

## Water Based Fragrances

SITARAM DIXIT

Senior Manager — Fragrance Applications  
International Flavours & Fragrances India Limited

In today's time, prosperity and comfortable living are closely related. The quality of the fragrance is taken for granted as good if the brand is well known and the container elegant.

Personal fragrance is no longer a luxury today, with both men and women considering it as a daily commodity to improve aesthetics. Developing an attractive fragrance is never a matter of chance. Creative imagination, systematic study of the behaviour of odorants, combined with years of practice is required to develop a product designed to appeal to others. Use of top quality raw materials having absolute purity of odour is a prerequisite.

Consideration must also be given to other factors like environment, government rules and regulation and other subjective influences that directly affect fragrance development, manufacturing and marketing. Patience and time are required to create a fragrance, to evaluate, and make changes necessary to balance it before launch. Only a fragrance that has attained the desired degree of perfection demanded by today's discriminating consumer will make it to the best seller list and conquer the world.

A cursory look at the world fragrance market will reveal the trend of alcohol-free fragrance sprays becoming popular. The basic underlying reason for this global market trend might be different. However, we cannot ignore the fact that aqueous dispersions of fragrances are becoming popular in the world market. Volatile Organic Chemical (VOC) restrictions in the US, environmental pressures in Europe, religious constraints in Islamic nations, and political climate coupled with Indian government restriction of alcohol usage in consumer products has helped to create this new market segment of non-alcoholic fine fragrances.

Use of water as a solvent in place of alcohol has its limitations. The biggest constraint with water based fragrances, is our inherent desire to achieve near iden-

tical drying effect, odour diffusion, application methods, appearance and skin feel in comparison to conventional alcoholic fragrances.

The limitations of water as a solvent are equally divided on both the manufacturer and the user. Oil based fragrances, although present in the market, is not very popular, and is limited to a small section of the populace. Microemulsion technology is one route to realise a clear to opalescent solution of the fragrance oil in water. Water based fine fragrance formulations largely consist of the fragrance oil, surfactant blends and other minor additives like actives, UV absorbers, antioxidants, preservatives, colour, etc.

Marvin Balsam almost three decades ago pointed out that solubilisation of fragrance oil is easier if the perfumer avoids use of terpenes, sesquiterpenes, resinoids, crystalline ingredients and materials that have more than 12 carbon atoms (e.g. benzyl benzoate or salicylate).

Although in the pure form the above materials are difficult to dissolve, they generally form stable solutes when used as one of the many ingredients in fragrance oil. Avoiding use of limonene and pinenes does not significantly change the odour quality of the fragrance created. However, it enables the fragrance compounded to be used at a higher level, as the solubility is significantly greater.

One important observation to be noted is that natural essential oils comprising of various ingredients show a high solubility in comparison to pure chemicals. In short, creative expertise, patience, and time are needed to formulate a fragrance if solubility, in addition to a high degree of odour perfection, is desired.

To formulate water based fragrances we have to take recourse to using solubiliser surfactants. Lower the lever of solubilisers, lesser the stickiness perceived in the final product. The optimum quantity and type of the solubilisers used is therefore an important factor in

the formulation. A variety of solubilisers are available for use. However, comparative solubilisation data is not available. Solubiliser requirement also changes with specific fragrance types, making it all the more difficult to choose the correct one. Only by tedious trials and expertise gained thereby, an optimum quantity of the selected solubiliser can be determined.

Typical solubilisers popular with development chemists are:

- PEG 40 Hydrogenated Castor oil isostearate.
- PEG 60 Hydrogenated Castor oil.
- Nonyl Phenol (10M Ethoxylate)
- Polysorbate 20
- Polysorbate 80
- Cateth 20
- Ethoxylated alcohol
- Trideceth -11
- Fatty alcohol ethoxylate
- PPG 2 Cetareth 9
- Laureth -35
- Cocodimethyl amine oxide.

Commercial fine fragrances normally have 5 to 25% of fragrance oil dissolved in a solvent. Experience indicates that to get an aqueous fragrance, 1 to 2 times the weight of the solubilisers is required to achieve a stable clear solution. A typical spray fragrance formulation will look like this:

Fragrance (deterpenated)	6.0
Solubilisers	9.0
PPG 20 (Antifoam)	0.02
Preservatives/Antioxidants/ UV absorbers/Colour	q.s.
De-ionised water	to 100

Normally the aqueous fragrances obtained have a faint opalescence, the microemulsion remaining clear between 10-40°C. As the fragrance oil percentage increases, the solubiliser requirement will also change for the higher. Sometimes, higher proportion of

solubilisers gives a viscous product not suitable for use in pump spray dispensers. Another important point to be noted is the tendency of the final product to foam in the bottle when relatively high concentration of solubilisers is used in the product formula.

Small amounts of silicone anti-foaming agents when added can reduce high foaming; however the clarity of the solution is disturbed with an increase in opalescence. Use of high molecular weight polypropylene glycol (20M) is better suited for this purpose instead.

Solubilisers used generally are non-ionic surfactants with polyoxyethylene chains. They all exhibit inverse solubility coefficients with temperature (i.e. higher the temperature, lower the solubility). Lower the solubility, lesser the effectiveness of the solubiliser. Solubilisers perform better at lower temperature. However lower temperature limit lies between 5-15 °C just as the higher temperature when the products become insoluble ranges between 35-80°C.

Generally, all fragrance microemulsions are thermodynamically stable. A fragrance solution that is clear at room temperature and becoming cloudy at 50°C or separate at 10°C will again become clear when temperature is brought back to room temperature. This rule is general and only storage studies at various temperature conditions and cycles can provide data on long term adverse effects on emulsion consistency and product stability.

Contrary to general belief that only alcoholic fragrances give better lift to a fine fragrance, water based products also give good diffusion, but after the elapse of a first few seconds of application on our skin. Substantivity and retentivity of the fragrance is comparable to the one obtained by alcoholic fragrances. Although water based fragrances do not necessarily give rise to changes to odour profile, it is essential to control the residual acidity and alkalinity in the final product.

The pH of the formulation should be maintained between 5 and 6. Utmost care has to be taken when use of buffer is resorted to maintain pH levels, as some buffers (e.g., EDTA-Na<sub>2</sub>) themselves can catalyse malodour development in the product.

When water based fragrances have a viscosity of more than 15cps then the pumps used for alcoholic fine fragrances are not suitable and special nylon based pumps may have to be designed.

Water has a slower rate of evaporation as compared to alcohol. This apparent disadvantage can be addressed to by lowering the pump capacity from the usual 150  $\mu$ l to 100 $\mu$ l. The reduced capacity will allow the pump to give a finer spray, which, in turn, will give a better spread on the skin. In any case, the consumer should also be tolerant while using water based fragrance sprays, as it will take a longer time to dry.

Use of solubilisers in the formulation can give a feeling of stickiness during the transitory drying period. However, if correct solubilisers are chosen and levels optimised, excessive stickiness can be avoided. Moreover, this inherent disadvantage can become a marketing claim if consumers perceive a moisturising effect during use. Although solubilisers are specific for a fragrance oil chosen, solubilisers having an HLB value of 11 is optimum. This is achieved by blending solubilisers having lower and higher HLB values. If

products with higher fragrance oil concentration are required then the solubiliser requirement will be higher. The product will naturally be in the form of a viscous cream or lotion. Sometimes solubilisers alone are not sufficient and colloids or soluble acrylic resins may be necessary for solubilising the fragrance oil.

Although water-based fragrance do offer some advantages to conventional alcoholic fragrances, it is also necessary to adhere to some specific requirements. Optimum olfactive stability is achieved by minimising the exposure of the final product to air and oxygen as this invariably leads to rancidity on ageing, even if antioxidants are used in the preparation. Emulsifiers with oleate or ricinolate groups is avoided, as they are prone to get rancid on ageing, especially when the top notes of the fragrance are reduced by natural evaporation.

Creating a successful water based fragrance is a time consuming process. Joint effort and co-operation between the perfumer, development chemist, and the surfactant supplier is of paramount importance if one has to taste success.