Soap and Detergent Fragrances — Natural vs. Synthetic

E.A. MORRIS, Bush-Boake-Allen Ltd., Blackhorse Ln., Walthanstow, London E17 5QP, England

ABSTRACT

A brief resume of synthetic aromatics development and their role in soaps and detergents will be presented along with comparison and evaluation of natural and synthetic routes to fragrances. The discussion also will include economic factors and future trends, with some conclusions as to growth and pattern of demand.

Nature provided a range of fragrances that have pleased and excited people over the centuries. Some were bold and demanding of recognition, others subtle and of delicate impact. We are allowed the full enjoyment of these odors via an olfactory sense that is capable of extraordinary development, and this facility has been an essential feature in the production of synthetic fragrances that both match and challenge their natural forerunners. All races desire an association with fragrance, and the more sophisticated the society, the more demanding is the need for a widening application of fragrance materials. The soaps and detergents industry has long since recognized and prospered by its affiliation with perfumery, and none will doubt the importance of immediate odor appeal to the potential consumer.

In referring to natural fragrances, we should visualize such as natural absolutes, ottos, resinoids, musks, castoreum, civet, and ambergris, all of which are still employed. However, it is important to realize that these now represent a modest part of today's perfumery market. Although the title of this paper suggests a contest, in fact, little contest still remains. Figure 1 illustrates the dominant position that synthetics have attained in the bulk perfumery field and with continuing growth, you will readily accept the impossible challenge that the naturals face.

Rose alcohols are traditional feedstocks for soaps and detergents and prior to the introduction of synthetics, these were principally obtained from citronella and lemongrass oils. Citronella is available in two main commercial varieties by distillation of citronella grasses which occur in Java and Sri Lanka (Ceylon). Lemongrass occurs widely and also yields oil by distillation. The areas principally involved have a history of political and economic stress which has been reflected over the years in the price structure, quality, and availability of the natural oils. Users, in particular the soapers, mounted a pressure for synthetics that would be less subject to the fluctuations besetting the naturals market. As one brief example of their dilemma we need but consider the graph of price movements on citronella oil which shows the instability involved (Fig. 2).

The consumer pressure created a major technical challenge which demanded an expertise of the highest caliber in order to establish formulas and to evolve production and engineering techniques of considerable complexity with plant capacities well in excess of previous norms.

Synthetics have been with us for many years. Indeed the 1920s saw such as the development of synthetic menthol and hydroxycitronellal from natural oils, but it was the early 1950s that heralded the principal moves toward the bulk production of synthetic equivalents of the main natural isolates. This development firstly concerned the upgrading of turpentine as a raw material for chemical processing to perfumery materials. It is in this area that I am personally connected in a buying capacity.

The pinenes development which evolved mainly in the U.S. and the U.K. was soundly backed by a long term replaceable feedstock situation. The pulp and paper industry yields by-product sulfate turpentine to form a most significant supply source.

The synthetics story has been one of considerable achievement and alongside pinene-derived materials has been the parallel development of entirely different routes from petroleum. Nature is often complex and never more so than with her fragrance formulations. It has demanded the utmost technical expertise to both recognize and copy the extensively complicated structures involved, but today we can perceive a situation where these complexities have been largely overcome, and mainly now the user has simply to consider economic and availability factors in order to determine choice.

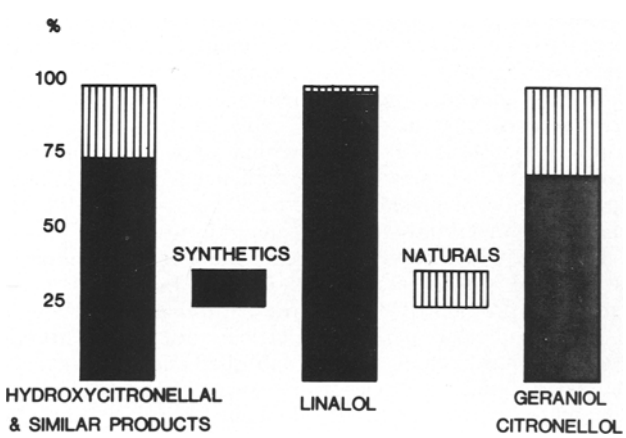

FIG. 1

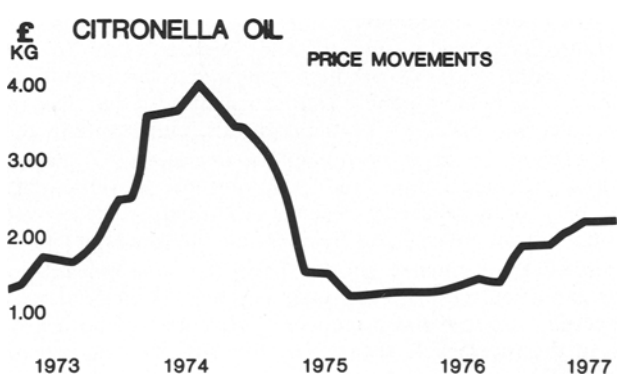

FIG. 2

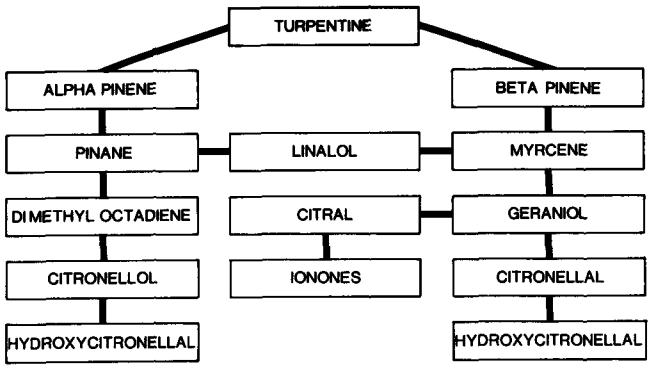

FIG. 3

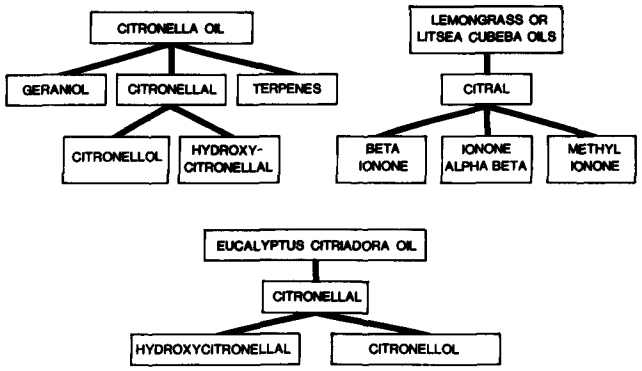

FIG. 4

Understandably, the synthetics were not given ready acceptance initially and indeed, being generally of a purer nature, they had a somewhat different character than the natural products. However, by commendable cooperation between user and producer, products were found that had the ready approval of both parties, not necessarily a precise match for the natural material but nevertheless suitable for the required application.

In rounding off these introductory remarks it is worth reemphasizing the particular part played by soaps and detergents in support of the synthetic arena. The sheer size of the industry has demanded stability and capacities that only synthetics could be expected to satisfy with long term continuity. Technical and commercial collaboration has promoted benefits to all concerned.

Now let us turn to a more specific examination of certain major perfumery materials employed in soaps and detergents. Let us examine the alternative routes currently available and attempt to expose the principal strengths and weaknesses of their relative positions. For this explanation, and to reduce complexity, I will discuss four materials that can be considered the frontrunners within the current demand pattern, these being hydroxycitronellal, geraniol, methyl ionone, and linalol.

Hydroxycitronellal imparts the popular 'Lily of the Valley' odor, and this product is now derived from both alpha and beta pinene from turpentine, the natural citronella and eucalyptus citriodora oils, plus isoprene and isobutylene of petroleum extraction. Pinene hydroxycitronellal pioneered bulk synthetic development, and it is only relatively recently that petroleum-derived products have entered the field. Of all the routes, it can be observed that pinenes should have the cost advantage. This is particularly true where alpha pinene is the feedstock concerned, since it has a relatively weak market both now and in the foreseeable future. In 1975/76, the essential oil prices fell back to levels which few marketers could have previously envisaged and for a brief spell they became competitive feedstocks. However, we have now seen a return to more normal trading conditions, and the oil prices have hardened to levels that are economically unattractive, at least for bulk production.

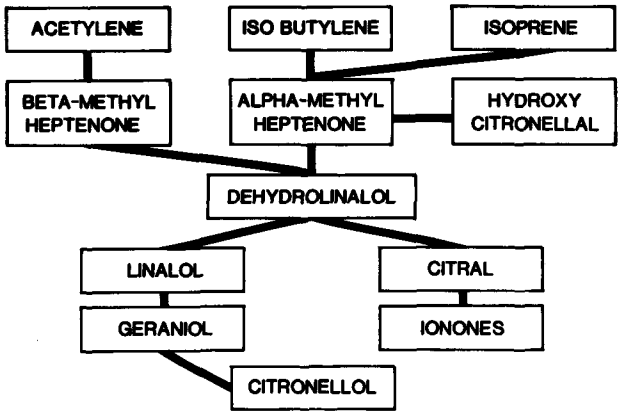

FIG. 5

It is worth observing that these oils are largely the products of developing countries, and as such, it is important that their return shows a proper economic advantage. If such is not achieved, then one can expect them to turn to more lucrative crops.

The competing routes to hydroxycitronellal are shown in Figure 3. Pinenes progress from turpentine via beta pinene, myrcene, geraniol, and citronellal, while the alpha pinene route is via pinane, dimethyl octadiene, and citronellol (Fig. 4). Citronella oil has a citronellal content of about 30%, and eucalyptus citriodora contains some 60/80%. Manufacture from petroleum feedstock uses methyl heptenone (Fig. 5). From a quality standpoint, there is little to choose between the competing products of these alternative manufacturing routes. While the traditional product from essential oils will continue to be used, it is certain that synthetics will gain ascendancy by virtue of their price advantage.

For hydroxycitronellal, it is very difficult to see a future for the natural oils unless, as in 1975/76, extraordinary market conditions force the oil prices down to totally uneconomic levels. Of all the present routes there is reason to expect that pinenes will maintain their position as more production is centered on the cheaper and readily available alpha pinene feedstock.

Turning to geraniol (Fig. 5) you will recognize this as a highly popular floral note. The competing routes of preparation are from beta pinene, citronella oil, and isoprene. Isoprene proceeds via methyl heptenone, dehydro linalol, and linalol. Citronella oil (Fig. 4) contains about 60% geraniol, and it's a simple step from beta pinene via myrcene (Fig. 3).

Calculating the cost of these competing routes, one is forced to the conclusion that citronella oil will always be the most expensive, and the principal competition will be from the pinenes and petroleum sources. Pinenes are extremely strong in geraniol and its derivatives, while isoprene synthesis to linalol would appear the stronger product but this is now open to challenge from linalol from alpha pinene which is not expected to match on quality but which should certainly have an economic advantage.

There is a detectable difference between the odor of natural and synthetic material. Perhaps because it is the traditional product of decades the natural is often thought to be the better perfumery article, but the synthetic alternative has become firmly established and is in universal use as a building brick in its own right. Soaps and detergents are almost totally dependent on the synthetic products.

Looking ahead, one should not expect essential oils to

return to low price levels for anything but limited periods. It can be expected that, for volume use, albeit with certain reservations on quality, the synthetics will both maintain and improve their market share. The same can be said for the popular rose odor of citronellol which is derived from geraniol.

Methyl ionone is a floral woody odor of the violet type and while somewhat highly priced, it is nevertheless a big volume detergent chemical. In competition for the available market there are routes to prepare it from pinenes, litsea cubeba oil, isoprene, acetylene, and to an insignificant degree, lemongrass oil. The latter oil was the major feedstock until the 1960s, since then it has completely lost its position.

Pinenes proceed to geraniol and citral (Fig. 3) while litsea cubeba (Fig. 4) has around 70%/80% citral content which is taken on to methyl ionone and similarly lemongrass oil, when used. Finally, (Fig. 5) the petroleum routes work through methyl heptenone, dehydro linalol, and citral, there being two acetylene stages in the case of isobutylene. With regard to methyl ionone it is certain that the natural oil will seek to retain a positive position because litsea cubeba is a significant export of China and one that presumably China will safeguard as a currency earner. Litsea cubeba is obtained by steam distillation of a pepper-like fruit from the may chang – a tree that is used extensively in China as a windbreak. This is very significant because the producer does not have the ready ability to switch crops if the situation so demands, as is the case with regard to products from grasses. This means that market positions will be protected to the best extent possible.

Litsea cubeba, over the recent past, has certainly been the dominant feedstock but here we have a raw material from China only and to try to anticipate the future market provides an enigma to producers who have the capacity to use the alternative synthetic intermediates.

At present the market has seen nothing significant in the way of products from petroleum sources and hardening of the litsea price has left pinenes with the best market position for the time being. In the long term it is difficult to form an opinion as to the likely market development for so much does depend on the strength of the litsea cubeba market and undoubtedly China holds the key.

And now let us turn to linalol, a product whose growth has been stimulated extensively by soaps and particularly by detergents. The industry needed and created a demand for large quantities of linalol in perfumes for detergent composition. The trend toward washing materials at higher temperatures created the need to fashion perfumes to meet this requirement and for which synthetic linalol is particularly suitable.

Linalol can be isolated from bois de rose oil in which it occurs to the extent of 60/90%, being distilled from the wood, but labor and distance problems have made the tree increasingly inaccessible. Despite the fact that pinene and petroleum linalol did not appear until the mid-1960s, the essential oil-based linalol is now already passé.

The petroleum routes to linalol (Fig. 5) utilize methyl heptenone and dehydro linalols, while pinenes produce linalol (Fig 3) via beta pinene and myrcene or perhaps more economically from alpha pinene and pinane. So far as soaps and detergents are concerned, both the pinene and petrochemical linalols have proved to be highly acceptable in terms of odor. This is a floral woody note.

Although, by necessity, I have concentrated on synthetics from pinenes and petroleums, one must not forget the considerable range of products that are made synthetically, such as the benzyl group products, nitrated musks, and their modern successors, coumarin, aldehydes, phenyl ethyl alcohol, and simulated essential oils, all important synthetics that are available to the perfumery market of today.

Contrary to earlier opinions and as evidenced in 1975/76, given particular and favorable market situations, the naturals can still recover temporarily some of their lost ground. However, evidence and informed comment would suggest that, short of a major recession, essential oils will not be available at low prices in the future, and it is equally unlikely that the petroleum- and turpentine-derived alternatives will rise to an extent that could reestablish the natural essential oils into a competitive position.

Many essential oils are the product of developing countries and they do have this overriding need to assess their total economic position and to opt for crops that provide the most lucrative return. The result of this could also mean that essential oil availability will decline.

Although it is popular to link petrochemical routes to a diminishing supply line, this cannot be a limiting factor in the foreseeable future although of course, as already seen, their feedstock must continue to firm as time progresses.

Pinenes, based as they are on turpentine, will benefit greatly from the pulp and paper industry. Pinene production utilizes both gum and sulfate turpentine, and while the former is labor intensive and therefore subject to an obvious cost hazard, the sulfate turpentine, a by-product of the kraft pulp industry, should provide a more stable and regulating influence.

I would predict that major fragrance users, with full recognition of their supply choice, will seek blends of both natural and synthetics that would allow ease of modification in order to take the best advantage of market situations.

Pinenes will offer the soundest long term situation in all respects. More broadly, it is to be observed that synthetics have gained a supremacy within the realm of bulk production which is unassailable. Naturals will, of course, remain to satisfy specific and limited demands. With certainty, the perfumery interests of soaps and detergents will be well served.