Chapter 13

Applications II: Fragrance

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13.1 Introduction

A fragrance is not a single material of clearly defined properties, but rather a mixture of individual chemicals, each behaving according to its own unique attributes. Characterizing these chemicals separately, and then combining their effects, allows the behavior of the complete fragrance composition in diverse media to be understood. Important properties of fragrance chemicals include volatility, polarity, surface activity and stability. Each fragrance component interacts with the chemical and structural nature of the environment to determine the aesthetic and the physical characters of the final system. The combined talents of the perfumer and the technical staff, working closely together, are needed to create a successful commercial product.

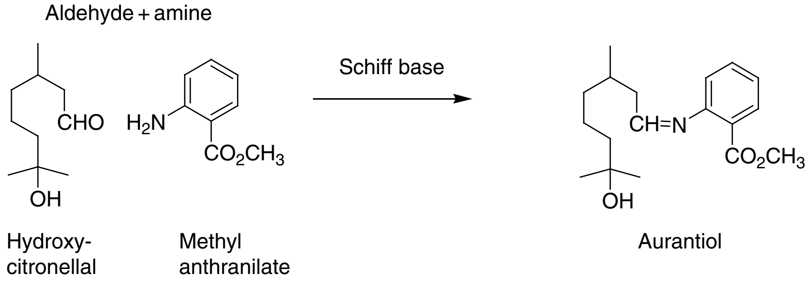
13.2 The basic structure of fragrances

Modern perfumers use an extensive palette of natural and synthetic chemicals. Until the end of the nineteenth century, perfumers worked with a relatively small number of materials, which were naturally derived, and they created a correspondingly small range of fragrance types, primarily in the citrus and floral families. Within this limited domain, perfumers could use an inefficient trial-and-error approach to create fragrances. The explosive growth of organic chemistry at the end of that century made innumerable new materials available to the perfumer, necessitating a rational method of fragrance creation. One of the pioneers of this period, Jean Carles, later wrote an invaluable series of papers [1], entitled “A Method of Creation in Perfumery”, which describes a widely accepted approach to the process. Carles considered volatility to be a key quality for judging how to best use an aromatic ingredient. Each material is placed on a blotter and evaluated for intensity and character over a period of hours. Very volatile materials, which disappear first, comprise the “top notes” of a finished perfume, those of intermediate volatility and tenacity are the “modifiers” or “middle notes”, and those with the lowest volatility, tenacious products constitute the “base notes”.

The characteristic odor of a single material is called a note. Mixtures of two or more materials, having a unified olfactory theme, are called accords. If individual chemicals are like words, accords are short phrases, the top, middle and bottom notes are sentences, and the finished fragrance is a paragraph. The ratio of 25% top notes, 20% modifiers and 55% base notes is typical of a well-balanced blend.

13.3 The simplest case: hydroalcoholics

The typical use of the fragrance construction described by Carles is hydroalcoholic applications such as perfume, cologne or eau de toilette. These systems, based on aqueous ethanol, are the least technically hostile of the environments where fragrance is used. Although the hydroalcoholics are chemically the simplest exemplars of fragrance intended for consumer use, there are still technical considerations that must be attended to. Even single perfume ingredients can change in storage, for example, the aerial oxidation of benzaldehyde to benzoic acid. Aldehydes routinely polymerize at room temperature, and citrus products easily oxidize. When the individual materials are combined into perfume oil, further changes can occur. Very few chemical reactions occur between perfume materials to a significant degree, but Schiff bases, which produce a new molecule by combining an aldehyde or ketone with a primary amine (Scheme 13.1), are an important exception.



Scheme 13.1

Additives are commonly used to enhance fragrance stability. For hydroalcoholics as well as more challenging systems, UV absorbers such as benzophenone-2 can improve stability toward light. Chelating agents, such as EDTA and its salts, are useful in removing iron and other contaminants before discoloring reactions occur with sensitive fragrance chemicals. Antioxidants such as BHT (butylated hydroxytoluene), citric, tartaric, or oxalic acids help prevent rancidity. A combination of these ingredients often works synergistically. These materials can be added to the perfume if they are oil-soluble. Water-soluble materials must be added to the finished solution. It is best to incorporate the stabilizers as early in the process as possible, since unwanted reactions can rarely be reversed after the damage is done.

To make a perfume, the fragrance oil is added into a solution of alcohol and water. The commercial alcohol is not a single ingredient, but contains ethanol, water and a denaturant. Commercial alcohol is typically 95–96% ethanol and 4–5% water. This mixture is termed an azeotrope, because it boils at a lower temperature than either component separately. Thus, it is impossible to distill it further to increase the proportion of alcohol. To obtain anhydrous alcohol, it is necessary to add a third component to alter the evaporation properties of the mixture. To discourage drinking the ethanol, which is the essential ingredient of alcoholic beverages, it is poisoned with a denaturant. The denaturant is selected from materials that cannot readily be distilled out, which would return the alcohol to its original state. Denaturing exempts the alcohol from the taxes that are normally imposed on the potable version.

The best solubility is obtained if the perfume is added first to the alcohol, mixed, and the water is then added. When the perfume oil is placed in the hydroalcoholic solution, an aging process begins. The container is important; stainless-steel and glass-lined vats are best. Iron should never be in contact with the solution. All hoses, gaskets and stirrers should be carefully chosen to ensure inert response to the product. Aging was much more common in the past than now, and more important when a large amount of natural products are present in the oil. Contemporary mass-market fragrances are frequently not aged at all, with mixing, chilling, filtering and filling done in a continuous process.

A typical formula for a cologne and perfume would be:

	Cologne	Perfume
Alcohol SD39C or 40B (190 proof)	79.60	79.60
Fragrance	8.00	20.00
Distilled water	12.00	–
Benzophenone-2	0.40	0.40
	100.00	100.00

Smaller batches are chilled and run through filter presses. Clarity may be improved by the addition of a filter aid such as diatomaceous earth. Many modern fragrances, containing a high proportion of synthetic aroma chemicals, have excellent solubility in alcohol. Fragrances with a slight haze in solution can frequently benefit from the addition of a solubilizer such as polysorbate 20. The use of solubilizers should be minimal, since they can have an adverse effect on skin feel.

Natural oils are complex mixtures, and often contain waxes that are insoluble in alcohol. If the fragrance contains crystals and resins, some precipitation can occur. The level of crystals in a fragrance should never exceed 30%, although the exact amount that can be tolerated depends on the other materials in the formula and the percentage in the final product. The amount of water that can be incorporated into the system is affected by the nature of the perfume composition and the percentage of oil. Water is desirable because it reduces the sharp odor of the alcohol and lowers the price of the finished product.

Aftershaves are the lowest, least prestigious of hydroalcoholic solutions. The alcohol content is limited to 60–65% to avoid stinging, since minor cuts and abrasions often occur during shaving. Water-soluble emollient oils such as glycerin and propylene glycol are frequently added to modify the feel. Healing agents such as allantoin are also common. The addition of menthol or its ester derivatives is sometimes done for cooling effect.

The fragrance materials can also react with the alcohol to form new compounds. Reaction between aldehydes and alcohol to form a hemiacetal commonly occurs as solutions age. Schiff bases, if they were not intentionally created prior to the fragrance compounding, can slowly form in solution, if the necessary materials are available, although only to a partial degree. The value of the aging process, known by tradition to be necessary to achieve the final effect of the hydroalcoholic product, has a basis of sound science.

Fragrance selection at the point of sale is heavily dependent on its top notes. During the development of a fragrance, the perfumer evaluates the creation as it evaporates off a paper blotter. As a fragrance evaporates it necessarily changes character, but the evolving fragrance must retain a consistency through these changes. A successful fragrance must also exhibit a pleasing effect on the skin. Users of personal fragrances sometimes spray their clothes, but the most important test of a fragrance is its character as it evaporates off the skin over a period of several hours. A challenge for fragrance marketing is that every individual has a different skin chemistry, which changes the quality of the fragrance on each person.

Mookherjee *et al.* [2] (1998) analysed the “aura” above the skin, the molecules in the air above the fragrance. It was found that the standard model of top note, middle note and bottom note did not apply to the aura. Indeed, the aura was not dependent on molecular weight, boiling point, vapor pressure or odor value. Instead, a property of the compound – coined “diffusivity” – was the key, attributed to the tendency of the molecules to pass into the air. Ultimately, evaluations are best obtained by smelling the fragrance on a variety of individuals over a period of several hours.

13.4 Personal care applications: emulsions

It is customary for a successful fragrance to spawn line extensions, traditionally cosmetics and personal care. With increasing frequency, fine fragrances have inspired environmental, household, and even institutional fragrances. Thus, a designer fragrance can evolve into skin- and hair-care products, air fresheners and candles, dish and laundry detergents, and ultimately in janitorial supplies. Obviously, the same fragrance does not find itself in these products, but rather modifications of the odor type.

The major changes involved in altering a fragrance for non-alcoholic vehicles are price, aesthetics, and stability. The challenge for the perfumer is to keep the character of the fragrance as close as possible to the original, while accommodating all the crucial economic and technical issues. Perfumers often learn how to meet these challenges through experience or trial-and-error, but the solutions arise more consistently if the underlying science is understood, and the technical staff is intimately involved in the process. The majority of personal-care products are either emulsions, such as creams and lotions, or surfactant systems, such as shampoos and bath gels. Examining the interaction of these two systems with fragrance reveals most of the essential issues that arise in fragrance applications. The breaking or discoloration of emulsions, viscosity changes in surfactants, and the effects of light or elevated temperatures are key indicators of product integrity.

The first obvious effect of mixing perfume oil in an emulsion is an aesthetic change in odor character. Fragrance oil smelled directly out of the bottle, or in a hydroalcoholic solution, does not accurately represent the olfactory character it will exhibit in an emulsion. Odor changes taking place over time include the loss of strength and character, and the development of sour or rancid notes, particularly at elevated temperatures. An acidic note may also be detected. Furthermore, the fragrance in the emulsion will not smell the same after application to the skin, when the emulsion breaks, and an individual's natural odor and skin lipids become factors.

The quality of the emulsion raw materials can decisively impact performance and stability. Poor grades of emollient oils are generally more prone to rancidity than purer grades. The odor problems associated with raw materials become increasingly obvious with aging at elevated temperatures. These problems can sometimes be overcome by the addition of antioxidants such as BHT. Another important variable in emulsion bases is pH; a fragrance may be fine in a lotion of pH 7 but become unstable at the low pH of an AHA (alpha hydroxy acid) treatment cream. Hydrolysis of esters is common in acidic environments. Fragrance can also trigger changes in viscosity, which become more pronounced as the fragrance level rises. In extreme cases, the fragrance can cause the emulsion to break. Some aroma chemicals trigger the discoloration of a white emulsion, usually toward a brown or yellow hue.

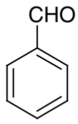
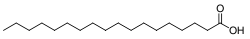
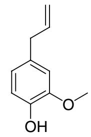
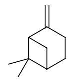
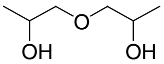
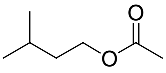
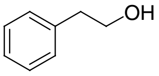
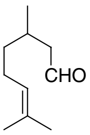
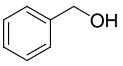
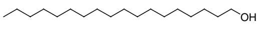
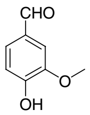
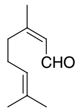
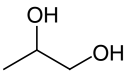
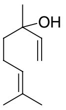
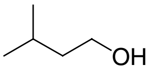
The polarity, solubility, surface activity and stability of fragrance materials can explain their behavior in diverse environments. For example, hydroxycitronellal contains two polar groups, hydroxyl and aldehydic. Its polarity enables it to compete for space on the surface of a micelle, leading to either a decrease in viscosity or a breaking of an emulsion. α-Terpineol has one hydroxyl group on a relatively rigid molecule, less disruptive than hydroxycitronellal, but still capable of destroying the balance of the emulsion. It is also possible for perfume ingredients to produce closer packing on the micelle surface, in which case, emulsion stability will improve.

A useful tool for understanding the location of fragrance materials in an emulsion is to examine the solubility parameter (SP) and surface activity of all the components in the system, combined with knowledge of all the associative structures present in the emulsion. The SP is the sum of all the cohesive forces in a molecule. The SP can be measured by laboratory experiments, calculated based on the molecular structure, or derived using commercially available computer programs. It is much more refined than the simple division into either water-soluble or oil-soluble. Materials used in cosmetics have an SP range of 5–25, with most fragrance materials in the range of 7–13. There can be regions at both extremes of polarity with very limited fragrance solubility. The SP of selected fragrance materials and some common emulsion ingredients are shown in Table 13.1.

The water/octanol partition coefficient (P) is another valuable measure of polarity. The logarithm of P exhibits more linear behavior than P itself, and computer programs are available that derive calculated values of log P, based on chemical structure. The calculated value of the logarithm of the partition coefficient is abbreviated Clog P.

In 1970, Anonis [3] reviewed some empirical quidelines for fragrancing emulsions and summarized the situation as follows: avoid indole, replace methyl anthranilate with methylnaphthylketone when aldehydes are present, replace hydroxycitronellal with cyclamen aldehyde, use aliphatic aldehydes at low levels or replace with acetals

Table 13.1 Solubility parameters and chemical structures of selected cosmetic and fragrance materials

White mineral oil	7.09	$CH_3(CH_2)_nCH_3$	Benzaldehyde	11.00	
Stearic acid	7.75		Eugenol	11.12	
ß-Pinene	8.03		Dipropylene glycol	11.78	
(Iso)amyl acetate	8.43		Phenylethyl alcohol	11.79	
Citronellal	8.83		Benzyl alcohol	12.31	
Stearyl alcohol	8.90		Vanillin	12.34	
Citral	9.34		Propylene glycol	14.00	
Linalool	9.62		Water	23.40	H_2O
(Iso)amyl alcohol	10.84				

(always, in the case of phenylacetaldehyde), replace coumarin with dihydrocoumarin, replace vanillin with ethyl vanillin, avoid quinolines, cresols, and animal fixatives.

Anonis and his predecessors established these principles primarily through trial-and-error. By the 1970s, theoretical knowledge of emulsion technology had reached a higher plateau, and it was possible to understand the scientific foundations of fragrancing emulsions. Friberg [4] had established the necessity of liquid crystal structures in the external phase to guarantee stable emulsions, and concepts like the SP and water–octanol partition coefficient made characterizing the interaction of fragrance and emulsion ingredients much more precise.

By 1980, Bonadeo [5] published a paper where K_d, a water/dioxane partition coefficient, was proposed to explain the effect of fragrance on emulsions. This concept relates to the classic hydrophilic/lipophilic balance (HLB) developed by Griffin to systematize the formulation of nonionic emulsions. The HLB of a surfactant is determined by the weight ratio of the oil-loving and water-loving parts of a molecule. The aromatic material is considered part of the oil phase, and an HLB_r is assigned, corresponding to the required HLB of Griffin. One additional concept was proposed, the critical limit of the water phase (CLWP), which quantifies the water that can be tolerated by the emulsifier system.

Bonadeo concluded that the olfactory properties of a fragrance in a water-in-oil (W/O) or oil-in-water (O/W) emulsion is the same if the system is properly balanced; otherwise, a mixed system is formed which upsets the fragrance distribution. He firmly places the fragrance in the oil phase, thus making fragrance a determinant in calculating the total HLB, and that the CLWP of each perfume component contributes to the limit of water which can be tolerated.

The most common type of emulsion is oil-in-water (O/W), formulated either with anionic or nonionic emulsifiers. The emulsion has an oil phase of small droplets covered by emulsifier molecules (micelles), an external phase, and liquid crystal structures in the water phase. Four common fragrance materials, pinene, hydroxycitronellal, phenylethyl alcohol and amyl alcohol, can illustrate how a fragrance can partition in an emulsion.

When the fragrance is mixed into the emulsion, the individual components of the fragrance partition in varying degrees into the different structures of the product [6]. Figure 13.1 shows the areas where the fragrance components can preferentially concentrate, although the partitioning is not absolute. Pinene, with a SP under nine and no oxygen groups, will migrate entirely into the internal oil phase. Hydroxycitronellal, with its surface activity, can inhabit the micelle surface, where it can displace some emulsifier, making it possible for it to lower the viscosity or break the emulsion. Phenylethyl alcohol and vanillin, with SPs over 11, can have a substantial presence in the external aqueous phase. The amyl alcohol, with a fatty chain and hydroxyl group, can partition into the liquid crystal structure. The partitioning takes time, accounting for the aging necessary before an accurate evaluation can be made of the effect of the base on the fragrance's olfactory performance.

Studies of the location of fragrance in emulsions by Friberg [7] and his colleagues confirm the results deduced from the partitioning of ingredients. Friberg's phase diagrams are valuable in illuminating basic principles, but only apply to simple, clearly defined systems. It seems unlikely that the phase diagram approach will fully elucidate the interactions of an emulsion, with 20 ingredients, interacting with a fragrance oil, of 200 aroma chemicals, in the near future, although computer programs are making progress in this area.

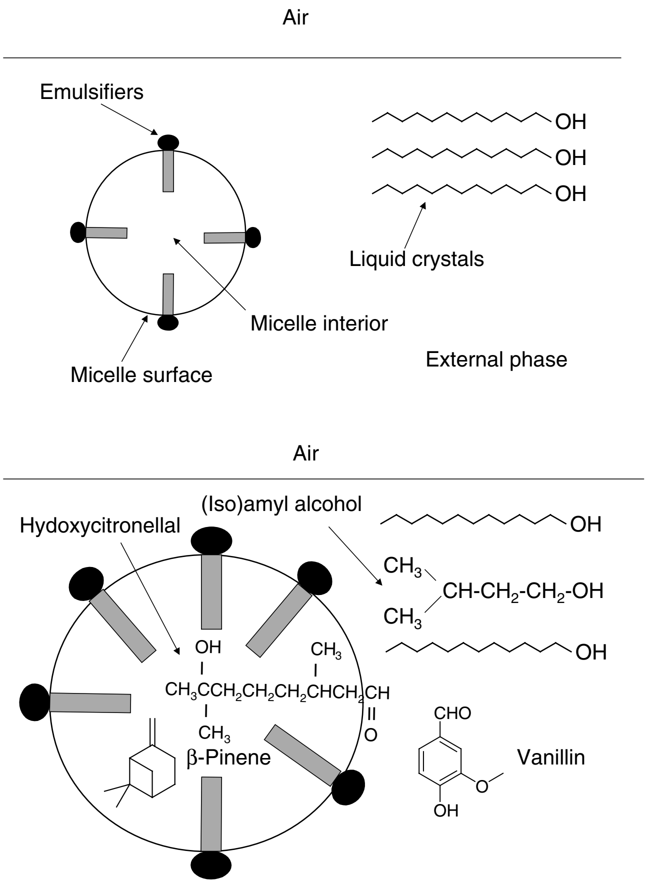


Figure 13.1 Partitioning of selected fragrance materials in an emulsion system.

Traditional fatty-acid soaps exhibit many of the fragrance problems found in emulsions. In addition to its fundamental similarity to emulsions, soap also has a high pH, which immediately restricts the fragrance palette. Vanillin is a notable cause of discoloration, as are eugenol and isoeugenol, heliotropin, indole, citral and Schiff bases. Any qualified perfumer must be aware of the materials that are appropriate for use in a conventional soap.

By understanding the relation of the chemistry of fragrance oil components to the structure of emulsions, it is possible to create a complete picture of the process of developing a successful product. Dellas and Lenoci [8] published an example of how a fragrance is modified from a cologne to a cream version, requiring attention to price, safety, stability and aesthetics. They showed the thought process of an experienced perfumer, rather than that of a chemist. Economics becomes a concern, since normally a fragrance for a lotion must cost significantly less than a hydroalcoholic creation. Some price reduction changes can have almost irrelevant aesthetic impact, since some of the delicate nuances of a fine fragrance are lost in a functional product. Residual fixative notes, which tend to be large, costly ingredients, can also be reduced or eliminated. Some materials must be eliminated because of stability concerns, and replaced with stable ingredients. The balancing of the fragrance to achieve the same olfactory effect in the new base either involves boosting the levels of ingredients muted by the emulsion, or adding new materials with a similar odor profile but greater impact.

13.5 Personal care applications: surfactants

The end of World War II saw the creation of a mass market for surfactant systems based on new synthetic anionic and nonionic materials. As the market expanded and matured, the importance of fragrance as a sales and marketing tool increased. Indeed, fragrance became perhaps the most important attribute of brand differentiation. New product formulations and significant fragrance levels made it crucial to understand the effect of fragrance on the surfactant systems, and the influence of the surfactant systems on fragrance performance.

Basic research clarified the concepts of the micelle and critical micelle concentration, and it became clear that different perfume components could concentrate in different areas of a micelle or the continuous phase. Some materials are solubilized by incorporation in the micelle, and any increase in the capacity of the micelle core is helpful. Materials with some true water solubility, such as phenylethyl alcohol or vanillin, become less soluble if the polarity of the external phase is increased by the addition of salt.

The most common product forms of surfactant systems for personal care are shampoos and bath gels, and their composition is similar. A typical formula contains a primary surfactant, secondary surfactant, foam boosters, viscosity builders and specialty additives. The primary surfactants are usually anionics. Amphoterics, nonionics, betaines, amides and amine oxides can be incorporated to obtain special properties such as foam or viscosity boosting. Common additives for conditioning hair shampoos are silicones and proteins. Medicated shampoos also contain actives such as coal tar or zinc pyrithione.

Viscosity can be built in different ways. The best, but the most expensive, approach is with a properly chosen blend of primary surfactant, secondary surfactant, and a betaine or alkanolamine. The inexpensive way is to add salt or a polymer network such as carbomers or similarly performing materials. Such systems have a minimum of surfactant activity. It may be hard to maintain clarity while adding fragrance to salt-built systems for two reasons: the low level of surfactant, and the excessive polarity of the external phase.

It is now possible to view the problems of fragrancing surfactant systems using the current state of theoretical knowledge of micellar aggregates. The fragrance can be considered an additive, and its effect on the critical micelle concentration (CMC) will determine the consequences for the viscosity. The shape of the micelle can be determined by a relationship between three parameters: the volume occupied by the hydrophobic groups in the micellar core, the length of the hydrophobic group in the core, and the area occupied by the hydrophilic group at the micelle surface. There are two classes of organic compounds that can affect the CMC: Class I materials are incorporated in the micelle and Class II materials modify solvent–micelle or solvent–surfactant interactions. Fragrance materials illustrate this phenomenon, as they have a range of polarities. Whether a material is Class I or Class II will depend on the specific system involved.

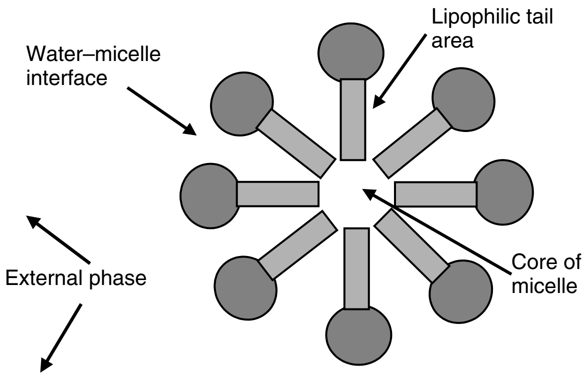


Figure 13.2 Fragrance partitioning in surfactant systems.

The individual aroma chemicals in a fragrance will partition into different areas of the surfactant system, as indicated in Figure 13.2. Some materials will migrate into the core of the micelle, some will align along the hydrophobic tails, some will be near the micelle surface, and a small amount will be in the external aqueous phase. The number, shape, and size of the micelles, and any thickening that has been created in the external phase, determine the viscosity of the system. The fragrance materials can change any of these parameters, and thus make the viscosity increase or decrease. The viscosity changes can be extreme and difficult to correct.

Munden [9] published a study on the effect of fragrances on viscosity. He used a perfume consisting mainly of phenylethyl alcohol, lillial, citronellol, hexycinnamic aldehyde, methyl dihydrojasmonate and Lixetone Coeur. The surfactant system consisted of 10% sodium lauryl ether sulfate, some minor additives, and sodium chloride to adjust viscosity. It was noted that fragrances usually decrease viscosity, but occasionally increase it. Of the materials considered, citronellol has the greatest effect, and thus was selected for detailed study.

Similar to the way in which a salt curve results from adding increasing amounts of sodium chloride to a surfactant blend, a viscosity curve can be established using increasing amounts of citronellol. The peak was found to occur at approximately 1% citronellol. In addition, the presence of citronellol affects the response of the system to salt. Without citronellol, a viscosity of 15 000 cts was achieved with 6% NaCl, while with 0.5% citronellol present, the highest possible viscosity was 7500 cts. Munden concluded that formulating a surfactant system before selecting the fragrance is ill-advised. If the fragrance is selected late in the development cycle, and a viscosity adjuster is used, then the effect of fragrance on the adjuster efficacy should be conducted to establish optimum values.

Blakeway [10] concluded that the odor of a solubilized perfume must be proportional to its concentration in the aqueous phase, not the fraction contained in the micelle. The greater the number of micelles, the less the odor intensity, and at higher surfactant concentrations the micelles must burst, releasing aroma chemicals into the solution.

A study by Behan and Perring [11] examined the vapor-phase concentration over a shampoo system using headspace analysis. Sodium dodecyl sulfate (SDS) was used at a range of 5–20%, but with 10% as the standard level. Aroma chemicals from 0.5 to 3% we used, with 1% as the standard. The aroma chemicals studied were octan-2-one, benzyl acetate, anethole, limonene and heptan-1-ol. A number of solvents/solubilizers were also considered: diethyl phthalate, dioctyl adipate, dipropylene glycol, 2-phenoxyethanol, triacetin, and Triton X100. It was found that the solvent could profoundly influence the headspace composition of the volatile components. Triton X100 was best for depressing vapor pressures. The perfume components will partition between the different structures in the SDS/water system. Increasing the surfactant concentration reduces the quantity of aroma chemicals in the headspace.

Fragrances are not intrinsically water-soluble. Some aroma chemicals, such as vanillin and phenylethyl alcohol, have moderate water solubility, but usually fragrances have to be solubilized by combining with nonionic surfactants. The phrase "water-soluble fragrance" is misleading, since the fragrances are actually located in microemulsions. Different solubilizers require testing to identify the one with optimum performance for each fragrance and vehicle. Once solubilized, water is a perfectly acceptable vehicle for fragrance delivery in terms of odor quality. It is best to maintain the pH at $5.5 +/- 0.5$ for optimum stability.

With water-soluble fragrances, the ethoxylated groups in the solubilizer are responsible for the hydrogen bonding that bridges the oil and water phases. The hydrogen bonds weaken with increasing temperature, resulting in a reverse cloud point, also referred to as the inverse solubility coefficient. When the temperature rises, the solution clouds, and upon cooling, clarity returns. Clouding normally occurs at 35–80°C, with a lower solubility range at 5–15°C.

Surfactant systems for skin and hair have similar chemistry, but the substrates have very different odor-retaining properties. The skin has fairly low odor retention, particularly when the fragrance is present in a wash-off product. Hair has much greater odor retention, but a marketing question immediately arises – Does the consumer want residual odor? Combining customer preference with knowledge of the retention characteristics of aroma chemicals on hair makes the design of appropriate fragrances more predictable. Hair exhibits more absorptive character based on its non-polar nature. The fragrance molecules penetrate the hair, much like dye intermediates before neutralization. There is competition for space in the keratin, leading to non-additive behavior. As a consequence, two materials do not exhibit their combined strength, unless a unique synergistic effect is present.

Just as fatty soaps are similar to emulsions, transparent and glycerin soaps show kinship to surfactant systems. Clarity and discoloration are crucial issues, although pH is not a contributing problem factor in these bases. Syndet (synthetic detergent) and combo bars (combinations of fatty soaps and synthetic detergents) have formulations significantly different from other soap formats, and their fragrancing must be attacked as unique situations. With all these alternative soap variations, it is essential to work with the exact customer base and with an awareness of the exact production processing employed.

13.6 Air fresheners

Air fresheners provide a significant category of fragrance use, and the products are dispensed in a constantly expanding number of forms. Room temperature systems include aerosols, pumps, gels, beads, pads, powders and plastic. Some dispensing involves

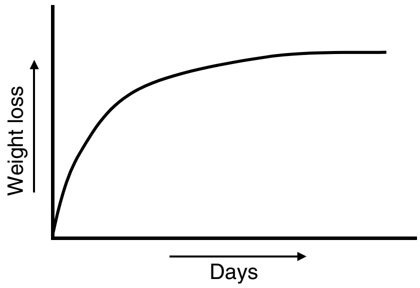


Figure 13.3 Typical fragrance evaporation curve.

heat, such as plug-ins and lamp rings. The simplest system involves the evaporation of a liquid, often through a wick or pad. Desirable features are fragrance impact, odor integrity during the life of the product and long-lasting performance. Marketers typically request 30- or even 60-day performance from these products. Evaporation curves generally show the most pronounced weight loss in the first 2–3 days (Figure 13.3). Since the weight of fragrance material present continually decreases, it is impossible to have significant impact at the end of the product's life cycle, unless some sustained release technology has been employed.

A typical fragrance will invariably change character as it evaporates. By focusing attention on the evaporation properties rather than on the odor character, it is possible to design a fragrance that will maintain an essentially uniform composition as it evaporates. These mixtures are called linear fragrances. The evaporative weight losses of different aroma chemicals are proportional to their vapor pressures.

The weight loss of four fragrance ingredients (1, 2, 3, 4) with vapor pressures $p_1 < p_2 < p_3 < p_4$ is shown in Figure 13.4(a). To create a linear fragrance with these materials, the proportions must be adjusted to conform to Figure 13.4(b). Of course, when other factors such as wick and pads enter the calculations, these linear effects are disturbed, but the basic principles are still valid. The interaction of ingredients also causes non-linear response during evaporation. Linearity is easier to achieve if the various components have similar vapor pressure, and some odor types are more adaptable than others to linearity. It is always true that formulating for linearity involves compromising olfactory quality for technical performance.

An early application of liquid air fresheners was a simple combination of a bottle containing a fragrance solution and a thick wick. A later refinement was to use a capillary to draw the liquid into a pad, usually composed of thick, porous cellulose. The fragrance must not clog the capillary; so testing of aroma chemicals, diluents and surfactants with the customer's components is necessary. The evaporation from pad will differ from the free liquid evaporation curve due to differing interactions of the aroma chemicals with the substrate.

The same laws that govern other combinations of liquids in physical chemistry rule the properties of fragrances. The vapor pressure is calculated by Raoult's law, which states that the vapor pressure of true solutions is dependent on the proportion of each component of the blend. The Phase rule of thermodynamics states that the vapor pressures of two immiscible liquids are not affected by each other. Thus, in a system with water and oil in

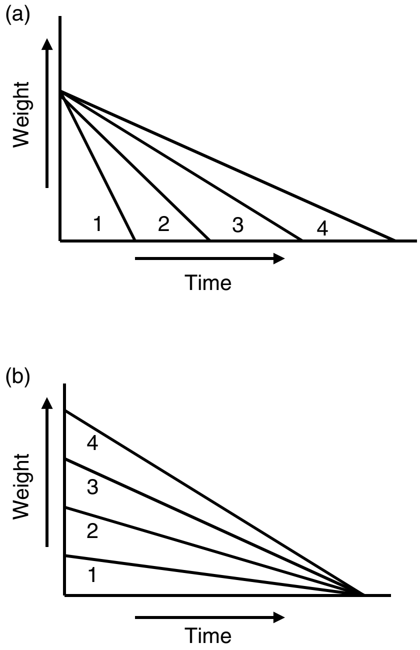


Figure 13.4 (a) Free evaporation of fragrance materials; (b) Evaporation of linear fragrance.

a gel, each behaves as if the other were not present. Altering the solvents in a fragrance is one method for changing the evaporation characteristics.

Water-based solid air fresheners based on carrageenan, a marine-derived polymer used as a thickener, have been manufactured for many years; the first US patent appeared in 1954. A key patent [12] disclosed a gellant mixture of:

Carrageenan	0.75–1.80%
Locust bean gum	0.20–0.75%
Potassium chloride	0.10–0.75%
Sodium carboxymethylcellulose	0.10–0.70%

During times of high carrageenan cost, stearates have sometimes been substituted.

Chlorophyllin was often incorporated in gels as a deodorizer, although it is unlikely that it was efficacious. These products are typically packaged in tightly sealed plastic containers that pull or twist open. The gels form hard surfaces during evaporation, significantly decreasing fragrance release with time. Their base color, a tannish brown, made attractive coloring impractical, and they shriveled into an unattractive, irregular lump. Fragrances require the addition of nonionic surfactants to become soluble in these bases.

Clear water-based gels became possible with refinements in the quality of gellan gum. Gellan gum is a polymer with a linear tetrasaccharide repeat unit comprised of four sugar units: 1,3-β-D-glucose, 1,4-β-D-glucuronic acid, 1,4-β-D-glucose and 1,4-α-L-rhamnose. High levels of fragrance are employed, necessitating the use of surfactants, glycols and alcohol for achieving complete clarity. Even these materials cannot always make a clear product with certain difficult fragrance types such as citrus. Since they are transparent, the gels can be easily produced in a variety of colors, and objects such as botanicals and fruit slices can be suspended in the base for added marketing appeal. These gels, while visually appealing, unfortunately, have poor fragrance release.

Pennzoil patented a hydrocarbon gel [13] for air fresheners in 1999. The typical hydrocarbon of this invention is mineral oil. Whereas fragrances need water compatibility in other gel systems, the Pennzoil form, being non-aqueous, is clear with non-polar fragrances, or on some occasions solubilized with an amphiphilic molecule such as glyceryl oleate. The fragrance evaporation from this base is superior to that of a water-based gel, and the crystal-clear appearance has excellent consumer appeal.

Air fresheners are always most effective when the fragrance can be efficiently distributed in the environment, and the best means of accomplishing this has always been the aerosol. The best performing sprays are solvent-based, which creates the finest particles and the best suspension. In response to VOC regulations, aerosol air fresheners are usually water-based. Hydrocarbon propellants such as propane, butane and isobutane are not good solvents for polar aroma chemicals. Crystals such as coumarin and vanillin, and resins such as oakmoss, must be kept to a minimum in the formulation.

The basic components of an aerosol are shown in Figure 13.5. The possible interactions of the fragrance with the other components of an aerosol are extensive. The concentrate for a water-based formula resembles an emulsion, and can exhibit the same stability problems, such as the discoloration of vanillin. Hydrocarbons such as A46 are supplemented with other propellants, such as dimethyl ether (DME), for reduced VOC products. DME does not react adversely with aroma chemicals. The propellants and fragrance materials can also react with the valve and gasket material. DME, for example, requires butyl inner gaskets.

Fragranced polymers can be used for a variety of applications, from novelty jewelry to air fresheners. Fragrance levels vary from 0.5 to 1% for masking, 4–8% for a long-lasting but low-impact impression, 20–40% for intense effect in jewelry and toys, and to 50%

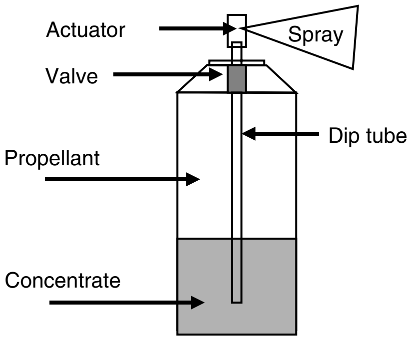


Figure 13.5 Aerosol components.

in air fresheners. Appropriate base resins for fragrance concentrates are LDPE (low-density polyethylene), LLDPE (linear low-density polyethylene), HDPE (high-density polyethylene), PP (polypropylene), EVA (ethyl vinyl acetate), PVC (polyvinyl chloride), styrene copolymers, cellulose acetate, TPE (thermoplastic elastomer) and TPO (thermoplastic olefin). Resins that do not fragrance well are polystyrene, ABS (acrylonitrile butadiene styrene), acrylic, PC (polycarbonate), nylon and polyester.

Meder [14] used the SP to determine the compatibility of a fragrance with a polymer. PVC was an example because it is a major polymer based on tonnage produced, and it is usually compounded with a plasticizer. The fragrance can be added to the plasticizer with no additional processing. PVC has a solubility of 19.4 $\text{MPa}^{1/2}$. Since compatibility exists when the plasticizer SP is within 2 $\text{MPa}^{1/2}$ of the plastic, the range of acceptable perfume materials is 17.4–21.4.

The characteristics of a good plasticizer are: high boiling point, high molecular weight, low color, low odor and good solubility in the polymer. Odor aside, fragrances fit these parameters, and ethylene brassylate was an example of a plasticizer for PVC. In a reverse example, a polymer compatible with a vanilla was determined. Three common primary vanilla chemicals were considered: vanillin, ethyl vanillin and ethyl vanillin PG acetal. Since these chemicals are polar, water-soluble polymers were candidates; namely, PVOH (polyvinylalcohol), PVP (polyvinylpyrrolidone) and PEOX (polyethyloxazoline). After a series of experiments, the following was determined for a vanilla-fragranced label adhesive: 51 g of vanillin, 56 g of ethyl vanillin, 357 g of PEOX and 536 g of water. This indicates that by matching the polymer to the fragrance, polar crystalline materials can be incorporated successfully.

13.7 Candles

Candles are a key segment of the United States home fragrance market. Fragrance is what drives the sale of candles, followed by color and packaging. It is essential that the fragrance translation into candles is executed with the same care that personal-care products receive. Candles appear to be simple systems, but they can present great technical and aesthetic challenges to the formulator. The correct balance of base, fragrance, color and wick is essential to create a satisfactory product (Figure 13.6). Consumers are increasingly demanding products that are attractive, economical, safe, and perform well. Achieving this requires close cooperation between the candle manufacturer and the fragrance supplier.

The evaluation of a candle fragrance, besides the assumed fidelity of the odor character to the customer's expectations, hinges on "cold throw" and "hot throw". Cold throw is the impact of the fragrance in the candle before burning. A candle is not customarily lit in a retail store; so a purchaser almost invariably selects a candle based on its cold throw. It is crucial that the fragrance balance emphasizes the top and the middle notes. Bottom notes, often the most expensive part of a fragrance, have little place in a candle. Hot throw is the odor impact when the candle is burning, particularly when the pool of molten wax on the top has completely formed. The fragrance should give a strong and characteristic odor, filling an average room with scent.

It is essential that the fragrance performs well in the customer base. Most candles are paraffin-based. Paraffin is a complex mixture, and the detailed chemical composition of a particular material is rarely available. The standard specifications for wax

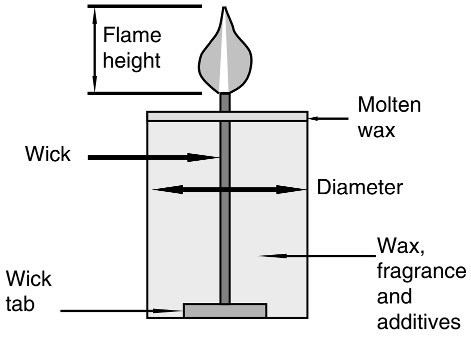


Figure 13.6

are melting point and penetration. Changing suppliers of 145°F paraffin – based on the assumption that all 145°F paraffins are essentially the same – has been the cause of countless difficulties.

The key determinants of paraffin chemistry are the source of the petroleum oil and the refining process. Some oil fields have aromatic or cyclic components, while others do not. Most paraffins are straight chains, but some paraffins contain a significant amount of branched-chain compounds. The melting point rises with increasing chain length, and branched chains are lower-melting than straight chains. The boiling range, melting point, and paraffin composition can all be controlled, in theory, to fairly tight specifications by the refining operations, but rarely is the paraffin purchased by candle companies actually held to these rigid standards.

Candles are made in different forms. The most common types are tapers, votives, pillars and jars. Each should have a different wax blend. For example, tapers must have higher melting points than glass jars. The oil content of the paraffin (excluding the additional fragrance) should be no higher than 0.5% in straight paraffin for a free-standing candle, while a jar candle can contain as much as 1.5% oil. It is important that candles in glass do not pull away from the surface upon cooling. It is equally necessary that a votive has good mold release. Materials added to paraffin to change the properties include stearic acid, petrolatum, mineral oil and microcrystalline wax.

Regardless of the exact composition of the paraffin, the key fact is that paraffin is non-polar. There are a few non-polar aroma chemicals, but the majority of the fragrance ingredients have some polarity: aldehydes, esters and alcohols are a few examples. Bleeding out, or syneresis, occurs when the wax matrix of the candle cannot hold the fragrance, like a sponge holding too much water. An oil that seems perfectly soluble initially may bleed out over time. Observation after a minimum of one day is necessary to ensure that no solubility problem exists.

A second polarity-related problem is sublimation. Materials that are totally incompatible with paraffin, particularly crystalline materials such as vanillin, can sublime. These materials can migrate up the wick and deposit on the glass cover if it is a jar candle, resulting in an observable film.

The perfume percentage in a candle is frequently at a very high level, compared to most household products. In modern candles, where color and fragrance are prime selling features, 5% fragrance is often used. The fragrance must be completely soluble in the molten wax blend. Some manufacturers will accept a slight haze, but there should certainly not be insoluble droplets or particles settling to the bottom.

The solvent for the fragrance must be compatible with the wax. DPG, the solvent of choice for many personal-care applications, is totally inappropriate. DEP, dioctyl adipate, Hercolyn D, benzyl benzoate, mineral oil, isopropyl myristate, IsoPar, NorPar and capric/caprylic triglycerides are all possible candidates. Low HLB solubilizers are occasionally used for some problem fragrances. Which solvent performs best is determined by testing the individual fragrance oil and candle base. Proper choice of solvent can also be used to adjust the flash point of the fragrance, which is a critical factor for shipping.

Besides solubility, the fragrance must not adversely affect the burning characteristics. Burn tests are commonly performed by manufacturers, both on new submissions and on each individual lot of fragrance oil received for production. The flame must burn well both initially and when relit. In a properly burning system, the paraffin will totally combust, yielding carbon dioxide and water. Most aroma chemicals are primarily carbon, hydrogen and oxygen, and do not create significant quantities of byproducts upon combustion, especially since the bulk of fragrance chemicals evaporate intact from the molten pool, rather than burn in the flame.

Once the diameter, wax base, and percent perfume are all fixed, only one variable remains to achieve proper burn – the wick. In general, the thicker the wick, the more rapidly the candle will burn. Wicks come with and without cores, coated and uncoated, and with different weaves. A large selection from wick suppliers should be tested, and the most appropriate one chosen through burn tests. The flame should burn clean. Holding a clean broad metal spatula over a flame will quickly reveal the amount of carbon residue produced. The desired pool of molten wax should form in about an hour. The candle should also perform well when relit.

The addition of color increases the potential stability problems. Candles are not restricted in the US to the certified-type colorants (FD&C, D&C, ext D&C), and other colors are available as powders, liquids and waxes. Generally, these colors contain nitrogen in the form of an azo bond (–N=N–), which can react with aroma chemicals. Stray metal contamination can also come from the wick, wick tab, a poor grade of wax, or iron present in the processing equipment. Dark perfume oils, usually yellow, orange or amber, when incorporated at 5%, can add significant color to a base, making a blue into a green or a white candle yellow. Light, either from the sun, fluorescence or UV, can trigger unwanted color reactions. UV absorbers, chelating agents and antioxidants, alone or in combination, may eliminate or alleviate some unwanted reactions – sometimes. Raw material studies on the fragrance in the colored base may be necessary.

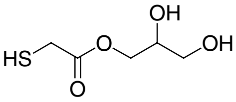
Clear candles based on polyamide resins have been available since the 1960s. The clear candles did not burn well, and were at best novelty items. By the early 1990s, the clear gel, invariably in a jar due to their soft structure, became popular, although never popular enough to displace the wax candle. Unfortunately, a major company marketed unsafe clear gel candles, which caused several fires. This resulted in a well-publicized recall and consequent loss of consumer acceptance. The flare problem involved fragrances that were not perfectly soluble and a solvent base that was not properly engineered. These fragrances also had flash points that we now know to be too low. When areas of fragrance concentration encountered the molten pool, and the wick dipped into the liquid, a fire could result.

In response to this problem, Penreco developed a new, patented base [15]. A special cut of mineral oil, having a high flash point, was gelled. The composition is approximately 92% mineral oil and 8% polymer. Fragrances, which have specific solubility and flash point characteristics, are specified. The fragrances must be completely soluble in mineral oil in blends of 25% fragrance and 75% mineral oil, and 75% fragrance and 25% mineral oil. The fragrance must thus be as non-polar as possible. The flash point must be at least 140°F, and preferably 170°F. A special self-extinguishing base developed by Penreco incorporates silica in the gel. The wick clogs when the flame reaches the bottom; this removes a safety issue, since the users frequently forget to blow out the candle at that point.

13.8 Reactive hair care

Products that chemically interact with hair provide great technical challenges for perfumers. Permanent waves, hair dyes, depilatories and relaxers are diverse in composition and purpose. As a group, they have very high pH. Permanent waves and depilatories also have extraordinary base odor, hair dyes are unusually reactive chemicals, and relaxers have an extreme pH coupled with a base formulation that is not very stable even without fragrance, due to the sensitive nature of the active ingredients. Some of these products require a neutralizer, usually ammonia, which is not strictly an odor but a chemical irritant. The chemical interactions with hair provide an additional source of odor problems.

Permanent waves have a severe base odor, both in product and in use. The characteristic smell comes from thioglycolates, usually ammonium thioglycolate ($C_2H_4O_2S{\cdot}H_3N$) or glyceryl thioglycolate (**1**).



(1)

No fragrance can mask the odor completely. Sagarin and Balsam published the basic reference [16] concerning perfume materials in these bases in 1956, offering data on 200 aroma chemicals, and surprisingly little information has since been published.

Sagarin and Balsam found it impossible to draw conclusions based solely on structure. Aldehydes would be expected to react with thioglycolates, but some proved stable, such as methyl nonyl acetaldehyde. Some materials mask but do not retain their odor value; cinnamon oil and citronellal change odor but have good masking ability. Phenylethyl alcohol maintains its character but covers poorly. Some materials can maintain odor and coverage but exhibit other problems, such as trichlorostyralyl acetate, which is useful, except for the deep yellow color it produces.

The odor stability and coverage achieved by blends of aroma chemicals are hard to predict. Some materials perform better in mixtures; others require careful blending to be effective. Certain materials that tested well, such as cade oil and methyl acetophenone, are unpleasant by themselves and must be carefully added in small proportions to be useful.

An approach to reducing the thioglycolate odor was disclosed in US patent 5,554,363 [17]. In 1888, Bongartz observed that thioglycolic acid combines with benzaldehyde over a span of a few hours, and with cinnamic aldehyde in minutes, with the release of significant heat. The patent builds on these observations. It specifies benzaldehyde, methyl hydrocinnamic aldehyde, and mixtures of the two, for being more reactive with the cysteamine reducing agent, than with the aldehydes that naturally occur in hair. The reducing agent thus attacks the fragrance aldehydes rather than the hair aldehydes, resulting in reduced odor during the permanent waving process.

13.9 Depilatories

Depilatories use calcium thioglycolate as the active of choice, combined with a nonreactive filler (typically calcium carbonate) to reduce irritation, a wetting agent to improve contact with skin, and an emollient such as cetyl alcohol. Raising the pH to 10–12 can reduce the time required for effective depilation. Above pH 12, there is a high risk of skin damage. Below pH 10, the depilatory action falls off rapidly.

Barry [18] provides some guidelines on perfuming depilatories. Alcohols can form mercaptans, esters may be hydrolyzed to odorless alcohols, and aldehydes undergo aldol condensations. Many aroma chemicals are discolored by alkali. Linalyl acetate maintains floral note after hydrolysis, making it a valuable odorant. Generally, the best performing ingredients are ionones and rose alcohols (citronellol, geraniol).

Deplilatories can be important as an alternative to blade shaving for men of African ethnicity. The hair is typically curly and wiry, and conventional shaving leaves the ends of the hair shafts with points, and these can penetrate the skin, a condition named *pseudofolliculitis barbae*. A depilatory system should work quickly, finishing its task in 3–7 minutes. Barium sulfide and calcium thioiglycolate are effective actives, but the former is banned in the EU. Fragrances used in perms and depilatories can be used in these products, but the base odor during use is so severe that no coverage is truly effective, and the consumers seem resigned to its offensive odor.

13.10 Dyes and perms

Hair dyes are possibly the most difficult systems to fragrance. Besides the high pH, the active ingredients of the dye are extremely aggressive to aroma chemicals. Some oxidative dyes contain perfume, while others do not. Ammonia adds a strong impression that masks the fragrance, but when the product is applied, the ammonia dissipates, and it is possible to smell the fragrance. Any aroma chemical should be able to resist alkali and hydrogen peroxide during the brief time when it is combined with the dye. No aldehydes are appropriate, because they react with amino compounds.

A typical relaxer base is shown in Table 13.2. The pH is very high, and the base has only moderate stability even without fragrance. The base odor out of the container and

Table 13.2 Cream hair relaxer

Ingredient	% by wt
Water	48.30
Propylene glycol	3.00
Petrolatum	20.00
Mineral oil	15.00
Cetearyl alcohol	8.00
Ceteareth-20	2.50
Steareth-10	1.00
Sodium hydroxide	2.20
	100.00

during use is not offensive, and hence many commercial products use no fragrance. The most successful fragrance is a simple rose, essentially phenylethyl alcohol, which is an exceptionally rugged molecule. Comber [19] examined some of the difficult chemistry involved in the bases: sodium, lithium or calcium hydroxide in relaxers, guanidine carbonate in the activators for relaxers, and guanidine in the activated relaxer. Most relaxers, about 85% of the market, use sodium hydroxide; they are termed "lye relaxers". Lye relaxers have a pH of 13.5, putting a severe restriction on the aroma chemicals that can be used. The so-called "no-lye, no mix" lithium hydroxide relaxers have a slightly more moderate pH range, 12.5–12.8. The no-lye, guanidine/hydroxide relaxers are back to pH 13.5.

The consumer use of the guanidine/hydroxide relaxer involves mixing a calcium hydroxide containing cream emulsion base (pH 12.4–12.6) with a liquid guanidinium carbonate activator (pH 11.0–11.2) to produce the activated relaxer base (pH 13.5). The cream emulsion base is sometimes fragranced. It is necessary that the fragrance be stable not only in the emulsion base, but also in the final activated base.

13.11 Bleach

There are three common types of bleach products available, with significantly different levels of activity. A 5.25% sodium hypochorite solution sold principally for whitening laundry can be termed simply "bleach". Concentrations up to 15% available chlorine with reasonable stability are available for commercial use. Cleaners containing sodium hypochorite as a functional ingredient but also possessing other surfactants and/or thickeners comprise a second category. The final group consists of non-hypochorite bleaching products, such as peroxides.

Sodium hypochlorite poses a unique combination of challenges for the perfumer. Not only must the fragrance itself be stable; it also must not adversely affect the chlorine stability. Few solubilizers have satisfactory stability, and those available are not highly effective, compared to the solubilizers used in other applications. The solubilizers can also have a negative effect on stability and create unwanted foam. The high pH required for hypochlorite would alone limit the palette of allowed raw materials. The packaging, including the cap and cap lining, can create problems. The cumulative constraints result in a narrow range of creative options.

The key factors effecting bleach stability are hypochlorite concentration, temperature, pH, chloride ions and metallic impurities. When the pH drops below 10.5, the decomposition becomes precipitous. A sealed, full container stored in a cool environment will have the best shelf life. As the product is used, the increased presence of air becomes problematic. Currently, the most frequently used solubilizer for fragrance in bleach is Dowfax, a series of alkylated diphenyl oxide disulfonates (ADPODS). While Dow was the innovator with these products and their trade name is familiar to the industry, other companies now make similar chemicals. The standard member or the series in bleach solubilization is Dowfax 2A1, which consists of a C_{12} branched hydrophobe, sodium salt form, with 45% activity. Phosphate esters have also found use as bleach compatible surfactants.

Liquid bleach is usually, but not always, fragranced with solubilized perfume oil. Some manufactures have successfully marketed products where the insoluble fragrance oil lays on the top as a film. When the product is used, the top layer does not pour off with the first use. Rather, the fragrance percentage stays relatively uniform during the life of the product. There is considerable psychological resistant to this approach, despite any advantage it may have in terms of economics or foam reduction during processing.

Testing bleach stability requires great care. Chlorine has the potential of adding to unsaturated bonds in aroma chemicals. The resulting adduct may still have an acceptable odor; thus, a chemical may smell fine, yet adversely effect the chlorine content. Conversely, an aroma chemical may have no effect on the chlorine content, but may have its odor value destroyed. Analytical and olfactory testings must both be satisfactory before a product is appropriate for use.

Available chlorine is the basic measure of the oxidizing power, present as hypochlorite. To measure available chlorine, the bleach solution with potassium iodide is acidified, and the iodide titrated with sodium thiosulfate.

Test samples are prepared with either complete fragrances or individual raw materials. Fragrance levels are very low; a starting point could be 0.02% fragrance solubilized with 0.06% Dowfax 2A1. Unfragranced samples are used as a control, as hypochlorite levels in bleach fall with time, even in the absence of fragrance. Samples require testing by titration, each week, for four weeks. Samples at room temperature, elevated temperature (35 or 40°C), refrigeration (4°C) will give a complete stability profile. There is a non-linear degradation at higher temperatures, so test conditions should not be higher than 40°C.

Odor evaluations of the samples are an essential part of the stability testing. Assuming the odor test is satisfactory, the chlorine content of the fragranced product should be 85–90%, compared to that of the unperfumed sample. At what point a material is unfit to use is a matter of judgment. If an aroma chemical is used at a low level in the fragrance, and has an important odor contribution, perhaps, its stability can have a lesser standard.

Many cleaning products have lower levels of bleach. Bleach deteriorates more slowly at lower levels, and the bases may contain surfactants that help solubilize the fragrance. In products where the bleach gains protection from an encapsulation process, the perfuming problems are much easier. Powder products protect the fragrance more than liquids.

13.12 Malodor counteractants

Fragrance companies are frequently required to reduce or eliminate unpleasant odors. Intrinsically unpleasant molecules cause some malodors. Others arise from the products of organic decay. A common characteristic of many offensive smells is the presence of sulfur, nitrogen, or halogens. Some osmophoric groups to be focused on are $-NH_2$, –SH, and C=C. Thioglycolates, mercaptans and pyrazines are examples of foul smelling compounds used in personal care and perfumery. Sour milk and underarm odor are some common products of organic decay.

The earliest use of fragrance in malodor control was the use of a large dose of aromatic materials to overwhelm a foul smell. The incense used in churches helped to reduce the cumulative olfactory impact of the assembled masses of unwashed individuals. These materials were not designed to be effective malodor counteractants, and the effect could be achieved only by employing a heavy application of odor-masking materials.

The first modern approach was the design of fragrances composed of aroma chemicals known to be particularly efficacious against malodors. Aldehydes and esters were the key components; the neutroleum fragrance of the 1960s was a characteristic example of this approach. US4840792 [19] suggests a mixture of citral, eugenol, coumarin, and helional for odor control. US5683979 [20] prefers 20–60% musk, 30–70% citrus and 1–20% mint.

An extension of this idea is the patented use of two aldehydes selected from certain defined groups. There must be a minimum of 20% of each aldehyde in the mixture. It is required that one aldehyde must be selected with a double bond in the alpha position, R–C=C–CHO, and one from all the remaining aldehydes used in perfumery. Examples of materials with the double bond in the alpha position are citral, cinnamic aldehyde, benzaldehyde and vanillin. The finished fragrance must contain a minimum of 10% of the aldehyde blend with a total fragrance level of 1% in the finished product, with the proportion adjusted appropriately as the fragrance level goes up or down.

The next technical advance was the use of nonodorous materials that could complex with the malodor molecules and effectively eliminate their odor. Not only are these ingredients not aroma chemicals, they could potentially neutralize selected components of standard fragrances. A number of proprietary materials, generally recognized by trade names, are typical of this category of modern malodor counteractants.

Metazene is one of the first malodor counteractants. It originated around 1950 and is still available. The structure of Metazene shows it to be a mixture of fatty alcohol esters of methacrylic acid, primarily lauryl methacrylate. The molecule can react with osmophores such as –SH, $-NH_2$ and –CHO to produce large molecules, whose vapor pressures are too low for olfactory detection.

Meelium is a blend of polyhydroaromatic sulfonates. Neutrolair D-7 is a mixture of geranyl crotonalte and dihexyl fumarate, Vandor B is principally 3,5,5-trimethylhexanal. Forestall is soyaethyl morpholinium ethosulfate.

Grillocin® contains a clearly defined substance, zinc ricinoleate, synergistically combined with other zinc compounds made up of multiple hydroxylated sebatic acids, oxamines and resinic acids. Other metal salts, such as copper, cobalt or nickel show similar deodorizing properties but have toxicological problems. The properties of the ricinoleic anion are important, and similar fatty acids are not effective. Grillocin® reacts with low molecular weight fatty acids, amines, mercaptans and isovaleric acid, a prime component of body odor.

Some structures form cavities that can effectively encapsulate an odor molecule. One aspect claimed for Odorone® is the entrapment of the odorant in a cavity. Cyclodextrin is a notable example of this phenomenon, as expounded in various patents. US5783544 [21], assigned to Procter & Gamble, is the basis of Febreze™, a popular fabric deodorizing spray. Cyclodextrin is available in different forms, α, β and γ, which have different cavity sizes. The α and β forms are available from several suppliers, but the γ version is only available from Wacker [22]. The inside of the cavity is hydrophobic, while the outside is hydrophilic. The solubility characteristics allow cyclodextrin to disperse in an aqueous system, while trapping oily materials such as fragrance or malodors in its cavity.

The fragrance materials preferred in patent US5474917 [23] have a Clog P of 3 or less. This value indicates some hydrophilic tendency, which the patent claims enhances the performance in the base and during product use. Some examples cited in the patent are benzaldehyde, benzyl acetate, coumarin, dihydromyrcenal, ethyl vanillin, eucalyptol, eugenol, geraniol, hydroxycitronellal, linalool, methyl anthanilate, nerol, phenyl ethyl alcohol, terpineol and vanillin. The patent also prefers fragrances with at least 25% of these materials, more preferably 50%, ideally 75%.

13.13 Stability testing

A product must be stable if it is to succeed. The more rigorous the stability testing during the development process, the more likely that success will be. The base, fragrance, color, packaging, and even labeling, must all be carefully scrutinized. Time is needed to carry out these tests, and a last-minute or haphazard approach to stability and compatibility studies is an invitation to commercial failure.

Products being tested should be as representative of the final marketed version as possible. In addition to the exact base and fragrance, it is necessary to have the packaging, including details such as the label and closure. A control run in glass will show if any troublesome situations are due to the product itself or the package. Different plastics vary in qualities such as thermal resistance, color fastness and oxygen permeability. Some fragranced products may be packaged in paper, like sachet stones, or wrapped in cellophane, like cellulose car air fresheners, and unwanted permeation is always a possibility.

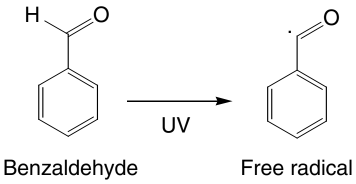
Among the parameters requiring close monitoring during the test period are pH, physical separation, color, odor, particle size, viscosity and weight loss. Of course, not all test parameters are appropriate for all product types; particle size is important for emulsions, not bath gels. Stability requirements are generally more difficult for emulsions, and more tests are applicable for them. Certain changes of appearance are more critical in clear packaging, such as a slight haze in the base or slight color shifts. Often perfection is unobtainable; comparison with a successful product that has been on the market for years reveals a great deal about the acceptable range of key variables.

Elevated temperature is the most universal stability test. As a rough rule, reaction rates double for every 10°C. Assuming room temperature to be 25°C, then one year at room temperature would correspond to three months at 45°C or one month at 50°C.

These conditions, while useful, are nevertheless misleading. Reactions can occur at 50°C, which will never happen to the product in its normal lifecycle. Confidence can reasonably be placed in a product that passes a 50°C test; however, a product that fails at 50°C may still be suitable for the marketplace. Other commonly employed temperature conditions include low temperatures (4°C), subfreezing temperatures (−20°C) and freeze–thaw cycles. These tests attempt to simulate all the shipping and storage conditions that can occur in all seasons through the entire region to be served. The centrifuge test is also useful for emulsions. Separation of emulsions can occur due to differences in specific gravity between the discrete and continuous phases, and the centrifuge increases this gravitational effect. The test sample is first warmed to 50°C, and then centrifuged at 3000 rpm for 30 minutes.

The effect of fragrances on the stability of emulsion and surfactant systems and in a number of other systems has been dealt with in other sections. Bath gels and shampoos often combine color and high fragrance level to enhance consumer appeal. Color molecules have color because of structural groups called chromophores. Chromophores are configurations that can alter the energy levels of delocalized systems. Benzene absorbs around 200 nm, but our eyes see radiation only between 400 and 700 nm. Thus, benzene is colorless, despite its delocalized electrons. The addition of a chain with conjugated double bonds or an azo group can shift the radiation into the visible region.

Fragrance materials can change properties when exposed to light. Benzaldehyde is difficult to stabilize with red dyes. Benzaldehyde is a relatively unreactive molecule in its ground state, but UV readily converts it into a free radical (Scheme 13.2), which attacks the chromophore structures of the red dye molecule. One way to combat this phenomenon is to introduce UV absorbers into the system.



Scheme 13.2

13.14 Conclusion

The fundamental key to dealing with the technical aspects of fragrances is to treat them as mixtures of chemicals – and, of course, to know what those chemicals are and their properties. The environment contributes additional chemistry plus larger structures susceptible to interactions, such as micelles and liquid crystals. It is essential to have clearly defined technical parameters at the beginning of product development, such as specific stability requirements or the presence of sensitive base materials.

Open cooperation between perfumer, chemist and customer is necessary for the most effective resolution of problems, since each can hold a piece of the solution. Since aesthetic considerations enter into most fragrance applications, marketing concerns impose yet another level of issues. Taking every possible variable into account, encouraging input from everyone contributing to the product development chain, and allowing adequate time for testing and the resolution of problems, will maximize the opportunities for success.

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