Creative Perfumery in the Soap and Detergent Field

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The quantity of detergent powders and liquids produced in the USA in 1982 was 2,400,000 tons. In Western Europe 2,600,000 tons have been manufactured (Table I).

The share of liquid detergent of the total quantity produced is about 20% in the USA, while it stays below 5% in Europe. Production value of detergents in the USA and in Europe is as high as $7 billion.

In the same period one million tons of soaps and bath additives have been produced representing a value of approximately $3 billion (Table II).

The ratio between solid and liquid products in the USA compared to Europe is nearly inversed. While the market share of liquid bath products is as low as 10% of the bar soaps in the USA, they are produced in nearly the same quantity in Europe.

Considering these figures we estimate the fragrance value in the USA and in Western Europe as shown in Table III.

The figures are of course only rough estimations. The fragrance quantities needed are about 12-13,000 tons with a value between $130-140 million.

The total value for detergent fragrances in the USA is estimated at about $40 million. For Western Europe we calculate the value at around $33 million (Table IV).

We estimated the total value of fragrances for soaps and detergents worldwide at approximately $300 million.

The great economical impact of soap and detergent compounds becomes very obvious when costs for perfuming are compared to the selling price of the finished product (Table V).

Fragrance costs for soaps amount to 7% of their retail price in Europe; in USA up to about 4%. In detergent powder, usually containing 0.1 to 0.2% of perfume, its costs amount to 1% of the selling price of the finished detergent.

It is interesting to realize that fragrance costs for extraits and Eaux de Toilette represent only 1% of the retail prices.

This short view on economy illustrates the importance of soap and detergent perfumery.

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Table I

Detergents (Powders and Liquids) 1982
(Estimation based on two Different Sources)

	USA		W-Europe	
	Mio $	1.000 t	Mio $	1.000 t
powders	3.000	2.000	3.000	2.500
liquids	600	400	170	100
total	3.600	2.400	3.170	2.600

Table II

Soaps and Bath-Additives 1982
(Estimation based on two Different Sources)

	USA		W-Europe	
	Mio $	1.000 t	Mio $*	1.000 t
bar soaps	1.100	300	900	350
liquid soaps	90	30	< 4	< 1
bath-additives	10	1	700	330
total	1.200	331	1.600	680

*Rate of exchange (1982): 1 $ = 2,43 DM

Table III

Fragrances for Soaps and Bath-Additives 1982

perfumes for	USA		W-Europe	
	Mio $	t	Mio $	t
toilet bar soaps	40	3.300	50	4.200
liquid soaps	5	300	negl.	negl.
bath-additives	< 1	20	40	5.000
total	46	3.620	90	9.200

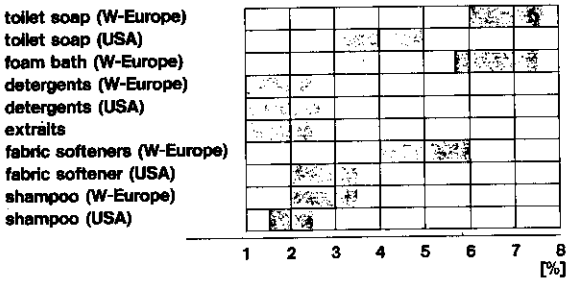
Table IV

Fragrances for Detergents 1982

perfumes for	USA		W-Europe	
	Mio $	t	Mio $	t
powders	30	3.000	30	3.000
liquids	10	1.000	3	300
total	40	4.000	33	3.300

Table V

Fragrance-Costs
in % of Selling Price of Finished Product



Fragrance Creation for Application Areas

The creation of a soap and detergent fragrance is basically not very different from the creation of a fragrance for extraits or Eaux de Toilette. Buongiorno even dared to say that the creation of a good soap fragrance is more difficult than the development of an extrait fragrance.[1] The perfumer only has to be very much aware that an aroma chemical has a totally different performance in soap and detergent than in alcoholic solution. Working on a soap fragrance we have to consider:

—stability of the raw materials
—intensity and power
—possible discoloration of the soap base
—odor performance when washing
—substantivity on the skin after washing
—the price of the raw material

Successful fragrance development in the soap and detergent area is heavily dependent on close cooperation between creative perfumers and the application department.

While 95% of all existing materials may be used for creating an alcoholic fragrance, the number of suitable materials for soaps and detergent powders is very limited (Table VI). About 80% of all odorants are suitable, from a technical point of view, for perfuming toilet soaps. The same is true for American detergents and light duty detergents in Western Europe.

The number of suitable materials for use in detergent powder containing enzymes and bleach activators is restricted to 70%. For white toilet soap one can only make use of 65% of the total.

What do we mean when we talk about the suitability of a raw material? Usually perfumers and application people don't talk about suitability but about stability. But is it really only the stability of the raw material which is of interest to us?

Burrell describes an analytical method enabling the formulator to measure by GLC the remaining quantity of the fragrance material incorporated in soap or detergent[2] and, therefore, to draw conclusions on stability and volatility. The results of this method are, in our opinion, not sufficient to prove whether the fragrance is suitable for use in soap and detergents or not.

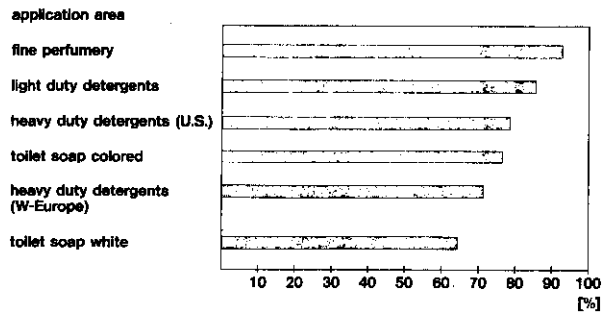
What is the usefulness of a raw material which is analytically detectable in a rate of 80-100% after one year's storage if it is not perceptible by the nose or doesn't have any performance?

This is very often the case and certainly not exceptional.

It occurs, for example, when the odor of the soap or detergent has altered after prolonged

Table VI

Raw Materials Allowed to be Used



storage and rancid off-odors cover the perfumery material. The soap base or the surfactant of a detergent may also have such a fixative effect on a material that it is no longer perceptible. In both cases the raw material is not suitable for use in soap and detergent compounds in spite of its stability.

Problems not only occur during storage: some soap bases develop a strong odor immediately after production. This can be attributed to processed active ingredients or to fatty acids of inferior quality. For this reason test results obtained with one soap base are not relevant for other soap bases. This means that tests have to be repeated whenever it is necessary to work on a different soap base. It is obvious that materials with a bad performance in good quality soap base do not have to be tested in an inferior quality. This brings some kind of relief.

In 1980 and 1982 we already described how to carry out a suitability test for detergent and soap perfumery raw materials and how to evaluate its results.[3,4] We think this method is very effective and therefore it seems interesting to repeat the description starting with the method for soaps.

Each individual raw material is incorporated in a concentration of one percent in the representative soap base.

The tablets are stored in soap boxes at room temperature for one year. After this storage the tablets are evaluated by a team of at least three perfumers. According to our experience it is very important to have this evaluation done by at least three perfumers because each person has a different perception of an odorant and therefore the judgment on its suitability may differ largely from person to person. One observes this phenomenon not only in the case of the musks, but also that of sandalwood odorants, salicylates, esters of p-cresol and some woody odorants.

Parallel to this it is possible to carry out a short storage test at higher temperature. We found that in this kind of test the results often are very different from the results of a one year storage test at room temperature. Materials which perform very well after a year's storage at room temperature may give poor results when tested at higher temperatures. We prefer to decide about the use of a certain material on its performance after a one year's test at room temperature. In our opinion this represents more truly the real life of the soap cake.

Many application laboratories rate the stability for instance on a scale from 1-6. We feel that a good evaluation can be done with three different ratings.

- Rate 1: good
  The raw material to be tested can be identified easily. Its odor has remained unchanged and its performance is good.
- Rate 2: fair
  The raw material is identifiable but its intensity has suffered or it does not sufficiently cover the odor of the soap. Raw materials which have been slightly altered also belong to this group.
- Rate 3: poor
  The odor cannot be identified or is not perceptible or has an off-note due to chemical reactions (e.g., saponification or oxidation).

Evaluation is done at round tables and odorants are rated by majority decision. This judgment is not only based on the odor of the soap tablet but also on the lather smell and on the smell on the skin during and after washing. Moreover we notice any possible discoloration. The ratings are listed and can be expressed clearly either by numbers, symbols or by colors. Table VII shows an example of such a list.

Table VII

product	after one year		odor of	
	odor	color	lather	skin
Aldehyd 13-13	++	++	++	++
Ambroxan	++	++	++	++
Bigaflor	–	+	++	++
Herbavert	++	++	+	+
Irotyl	++	++	++	+
Jasmacyclat	++	++	++	+
Lavandin oil grosso	++	++	++	+
Lemon oil, Sicily	–	+	+	+
Litsea cubeba oil	+	–	++	+
Mandarin oil, Ital.	+	+	++	+
Orange oil, Florida	+	++	+	+
Patchouli oil, Karimun	++	++	++	++

Note: ++ = good; + = fair; – = poor

Bigaflor is an interesting example. After the one year storage test the soap tablet containing Bigaflor no longer smelled like Bigaflor due to a chemical reaction which produced acetophenone and hydratropic aldehyde. This was a pity because the results with Bigaflor in lather and on the skin were excellent.

We also show some examples of suitable essential oils: Lavandin grosso is, as commonly known, a good performer. Lemon oil, on the contrary, cannot be recommended, as reported in literature. Mandarin oil performs surprisingly well. The oil of Litsea Cubeba causes many discoloration problems and is therefore not recommended for white soaps. The performance of orange oil is fair, whereas the results with patchouli are, as commonly known, excellent.

Each perfumer has this list (Table VII) at hand for creative work and will try to employ mostly the raw materials marked ++. The use of + marked materials is allowed within certain limits, but not recommended. The employment of those marked – is absolutely forbidden. It is quite certain that a perfume which is developed according to the above described methods will present excellent stability and great power. Its beauty and its acceptance on the market only depend on the perfumer's creativity.

Fragrance for Powder Laundry Detergent

When creating a soap perfume one hardly needs to consider consumer habits in the different countries. In contrast, one has to consider many different points before starting creative work on a detergent powder perfume. On the one hand one should be concerned with the formulation of the powder detergent itself, on the other hand with the consumer's laundering habits.

Europe

The heavy duty detergents in Europe have a market share of 90%. Only 5% of these are liquids. The remainder of the market are light duty detergents used for wool and fine fabric. The light duties do not cause too many problems for a fragrance from a technical point of view. According to their purpose they usually contain more delicate perfume notes than the heavy duties. The development of a fragrance for a European heavy duty detergent is much more complicated. Many raw materials are not compatible with a number of active ingredients, as shown in Table VIII.

Washing Habits. Front loading washing machines are widely used. Washing temperature is usually 60° or 95°C. Rinsing is done mostly with fabric softener.

Standards for the Fragrance. Performance in the powder is very important. Performance in detergent solution is less important because in most cases the washing machine cannot be opened during the washing process. The residual odor on the laundry is not so important since it will be scented by the fabric softener.

Table VIII

Product Formulation of Powder Detergents (heavy duties) in W-Europe and their Influence on Fragrance

ingredient	contents (%)	influence on fragrance
Anionic and nonionic surfactants	8-25	without any problem
Builder (Triphosphate, Zeolithes)	20-50	perfume should be alkali resistant
Bleaching agent (Sodium perborate)	0-30	perfume should be alkali resistant
Bleach activator e. g. TAED*	0-2	very problematic reacts with many fragance materials
Foam inhibitors (soap, Silconoil etc.)	0,1-4	odor of rancid soap is difficult to cover
Enzymes	0-0,5	negative odor problems during storage

*TAED = Tetra Acetyl Ethylene Diamine Pentaacetylglycose

South America

High sudsing detergent powders are used in South America, mainly in Brasil. Liquid detergents are not common (Table IX).

Washing Habits. Hand washing is still very common although washing machines are increasing in number. In these top loading machines the water is cold or only fairly warm, but never hot. Bleaching is done, if at all, by means of chlorine bleach. The employment of fabric softeners is increasing, but is still at a low level.

Standards for the Fragrance. Performance in powder is very important; it has to cover the strong odor of the powder. Performance in the solution is obviously also very important. Residual odor on the fabric is important, too, since fabric softeners are not commonly used and the consumer wants a pleasant smell on the fabric.

Table IX

Products Formulation of Powder Detergents in Brasil

ingredient	contents (%)	influence on fragrance
A B S (alkylbenzene sulfonate)	10-25	unpleasant odor of ABS is difficult to cover
T P P (triphosphate)	5-20	fragrance should be stable against alkali
bleaching agents	0	without any problem

North America

80% of the heavy duty detergents are powders, about 20% are liquids. Light duty detergents are not of great importance (Table X).

Washing Habits. Big top-loading machines with washing temperatures ranging from 40° to 50°C. For disinfecting and bleaching mainly chlorine bleach is used, but there are also perborate-caustic soda mixtures on sale. Softening and drying is mostly done in tumblers.

Standards for the Fragrance. Good performance in powder and solution because the washing machine can be opened easily. Residual odor is not provided by detergent but by fabric softener.

It may be concluded from the above mentioned points that fragrance development for USA detergents is not very complicated from a technical point of view. The essential problem is to create an attractive fragrance with low priced raw materials. This task itself is difficult enough.

Table X

Product Formulation of Powder Detergents in USA

ingredient	contents (%)	influence on fragrance
surfactants	10-25	without any problem
builder	35-45	aromatic chemicals should be alkali resistent
bleaching agents	0	without any problems
bleach activators	0	
foam inhibitors	0	
enzymes	0	

Doing perfumery work for South American countries, especially Brasil, is more difficult because of the usually poor sulfonate qualities in South American detergents, the odor of which is difficult to cover.

When the task is to create a perfume for a European detergent powder, the perfumer faces a multitude of problems. All raw materials have to be strictly tested. As with the above mentioned material test in toilet soap, this test should not only determine a raw material's stability but also its suitability, by which we mean a joint evaluation of stability and intensity.

Test Procedure in Detergents

For this purpose each odorant under test is incorporated in detergent powder at a 0.1% level. The samples are examined for odor after one year's storage in glass bottles at room temperature. Again, there must be at least three perfumers to do the rating. Since washing is done to some extent by hand, a raw material's ability to cover the solution's odor should also be examined. This is very important in particular if the detergent powder contains any bleach activators which may develop, during washing, a strong and unpleasant smelling material as peracetic acid. A good fragrance compound should cover these malodors which is only possible if most of its constituents already have this covering ability.

The results of the above mentioned test can be listed as shown previously with soaps, or can be computerized. Computerization of data is extremely helpful when carrying out different research programmes with different parameters.

The importance of collaboration between perfumers, application specialists and research chemists and the use of the above described method is illustrated by the following example. The salicylates are widely used, low priced and very interesting materials to the perfumer.

With the exception of the ethyl- and methylsalicylate they all have very similar, pleasant and more or less balsamic and floral notes.

In the past we have been confronted with the problem that the most important members of this family, the amyl- and isoamylsalicylates develop very unpleasant and dirty-smelling off-odors when incorporated in detergent powder.

The commercially available benzylsalicylate does not show this off-odor in detergents. Its performance, however, is much weaker and its odor effect is not comparable to those of the amyl- and isoamylsalicylate. Though the cis-3-hexenylsalicylate is of outstanding value for use in detergent powder, it can't be employed in desirable quantities because of its high cost.

We have discussed the situation with our research chemists and made a survey of all salicylates not commercially exploited. A large number of esters were prepared. We limited the preparation to alcohols with a maximum of 8 C-atoms.

First of all, an olfactive evaluation was done with the prepared materials. The salicylates described in Tables XI and XII gave positive results.

In the next stage we evaluated the power and tenacity in comparison with the well-known salicylates (Table XIII). The cyclopentyl salicylate has the strongest odor, followed by the amylsalicylates, the prenylsalicylate and the various hexylsalicylates. The evaluation of tenacity gave surprising results. Cyclohexylsalicylate was clearly perceptible even after 18 days on a blotter. Most of the other salicylates disappeared after one week.

This superior tenacity has also been observed during tests on dry fabric treated with softener.

We then went back to our basic problem: how do the new salicylates behave in detergent powder?

Table XI

Odor Description of Aliphatic Salicylates

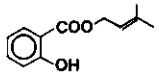
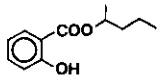
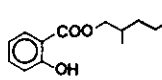
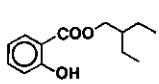
salicylate	formula	odor
Prenyl		sweet, floral, balsamic
2-Hexyl		sweet, slightly balsamic
2-Methylpentyl		flowery balsamic, slightly green
2-Ethylbutyl		fresh floral, herbal green

Table XII

Odor Description of Cyclic Salicylates

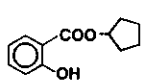
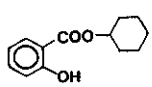
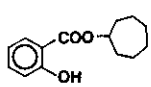
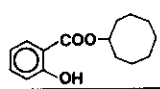
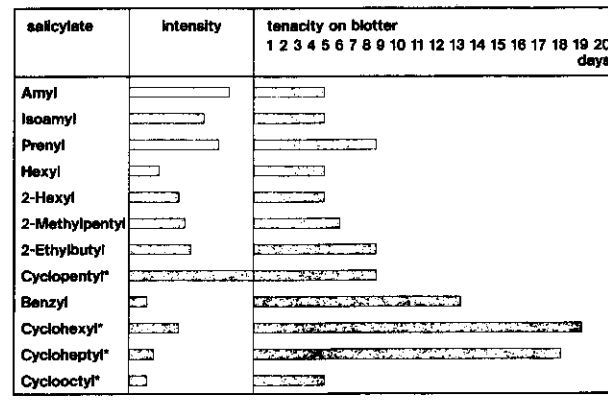
salicylate	formula	odor
Cyclopentyl		very sweet floral, slightly balsamic
Cyclohexyl		aromatic, floral, balsamic
Cycloheptyl		delicately spicy, balsamic
Cyclooctyl		delicate, balsamic

Table XIII

Intensity and Tenacity of any Salicylates



Average rated by 6 perfumers
* patents applied

Table XIV

Comparative Valuation of Different Salicylates after 6 Months Storage at Room Temperature

salicylate	heavy duty detergent			
	american type		european type (with TAED)	
	powder	washing bath	powder	washing bath
Amyl	poor	good	very poor	good
Isoamyl	very poor	good	horrible	good
Hexyl	poor	sufficient	very poor	sufficient
Benzyl	very weak	very weak	very weak	very weak
2-Ethylbutyl	very poor	excellent	very poor	very good
Cyclopentyl	very good	excellent	very good	excellent
Cyclohexyl	good	excellent	good	excellent
Cycloheptyl	sufficient	sufficient	poor	sufficient
Cyclooctyl	too weak	very weak	odorless	very weak

We carried out a comparative evaluation incorporating them in detergent powder in amounts of 0.1%. For these tests we used powder from U.S. and European manufacturers. The perfumed powders were stored for six months in glass bottles at room temperature. After this period we judged the performance in powder as well as in solution. The results are shown in Table XIV.

We very much improved the fragrance performance in detergent powder by using cyclic salicylates, mainly cyclopentyl- and cyclohexylsalicylate, instead of the noncyclic salicylates. In the laundry water the differences are not as clearly perceptible. Nevertheless, the strong off-odor caused by isoamylsalicylate in powder detergent gives reason enough to consider the replacement of this material by cyclohexylsalicylate or a combination of cyclohexyl- and cyclopentylsalicylate.

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