C&T

What Every Formulator Needs to Know about Fragrance

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Key words

Fragrance, stability, color, compatibility, solubility

Abstract

This overview of the types of problems encountered when fragrancing personal-care products discusses issues of stability, solubility, color change, and compatibility of fragrance and product ingredients.

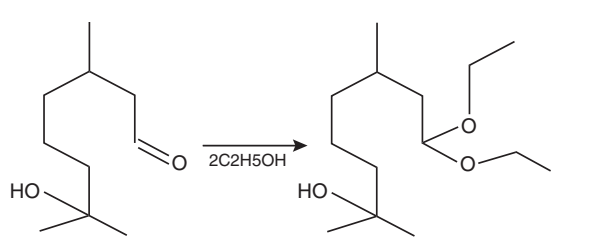
Fragrancing personal-care products can present a variety of problems, such as fragrance/product compatibility, color changes, solubility, and reactions between fragrance and product. This article will provide an overview and checklist of the types of problems that one can expect when fragrancing a variety of products. The good news is that these problems can be minimized when product construction and requirements are understood in advance, so fragrance construction can be tailored to accommodate the product system.

Questions from the Fragrance Supplier

What questions should any product formulator ask of the fragrance supplier? This question is a bit like the tail wagging the dog. Since the perfumer has an intimate knowledge of the chemical and physical properties of the materials being used in fragrance, it would be more productive if the fragrance supplier raises certain questions with the formulator.

The basic question asked by the fragrance supplier is, "What product are you making?" This deceptively simple question is the key to understanding the type of fragrance that will be required. It suggests numerous hidden questions (see sidebar).

In order to convey effective information, the question must be answered very specifically. For example, a response such as "personal-care product" will not provide any information that would be sufficiently revealing or helpful. A more specific answer such as "Clear Shower Gel" or "Conditioning Shampoo" will provide a different framework for fragrance selection in both odor and stability performance as well as base compatibility. Additionally, each answer starts a series of questions down a different path.



Hydroxy Citronellal **Hydroxy Citronellal Diethyl Acetal**

Figure 1. Aldehyde transformation to an acetal

Stability

All chemists know that nothing is completely stable. There are very few things in the universe that are not changing all the time. Seemingly innocuous environments or simple formulations like fragrance and alcohol start making changes as soon as they are mixed together.

Aldehydes begin to be transformed to acetals within minutes and their presence can be analytically identified within hours. A classic example is hydroxy citronellal (Figure 1).

We have made a solution of hydroxy citronellal and SDA alcohol 39C (a commonly used perfume alcohol) in our laboratory and left it in the light and in the dark. Analysis by gas chromatography showed that both samples formed diethyl acetal within one day and continued at a steady pace throughout the week.

The above example clearly indicates that almost any aldehyde when mixed with ethanol will undergo rapid changes. This should be an indication that other reactions, known or unknown, will be taking place. The experienced chemist realizes that there are many more unknowns than knowns. One has to take some time and anticipate, as best as one can, the obvious problems and be alert to the possibility that other reactions will be taking place. There is no substitute for testing and

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keen observation. This is the only way to provide assurance that a reasonably stable system has been accomplished.

Compatibility and Solubility

Each product will have its own set of problems that need to be addressed and overcome. Often, a fragrance is selected or requested by the type of odor desired without regard to the system or stability requirements. A great example would be selecting a fresh lemon or citrus for clear shower gel. Since all citrus products tend to oxidize and are naturally hydrophobic, there is definitely going to be a problem with stability as well as solubility. This will leave the cosmetic chemist with the problem of how to solubilize to clarity.

This is something that should be thought of in terms of properties of fragrance materials or overall properties of the base. In a wax or lipstick or petrolatum, the base is lipophilic; therefore, the fragrance has to be completely lipophilic and should contain no glycols or polar ingredients. In a shower gel which has a preponderance of water, the base is hydrophilic and 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 extremely hydrophobic.

The good news is that most cosmetics, shampoos and lotions can tolerate a wide range of solubility characteristics in this area. Solubility usually only becomes an issue when the base is extreme. An example is mineral oil, which is very non-polar. Consequently, it is difficult to achieve clarity in mineral oil unless it is tested and unless one uses only the minimum amount of almost any fragrance.

The goal for the fragrance creator should be to prevent this type of problem from the outset. This will also minimize the occurrence of phase separation or haziness over a range of temperatures that a product has to endure during manufacture, shipping, storage and shelf life.

In many cases a "clear" product packaged in a "clear" bottle is the recipe for difficulty. A clear package allows the consumer to see a product completely with all the potential pitfalls of change in clarity, color or phase separation. These changes may be initiated or caused by temperature and/or light, both natural sunlight and UV from artificial lighting.

The first step in achieving compatibility between the product and the fragrance ingredients is to examine the product. Usually the product is formulated with a significant amount of water. In general, most fragrance components are lipophilic: they do not like water at all, and in the best cases are only marginally soluble. They are usually compatible with oil depending on the fragrance type. Within that general guideline there are degrees of solubility. Terpenes, sesquiterpenes and other aromatic, cyclic or polycyclic materials are extremely insoluble in any type of water system.

It can be a significant challenge to make a clear product that can be easily manufactured, tested through several freeze/thaw cycles and survive extreme storage conditions without phase separation. These challenges must be overcome. An experienced, knowledgeable perfumer with reasonable chemistry experience is needed to accomplish this daunting task.

In the end, the task is reduced to understanding the physical properties of the fragrance materials as well as the physical properties of the preponderance of the materials used in the

What Product Are You Making?

These are the questions that a fragrance supplier should ask and a formulator should answer early in the process of fragrancing a product. They will help the fragrance supplier obtain an answer to the basic question, "What product are you making?"

What is the end product?

What are the base ingredients likely to be?

- Hydrophilic? Lipophilic?
- Acidic? Basic? pH?

What will the product look like?

- Color?
- Single phase?
- Clear? Pearlized? Opaque?

Who is this product going to be marketed to?

- How will they use it?
- What is the targeted age group?
- What geographic area?

How will this product be processed?

- Time?
- Temperature?

How will this product be packaged?

- Clear Bottles? Glass? Plastic (What type)?
- Opaque?

What are the pricing guidelines?

What is the intended percentage of use? (Maximum/Minimum)

Are there stability requirements or protocols?

How long will the product remain on the retail shelf and in the hands of the consumer?

product. The objective is the selection of materials with the correct physical-chemical properties and elimination of the materials with the undesirable properties. The odor properties must be considered separately and secondarily.

Color Changes

The nemesis of all product marketers is color change. There are so many areas of instability here that many doctoral theses could be written and in the end the problems would not go away. Color change can come from fragrance and often does, but fragrance is *not* the only source. Color change can be caused by dye instability, fragrance/fragrance interaction, fragrance/dye interaction, fragrance/base interaction, and light-induced change, as well as base/package and fragrance/package interaction. I am keenly aware that I have not included all possible causes of color change. These are the most common causes.

When the fragrance supplier and the formulator first meet to discuss the fragrancing project, it is a good time to consider any items that are prone to color change due to UV and/or sunlight radiation. UV light, often from artifcial flourescent lighting in department stores, is a major cause of color change. This change can often be mitigated by a UV absorber in the product as well as in the plastic or glass packaging.

Color is one of those issues that can be quite frustrating. Often the odor change is insignificant, but a visual change draws a strong customer response. If a product does not look good, it cannot be good.

Other factors that contribute to color change are oxidation, subsequent condensation reactions and interactions between fragrance ingredients. These can be further catalyzed by trace elements of iron or other materials, such as negatively or positively charged particles that come from water, mixing vessels or the components themselves.

The drums that fragrances are normally shipped in are drums that are double coated with an inert resin, but the threads of the bung openings are not. An example that occurs frequently is that the fragrance is ordered, shipped to the customer, who uses a portion of the drum. The fragrance material "touches" the unlined threaded portion of the steel drum. A portion of the material drips back down into the liquid carrying parts per million of iron from the steel drum and catalyzes color changes over the next few weeks. The color of the fragrance material changes and also may cause a color drift in the finished product.

This cantankerous problem can be somewhat mollified by using all the fragrance at one time from a single batch. However, we know that this is not always practical. Another solution may be to incorporate a sequestering agent in both the fragrance and the product. This agent will scavenge any free metallic ion contamination and help maintain color stability.

It is extremely difficult to accurately predict color changes because there are so many variables and sources of contamination in the manufacture of any product.

Problems With Products

The wide range of personal-care products means that one can expect a variety of problems in fragrancing them. We've already mentioned stability, color changes, and compatibility between fragrance and product. Other concerns are solubility of the fragrance, and reactions between the fragrance and the product. Here we consider some of the typical problems that may arise in fragrancing particular product types (Table 1).

Clear shower gel: With a clear shower gel, compatibility with a specific regard to solubility becomes the initial and primary concern. If a citrus fragrance is requested, the formulator can expect problems with both stability and solubility, as described earlier.

Conditioning shampoo: In a conditioning shampoo, the pH is often the determining or limiting factor. If the conditioner is very basic, it can cause an equilibrium shift and hydrolyzation of esters (Figure 2). Additional problems may include discoloration and phase

Table 1. Typical fragrance types and the problems encountered in using them to fragrance selected personal-care products

Product	Fragrance	Color	Solubility	Stability	Comment
Clear Shower Gel	Orange/Citrus	X	X	X	Oxidizes and is hydrophobic; often adds color
Shampoo	Orange/Citrus	X		X	Oxidizes or affects viscosity
Conditioner	Citrus or Fruits	X		X	Adds color; oxidizes or hydrolysis of esters
Lotions & Creams	Balsams	X		X	Color changes; some materials affect viscosity
Antiperspirant	Citrus or Fruits	X		X	Oxidizes; hydrolysis of esters
Talc	Citrus or Fruits	X		X	Oxidizes or volatilizes away prematurely
Aerosol	Vanilla/Powder	X	X	X	Crystal may form in actuator and clog orifice

separation. Effects on viscosity may also be a consideration.

The fragrance selected should also be one that is resistant to large changes due to oxidation. This means a minimum use of citrus products. These products are high in unsaturated terpenes, which are prone to oxidation under basic conditions.

Another class of chemicals that are unstable under basic conditions are lactones. They tend to open up to the hydroxy acid from which they were originally made (Figure 3). This might be a small chemical change, but it could create a very different and negative odor profile (see sidebar on odor profile).

Shampoos and liquid detergents: Shampoos and liquid detergents can be viewed as similar products in terms of stability requirements. A pH that is neutral or slightly alkaline is the norm for these product types. Still, one has to be aware that oxidation and a slight equilibrium shift due to alkalinity can compromise the stability of many esters that are normally used in fragrances.

Additional performance loss might be attributed to volatilization through the packaging. Most shampoos and liquid detergents are fragranced at a concentration range 0.2-0.8%. However, a loss of top notes or volatiles at the lower concentrations will be more dramatic than at the higher concentrations. The fragrance should be constructed accordingly, using more of the mid-range notes.

Conditioners: Conditioners and high pH preparations that may contain a quaternary agent or ammonium hydroxide may exhibit instability when unsaturated terpenes are used for fragrancing. These items are common in all citrus products.

Since citrus is such a popular trend and often used in a wide variety of products, you might wonder how is this accomplished. There is a wide variety of citrus-like products at the disposal of the perfumer. These "surrogate" citrus notes possess a citrus-like character without the unsaturated terpene content that can be so problematic in functional products.

Alternate choices for citrus fragrances would be deterpinated or terpeneless products that are low in unsaturated molecules and are less prone to oxidation. Examples include straight chain or branched alcohols that possess a citrus character.

Lotions and creams: Lotions and creams have fewer problems than most of the products already mentioned. There

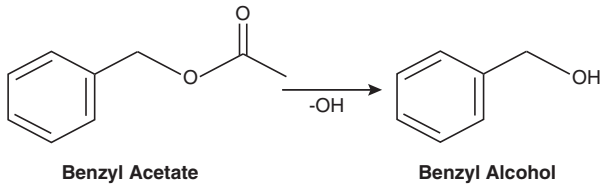

Figure 2. Equilibrium shift and hydrolization of an ester

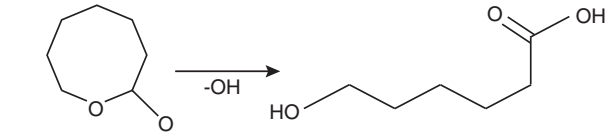

Figure 3. Hydrolization of a lactone

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.

is little problem with compatibility. However, there can be problems of color stability.

Color stability is the bane of every marketer who wants the consumer to actually see the product. Color stability problems can be mitigated by packaging and by the use of antioxidants and UV absorbers in both the product and the packaging.

Problems of viscosity are generally easily solved, but one should always be aware that many fragrance ingredients can alter the viscosity drastically and occasionally some alternate fragrance types or ingredients must be substituted.

Antiperspirants: Antiperspirants use aluminum chlorohydrate, which produces a very acidic solution in the presence of trace metals that serve to catalyze a variety of reactions. This type of medium requires the elimination of unsaturated aldehydes and terpenes.

As can be seen in Figure 4, unsaturated molecules will be oxidized and or catalyzed to the aldehydes, and subsequently to acids. These reaction products can have quite a negative effect on the fragrance. They can also create additional reactive chemicals that, in turn, can react with some of the base components.

Talcs and powders: Any talc or powder formulation presents a different medium for chemical reactions. The vast surface area of a powder provides an ideal environment for evaporation, volatile oil loss and rapid oxidation. These problems must be addressed in the earliest phase of fragrance selection.

Citrus-based fragrances, which are prone to evaporation as well as oxidation, must practically be eliminated at the outset. The use of deterpinated or terpeneless materials should be a standard practice, as should the use of saturated molecules to replace those that are unsaturated.

In general, floral or powder oriental blends fare better, but an effort to control color stability must be made.

Aerosol sprays: Aerosol sprays can pose problems of compatibility with the medium used for delivery. Will the product be hydrocarbon, alcohol or water-based (see Table 2)?

In addition to compatibility some attention must be paid to the type and amount of materials which may crystallize in the spray orifice. They may come from naturally crystalline materials from the fragrance. As volatile materials evaporate, the concentration of the crystalline material increases and crystals, formed on the surface of the valve, can eventually block the spray orifice and prevent proper spray. This can take place slowly and accumulate over time. Experienced formulators know not to use too much crystalline material in this type of product.

Problems With Scale Up

Scale up presents another area for surprises. Prototype products that are developed in glassware or ceramic in the laboratory can be markedly different from batches prepared in a manufacturing plant environment. Stainless steel is not an inert mixing vessel material. Often, times and temperatures that are easily controlled in the laboratory are impossible to control in a manufacturing plant.

Another variable is the personnel and their training, education and ability to recognize where a seemingly insignificant change in procedure may affect subsequent stability. An example might be the simple change in the order of addition of ingredients in a formula calling for 90% water, 5% surfactant and 5% fragrance.

In Example 1, the water, surfactant and fragrance are added to a tank and mixed. If these ingredients are added in this order, two things happen: the fragrance will not be evenly dispersed in the water; and the batch will foam considerably, making mixing a problem.

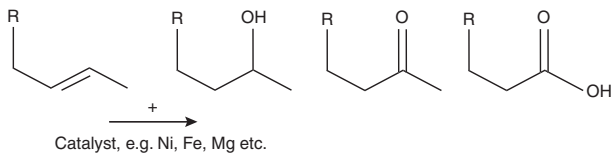

Figure 4. Possible oxidation products in the presence of trace metals

Table 2. Compatibility considerations for aerosol sprays

Base delivery material	Fragrance properties
Hydrocarbon	Non-polar ingredients
Alcohol	Usually all soluble, but limited amount of terpenes
Water	Polar ingredients and no terpenes or sesquiterpene hydrocarbons

In Example 2, a three-step procedure is used. In Step 1, water is added to the tank. In Step 2, in a separate vessel, the surfactant and the fragrance are thoroughly mixed. In Step 3, the surfactant/fragrance mix is added to the water in the tank. Example 2 solves many problems by having the fragrance completely enveloped by the surfactant, allowing proper micelle formation. This also minimizes foaming during mixing.

Keep in mind that order of addition and procedures can be very important for ease of manufacture. This type of thinking can alleviate many problems.

Unpredictability

Despite everyone's best efforts, there are always elements of unpredictability. We are trying to predict what will happen when we mix several hundred ingredients with the variables of time, temperature, light energy exposure, as well as shipping, storage and use conditions. These reactions occur at extremely low levels often catalyzed by trace elements. It is not uncommon to go through testing and refinement and then nearly at the eleventh hour make a small, seemingly insignificant base change. It can be as simple as a supplier change with no apparent difference in quality.

References

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