

Formulation notes

Fragrancing Detergents

Creating functional, effective and stable scents

Felix Buccellato, Custom Essence Inc.

Why do you wash your clothes? It is probable that the first clothing consisted of animal skins, an auxiliary spoil of the hunt. This additional layer of protection allowed early Man's fragile bodies to survive in climates and seasonal changes that were previously not possible or uncomfortable at best. There is little doubt that the women, with more sensitive and discriminating olfactory senses, discovered the need to wash out the animal skins in a nearby river or lake.

As time progressed and textiles and weaving developed, clothing became more delicate and refined, and the women washing the clothes became increasingly discriminating. (There is little doubt that the more affluent, in addition to washing their clothes, also fragranced their bodies, hair and clothes with natural oils and plant extracts or natural fragrances.) The story of soap supposedly begins at the base of Mount Sapo, where, according to Roman lore, the water foamed and washed the clothes better than in other spots. Why was this?

It so happens that at the top of the fictional mountain was an altar where animals were routinely sacrificed. The animal fat mixed with ash as rain washed the fat down the mountainside to the river at its base. Along the way the fat reacted with the ash (saponification) to create the first soap. The Italian name *sapone* (soap) is derived from Mount Sapo.¹

Using animal fat (or any fats for that matter) in the soap making process to produce surfactants often results in a fatty rancid animal fat odor. While all the grime and dirt and perspiration odors can be removed, there remains an unpleasant fatty odor, hence the need for fragrance. Over time, soap manufacturers have improved the base odor but have never been able

to make the end product fresh and clean smelling without the use of fragrance. This situation holds true today; although the levels of malodor (odor perceived as unpleasant) have been reduced, they are not completely eliminated ... so far.

Perhaps the most difficult attribute to define or create is likeability.

Detergent technology continues to advance, along with more efficient and cost-effective chemical reactions and improved antioxidants, whiteners and brighteners. These and other phases of refinement have brought continuous change barely noticed by the consumer—excepting negative aspects that can lead to formulation changes and legislation. One glaring case is phosphates, which may be harmful to the environment. Today, it is difficult to find a detergent that still uses phosphates. Some may be used in dishwashing detergents, but likely will be replaced in the future.

T-1 lists the major detergent brands.

Understanding the Product and Process for Detergents

There are a number of key points that must be understood when formulating detergent fragrances:

- 1. Product:** Fragrance should cover the base odor of the detergent before use.

Brand	Manufacturer	# Liquid	Powder	Notes
All	Unilever	2	X	1. Citrus, 2. fruity floral and 3X
Ariel	Procter & Gamble			
Arm & Hammer	Church & Dwight	2	X	Fragrance Free and Clean & Fresh
Cheer	Procter & Gamble	2	X	Color Guard fruity floral and True Fit
Clorox	Clorox Corp.			
Daz	Procter & Gamble			United Kingdom
Downy	Procter & Gamble	4		Simple Pleasures, Rose Violet, Magnolia & Orange Blossom, Vanilla & Lavender, Water Lily & Jasmine
Dreft	Procter & Gamble	1		Powder aroma
Dropps	Cot n Wash			Pre-measured packets
Dynamo	Colgate Palmolive	2		Two variations in liquid
Ecover	Ecover Sweden			Environmentally friendly
Fab	Colgate Palmolive	X		
Gain	Procter & Gamble	X		
Ivory Snow	Procter & Gamble	1	X	Powder
Persil	Unilever			
Purex	Dial	4		Original, Mountain Breeze, Fresh Scent, and Unscented
Rinso	Unilever			
SA8	Amway			
Solo	Heritage Brands			
Sunlight	Unilever			
Surf	Unilever	X	X	
Tide	Procter & Gamble	4	X	At least four variations in liquid—Original Scent (powder floral), Mountain Breeze (fresh floral with green fresh notes) are the two main characters; unscented (Tide Free) also available; Simple Pleasures Line features Febreze and Downy Scents
Ultra	Procter & Gamble	X	X	Concentrated detergent
Wisk	Unilever	2	X	Crisp Scent (fruity floral) and Invigorating (citrus floral)

*number of odor variations or X means product is there in at least one fragrance or type

Conditions	Liquid Detergent Disadvantage	Liquid Detergent Advantage
Liquid/water	Ionic or charged particles in water system Water system provides a medium in which fragrance reactions can take place more easily. pH range from 7.8 to 8.2	No high oxygen exposure; oxidation potential significantly lower Volatile more easily retained in a liquid system

- 2. Wash:** The fragrance is distributed into the wash cycle; a good portion will be lost at that time and then again during the rinse cycle. Note: If bleach is added at this phase, as is common when washing white clothing, another factor is imposed on fragrance stability and reaction. Of course, there are fragranced bleach products that contain stable materials which also have good substantivity on fabric.
- 3. Rinse:** The residue left on the wet, cleaned clothes—water, soap/surfactant and a minor amount of fragrance—then goes to the dry cycle.

- 4. Dry cycle:** The water as well as fragrance are driven off by heat. This is where the challenge for fragrance performance becomes most important.

The combination of fabric/fragrance bonding, molecular weight and odor threshold all play an important role in fragrance delivery. The *less* water-soluble the materials are, the greater the likelihood it will not be washed away with the water surfactant mixture. This is difficult because detergents are designed to solubilize the less soluble oils into the water to wash them away.

The active ingredients for powdered laundry detergent are usually surfactants, which can be nonionic and anionic. Cationic surfactants are used to a lesser extent, often for fabric softening, and can also include various enzymes.

It may help the formulating perfumer to look at the advantages and disadvantages of the liquid detergent listed in **T-2**.

When the pH shifts to the basic side (~ 8.0), the environment becomes protic and can shift the equilibrium and ionize water, driving various reactions and perhaps causing hydrolysis. This can affect esters as well as lactones. The liquid (water medium) provides a gradient, or a good place for the resultant water molecules, as a leaving group, to migrate.

Liquid and Powder Considerations

What are the unique conditions for liquid or powder, and what are the performance expectations?

A fundamental problem is that the function of surfactants—almost any type—is to solubilize oils into a water phase and remove them from the clothes. As irony would have it, *almost* all fragrance ingredients are highly oil-soluble with a marginal solubility in water. So, the challenge is to add the correct fragrance ingredients that will remain on the fabric, survive the drying cycle, and leave a clean fresh smell that reminds consumers that the clothes are in fact clean, and *not* perfumy.

If the detergent is a liquid, what are the active ingredients and what types of reactivity do they display? It should be noted that the majority of laundry detergents used today are liquid or liquid concentrates. There are at minimum 20 types of liquid laundry detergents on the supermarket shelves while one has to search for the four major brands of pow-

Ingredient that should not be used in powder detergents

Almost any natural citrus: orange, lemon, lime, bergamot and tangerine oils

Almost any low-molecular weight components or aldehydes: ethyl butyrate, amyl acetate

Aldehydes: hexanal through decanal or hexenal to decenal

Reasons

Primarily limonene, which is volatile and easily oxidized, along with characterizing aldehydes including octanal, decanal, and citral

Very volatile, usually poorly contained in cardboard packaging, easily oxidized to the acids that can create undesirable odor changes

Both unsaturated aldehydes and aldehydes are easily oxidized to acids

dered detergent, of which Tide is the leading brand (over 30% market share).

If the detergent is a powder, what are the active ingredients and what type of reactivity will occur with the fragrance ingredients? Serious consideration must be given to the enormous surface area of the detergent. The materials selected for this application should be stable and not prone to oxidation or degradation.

Achieving the “Fresh and Clean” Effect

Consumers still prefer detergents that have a fresh and clean smell, leaving a pleasant—not perfumy—aroma. What is “fresh and clean?” For the purpose of this article, fresh and clean will be defined as any odor that does not smell like any food item. It might be best to describe the aroma as something not easily recognized, or to relate to an aroma that reminds one of fresh air or the outdoors. An unrecognizable aroma that is somewhat nondescript but pleasant. Perhaps the most difficult attribute to define or create is likeability. What items might be used to create such a likable scent for use in laundry detergent?

To create an effective detergent fragrance, a specific set of questions must be answered. Is the fragrance ...

- ... **functional?** A major consideration is functionality, meaning the fragrance must be phase-compatible and deliver odor that covers

the base and leaves a fresh clean residual aroma on the clothing after washing and drying.

- ... **effective?** The fragrance must be effective in covering the base odor as soon as the package is opened and substantive enough to leave residual clean fragrance on the clothes after the wash and dry cycle.
- ... **stable?** The fragrance must be stable for a minimum of one year on the market shelf as well as in the consumer’s laundry room. Additionally, the fragrance items themselves should be stable—not interact with each other or the fragrance base—and should not leave discoloring residue on clothing, especially whites.

Troubleshooting

Now, examine a powder detergent and focus on items that should *not* be used. Detergents are granular powders with low water content. Their formulary disadvantage is an extraordinarily high surface area through which fragrance materials must be absorbed, and, as a result, are exposed to oxygen—the enemy of a variety of fragrance materials.

The disadvantages and advantages of working with powder detergents are:

- **Conditions:** Granular powders have low water content.
- **Disadvantages:** High surface area molecules are prone to oxidation; volatile materials in fragrance do not retain in product as well as in liquid.
- **Advantage:** No liquid spills or extra weight in shipping; therefore, less potential for fragrance interaction and reaction in powder.

Materials that should be avoided in powder detergents are discussed in **T-3**.

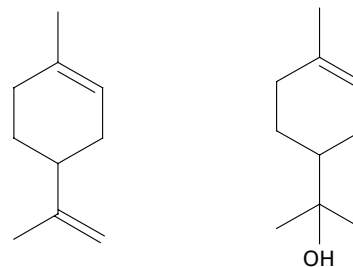
Terpenes possess low molecular weight (136), and so their volatility limits or prevents their use in powder detergents. Additionally, terpenes are unsaturated, easily react with oxygen and are not stable

(**F-1**). This precludes the use of any citrus products.

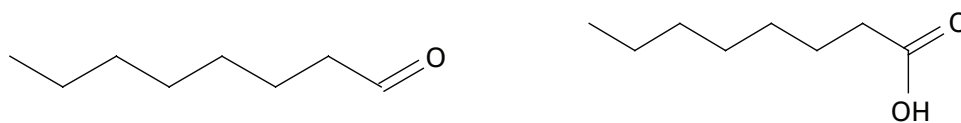
Aldehydes are another area for concern. While they are usually in the C-8 to C-12 range, *all* aldehydes are prone to oxidation, which can form acids that often display undesirable odor characters (see **F-2** and **F-3**).

If there are any alcohols or glycols present in any significant quantity, aldehydes will thereby react to form acetals or hemiacetals (see **F-4**).

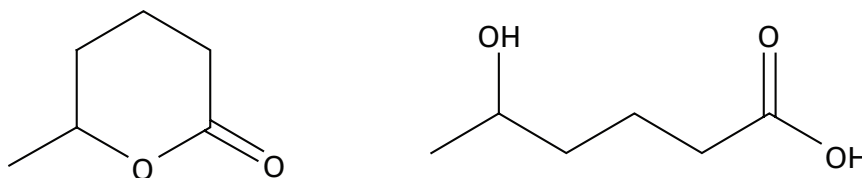
Limone oxidizes to α -terpineol

F-1

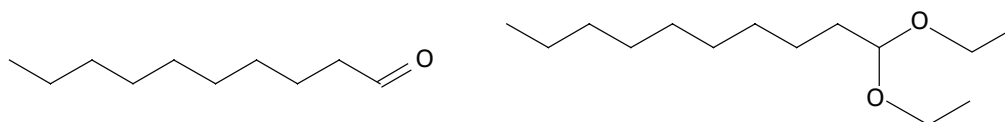
Octanal oxidizes to octanoic acid

F-2

δ -Hexalactone hydrolyzes to the parent hydroxy acid

F-3

Decanal reacts to form acetal formation

F-4

Ingredients that are suitable for powder

High molecular weight > 150
 Materials with low-threshold values
 Polar materials

Reasons

Do not easily volatilize away during wash or dry cycle
 Low amounts are left on fabric that can be perceived
 These have a tendency to bond to fabrics

Classes of materials to consider for powder detergents

Chemical class

MW range

Odor

Musks of all types	236–284	Musk: very good substantivity on cloth
Salicylates of all types	150–250	Powder floral: very good
Anthranilates all types: cyclic and bicyclic esters, alcohols (cyclic or straight chain)	153–273	Floral: good body and substantivity
Ketones (cyclic or straight chain)	130–280	Various fruity and floral: good fruity notes or modifiers
Nitriles	150–220	Improved stability over aldehydes, with good substantivity, stable citrus character as well as clean residual notes

Because acetals are inherently more stable, they are generally a good class of chemicals to include in detergent formulation. This is especially true for powder detergents.

An effective detergent fragrance usually imparts a fresh and clean aroma at all phases of use. This means a good initial impression and base odor coverage as perceived by the consumer. At the same time, this fragrance must leave a signature fresh and clean aroma on the fabric, whether the fabrics are dried on a clothesline or heated in a dryer. Commercial dryer temperatures can exceed 200°F. **T-4** lists a number of materials appropriate for powder detergents. **T-5** lists classes of materials for consideration in powder detergents.

What Will the Future Bring?

There is an increasing awareness of how chemicals of all sorts affect the environment. Phosphates have been largely eliminated in laundry detergent due to phosphate-induced eutrophication in lakes and rivers. The next phase is to remove them from dishwashing detergents and replace them with citrates, zeolites and materials that help in removing the calcium residue on glassware.

Coldwater detergents utilize surfactants that satisfactorily solubilize oily materials in cold water. The time is right for this type of product on a large scale. It can be an easy and immediate start to reduce the energy demands and associated expense

of our increasing population. Consumer demand and behavioral changes can be a very effective way to quickly alter energy consumption.

Delivery systems are constantly being researched, devised and implemented by manufacturers as well as fragrance companies. Delivery systems include: encapsulation, malodor neutralization, enhanced substantivity and precursor technology. The notion of precursor technology has been known for many years. It is the opposite process of instability, where a molecule is formed with negative olfactory or performance characteristics. The precursor approach starts with the question, "What molecule do we want delivered onto the fabric?" followed by, "What molecule can we introduce that has no olfactory or performance negative, but when introduced into the water/surfactant or high heat exposure will generate either through hydrolysis, oxidation or charge reaction a desirable odor or performance character?" This type of information has been and will continue to be a highly regarded trade secret by the fragrance companies who

develop this technology. It is noteworthy to mention that Henkel developed a precursor technology based on silicic acid esters that bear fragrance molecule appendages. They patented the mechanism more than 10 years ago.²

Liquid fabric detergents have become the dominant product type in the category, with typically 16–20 shelf-keeping units (SKU) on the market shelf in contrast to only four to five SKUs on average for powder detergents. Because the two major detergent types are liquid and powder, it may be best to determine the philosophical direction for the selection of fragrance requirements. One should also consider what performance will be needed. It may well be the case that powdered detergents will become a thing of the past with many brands vanishing in the next 10 years.

Address correspondence to Felix Buccellato, Custom Essence Inc., 53 Veronica Ave., Somerset, NJ 08873.

References

1. Soap & Detergent Association publication, 1st Ed., New York (1981)
2. *Chemical & Engineering News*, 85(5) (Jan 29, 2007)

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