What Every Formulator Needs to Know about Fragrance

The types of problems encountered can be fragrance/product compatibility, color changes, solubility, and reactions between fragrance and product.

I. Questions from the Fragrance Supplier
   a. Basic question asked by the fragrance supplier: “What product are you making?”
   b. Descriptive answers such as: “clear shower gel” or “conditioning shampoo”
   c. Address issues of stability, compatibility, performance

II. Stability
   a. Nothing is completely stable
   b. Some more than others
   c. Addition of a fragrance to an alcohol base – main consideration
      (e.g. formation of an acetal in the following example)

   \[
   \begin{array}{c}
   \text{Hydroxy citronellal} \\
   \text{HO} \\
   \text{C } \text{O} \\
   \text{HO} \\
   \end{array} \xrightarrow{2\text{C}_2\text{H}_5\text{OH}} \\
   \begin{array}{c}
   \text{Hydroxy Citronellal Diethyl Acetal} \\
   \text{HO} \\
   \text{O} \\
   \text{O} \\
   \end{array}
   \]

   d. A solution of hydroxy citronellal and SDA alcohol 39C was left in light and another sample kept in the dark. Analysis by GC/MS showed that both samples formed the diethyl acetal within one day and continued to undergo acetal formation (complete conversion = one week)
   e. More unknowns than knowns
   f. Must have an initial understanding → testing and observation

III. Compatibility and Solubility
   a. Fragrance often selected by the type of odor desired without regard to system or stability requirements
   b. Example: selecting a fresh lemon or citrus for clear shower gel
      i. Citrus products tend to oxidize and are naturally hydrophobic – both the problem of stability and solubility
      ii. How to solubilize to clarity?
   c. Properties of fragrance materials or properties of the base
   d. In a wax or lipstick or petrolatum, the base is lipophilic; the fragrance has to be lipophilic and should contain no glycols or polar ingredients
e. In a shower gel, the base is hydrophilic; the fragrance should be skewed to be as polar as possible and minimize the use of non-polar types like citrus or wood-based fragrances that are hydrophobic.

f. Most cosmetics, shampoos and lotions can tolerate a wide range of solubility characteristics.

g. Exceptions occur when the base is extreme (mineral oil – very Nonpolar – use minimum amount of fragrance).

h. A “clear” product in a “clear” package is difficult to accommodate.

i. First step in achieving compatibility between the product and fragrance is to examine the product.

j. Does the product contain water? Most likely answer is “yes.”

   i. Terpenes, sesquiterpenes, aromatic, cyclic, polycyclic compounds insoluble.

k. Best to regard odor properties separately and secondarily.

IV. Color Changes


b. Often comes from fragrant compounds, but not always (of course).

c. Most common issues:

   i. dye instability.

   ii. fragrance/fragrance interaction.

   iii. fragrance/dye interaction.

   iv. fragrance/base interaction.

   v. light-induced change.

   vi. base/package.

   vii. fragrance/package.

d. First consider photolytic issues.

   i. Include UV absorber in the product as well as in the packaging.

e. Consumer market – if the color isn’t good, the product must not be good.

f. Other factors that influence color.

   i. Oxidation.

   ii. Condensation reactions.

      1. can be accelerated by heavy metal impurities (Trace Fe, for example).

g. Drums used to ship fragrances are double coated with an inert resin, but the threads of the bung openings are not.

h. Generally use all the fragrance at one time from a single batch.

   i. Not always practical.

   ii. Another solution is to incorporate a sequestering agent in the fragrance and the product (metallic ion scavenger).

V. Problems with products.

a. Clear shower gel: solubility main concern (e.g. citrus fragrance described earlier).

i. If the conditioner is basic → hydrolysis of esters
ii. Additional problems include discoloration and phase separation
iii. Effects on viscosity is another major consideration
iv. Fragrance should be resistant to oxidation (minimum use of citrus)
v. Lactones are also unstable under basic conditions (open to the hydroxy acid – can create a negative odor profile)

\[
\text{Benzyl acetate} \xrightarrow{\text{OH}^-} \text{Benzyl alcohol}
\]

\[
\text{Epsilon hexalactone} \xrightarrow{\text{OH}^-} \text{6-Hydroxyhexanoic acid}
\]

c. Shampoos and liquid detergents: similar in terms of stability requirements
   i. pH is neutral or slightly alkaline
      1. watch out for esters
   ii. volatility (through packaging)
   iii. fragrance concentration range 0.2 – 0.8%
   iv. loss of top notes or volatiles at the lower concentrations will be more dramatic than at the higher concentrations
   v. fragrance should be constructed to contain more of the mid-range notes
d. Conditioners: high pH preparations
   i. A lot of citrus scented products – how is this accomplished?
   ii. “surrogate” citrus notes that have fragrant properties similar to citrus scent but do not contain the unsaturated terpene content (branched alcohols that possess some citrus character)
e. Lotions and creams: fewer problems
   i. Compatibility not as big of an issue
   ii. Color stability a bigger problem
1. packaging, use of antioxidants and UV absorbers in product and packaging
2. viscosity (fragrance ingredients can alter viscosity drastically)
   
f. Antiperspirants: use aluminum chlorohydrate (produces acidic solution in the presence of trace metals that serve to catalyze a variety of reactions)
   i. Requires the elimination of unsaturated aldehydes and terpenes
   ii. Negative effect on fragrance not to mention production of reactive chemicals that can react with base components

\[
\begin{align*}
\text{R} &\text{Ni or Fe} \\
\rightarrow & \text{R} \text{OH} + \text{R} \text{CO} + \text{R} \text{CO}
\end{align*}
\]

   
g. Talcs and powders: large surface area – very different media
   i. Evaporation an issue
   ii. Volatile oil loss and rapid oxidation
   iii. Citrus-based fragrances (prone to evaporation and oxidation) must be eliminated at the outset
   iv. Terpeneless materials should be standard practice
   v. Saturated compounds only
   vi. Floral blends fare better in general

h. Aerosol sprays: the base can vary (table 2)
   i. Type and amount of materials which may crystallize in the spray orifice
   ii. Do not use too much crystalline material in this product

<table>
<thead>
<tr>
<th>Base delivery material</th>
<th>Fragrance properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>Non-polar ingredients</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Usually all soluble, but limited amount of terpenes</td>
</tr>
<tr>
<td>Water</td>
<td>Polar ingredients and no terpenes or sesquiterpene hydrocarbons</td>
</tr>
</tbody>
</table>

i. Problems with scale-up
   i. Prototype products that are developed in glassware or ceramic in the lab can be markedly different from batches prepared in a manufacturing plant environment
   ii. Example problem: formula calling for water (90%), surfactant (5%), and fragrance (5%)
1. example 1 (added in the order): water, surfactant, fragrance
   a. fragrance will not be evenly dispersed; the batch will foam considerably making mixing a problem
2. example 2 (three-step process): step 1-water is added to the mixing tank, step 2-in a separate vessel, the surfactant and the fragrance are thoroughly mixed, step 3-surfactant/fragrance mix is added to the water
   a. allows proper micelle formation and minimizes foaming during mixing

j. Unpredictability
   i. Variables: time, temperature, light energy exposure, shipping, storage, use conditions

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What is an Odor Profile?

In describing the nature of fragrance, many people use the terms top note, middle note and base note (often referred to as dry down). This description gives one an overview of the relative volatility of materials used in fragrance. However, it is not a very good representation of reality.

A better way to look at fragrance construction is from a compositional point of view, as with a piece of music. All music has sections that have general tonal frequencies. The melody is usually—but not always—positioned on top; the chords are generally the body; and the foundation is supported by bass and drums. The analogies would be top note to melody, middle notes to chords or basic structure, and base note to bass and drums. One can quickly see that a top, middle and base note analogy does not make complete sense because we do not listen to music in sections. Rather, we hear all the musical sections (melody, chords and bass section) blended together simultaneously.

This is also true of fragrance. It is really the balance and blend of all the sections that make the fragrance what it is. When one ingredient is adjusted, its section looms into or out of balance with the remaining sections. This analogy gives a more accurate portrayal than the top, middle and base note explanation.