Fragrancing Emulsions

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The last step in creating a cosmetic emulsion is the addition of a little perfume. After all the technical and esthetic considerations of formulating the product, the fragrance appears to be an afterthought. In fact, the consumer, blissfully unaware of micelles or lamellar liquid crystals, may likely place more value on the aroma than the scientific niceties of the formulation.

The formulator may look to the literature for guidance and as often as not will see the following:

Fragrance.....qs

Since fragrance is not a standardized, clearly specified functional material like cetyl alcohol or methylparaben, its application is not clearly defined. The formulator has no indication of the importance of the fragrance on the product's sensory appeal or physical performance.

What is "Fragrance"?

Hydroalcoholics are what we typically think of as "perfume." To create these fragrances, perfumers evaluate the relative volatilities of thousands of materials. A pleasing blend, termed an *accord*, is made of the least-volatile materials. A mixture of medium volatility is added to form the *middle note*. Finally, very fleeting materials which give sparkle and immediate impact are added as the *top note*. As the fragrance is observed over time, the top, middle and bottom notes become prominent in turn. A balanced fragrance will naturally change as it evaporates, but in a pleasing and consistent way.

The physical and chemical effects of perfume oils on emulsions can be significant. A perfume can easily contain over 100 components, including aldehydes and ketones, terpenes, aliphatic and aromatic alcohols, heterocyclics, aliphatic rings, esters and lactones, and amines and amides—a range so extensive that almost any conceivable reaction is possible. A good brief account of fragrance chemistry was provided by Seldner.[1]

Effects on Emulsions

Little consideration was given to the effect of perfumes on emulsions until the 1940s. Other than the need to eliminate materials which obviously discolored or were known irritants, perfume at typical-use levels was not deemed a potential complication.

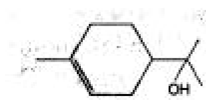
World War II created a shortage of alcohol, which required alternate fragrance delivery systems. Thin emulsions with high fragrance levels were concocted. These formulations experienced severe stability problems and were highly sensitive to the specific components of the fragrance oil.

Early work on the effects of aromatic chemicals on emulsions was published by Morel,[2] Karas,[3] Wynne,[4] McDonough[5] and Pickthall.[6] Each of these authors presented empirical raw material studies. Pickthall was particularly valuable for adding a theoretical picture of the potential surface activity of aroma chemicals. A number of papers[7-10] published since Pickthall have dealt with aspects of perfuming emulsions without significantly extending the foundations established by these early researchers.

Pickthall used hydroxycitronellal and terpineol as examples of aromatic raw materials with the potential of destabilizing an emulsion (Figure 1):

$CH_3C(OH)(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH{=}O$

Hydroxycitronellal ($C_{10}H_{20}O_2$)



α-Terpineol ($C_{10}H_{18}O$)

Figure 1

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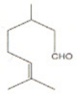
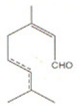
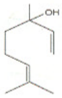
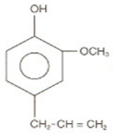
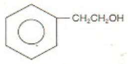
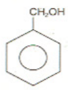
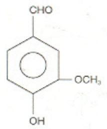
Table I. Solubility parameters and structures for selected cosmetic and fragrance ingredients

White mineral oil	7.09	
Stearic acid	7.75	$CH_3(CH_2)_{16}COOH$
β-Pinene	8.03	
Amyl acetate	8.43	$(H_3C)_2CH-CH_2-CH_2-OOC-CH_3$
Citronellal	8.83	
Stearyl alcohol	8.90	$CH_3(CH_2)_{16}CH_2OH$
Citral	9.34	
Linalool	9.62	
Amyl alcohol	10.84	$(H_3C)_2CH-CH_2-CH_2-OH$
Benzaldehyde	11.00	
Eugenol	11.12	
Dipropylene glycol	11.78	$CH_3-CH(OH)CH_2-O-CH_2CH(OH)-CH_3$
Phenylethyl alcohol	11.79	
Benzyl alcohol	12.31	
Vanillin	12.34	
Propylene glycol	14.00	$CH_3-CH(OH)-CH_2-OH$
Water	23.40	

Hydroxycitronellal has two polar groups, hydroxyl and aldehydic. It can compete for space on the surface of a micelle. The most likely adverse effect on an emulsion would be a decrease in viscosity, with the possibility of a complete breaking of the product. α-Terpineol works less drastically, with only its alcohol group sticking out of a relatively small and sterically rigid molecule, but still has enough disruptive influence to break some emulsions.

Occasionally, the perfume material may produce closer packing at the interface. Thus, it improves stability. More likely, it will disturb the balance either by loosening the packing or displacing the intended emulsifier. The effect is more apparent in thin lotions than in thick creams.

Solubility Parameters and Stability

The simple view of solubility, that materials are either water-soluble or oil-soluble, has been considerably refined by the concept of solubility parameters.[11-12] Besides the obvious polar components of aromatic chemicals (usually oxygen-containing groups), such factors as double bonds and van der Waals forces can produce slight water solubility. Even the most hydrophobic material can have some water affinity created by dipole-induced dipoles. Induced dipoles can only be explained by quantum mechanics. The electron cloud around a molecule is a time-averaged visualization. London[19] noted that a molecule with a zero time-averaged dipole has an instantaneous non-isotropic charge distribution. This results in a short-range attractive force, proportional to the inverse sixth power of the intermolecular separation. Polar molecules induce more stable dipoles in non-polar molecules. The interaction is termed a "dispersion force." Thus the fragrance in an emulsion cannot be assumed to be exclusively in the oil phase.

The solubility/structure table (Table I) gives some indication of the properties of fragrance chemicals and a few basic materials that might be in a TEA-stearate emulsion.

The most complete account of aromatic chemicals was provided by Arctander.[13] Although the description of solubility properties is not always quantitative, here are a few that Arctander provides:

Benzyl alcohol	4.00%
Amyl alcohol	2.70%
Phenylethyl alcohol	2.00%
Benzaldehyde	0.30%
Amyl acetate	0.25%

The correlation between the solubility properties and Arctander's descriptions are not exact, but the general tendencies are clear. Benzene is slightly soluble in water, so the substituted benzenes have greater water solubility than the terpenes. Aromatic alcohols are among the most water-soluble fragrance materials commonly used.

In addition to the growth of our perception of solubility, the theoretical framework of our knowledge of emulsions has blossomed since the time of Pickthall. The old view, where an amphiphilic molecule provided adequate stability merely by lowering interfacial tension, has been augmented by electrical effects and liquid-crystal structures in the external phase. This makes it possible to locate the perfume

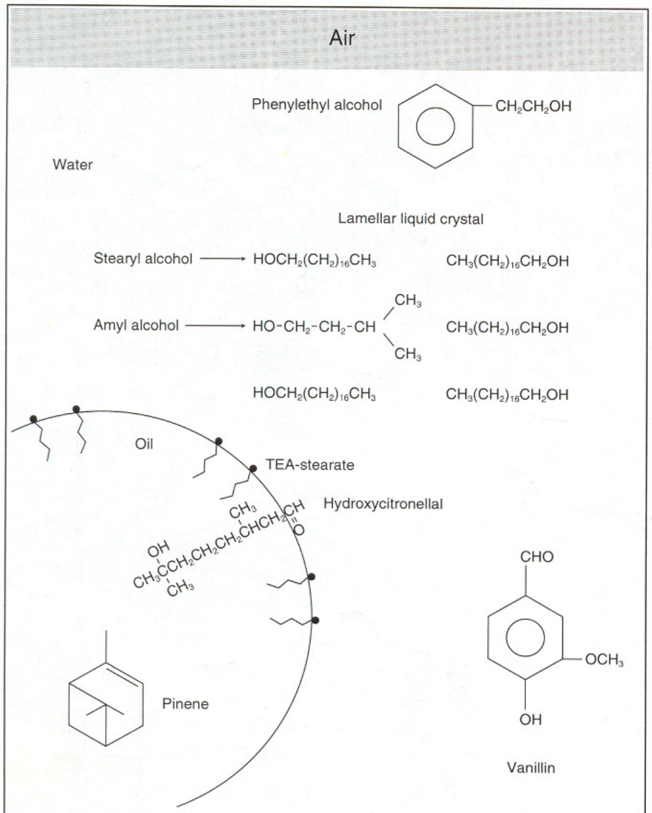


Figure 2. Schematic drawing of emulsion with fragrance elements that may affect emulsion stability

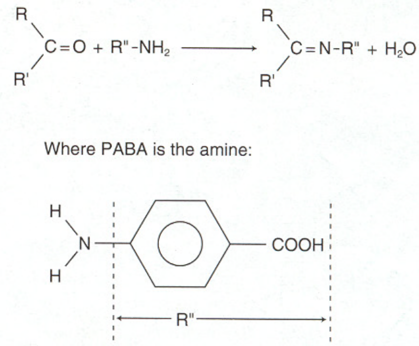


Figure 3. PABA's reaction with ketones to produce a bright yellow product

ingredients in the emulsion and to analyze their effects much more specifically than in the past.

When a fragrance is mixed into an emulsion, an equilibrium is established between the individual components of the fragrance and the phases of the emulsion. In the schematic of a very over-simplified TEA-stearate emulsion (Figure 2), some fragrance materials have been shown in possible locations. Pinene, along with many other materials with solubility parameters under nine and negligible oxygen-containing groups, will be almost entirely in the internal phase. Hydroxycitronellal is shown on the micelle surface, where it can significantly effect emulsion stability, or at least lower the viscosity. Phenylethyl alcohol and vanillin, as well as other materials with solubility parameters above 11, will have some presence in the external phase. The amyl alcohol can potentially squeeze into a liquid-crystal structure, as can other materials with polar character. The partition of materials takes time, which explains the difference in character of a newly made, fragranced emulsion and the same product a few days later.

Adapting a Fragrance for Emulsion Use

The normal standard for a fragrance type is the hydroalcoholic. The fragrance thus constituted is never appropriate for an emulsion without modification. We have seen some reasons for this at the molecular level. Now, we can briefly examine the practical consequences. Levy[10] described the potential negative effects of a fragrance in an emulsion as *odor changes* and *esthetic changes*.

Odor changes include loss of character and development of sour notes. The chief esthetic problems involve color changes and viscosity loss.

The reaction of a perfumer to these problems was described by Dellas and Lenoci.[14] In the translation of a target fragrance to a functional product, price is an initial concern. The desired cost for a lotion is significantly lower than that allowed for a hydroalcoholic. Stability is the next factor; aspects of that concern have already been raised. Unstable materials must be removed or significantly reduced, and replaced by stable products of similar odor character. Some notes suppressed by the base must be "pushed," either by increasing their proportion or adding other ingredients of similar nature. Subtle nuances are often lost in the base, and they can be eliminated. If the base has special odor problems, they must be masked using a fragrance designed to work with the specific odor(s).

Fragrance materials can also react with specific ingredients in the emulsion to deactivate the product or form colored compounds. An example is the formation of a Schiff base by the reaction of an aldehyde or ketone with a primary amine. PABA can react with ketones to produce a bright yellow product (see Figure 3).

An additional consideration is the effect of the fragrance on the skin. As the emulsion is rubbed on and begins to evaporate, phase changes commence. This process was described by Langlois and Friberg.[15] As the water evaporates, the surfactant concentration increases and the perfume can re-emulsify. The result is a suppression of the fragrance. Use of a steric emulsifier such as acrylates $C_{10\text{-}30}$ alkyl acrylates crosspolymer, which breaks on contact with salt and cannot re-emulsify, can eliminate this effect. The application of these materials has been thoroughly considered by Lochhead.[16]

The lipids present on the skin are included in the phase changes as the emulsion evaporates. Individuals vary in the exact composition of skin lipids. They also have slightly unique skin odors and reactions to fragrance materials. Thus, the same product will vary in odor character on different subjects. The choice of a proper fragrance for an emulsion must, in the end, be a subjective sensory decision.

Other Considerations

Fragrance can also react with or migrate through packaging. Lotions are usually sold in plastic bottles, and it is always essential that stability be tested in the final container. Frequently, an empty plastic container has an unpleasant residual odor. This can adversely affect the esthetic appeal of the product. Reaction of product with plastic can also result in the softening or physical collapse of the container.

Besides the references already cited, the interested reader is directed to the work of Jean Carles[17] for a classic account of the creation process. A brief overview of fragrance chemistry with additional references can be found in Herman.[18]

Summary

A fragrance designed for hydroalcoholic use must be modified for emulsions. This article has briefly considered the complex chemistry of aroma chemicals, their distribution in the emulsion based on solubility, structure and surface activity; the odor and esthetic effects on the product; and the practical steps perfumers take to create a satisfactory, translated fragrance.

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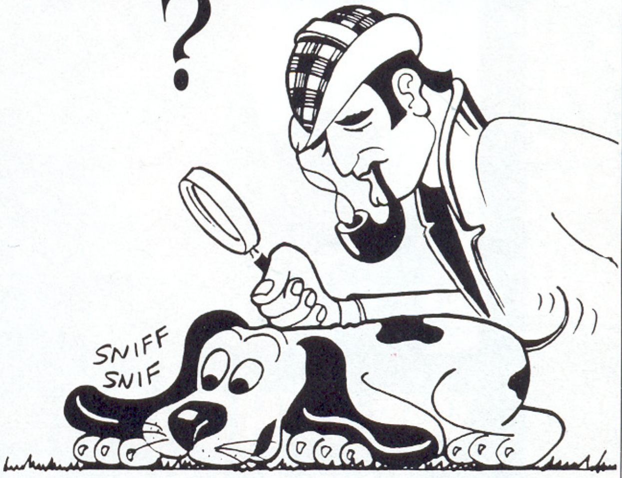

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