

PERFUMERY CHEMICALS

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A lecture delivered before the Society on 17th December 1958.

The purity of perfumery chemicals is discussed, and illustrated by means of a number of chromatograms. The influence of various "impurities" on odour is also dealt with.

INTRODUCTION

IN INDUSTRIES of all kinds the accent is on development in the form of improved and new manufacturing techniques. In particular, this is true of the industry which produces perfumery chemicals. Equipment now in operation is far in advance of that of even a few years ago, and is responsible for a much higher through-put, closer control and superior operating conditions. This satisfactory state of affairs is due to improved instrumentation and progress in chemical engineering, coupled with new techniques and greater know-how. In addition, new methods of testing and controlling the products during and after manufacture have become available and these enable the fullest advantage to be taken of improved manufacturing processes. Finally, a number of new starting materials have become available to the manufacturer during the last few years.

As a result of these changes, new odorous chemicals are being produced, but of even more importance, we are offered the opportunity to raise the general standard of a large proportion of the perfumery chemicals which have been known for years. It is here that the manufacturer turns to the perfumer for guidance. Krajceman¹ gave you an excellent review of the difficulties of this subject and I am sure he will be the first to acknowledge the fact that, even in the short space of two years, a considerable amount of water has passed under the bridge. There is plenty of evidence to show that many perfumers are conscious of these new possibilities and eager to take advantage of them. So that maximum advantage may be derived from the recent developments, it is necessary for the perfumer to become more fully aware of the nature of his raw materials. The manner in which the perfumer tackles the problem of obtaining better perfumery chemicals is of paramount importance, and the more clearly he understands and states what it is he requires, the sooner will he be satisfied, and furthermore, less of his time will be wasted examining a large number of uninteresting substances.

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THE PERFUMER'S REQUIREMENTS

All the foregoing may seem obvious on the one hand, and perhaps difficult to achieve on the other, but on further consideration it becomes clear that much time could be saved by a little thought. As an example of this, one of the most difficult requests met with by a supplier is for a purer or maybe even a pure perfumery chemical. Ignoring the point that in practice there is no such thing as a pure substance, the difficulty with this request is not in producing the material, but in ascertaining what it is the customer really requires. Maybe his desire is actually for a purer product, but, as will be shown later, with many of our products this is not the case and it is then that we are faced with the fact that the removal of minor constituents from the product may increase the price out of all proportion and also frequently result in a product with an uninteresting odour or one which is unsuitable for the purpose in mind. It is easy to understand how this request has originated. The existing material has been found unsatisfactory because it has a crude or unpleasant note or it may be that it is satisfactory by itself, but that the resulting perfume in which it is incorporated lacks desirable characteristics such as a fine, clean note. The perfumer, by his art and instinct, senses that certain by-odours in one or other of his raw materials have combined and are accentuating each other to give this effect. Obviously, this results in a desire for a higher quality perfumery chemical and the word "pure" has a fine ring to it, but beware—both the words "pure" and "impurities" should be used with the greatest care.

I am reminded of an instance when visiting an exhibition: I called at the stand of one chemical manufacturer and asked whether he could supply a certain chemical. He was most enthusiastic and we had discussed it for some time when we got to the point when he enquired as to the purpose for which it was to be used. When he was told for perfumery, his face dropped and his enthusiasm vanished. He explained that he had had many unhappy experiences when dealing with perfumers; in particular, he quoted a case where he submitted many samples, all of which were rejected as unsuitable on the grounds of the quality of their odour. He finally requested a sample of the material which the customer considered was suitable. When he tested this in his laboratory, he found that it contained less than 95 per cent of the active ingredient, whereas his later samples had all been better than 99 per cent pure. At this he gave up. By the way, I never received a sample of the material in which I was interested.

Without attempting to define the term "perfumery chemical", let us discuss the group generally and examine some of the members in detail to obtain a better understanding of this important class of compounds.

The materials in this category range from chemicals of known composition

in a very high state of purity, to mixtures of doubtful chemistry and very varied composition. They include aldehydes which are not aldehydes, Geraniol which is not Geraniol, Ionone 100 per cent which is far from 100 per cent, and a large number of other substances of undefined composition. Nevertheless, the perfumer is in no doubt when he receives one of these products as to its usefulness for his particular purpose. After all, a rose by any other name, etc.

Hundreds of organic compounds have been identified among the naturally occurring essential oils and to these have been added many hundreds of synthetic chemicals to form the group which we now term "perfumery chemicals". The perfumer's interest in this large number of compounds can be split into three sections :

Firstly, he requires stable compounds of constant quality which are pleasant smelling and of moderate price. These are of prime importance and form the backbone of his perfume.

Secondly, he is interested in those products which have specific or unusual odours so that he can formulate perfumes with different characteristic notes. Perfect stability and moderate price may not in this case be of first importance.

Thirdly, he is greatly interested in low priced products having a pleasant odour and good stability which can be used in deodorants and other industrial perfumes. Here, cost may be his main consideration.

The first of these three sections forms the main subject of this talk, but the observations apply also to the other two sections. By long use and custom, the trade identifies a particular chemical by a particular odour, but it is known that this odour can be considerably modified by the presence of subsidiary constituents. This is especially so with the isolates. It is fully appreciated that when a successful perfume has been known to the public over a period of years, it would be disastrous for a manufacturer suddenly to compound this perfume wholly or partially from pure products ; the odour of the resulting perfume would, in most cases, be drastically altered. Despite these statements, there is a need for perfumery chemicals of improved quality, and considerable advantage could be obtained by the use of chemicals of a relatively high degree of purity.

In the first place, there is advantage to the perfumer who wants, above all things, reproducibility of odour. Once he has decided upon his odour standard for a given chemical, then each succeeding delivery must be reasonably close to that standard. The nearer the approach to *one* constant odour, the easier it becomes to repeat that odour effect in subsequent batches. Impurities, as distinct from subsidiary constituents, are by-products or residuals which remain in the product during its manufacture, and it is frequently difficult to ensure that the same amount and the same kind of

impurity will be left in every batch. Naturally, the smaller the amount of impurity present, the less a change in amount will affect the final odour.

Secondly, a higher degree of purity is of great assistance in laboratory control of quality, as variations in trace impurities with strong odours may have little or no effect on the physical or chemical constants, but a very great effect on odour. This places an undue strain and responsibility on the perfumer, who must decide whether a product is satisfactory and similar to that previously supplied. It is possible to produce synthetic chemicals in a very pure state, and these obviously suffer less from variations in quality, but whether they will be useful as perfumery materials is open to doubt.

THE MODERN TREND

To sum up the situation, it appears that the modern trend is to use materials of the highest possible degree of purity. Although there are reasons why this is a most desirable trend, there will be many cases where the pure product will be of little value to the perfumer. The question is, how can these opposing points of view be reconciled? The first approach is by a better understanding of the nature of a perfumery chemical and an appreciation of what the perfumer really expects of that particular chemical by way of odour performance. There is no doubt that the modern methods of analysis are helping us to appreciate the foregoing points.

When a perfumer feels there is a desire for a superior grade of perfumery chemical, then he must distinguish between unwanted, unpleasant impurities and other subsidiary constituents. The subsidiary constituents referred to fall into three classes :

1. Those which have little or no effect on the odour.
2. Those which are essential to the odour of the main chemical to impart life or fullness and roundness.
3. Those products where the minor constituent is almost entirely responsible for the odour of the named substance. These cases are by no means rare.

The present position has come about by the fact that with the older type of plant it was impossible to separate traces of undesirable impurities from the subsidiary constituents. The result was that the subsidiary constituent was often unjustly blamed for the unpleasant odour. Using modern techniques, it has been shown that in many cases high proportions of subsidiary constituents actually fortify the main odour and are absolutely essential, always providing that these constituents are free from unpleasant trace compounds.

PRACTICAL EXAMPLES

As a practical illustration of the points so far outlined, I should like to take as an example one of the extreme cases, namely, Rhodinol. Consider

for a moment the chemistry. The structure of Rhodinol has been the subject of numerous investigations, and many chemists believe that the problem is still far from solved. To-day it is thought that Rhodinol and Citronellol are functionally identical, but that both are mixtures of certain isomers. So much for Rhodinol from the chemist's standpoint, but commercial Rhodinol is again very different from the Rhodinol of scientific literature, supposing this substance actually exists and it contains among other things, Geraniol, *d*-Citronellol, *iso*Menthone or Menthone and various terpenes. It is therefore obviously unreasonable to ask for a sample of pure Rhodinol. We could more sensibly ask for a supply of Rhodinol obtained from genuine Geranium Oil and request the highest possible total alcohol content. This would probably be the nearest one could get to a pure Rhodinol, but would it be satisfactory? The opinions of perfumers differ vastly on the question of the percentage of minor constituents they expect to find in their Rhodinol. Of these the most important is stated to be *iso*Menthone or Menthone.

Without this constituent, Rhodinol is flat and uninteresting, and in fact has little advantage in odour value over a mixture of Geraniol and Citronellol. *Iso*Menthone occurs in the lower boiling fractions of the Rhodinol and can be associated with the still earlier fractions of a terpene nature which have a most unpleasant and crude note. This, therefore, is a case where undesirable characteristics have, quite unjustifiably, been attributed to a secondary constituent. The following chromatograms furnish visible proof that it is possible to produce a Rhodinol having a considerable *iso*Menthone content, but free from harsh impurities.

The first chromatogram (*Fig. 1*) shows a Rhodinol which is very "pure", but it will be seen that it still consists of quite a number of substances. Its odour is, however, flat and uninteresting. The second chromatogram (*Fig. 2*) shows a Rhodinol with a higher *iso*Menthone or Menthone content—more acceptable to those who require a "minty" note. It will be seen that in addition to the higher *iso*Menthone content, the material contains the small fractions at the front which are the residues of the terpene present in the original oil. The third chromatogram (*Fig. 3*) shows the "minty" fraction which is contained in the second Rhodinol. This has been fractionated out and the chromatogram run with greater resolution. It can now be seen that there is a considerable proportion of early fractions. The fourth chromatogram (*Fig. 4*) shows the "minty" fraction when it has been further purified to give mainly two components, one the double peak which is associated with the mint-like odour, and a second peak which is an unknown component with a very fine odour. If a fraction of this type is now blended back in the right proportion with the so-called pure Rhodinol, the result is a very fine product having plenty of life, but lacking the crude notes of the

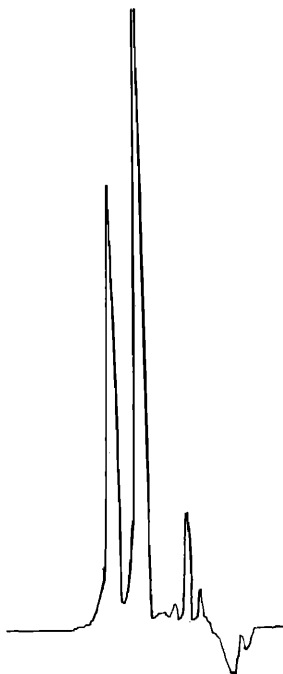


Fig. 1. A chromatogram of a "pure" Rhodinol. Odour flat and uninteresting.



Fig. 2. A chromatogram of a Rhodinol with a relatively high *iso*Menthone or Menthone content with a fine "minty" odour.

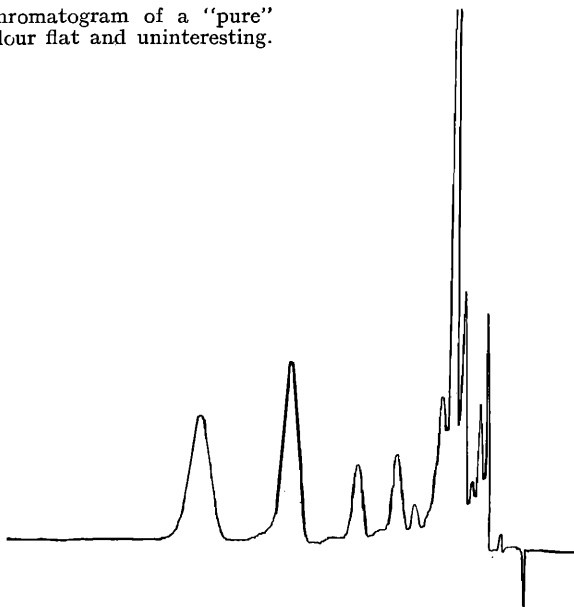


Fig. 3. A chromatogram of the "minty" fraction contained in the Rhodinol shown in *Fig. 2.*

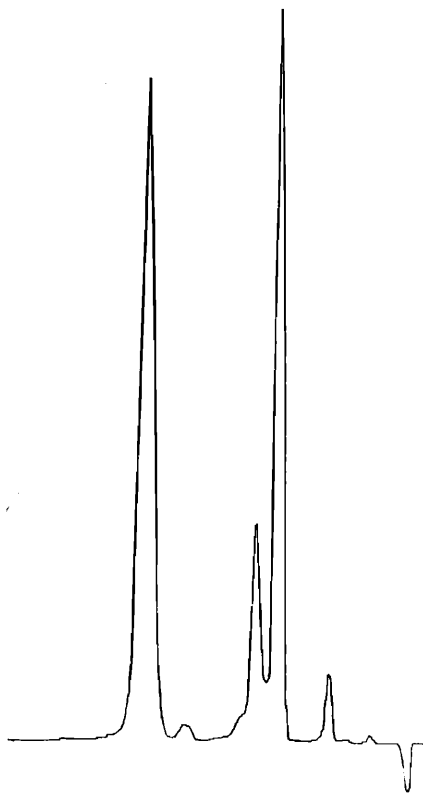


Fig. 4. A chromatogram of the purified "minty" fraction. The double peak is associated with a mint-like odour and the second peak is provided by an unknown component with a very fine odour.

early fractions. In other words, the clean odour of the purest Rhodinol has been fortified by a valuable top note without impurities of unpleasant odour.

Another example lies in the terpeness oils, where it is generally accepted that a terpeness oil which does not contain some terpenes is a most uninteresting product both for the perfumery and flavour industries.

It will, of course, be said that these cases are not quite fair, as they are materials which cannot be considered as chemicals; nevertheless, they illustrate very forcibly that the value of a product can be varied considerably by the other components which are present.

When we turn our attention to perfumery materials which can be more accurately described as chemicals, we find a similar situation in very many instances. To give a few examples:

Krajckeman¹ spoke about a paper by Mitchell², suggesting that a really

pure tri-chlorophenyl methyl carbonyl acetate had really little or no odour and that the odour value of the commercial product stemmed entirely from the presence of impurities. Methyl ethyl phenyl glycidate, the so-called strawberry aldehyde, is frequently asked for in a state of high purity and, in particular, the acetophenone content is expected to be almost zero. Here we have a case where the actual amount of the by-product or secondary constituent appears to be important, as it is found that while an excessive amount of acetophenone is undoubtedly undesirable, a strawberry aldehyde completely free from acetophenone is frequently rejected on the grounds that it is flat and lacking in odour. This may be purely a case of individual opinion, or an impression which has grown up over the years when it was not possible to obtain a very low acetophenone content for this product.

Ionone 100 per cent, which as already mentioned is not 100 per cent, gives another example, as the use to which this product will be put frequently controls the quality which is required. In many high-class perfumes an Ionone almost free from terpenes is required, but on the other hand, when the product forms part of a perfume to be used in soap, the terpene content can be much higher, for it is claimed that the Ionone terpenes perform very well in soaps. This also applies to methyl Ionone, *beta* Ionone and to a lesser extent, *alpha* Ionone. The list could be continued almost indefinitely; pure Hydroxycitronellal has very little odour indeed; pure amyl cinnamic aldehyde possesses an odour very different from the perfumer's normal product, and many perfumers would not "give a thank you" for pure, straight-chain fatty aldehydes.

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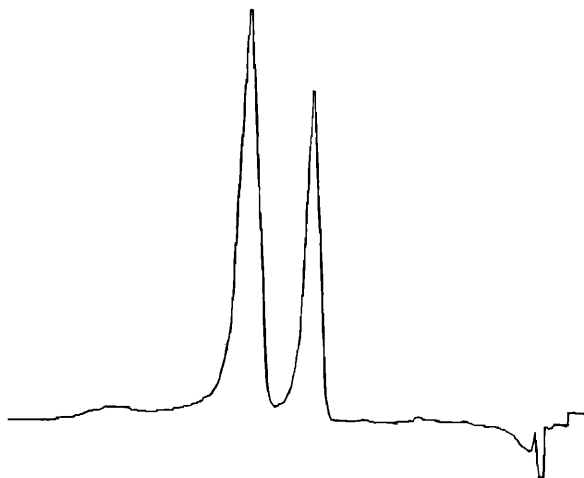


Fig. 5. A chromatogram of a Citral, Aldehyde content only 97 per cent by the Hydroxylamine method. Odour and flavour very fine. The tall peak on the left is Citral A and the peak on the right Citral B.

Another class of compounds is the higher esters of the terpene alcohols. Many of these are almost completely odourless if prepared in a high enough state of purity, as, for example, Geranyl Caprate, Linalyl Cinnamate, etc. The general idea is further extended by means of the following chromatograms.

CITRAL

Fig. 5 shows a chromatogram of a Citral which contains only 97 per cent of aldehydes when estimated by the hydroxylamine method. It is nevertheless a product with a very fine odour and is, in fact, superior in many respects to other Citrals with a so-called 100 per cent content.

This is due to the fact that one of the materials which may be present in Citral is Geraniol which, in small quantities, has no detrimental effect on the odour, but of course reduces the aldehyde content proportionally. On the other hand, a Citral can be produced which contains no Geraniol and tests approximately 100 per cent by the hydroxylamine method, but, nevertheless, contains impurities other than Geraniol testing as aldehydes and possessing a most objectionable odour and flavour. In this case, it may even be that attention should be directed to the ratio of Citral A to Citral B rather than to the total aldehyde content.

LINALYL ACETATE

Fig. 6 is a chromatogram of a Linalyl Acetate containing over 95 per cent of esters. It will be noted that it does not consist of a single substance and it could be claimed, therefore, that it is not pure Linalyl Acetate, but in actual fact, because it has been freed from undesirable impurities, it has a very satisfactory odour indeed and will in most cases perform better than pure Linalyl Acetate, which many people have described as having an odour no better than a high-class Terpinyl Acetate. The point here is that the work involved and the loss of yield due to the removal of other esters will increase the price very considerably, whilst at the same time in many cases making the product unsuitable for its intended purpose.

IONONE

It was mentioned earlier that Ionone Terpenes were claimed to perform very well in soap, whilst other people rate an Ionone containing terpenes as an unsatisfactory product. This chromatogram (*Fig. 7*) of a sample of Ionone Terpenes will probably explain this discrepancy, as it will be seen that the terpenes themselves consist of a very large number of components, some of which may be valuable and others undoubtedly detrimental to the odour of the product. In other words, the term "Ionone Terpenes" is not sufficiently descriptive. It is also possible that certain components of the terpene fraction are responsible for the instability of Ionones.

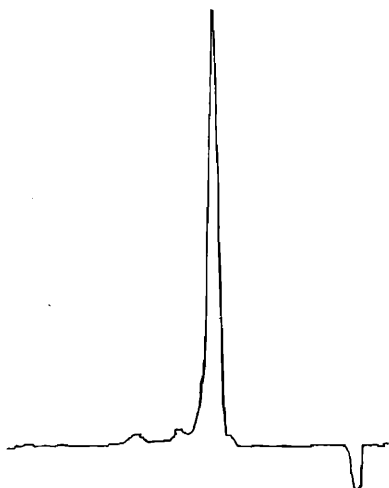


Fig. 6. A chromatogram of a Linalyl Acetate, possessing a fine odour despite the presence of subsidiary chemicals just before the main peak.

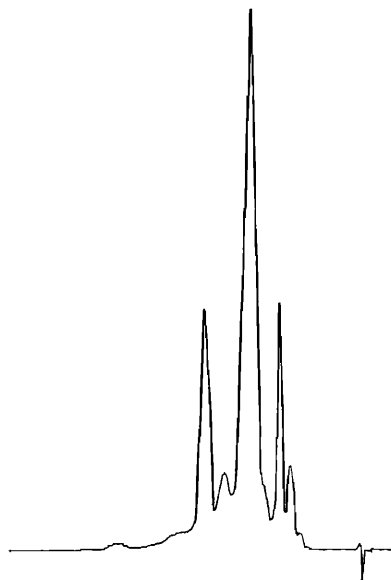


Fig. 7. A chromatogram of Ionone Terpenes, showing how this material consists of a very large number of individual components.

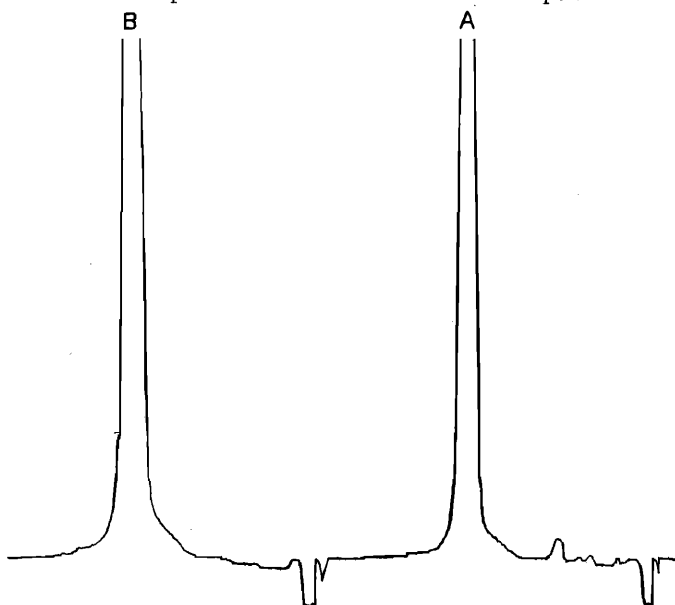


Fig. 8. A chromatogram of Phenyl Propanol. The figure on the left is virtually free of impurities but the odour is flat and uninteresting. The impurities shown in the chromatogram on the right impart a strong and sweet top note to this chemical.

PHENYL PROPANOL

Fig. 8 indicates chromatograms of two grades of Phenyl Propanol. The figure on the left shows practically no traces of impurities, but this particular product is soft, flat and rather uninteresting. The figure on the right, where traces of impurities are shown, possesses a strong sweet top note.

This then is the problem which has existed for so long between perfumers and the manufacturers of perfumery chemicals. We have seen how modern equipment has made it possible to appreciate more clearly the make-up of the materials we use. In fact, our problem appears to resolve itself into a distinction between unwanted impurities on the one hand and desirable or at any rate harmless subsidiary constituents on the other.

PASSING ON THE CORRECT INFORMATION

Now we come to the manner in which the perfumer can best assist his supplier to produce the exact type of material which he, the perfumer, requires. This is very much the perfumer's domain and I shall therefore tread warily. The perfumer's simplest approach will be via the smelling slip. Let us say his immediate problem is to improve the quality of a given perfumery chemical. A simple but careful examination of the slip will produce information of great use to the manufacturer. If the unpleasant odour is strong at first and then fades on standing to produce a substance of acceptable odour, this information means a lot to the distillation expert. If you can indicate whether the unwanted odour lasted for minutes or hours, then the manufacturer is even better armed to deal with the problem. On the other hand, if a product is acceptable at first but loses odour and becomes flat and uninteresting on standing, this information may well be an important clue to the producer. Finally, what of the residual odour? Tell your supplier whether this is to your satisfaction. If full details of odour performance are not given, you may find your next sample lacks your valuable top notes, but still retains the unpleasant residual odour.

The next request from supplier to perfumer is more difficult. Can you describe wanted and unwanted odours? Even a general description may be of value: sharp, sweet, crude, flat, burnt. For the better equipped perfumer, there are other aids to odour evaluation. Vacuum fractionation, employing modern laboratory column fillings, is an important weapon in the perfumer's armoury. Efficient stills may be constructed and relatively sharp separations of the various components of a perfumery chemical achieved. Examination of the various fractions should tell just which part or parts you require for your particular purpose. One point on the question of these stills: always use a form of reflux control, preferably electronic, as without this even a highly efficient column is almost useless.

There is, of course, gas chromatography, which as you have seen is

capable of giving an enormous amount of information even when the exact natures of the components are unknown. Chromatograms of the type of product which you like and those you do not like may indicate a trend which will enable you to obtain your ideal material.

CONCLUSION

The perfumer naturally wants the raw material which will give him maximum results and he wants the material to be identical with each delivery. He, the perfumer, can do a lot to help the supplier to bring about this highly desirable state of affairs. Finally, can I just say that the number of times when you find you really need a pure compound will be relatively small. That master perfumer—nature—never offers a pure chemical to us, she always shades it off with blending agents.

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AMPHOLYTIC SURFACE ACTIVE AGENTS

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Based on a lecture delivered before the Society on 16th March 1959.

The general characteristics of surface active ampholytes are discussed with particular reference to their similarities and dissimilarities to the better-known types of the surface active agents. A re-classification of the long chain betaines is proposed, and the reasons for this suggested change are given.

AMPHOLYTIC SURFACE active agents have been known for a considerable time, but they have remained little more than chemical curiosities until very recently, owing to the difficulty of procuring suitable intermediates for their manufacture. The situation has changed radically over the last few years, due principally to the pioneering work on Fat and Petroleum Chemicals, carried out mostly in the U.S.A. At the time of writing, however, it would be fair to say that owing to the still comparative novelty of the Ampholytics, little is yet known regarding their practical application.

* Glovers (Chemicals) Ltd., Leeds, Yorks.