm. The animals were closely observed, and dissected after the test. No changes could be discovered. No inflammation phenomena in the bronchials, lungs alveoles and the bronchial lymphknots were present. This is of particular significance in view of the present hairspray-thesaurosis controversy.

Shepherd's view⁷, that small quantities of vinyl chloride have an anaesthetic effect, could not be confirmed. Like Hoffmann⁸, no reference to the literature was given.

The anaesthetic concentrations of fluorohydrocarbons 11, 12, 113 and 114 have been examined by Scholz⁹. Rats and guinea pigs were exposed to increasing concentrations by volume, with the air circulating in a closed room. Carbon dioxide was absorbed, and the oxygen content was kept at a constant level. Rats and guinea pigs behaved differently.

Table 2
Anaesthetic concentrations for rats

| <i>Propellant</i> | <i>Condition</i> | <i>Concentration</i> % | <i>Time</i> <i>minutes</i> |
|-------------------|------------------|---------------------------|-------------------------------|
| 114 | G | 30 | 120 |
| | IN | 50 | 120 |
| | tN | 60 | 120 |
| | T | — | — |
| 12 | G | 30 | 120 |
| | IN | 50 | 60 |
| | tN | 60 | 60 |
| | T | — | — |
| 113 | G | 10 | 30 |
| | IN | 15 | 15 |
| | tN | 20 | 20 |
| | T | 20 | 45 |
| 11 | G | 5 | 40 |
| | IN | 10 | 20 |
| | tN | 10 | 90 |
| | T | 20 | 5 |

G — disturbance of equilibrium ;

IN — slight anaesthesia ;

tN — deep anaesthesia ;

T — death.

According to Scholz these results just about agree with American data. In addition, propellant 11 was compared with chloroform and carbon tetrachloride. With cats, already an exposure for one hour with approximately 1.5% chloroform and approximately 2% carbon tetrachloride has a lethal effect ; with propellant 11 an exposure with 10% by volume for one hour is necessary in order to obtain a lethal effect.

Scholz also explains, that such high concentrations (by volume) which were used for these tests, are not achieved when spraying from pressurized packs. In any event, mixtures of propellant 11 and 12 are mainly used. The tests carried out in the Battelle Institute confirm this insofar as a mixture of 2.5% by volume of propellant 11 and 2.5% by volume of propellant 12

did not cause any disturbance of the equilibrium in the test animals. Finally, inhalation tests were carried out by Scholz in currents of mixtures, with concentrations which did not cause the stimulating conditions which precede anaesthesia. With 114 and 12 this concentration amounted to 10% by volume, and with 113 and 11 to 2.5 or 1.25% by volume depending on the animal group. The blood and urine controls showed no change, nor did the liver show any signs of degenerative changes, as opposed to exposures with 0.25% by volume of chloroform.

While carbon tetrachloride should be rejected because of its high toxicity, and the importance of chloroform, a highly toxic solvent and anaesthetic agent, decreases, it is evident that a partial replacement of Cl by F atoms considerably reduces the toxicity of a substance. The anaesthetic and toxic properties are affected not only by the number of Cl atoms but also by the human absorption capacity and by the metabolic rate. The methane derivatives, as far as they are not fluorinated sufficiently, are more toxic than the ethene and ethane derivatives. Methyl chloride is more toxic than ethyl chloride and methylene chloride, although it contains only one Cl atom. Trichloroethylene has a greater anaesthetic effect than tetrachloroethylene, but neither surpass chloroform and carbon tetrachloride. The higher chlorinated ethanes are also more toxic than the ethenes. Vinyl chloride, another ethene derivative with only one Cl atom, is indeed the most harmless derivative of a chlorinated hydrocarbon.

It is therefore possible to state that propellants 11, 12, 113, 114 and vinyl chloride will not cause any definite injuries to health, in the concentrations obtained during the spraying of pressurized packs. The MAC values, and the classification into toxicity groupings permits the conclusion that the same is true for propellant C318, and for propane, butane and *isobutane*. We have no data on the inhalation compatibility of gaseous hydrocarbons, and we only know that the MAC values of the low molecular hydrocarbons is 100, and of the higher ones 500.

INHALATION

It is recommended that the general directions for the handling of pressurized packs should include the legend: "Do not spray into an open flame," because toxic gases can be formed during the thermal decomposition of halogenated hydrocarbons. This was investigated at the Battelle Institute, with propellants 11, 12, 114, vinyl chloride, and methylene chloride. The amount of carbon monoxide and phosgene, formed between 100 and 1000°C, and the amount of HCl, formed at 1000°C, were determined. The values for propellant 11 and for methylene chloride were derived from the results obtained with 11/12 mixture and with methylene chloride/12 mixture (both 50 : 50% by weight).

Table 3 indicates the amounts of carbon monoxide (ml), phosgene (mg) and HCl (mg), formed per 1 g of propellant.

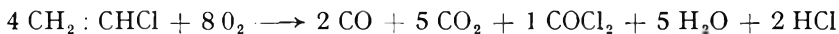
Table 3

| Temperature | CO | | | | | COCl ₂ | | | | |
|---------------|--------|--------|--------|--------|---------------------------------|--|-------------------------|-------------------------|-------------------------|---------------------------------|
| | VC | 11 | 12 | 114 | CH ₂ Cl ₂ | VC | 11 | 12 | 114 | CH ₂ Cl ₂ |
| 100° | <0.001 | — | — | — | — | 3.0 × 10 ⁻⁴ | <3.0 × 10 ⁻⁴ | <3.0 × 10 ⁻⁴ | <3.0 × 10 ⁻⁴ | <3.0 × 10 ⁻⁴ |
| 200° | 0.03 | — | — | — | — | 8.1 × 10 ⁻⁴ | 1.9 × 10 ⁻³ | 3.0 × 10 ⁻⁴ | <3.0 × 10 ⁻⁴ | <3.0 × 10 ⁻⁴ |
| 300° | 0.45 | <0.001 | <0.001 | <0.001 | <0.001 | 2.2 × 10 ⁻³ | 4.2 × 10 ⁻³ | 6.5 × 10 ⁻⁴ | 1.5 × 10 ⁻³ | 2.5 × 10 ⁻³ |
| 400° | 0.75 | 0.007 | 0.004 | 0.004 | 0.10 | 1.7 × 10 ⁻³ | 8.8 × 10 ⁻³ | 4.5 × 10 ⁻³ | 1.5 × 10 ⁻³ | 3.5 × 10 ⁻³ |
| 500° | 1.00 | 0.019 | 0.007 | 0.021 | 0.24 | 3.4 × 10 ⁻³ | 2.6 × 10 ⁻³ | 8.0 × 10 ⁻³ | 1.3 × 10 ⁻³ | 4.4 × 10 ⁻³ |
| 600° | 6.25 | 0.29 | 0.013 | 0.11 | 1.4 | 5.0 × 10 ⁻³ | 8.6 × 10 ⁻³ | 3.2 × 10 ⁻³ | 5.1 × 10 ⁻³ | 1.6 |
| 750° | 20.5 | 0.69 | 0.43 | 0.45 | 5.0 | 6.4 × 10 ⁻³ | 3.6 | 3.7 × 10 ⁻³ | 1.6 × 10 ⁻³ | 2.2 × 10 ¹ |
| 900° | 24.4 | 1.50 | 0.9 | 0.39 | 12.5 | 9.2 × 10 ⁻³ | 6.4 | 1.8 | 1.1 × 10 ¹ | 1.8 × 10 ¹ |
| 1000° | 31.6 | 1.20 | 1.2 | 0.63 | 12.2 | 1.1 × 10 ⁻¹ | 7.0 | 2.4 | 1.2 × 10 ¹ | 1.8 × 10 ¹ |
| HCl at 1000° | 102 | 79 | 51 | 28 | 81 | + calculated on the basis that the quantities of HF are equivalent to the quantity of HCl. | | | | |
| HF at +1000°C | — | 15 | 28 | 31 | — | | | | | |
| HX at 1000°C | 102 | 94 | 79 | 59 | 81 | | | | | |

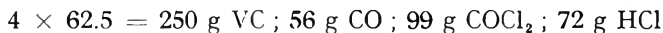
Accordingly, the following yields are obtained at 1000°C.

| | | |
|--|----|--|
| 1 g vinyl chloride | .. | 39.5 mg CO + 0.11 mg COCl ₂ + 102 mg HX |
| 1 g propellant 11 | .. | 1.5 mg CO + 7.00 mg COCl ₂ + 94 mg HX |
| 1 g ,, 12 | .. | 1.5 mg CO + 2.40 mg COCl ₂ + 79 mg HX |
| 1 g ,, 114 | .. | 0.8 mg CO + 12.00 mg COCl ₂ + 59 mg HX |
| 1 g CH ₂ Cl ₂ ,, | .. | 15.2 mg CO + 18.00 mg COCl ₂ + 81 mg HX |

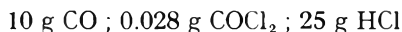
Assuming that the following reaction takes place during the oxidation of vinyl chloride at 1000°C



then the result should be

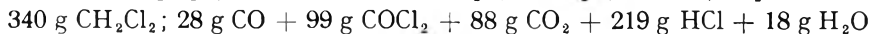


In practice, however, only the following were obtained :



Thus the vinyl chloride was only partially decomposed at 1000°C, with the HCl-formation at 35% of theory proceeded furthest.

Methylene chloride presents the following picture :



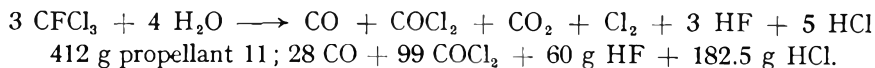
The experiments at 1000°C resulted in



Here too only a partial decomposition of the methylene chloride occurs.

The partial decomposition of the propellants is a function of the test methods described below. Repeated contact with the heated surfaces will continue the degradation of the propellant-air mixture.

With trichlorofluoromethane (propellant 11):



In practice : 0.43 g CO ; 2.88 g COCl₂ ; 39 g HCl.

Related to the contents of acid halide, only 25% of the propellant is decomposed, and with methylene chloride only 21.4%.

Supposing that 100 g of each gas is decomposed by a hot flame at 1000°C in a room having a capacity of 50m³, then the ppm value is as follows :

| | | | | |
|------------------------|----|-----------|--------------------------|---------------|
| For vinyl chloride | .. | 63.2 CO ; | 0.05 COCl ₂ ; | 126 ppm HCl ; |
| „ propellant 11 | .. | 2.4 „ ; | 3.10 „ ; | 98 „ „ |
| „ „ 12 | .. | 2.4 „ ; | 1.10 „ ; | 62 „ „ |
| „ „ 114 | .. | 1.3 „ ; | 5.40 „ ; | 34 „ „ |
| „ methylene chloride.. | | 24.4 „ ; | 8.10 „ ; | 100 „ „ |

The MAC value for carbon monoxide, which is near 100 ppm, has not been reached in any instance. On the other hand, the MAC value of phosgene, near 1 ppm, is exceeded by all gases with the exception of vinyl chloride.

The MAC value for HCl is near 5. The quantities of HCl obtained with all propellants are considerably in excess of that value despite the fact that the HF formed with propellants 11, 12 and 114 had been ignored. The irritation threshold for HCl is in the region of 35 ppm for brief inhalation, that for HF even lower, and is obtained in every case. This confirms the findings of Reed¹.

The concentrations of halogen acids formed are significantly greater than those of phosgene. They have such an irritating effect on the respiratory organs, that an individual cannot remain in this atmosphere for a long period. Although the halogen acids are an excellent warning, the danger of phosgene formation in a conflagration should, however, not be underestimated, because as little as 35 ppm have a lethal effect during a lengthy inhalation period. The halogenated hydrocarbons liberated after application of a pressurized spray cannot decompose into toxic gases, not even by decomposition in a flame of 1000°C. As a result a fatality reported in 1958 cannot be attributed to the use of an aerosol insecticide¹⁰.

R. C. Downing² has published a list of decomposition products obtained from propellants 11 and 12. Without defining the temperature he refers to warmed or heated surfaces, but no details of the experimental procedure are given. For the tests described above an exact amount of propellant was sprayed into a glass tube, through which an air current of 3.5–4 l/min

was sucked, and into which a hot plate or a gas flame was placed. The temperatures were measured electrically. Carbon monoxide was determined by means of the Auer apparatus, phosgene by measuring the absorption of 1,3-diphenyl urea in UV, and HCl by collection in 0.1N NaOH, neutralisation with H_2SO_4 , and titration with 0.1N $AgNO_3$ solution. The experimental errors were $\pm 5\%$. It was proven that the normal application of pressure packs, even in the event of decomposition of the propellants on hot or red-hot surfaces, cannot be injurious to health. In all instances, the considerable quantities of halogen acids developed will be a warning and the irritating effects will cause a person to leave or to ventilate the room immediately.

SKIN IRRITATION

It is necessary to distinguish between super-cooling of the skin by evaporation, which applies to all types of propellants, and definite skin compatibility. Spraying of an aerosol with a high propellant content from too short a distance on to the human skin may cause skin irritation, reddening or even blister formation. The possibility is the greater the lower the boiling point, and the more sensitive the skin is. We all know of the occasional consumer complaints that the pressurized product has a caustic effect. In actual fact, the directions for use have not been followed. Such cases are relatively unusual and it has never been reported that normal healing of the skin has not taken place after blister formation. Information concerning the compatibility of fluorinated hydrocarbons with the skin has been published by Quevaville *et al*¹¹ with the following conclusions: The treatment of the skin of rats, three times a day for two months, with propellants 11, 12 and 13 caused neither macroscopic nor microscopic changes.

The good compatibility of sesame oil and propellants 11, 12, 113 and 114 with the skin of rabbits, and with the mucous membrane of rabbits' eyes, was established by Scholz⁹.

A number of cosmetic preparations containing vinyl chloride as well as propellants 11 and 12 have been tested for compatibility with the skin. An oily suntan pack did not cause any skin reaction¹² with 600 separate tests on 50 patients including some suffering from eczema.

A similar test has been carried out with a hairspray¹³. The hair and skin of the head tolerated the product even after over-dosages and no differences could be detected between the various propellants. Only a concentration in excess of 20% methylene chloride caused structural damages of the hair, especially where subvisible changes of the hair have already occurred.

Tests with body deodorants¹⁴, footsprays containing vinyl chloride¹⁵, foam products containing propellant 12¹⁶ proved likewise positive.

CONCLUSION

This paper does not claim to be a complete summary of all tests with propellants, both published and unpublished. Nevertheless, the information presented is sufficient to draw the proper conclusion. All tests yielded identical results and there is thus no necessity to start further tests. Propellants 11, 12, 114, propane/butane and vinyl chloride, used in the aerosol industry, have a varying, but generally low or very low toxicity. The concentrations by volume formed when using a pressurized dispenser are normally not only completely nontoxic, but are considerably lower than, or near, the MAC-values. It is true that no tests have been carried out with propane/butane, but their chemical structure permits this analogous conclusion.

Actual practice confirms the good skin compatibility and the safe inhalation of the named propellants. A billion pressurized dispensers each year indicate the accuracy of the described tests. The problem of the thermal decomposition should not be exaggerated. Here, too, actual practice has shown that this danger is very small. From the physiological point of view, therefore, the pressurized pack, i.e. the propellant utilized, may be regarded as safe.

(Received: 2nd February 1963)

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BOOK REVIEWS

The Principles and Practice of Modern Cosmetics. Volume I. R. G. Harry. MODERN COSMETICOLOGY. Fifth Edition. Revised by J. B. Wilkinson, and R. Clark, E. Green and T. P. McLaughlin. Pp. xxiv + 683 + Ill. (1962). *Leonard Hill (Books), Ltd., London.* 84s.

Few cosmetic chemists can be unfamiliar with Harry's "Modern Cosmetics" and have not found this volume of some assistance in their work during the twenty-two years since the first edition was published. The need for a fifth edition reflects not only the tremendous advances in cosmetics technology but also the sound basis on which the book is written.

The revision has been undertaken by a team of leading workers in cosmetics technology who chose to retain the original basically sound framework. At first glance, the fifth edition appears to differ very little from the previous one but closer reading reveals how much thought and work has gone into this new edition.

Four chapters have been omitted: On toilet soap—impossible to deal with adequately in a book of this size, and those on diet and skin health, cosmetic stockings, and cosmetic facts and fallacies. A new chapter on "Pressurized Packs" surveys adequately the technical aspects of the aerosol package.

Practically every chapter has been revised in some degree but because of changing ideas and importance, some chapters have come in for more drastic changes than others.

The basic framework of the book has been retained and the treatment of Chapter 1 "The Skin" illustrates the general pattern of the revision. Much detail of lesser importance has been omitted and the nucleus of basic information rearranged, revised and expanded where necessary to give a sound, logically developed and highly readable account of the basic facts every cosmetic chemist should know about the skin.

Chapters 16 "Dertifices", 21 "Hair Shampoos", 22 "Permanent Waving", 24 "Hair Dressings and Conditioners", 25 "Hair Dyes" and 28 "Antiperspirants and Deodorants" have all largely been rewritten to incorporate recent developments and ideas.

The index is shorter than that in the previous edition and yet seems more comprehensive, indicating the care and selectivity exercised in its preparation.

The revisers have done a splendid job and produced a new work which at times differs not so much in the actual information contained therein but in its arrangements, and therefore in the ease with which it can be read and absorbed and a given piece of information found when required.

The new edition is produced to the usual high standard. Remarkably the revisers have managed to compress this new edition into over one hundred fewer pages than the previous edition but this has not prevented a one-third increase in cost. Nevertheless, at the price this volume represents good value and will undoubtedly be found a worthy addition to every cosmetic chemist's bookshelf.

R. P. REEVES.

The Principles and Practice of Modern Cosmetics. Volume 2. R. G. Harry. COSMETIC MATERIALS. Second Edition. Revised by W. W. Myddleton. Pp. xv + 803 + Ill. (1963). Leonard Hill (Books), Ltd., London. 84s.

This second edition is presented in an essentially similar manner to the first, i.e. an alphabetical listing of materials with details of synonyms, formula, molecular weight, occurrence or manufacture, physical and chemical properties, B.P. standard, use in toilet preparations and dermatological action.

A little over four hundred monographs are included in the main section and, in addition, the Standards and Methods of both the TGA and TPF are reproduced which appear to be complete up to mid-1962. An appendix includes monographs on the FDA approved colours. Almost one third of this volume is devoted to reproduction of these specifications and methods and one wonders whether this is justifiable.

The selection of materials for inclusion in this new volume leaves something to be desired. More than thirty monographs deal with materials which the authors state are not used, little used or should not be used in cosmetics. Surely this is sufficient reason for excluding them. To these I would add at least another forty materials which means that more than one in six of the monographs are on materials which are of negligible interest to the modern cosmetic chemist. Some of these are perfume and flavour materials and are better left to the specialist works such as Arctander's recent volume but most are adequately, and more aptly, dealt with in the pharmaceutical texts, B.P., U.S.P., B.P.C., N.F., 'Martindale', etc.

Some materials omitted are equally perplexing; for instance, PCMC and PCMX are included but not DCMX; U.S. permitted colours but no mention of British permitted food colours; methyl—and benzethonium chloride but not benzalkonium chloride, cetyl and stearyl dimethyl benzyl ammonium chloride nor alkyl pyridinium compounds; sodium but not stannous fluoride; stearic and palmitic but not other fatty acids; hairspray resin Devlex A.515 but not Ciba 325, Resyn 28-1310, Gantrez AN, etc. (the use of ethyl cellulose in hairsprays is not mentioned); menthyl salicylate but not its common cheaper alternatives homomenthyl and benzyl salicylates; phenylmercuric benzoate and nitrate but not the borate; a.s.o.

There is also a certain amount of unnecessary duplication. For instance, adjacent monographs describe acetic acid and glacial acetic acid ; separate monographs describe ethyl alcohol and I.M.S. ; sodium carbonate anhydrous, monohydrate and decahydrate ; calcium hydroxide and lime water ; chalk and calcium carbonate. The monograph on I.M.S. is particularly disappointing and gives a completely erroneous picture of a material the use of which is made complex enough by Excise regulations ; information on denaturation requirements could usefully have been included.

Probably the most important group of modern cosmetic materials are the surface-active agents and their treatment in this volume is very sketchy and inadequate in contrast to the lengthy discussion of some materials of comparatively minor importance.

Errors and misleading statements are all too frequent in this volume, making the reviewer's task the more difficult. The formula for D.D.T. (p. 165) is wrong ; the old numbering for the *Arctons* (p. 196) is used ; the *Isceons* and *Ucons* are not mentioned and the derivation of the present propellant numbering system is not given ; the formula for sodium perborate (p. 442) is wrong but the correct formulas for the two "hydrates" are given in the TPF standard on the adjacent page ! (its main use as a cold wave neutraliser is not quoted) ; is propenyl alcohol a synonym for glycerol (p. 202) ? The monograph on the Carbopols appears on page 113 but the TGA specification follows Polyvinyl alcohols on page 369 with no cross-reference. The monograph on cetyltrimethyl ammonium bromide incorrectly ascribes this constitution to Cetrinide and Cetavlon ; the latter are, of course, the mixed alkyl (average C_{14}) derivative. I cannot agree with the definitive statement (p. 27 referring to aluminium chloride as a deodorant) ". . . it is the aluminium ion which reacts with and precipitates the skin proteins with consequent obstruction of the sweat pore". Perhaps the most spectacular error however refers to the use of thioglycollic acid in cold waving (p. 502), ". . . it severs the S-S link in hair and forms an S-H group. An oxidizing agent is then applied to the hair and a sulphenic group is produced R-S-OH, which combines with another amino group in the hair molecule to give the 'set' " !

I found particularly irritating the inconsistent and sometimes quite erroneous presentation of references, and the extraordinary number of typographical errors indicate that the proof-reading leaves very much to be desired.

The presentation, binding and paper of this new edition are excellent but regrettably I cannot say that this volume is either a worthy successor to the first edition, or a worthy companion to the fifth edition of Volume 1.

R. P. REEVES.

SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

Annual General Meeting

THE FOURTEENTH Annual General Meeting of the Society took place on 24th May at the usual venue, 55 Park Lane. The Meeting was noteworthy for the presentation of scrolls to the two new Honorary Members, Dr. H. W. Hibbott and Dr. A. W. Middleton.



Scrolls of Honorary Membership being presented by Mr. G. A. C. Pitt, the retiring President, to :

Dr. H. W. Hibbott

Dr. A. W. Middleton

During his presentation of the Annual Report the retiring President, Mr. G. A. C. Pitt, underlined recent progress in the Society's affairs. Membership now stands at 392, and in the year under review six scientific meetings took place in London.

In 1963 the number of British issues of the Journal will be five, and these will, of course, be produced by Pergamon Press Ltd. on behalf of the Society. The increased number of British issues makes additional work for the Hon. Editor, Mr. Herzka. Fortunately our Symposia help in this respect but Mr. Herzka will still need all the contributions he can get.

By this new arrangement members will receive the Journal, British or foreign, monthly.

Education. The development in this activity is most encouraging. Twenty-four students entered for the course at Brunel College this session, amongst whom were a number of science graduates. Next session Dr. Skellon has agreed to arrange a part-time day release course. The course will then be completed in one year instead of two. Undoubtedly this raises both the standard and prestige of the course. Our congratulations and

thanks go to our Hon. Education Officer, Mr. Clark, to Dr. Scott and to the Education Committee who have worked hard to bring this about. Our thanks also to members who have lectured to the students in the past session.

A prize, to the value of £5, is to be awarded each year by the Society to the candidate who is placed first in the Diploma Examination. The first award will be made in the 1963-4 session.

The text book on Cosmetic Science will be published in the summer, and will be used for the Diploma course. Dr. Hibbott and his team of contributors are to be congratulated on this work which constitutes another advance for the Society.

The Institute of Weights and Measures Administration issued a Statement criticising many aspects of the cosmetic industry. A sub-committee was set up by Council to examine this. As a result the conclusion was reached that many of the criticisms were unsound. Accordingly, a Statement in reply was drawn up and circulated to the press and to all members.

International Federation of Societies of Cosmetic Chemists. Mr. Wilkinson, one of the British delegates to the I.F.S.C.C., has been elected Honorary Treasurer of the Federation. Mrs. Millman continues to be its General Secretary.

The Third International Congress will be held in New York in June 1964. The American Society has been most generous in making no charge to delegates from foreign societies for either the Congress or for board. At the time of writing over fifty members of the British Society have indicated their intention to attend.

Hospital Beauty Room. In October, the President and Vice-President visited the Mental Hospital at Menston, near Leeds, where the Society had equipped a Beauty Room similar to that in use at Halliwick Hospital. The hospital authorities were pleased with the results, the treatment was popular; on average twelve patients are treated a day.

Symposia are becoming a very important part of the Society's activities and more are planned, following those successfully held on "Perfumery" and "Aerosols".

During the year the Scientific Committee has been particularly concerned with Methods of Analysis and Toxicology. A list of accepted colorants has been published, and the initiative taken in calling a meeting of firms interested in the possible dangers in the use of hairsprays.

In the voting for 3 new members of Council, Messrs. R. E. Eckton, R. F. L. Thomas and N. J. van Abbe were elected.

The Officers for 1963-4 are :

| | |
|----------------------------|-------------------|
| President : | Mr. S. J. Bush |
| Immediate Past President : | Mr. G. A. C. Pitt |
| Vice-President | Mr. A. Herzka |
| Honorary Secretary : | Miss L. P. Torry |
| Honorary Treasurer : | Mr. D. F. Anstead |

Some 36 members stayed on to enjoy the pleasantly informal supper which followed the business meeting.

D.E.B.

SUMMARIES FOR CARD INDEXES

Summaries for card indexes are being included in this and the August issue on a trial basis. Such summaries can be cut out and mounted on 3" × 5" index cards for reference, without mutilating the pages of the Journal.

In order to establish whether this shall become a permanent feature, readers are requested to forward their comments to the Hon. Editor by the 31st October 1963.

Some economic aspects of perfumery: G. J. E. HACKFORTH-JONES. *Journal of the Society of Cosmetic Chemists* **14** 302 (1963)

Summary—Classical fragrances are often too dear owing to their dependence on a small number of very expensive natural products. Substitutes for these may be sought in both the natural and the synthetic field, but in both cases results may prove disappointing. Progress may result from the use of new chemical bodies, and it is to be hoped that manufacturers will offer more such materials for general sale.

Some aspects of contact sensitization due to perfumery raw materials: P. H. WITJENS. *Journal of the Society of Cosmetic Chemists* **14** 315 (1963)

Summary—Different factors which might influence the occurrence of contact sensitization due to perfumery chemicals are discussed.

Summaries for card indexes

Corrosion in aluminium containers: E. K. CLARKE. *Journal of the Society of Cosmetic Chemists*, **14** 322 (1963)

Summary—An investigation of a method to predict corrosion was made with cells constructed with electrodes of nickel, and aluminium taken from pressure containers. The electrolytes were a series of different hair sprays. The current flowing was plotted automatically as the cells were discharged over 24 hours. No general correlation was found between these results, and the results of storage tests except for formulations containing highly corrosive ingredients.

Lanolin derivatives for pressurized formulations: A. HERZKA. *Journal of the Society of Cosmetic Chemists* **14** 331 (1963)

Summary—The solubility of ten lanolin derivatives in nine different propellant and propellant/alcohol systems is described. The results indicate that most of the materials exhibit satisfactory solubility at 0°C.

Physiological properties of propellants: H. KÜBLER. *Journal of the Society of Cosmetic Chemists* **14** 341 (1963)

Summary—The properties, MAC and LD 50 values of the various propellants, all of which belong to the less toxic Groups 5-6, are referred to.

Inhalation tests indicate that up to 5% by volume of propellants 11, 12, 113, 114 and vinyl chloride is tolerated. The quantity of halogenated acids formed during the thermal decomposition of the propellants between 100°C and 1000°C is so great, that their irritation prevents the inhalation of carbon monoxide and phosgene.

The results obtained by various workers confirm the absence of skin irritation.

Symposium on
“The Toxicology of Cosmetic Materials”

A SYMPOSIUM on The Toxicology of Cosmetic Materials will be held at the Town Hall, Leamington Spa, Warwicks., on the 19th and 20th November 1963. The scientific programme includes seven lectures prepared by authors from Germany, U.S.A. and Great Britain.

Registration Forms will be sent to all members of the Society at the beginning of August.

Symposium on “Hair”

A SYMPOSIUM on Hair, organised by the Society, will take place in Brighton, Sussex, during the week commencing 13th April 1964. Anyone wishing to present a paper is requested to contact the Hon. Organiser, Mr. R. E. Eckton, c/o Givaudan & Co. Ltd., Whyteleafe, Surrey.

**3rd INTERNATIONAL CONGRESS OF
COSMETIC SCIENCE**

THE 3RD CONGRESS of the International Federation of Societies of Cosmetic Chemists is being organised by the Society of Cosmetic Chemists, and will be held in New York from 21st—28th June 1964.

The American Society chose New York City because the World's Fair will be held there at that time, and Thursday, 25th June 1964, has been designated as Cosmetic Chemists' Day.

The Congress will be held on the campus of Columbia University. Anticipating that accommodation in New York during the World's Fair will be costly and scarce, the Society of Cosmetic Chemists has reserved rooms for participants in New Hall, the newest residence hall on the campus which is built, and will be operated, like a hotel during the Congress.

SCIENTIFIC PROGRAMME

The Congress will have four morning sessions, Tuesday to Friday, 23rd—26th June 1964.

Seminar Areas

- (a) *Safety Aspects of Cosmetic Usage.*
- (1) Review of recent clinical experience.
 - (2) Advanced techniques for testing *in vivo*.
 - (3) Regulatory aspects.
 - (4) Statistical aspects.

(b) *Instrumentation's Role in Cosmetic Research and Control.*

- (1) Chromatography :
 - (a) Gas chromatography.
 - (b) Paper and other absorption media.
- (2) Spectroscopy.
- (3) Electron microscopy.

(c) *Cosmetics versus Skin Ageing.*

- (1) Physiology and biochemistry of the skin ageing process.
- (2) Radiation effects.
- (3) Action of steroids.
- (4) Atmospheric and environmental effects.

(d) *Cosmetics and Micro-Organisms.*

- (1) Preservation.
- (2) Control of skin flora.
- (3) Microbial aspects of hair and scalp problems.
- (4) Antibiotics versus antiseptics in cosmetics.

ACCOMMODATION

Through the generosity of the American Society of Cosmetic Chemists, members of the Society of Cosmetic Chemists of Great Britain, or of any other Society of Cosmetic Chemists affiliated to the I.F.S.C.C., will be admitted free of charge to the Congress under the "Package Deal", subject to the availability of accommodation. All reservations must be accompanied by a deposit which will be returned upon arrival at the Congress, or will be refunded up to 15th May 1964.

TRAVEL ARRANGEMENTS

Arrangements have been made for members to travel with a special flight of Aer Lingus Irish Airlines, in a Boeing 707 jet aircraft. The cost from **London** to New York and return, will be approx. **£75** per person, and from other **European centres**, approx. **£85** to **£95** per person, irrespective of age.

The proposed departure from London, is on the morning of 21st June 1964, thus arriving in New York during the afternoon (travelling time approx. 7½ hours). The return flight, which will last 6½ hours, is scheduled to leave New York between 7th and 12th July 1964, depending on the wishes of the majority of the participants.

Participants must also return as a group and the free baggage allowance is 44 lb. All rates are subject to confirmation, because the 1964 transatlantic fare structure will not definitely be known until the autumn of this year.

No deposits are required for the time being.

Registration Forms

Anyone interested in coming to the Congress, is asked to complete the attached coupon without delay, and to send same to the Hon. Travel Organiser.

SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

3rd International Congress of Cosmetic Science

New York—23rd to 26th June 1964

PRELIMINARY TRAVEL APPLICATION FORM

To : Hon. Travel Organiser,
A. HERZKA, B.Sc., F.R.I.C.,
Pressurized Packaging Consultants Ltd.,
Ashbourne House, Alberon Gardens,
London, N.W.11.

I wish to attend the 1964 Congress, and I will be accompanied by my *wife/*husband and *children, aged
(give ages of children).

I am interested to join the special flight with Aer Lingus Irish Airlines at approx. £75 return. Number of persons.....

I would be interested to stay in the U.S.A. for days.
(Present proposal : 17 or 21 days).

Title and Name (block letters).....

Address

Name of Company.....

Date..... Signature.....

Please type or write very clearly.

* Please delete as appropriate.

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One issue by the Gesellschaft Deutscher Kosmetik-Chemiker, e.V.
from Hamburg-Grossflottbek, Beselerstrasse 1, Germany.

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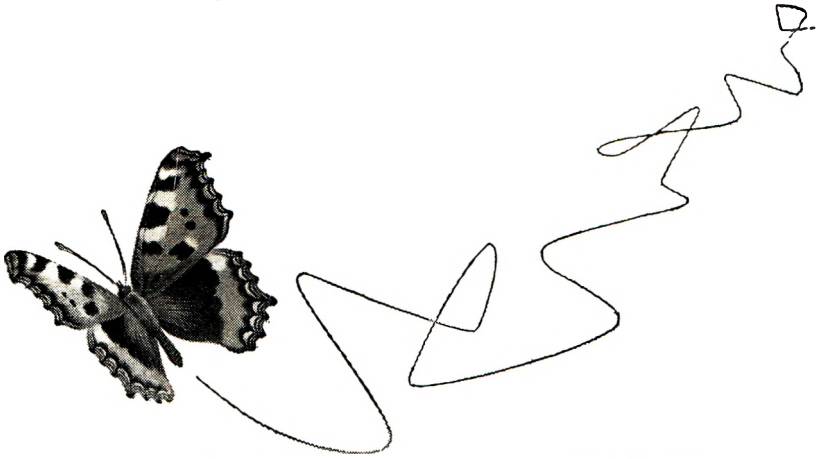
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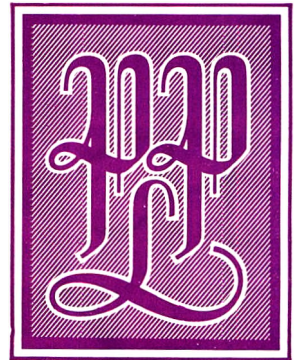


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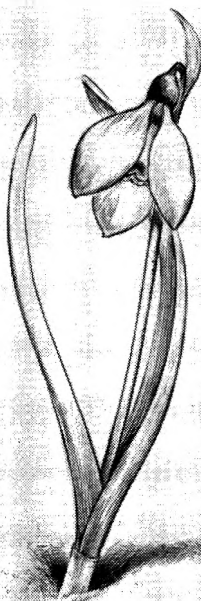
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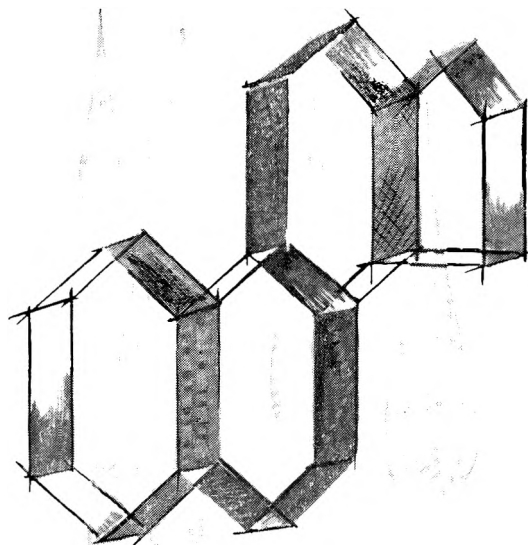
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