Aroma Chemical Usage Trends In Modern Perfumery

By Ronald S. Fenn, Vice President,
International Flavors & Fragrances Inc., Union Beach, NJ

In today's world, rarely does a perfumer have the freedom to create a fragrance at any price he chooses. The most successful fragrance products capturing large sales usually are backed by expertly organized and planned marketing campaigns, structured to yield a desired financial return to the marketing company.

In most major world markets there are a large number of companies prepared to compete for the privilege of supplying a fragrance. The net result is that many marketing companies set low level targets for the cost price of a fragrance that severely challenge the perfumers' creativity.

Therefore, there is a tendency to "push" the perfumer into using the lower priced commonly available materials. The better creative perfumers give the lower priced fragrances a quality and uniqueness by adding more "exotic" intensely odored specialty products which, although of higher price, offer excellent strength to cost ratio.

These materials, whether aroma chemical, or natural product, frequently comprise 80% or more of the total number of ingredients in a fragrance. In the case of fine fragrances, they often contribute the major part of the total cost. Such ingredients are beyond the scope of this paper, but will be the subject of a future article.

Significant Aroma Chemicals

Perfumers, external to IFF, have incorporated *significant* aroma chemicals into fragrances available in marketed products. "Significant" is defined as being present in the fragrance at more than 1% concentration. Please note that the fig-

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Table I. Frequency of occurrence in fine fragrances at > 1%

Product	% of tested
1. Linalool	90
2. Linalyl Acetate	78
3. Phenyl Ethyl Alcohol	82
4. Benzyl Acetate	74
5. Benzyl Salicylate	74
6. Coumarin	68
7. Terpineol	66
8. Hedione	56
9. Hexyl Cinnamic Aldehyde	51
10. Methyl Ionone Gamma	51
11. Terpinyl Acetate	50
12. Lilial	49
13. Lyral	46
14. Geraniol	43
15. Heliotropine	43
16. Galaxolide 50	41
17. Vertofix	41
18. Musk Ketone	38
19. Citronello	38
20. Amyl Salicylate	32
21. Eugenol	26
22. Vertenex	25
23. Iso Bornyl Acetate	23
24. Amyl Cinnamic Aldehyde	21
25. Hydroxycitronellal	21

ures presented do *not* include fragrances created by IFF and, for the sake of brevity, only the top 25 are listed in each category.

A study was made of nearly 400 fragrances used in major commercial products marketed around the world. These extracts of the results are presented in three product categories:

A. fine fragrances
B. household products, and
C. soap

The reasons for separating the results into three categories are somewhat arbitrary, but are roughly explained as follows:

Category A: Fine fragrances or perfumes in alcohol, also include toilet water, splash colognes, some creams, etc., as the fragrance level can be high; i.e., 10% of the finished product or more. They are the highest selling price group.

Category B: Household product fragrances. Generally lower price fragrances but with special need for chemical compatibility; i.e., for detergents, fabric softeners and cleansers. Lower fragrance concentration—up to 1% in most cases.

Category C: Soaps (in bar or tablet form). Medium price requirements. Usage level of fragrance is generally 1 to 2%.

Category A—Fine Fragrances

Table I shows the top 25 materials significantly present in the Category A fine fragrances studied. Linalool was found in 90% of the fragrances but, of course, its presence can be attributed not only to the use of the chemical as such, but also from the presence of various other products, particularly the essential oils. Many essential oils are rich in not only linalool, but also its acetate ester, which was second in terms of frequency.

The third product on the list, phenyl ethyl alcohol, although it does occur naturally, is much more likely to be present in formulas because of its deliberate addition as such by the creative perfumer. The fourth highest usage level is benzyl acetate, probably no surprise to anyone. The top four products in this list also feature in the top

eleven products of the other two categories.

Benzyl salicylate (5th), perhaps is somewhat surprising except to the highly knowledgeable perfumer. It has fixative properties with no significant depressant effect on the overall odor of a fragrance. In this respect it differs from diethyl phthallate (DEP) which is virtually odorless. (DEP and other solvents are omitted from this study as they are *not* odor contributing for the purposes of this study. However, they do have an effect on the odor of mixtures in which they are included.)

Coumarin is the first crystalline material most frequently used: 6th for fine fragrances and 7th in soaps. Another popular crystal, vanillin, would be a close contender in terms of frequency, however, it is usually found at levels below 1%.

Lilial and Lyral frequently are found in nearly half of the products in the marketplace and, in fact, are benefiting from the IFRA recommendations concerning hydroxycitronellal. Although this latter product still makes this list in the 25th position, it is likely to decline in terms of the perfumers' use of the product in new creative work, particularly for fragrances that come into contact with the skin.

Heliotropine (15th) is used frequently and can be expected to retain its position of importance. Two former specialty products that have established themselves for use in fine fragrance are Hedione and Galaxolide. As competition increases, Galaxolide will actually become easier for the perfumer to afford at high concentrations. Consequently, its usage should expand, to some extent, at the expense of other musk products.

Musk ketone (18th) long has been valued for its particular animal musk character, especially for use in alcoholic solutions. However, its frequency of use in soap and household products fragrances is nowhere near as high as for the fine fragrances. Other products included on the list are: terpineol, terpinyl acetate, geraniol, citronellol, amyl salicylate, eugenol, Vertenex and iso bornyl acetate. These products comprise a group of staple materials that are commonly used in all types of fragrances, regardless of purpose. They generally have proven reliable and are relatively inexpensive. However citronellol and geraniol have increased alarmingly in price this year.

The 24th product is amyl cinnamic aldehyde (ACA) which, although used in over 20% of the fragrances examined, is certainly not as popular as hexyl cinnamic aldehyde (10th) which features in 50% plus. Further growth of hexyl cinnamic aldehyde is expected. World production figures of HCA are more than twice that of ACA.

Table II. Frequency of occurrence in household products fragrances at > 1%

Product	% of tested
1. Linalool	68
2. Terpineol	66
3. Phenyl Ethyl Alcohol	63
4. Benzyl Acetate	63
5. Lilial	62
6. Vertenex	55
7. Cyclacet	51
8. Terpinyl Acetate	51
9. Methyl Ionone Gamma	50
10. Hexyl Cinnamic Aldehyde	46
11. Linalyl Acetate	44
12. Citronellol	40
13. Geraniol	36
14. Tonalide	35
15. Vertofix	32
16. Galaxolide 50	31
17. Iso Bornyl Acetate	28
18. Benzyl Salicylate	25
19. Amyl Salicylate	24
20. DMBCA	24
21. Amyl Cinnamic Aldehyde	23
22. Verdox	22
23. Vanoris	20
24. Iso E Super	17
25. Hedione	17

Table III. Frequency of occurrence in soap fragrances at > 1%

Product	% of tested
1. Linalool	91
2. Phenyl Ethyl Alcohol	87
3. Benzyl Acetate	85
4. Amyl Salicylate	74
5. Lilial	72
6. Vertenex	66
7. Coumarin	66
8. Methyl Ionone Gamma	64
9. Terpineol	62
10. Citronellol	60
11. Linalyl Acetate	59
12. Cyclacet	51
13. Phenyl Ethyl Acetate	45
14. Tonalide	42
15. Hexyl Cinnamic Aldehyde	40
16. Geraniol	40
17. Benzyl Salicylate	40
18. DMBCA	40
19. Eugenol	40
20. Heliotropine	39
21. Vanoris	30
22. Amyl Cinnamic Aldehyde	30
23. Terpinyl Acetate	30
24. Galaxolide	28
25. Musk Xylol	28

Category B—Household Products

Table II examines the pattern of usage found in fragrances for household products, Category B. Again the top of the list looks rather similar to the top of Category A except that Cyclacet plays a much more important part; it is contained in 51% of the fragrances examined. Tonalide or fixolide move onto the list at 35%. It must be emphasized that if IFF created fragrances had been included in our study, Galaxolide would have been much higher on this list and, in fact, higher on all three lists.

Not surprisingly, iso bornyl acetate shows a higher incidence of usage in household product fragrances than it does in fine fragrances (17th vs. 23rd). Other products that are featured in the top 25 for household products include DMBCA or dimethyl benzyl carbinyl acetate, Verdox, Vanoris and Iso E Super. Hedione is used less in Category B than in the fine fragrance category. Products that just failed to make the list include heliotropine in 26th position, Celestolide in 27th and musk xylol in 28th.

Category C—Soaps

Category C, soap fragrances (see Table III), constitute the final category and, here again, the ranking is similar to the previous two listings. Phenyl ethyl acetate (13th) is quite frequently used in over 45% of the samples tested. Products that did not quite make the top 25 include Vertofix, Cyclaprop, iso bornyl acetate, Hedione and musk ambrette.

Safety Restrictions

Safety and environmental considerations continue to exert severe constraints on perfumers. Some materials are restricted for use by various International Fragrance Association (IFRA) recommendations, or local governmental regulations regarding the environment. Long established materials such as hydroxycitronellal now have to be very carefully considered before they are incorporated into fragrances that may contact human skin, although there is no restriction for most other applications.

This type of activity slowly brings a change in

the perfumers' use of muguet odored materials where, as previously mentioned, there is increased activity regarding the demands of such products as Lyral and Lilial (generally thought of as being in the same odor family). Musk ambrette is similar. IFRA recommendations, coupled with strong surveillance by FDA, have resulted in a severe curtailment of the use of musk ambrette in skin contact fragrances. Fortunately replacements such as Ambrettex G, simulating the odor of musk ambrette, are available and have been specified in existing formulations by the marketing companies. Also for new creative work requiring the musk ambrette type of odor, either the simulations or the non-nitro musks enable the perfumers to achieve their objectives without inconvenience.

Such restrictions, although only affecting specific end product uses for the material, actually tend to affect the use of the material for *all* applications. Doubts concerning one application tend to raise the level of apprehension in the perfumer's mind for all activities. There will be a likelihood on the perfumer's part not to use the material at all, just in case further bad news develops affecting additional product applications. The natural conservatism of most companies; i.e., preferring not to use materials that may become a problem in later years, reinforces the perfumer's apprehension. Manufacturers of materials where restrictions apply should not be complacent and think they have only lost one outlet for part of their production.

The presence of a paper presented by IFRA at virtually all symposia or conferences relating to the fragrance industry is a constant reminder to all aroma chemical manufacturers of the need for vigilance concerning the total safety and hazard aspects of the fragrance ingredients used.

New Aroma Chemicals

In regard to new aroma chemicals, if one uses the old argument that there are only seven basic colors to the spectrum from which artists can produce an infinite number of pictures, then it surely must be true for fragrances—perfumers are well served by the several thousand materials they already have and, obviously, do not need more. However, this is entirely contrary to commercial reality. For example, the fine fragrance fashion world constantly seeks a new fragrance with a different note that will gain a large and faithful following for the new product. Today you would be hard pressed to find a fragrance containing the jasmin moiety that also does not incorporate Hedione. Similarly, for fragrances that require the precious "velvet on the skin" woody, amber character, most fragrance supply companies use Iso E Super. Both are comparatively new materials relative to the long history of perfumery. Perfumers must dare to be different!

Chemical Concentration

In Table I, frequency of occurrence for Hedione was in 56% (8th) of the products tested and for Galaxolide 41% (16th). Let us now take a look at fine fragrances but in order of concentration of the aroma chemicals used (see Table IV).

Surprisingly perhaps these two materials are used in the highest percentages of the more than 200 fragrances examined. This ranking takes on a very different appearance then in Table I. The most commonly occurring product, linalool, is 5th when expressed in order of concentration. Linalyl acetate is 7th. Phenyl ethyl alcohol is both 3rd in terms of occurrence and also average concentration. Vertofix is the 4th highest concentration and 17th in frequency of occurrence. Another product even newer than Hedione and Galaxolide, is Iso E Super. It jumps to 17th in terms of order of concentration. Although in terms of frequency of occurrence it was 27th. However, since IFF fragrances were not in-

Table IV. Average concentration of aroma chemicals in fine fragrances

Product	% of fragrance
1. Galaxolide 50	8.1
2. Hedione	6.5
3. Phenyl Ethyl Alcohol	5.6
4. Vertofix	5.0
5. Linalool	4.7
6. Benzyl Salicylate	4.7
7. Linalyl Acetate	4.5
8. Benzyl Acetate	4.3
9. Vertenex	3.6
10. Methyl Ionone Gamma	3.5
11. Citronellol	3.5
12. Hexyl Cinnamic Aldehyde	3.4
13. Lyral	3.2
14. Geraniol	3.2
15. Musk Ketone	3.1
16. Hydroxycitronellal	3.0
17. Iso E Super	3.0
18. Lilial	2.7
19. Musk Ambrette	2.6
20. Amyl Salicylate	2.5
21. Amyl Cinnamic Aldehyde	2.5
22. Coumarin	2.4
23. Iso Bornyl Acetate	2.4
24. Tonalide	2.4
25. Eugenol	2.0

Trade named aroma chemicals

Firmenich
Hedione
Givaudan
Lilial
IFF
Celestolide
Cyclacet
Cyclaprop
Galaxolide
Iso E Super
Koavone
Lyral
Vanoris
Verdox
Vertenex
Vertofix
PFW
Tonalide

cluded in the survey you can assume that the world average level of usage for Iso E Super comes in at higher than the 3% and, more importantly, that the material is enjoying a higher frequency of use in *new* creative work by most fragrance houses.

Traditional perfumery has long employed n-methyl ionone and then, more recently, the preferred alpha iso isomer, commonly known as gamma methyl ionone. These products have tremendous merit. However, if you want to make a fresher odored material, yet with the familiar characteristics of the methyl ionone, Koavone is now a fashionable product for the perfumer. Expect to see this product work its way onto these tables in the future.

Some Final Remarks

In short, new materials, preferably of a high cost effectiveness, are in desperate demand by the world's perfumers but few companies have the ability to meet that requirement. The higher cost associated with the testing of a new product to insure its safety has dissuaded many companies from spending substantial time on new chemical synthesis. If you couple the high cost factor with the "losing" attitude that the more chemicals you find the less there are to be found, then many a company has found it easier to take the conservative path. However, such an attitude inhibits further progress or certainly indicates the likely return is not worth a company's investment.

For the faithful few that do continue searching for new chemical structures useful to our industry, and IFF is one, there is an eager audience waiting. They know that when a new product is introduced they can reasonably assume the innovative producer will have exhaustively tested the product to make sure its future growth is worth the expense of the introduction, testing, etc. Therefore the product will be worthy of the perfumer's undivided attention.

Strategically, the creative perfumers who desire to be innovative and develop new winning fragrances are well advised to vary the ingredients they use. In so doing they will avoid the criticism of "house odor;" i.e., that fragrances from their company have an element of sameness or excessive familiarity. Also they will make duplication of their work by others far more difficult.

It is interesting to speculate on what the tables just reviewed will look like 10 years from now. I have opinions in this respect, but will leave the task to individual readers.

This paper was presented at the International Conference on Essential Oils, Flavors, Fragrances and Cosmetics in Beijing, October 6, 1988 organized jointly by the Ministry of Light Industry of the People's Republic of China and the International Federation of Essential Oils and Aroma Trades.

Address correspondence to Ronald S. Fenn, Vice President, International Flavors & Fragrances, 1515 Highway 36, Union Beach, NJ 07736, USA.