Multi-Sensory Technologies for Today's Effervescent Bath and Shower Products

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The more senses a product stimulates, the greater the chances for consumer delight. This paradigm leads product developers to incorporate as many sensory cues in their creations as they can. One of the beauties of effervescent technology is that it is ideally suited to produce bath products that can excite multiple senses. The fizzing sound of the effervescent reaction, the burst of fragrance delivered directly under the bather's nose, the dispersion of color throughout the bath water, and the tactile sensations of emollients both in the water and on the skin after the bath help create high levels of consumer satisfaction. Products that use well known effervescent technology do all of these things quite well. However, recent advances in this basic technology move the possibilities for sensory stimulation to new levels.

Effervescent Technology Basics

Before discussing new technologies, it is worthwhile to review the basics of effervescent chemistry. The chemical reaction is quite simple (INSERT FIGURE 1). An acid is used to neutralize a carbonate salt. This releases carbon dioxide gas, the salt of the acid, and water. Obviously, the carbon dioxide gas is the fizzing that characterizes effervescent products.

There are a few points here that are not so obvious, but are very important. First, water is needed to start the reaction. Without water, neither the acid nor the carbonate can dissociate. If there is no dissociation, the effervescent reaction cannot start. Once the reaction starts, however, it generates more water. This means that effervescent products must be carefully formulated, produced in appropriate environments, and packed properly; otherwise their inherent instability can ruin them.

Specifically, all raw materials used in an effervescent product must be anhydrous and must be stored so that they remain dry. The manufacturing environments where these products are made must also be designed to maintain dryness. Typically these facilities are dehumidified to less than 10%RH. To protect them from ambient humidity, effervescent products are usually packaged in high barrier foil and/or polymer films or in heavy wall jars that contain desiccant packs.

Raw Materials for Effervescent Products

Since it is the source of the carbon dioxide, the carbonate salt is a key material in an effervescent formula.

The most commonly used carbonate salts are sodium carbonate (soda ash) and sodium bicarbonate (baking soda). (INSERT FIGURE 2)

Sodium carbonate has a lower percentage of CO_2 than bicarbonate and since it requires 2 moles of acid per mole of the salt, it is slightly more difficult to neutralize than baking soda. However, these attributes cause products that are formulated with carbonate to be a bit more stable than those that contain only bicarbonate.

Bicarbonate has a higher proportion of CO_2 than soda ash and, due to its ability to easily break down, releasing water, products formulated with it tend to react more quickly and be less stable than carbonate-based products.

Both carbonate and bicarbonate have advantages and disadvantages. Therefore most formulations use a blend of the two. 50/50 is a typical ratio that generally achieves good reaction time and acceptable stability.

Although the sodium salts are the most commonly used carbonates, potassium and magnesium carbonate can be used successfully in effervescent products.

The other key component in an effervescent composition is the acid. It is used to react with the carbonate salt, releasing the CO_2 gas. (INSERT FIGURE 3)

The most commonly used acid is citric acid. It is low cost, easily available, very soluble and since it is trivalent, has good neutralizing power.

Fumaric acid is also frequently used. Even though it is only divalent, fumaric acid is actually a more efficient neutralizer than citric acid on a weight basis. This can be seen by comparing the equivalent weights of these materials. However, fumaric acid is much less soluble than citric acid and thus gives a slower reaction than citric. Probably because of this difference in solubility, fumaric acid products tend to be a bit more stable than citric acid products.

Adipic and malic acids are also commonly used in effervescent bath products.

Again, as in the choice of carbonate salt, the desired product performance and manufacturing method will guide the choice of acid.

Not only will the choice of acid affect performance, but the ratio of acid to carbonate will also affect the product. In general, higher ratios of acid to carbonate will yield faster reactions. Also, higher ratios of acid will assure that the carbonate is completely reacted. If the acid does not at least stoichiometrically balance the carbonate, some carbonate will be left unreacted and it will settle to the bottom of the bathtub. In general, 1:1 weight ratios of acid to total carbonate are common. However, highly reactive, highly soluble systems can use acid to carbonate ratios as low as 1:10.

Beyond the reactive ingredients, aesthetic and functional materials are usually incorporated in effervescent products.

Fragrances and essential oils are virtually always included in these products. Typical levels are 0.5% to 3%. Product design and intended consumer use will guide perfume selection and level.

Most fragrance houses can provide technical assistance in designing perfumes for use in effervescent products. They can formulate the oil to be compatible with effervescent bases by avoiding materials such as glycol solvents that may cause instability to occur by allowing partial dissociation of the acid or carbonate.

Color selection will depend upon the desired product performance and aesthetics. Most cosmetic colors work well in effervescent bases. If the product needs to color the bath water, use dyes. If coloring only the product itself is important, use lakes and/or pigments. Color stability, particularly in light, must be checked carefully.

Functional materials are included in virtually every effervescent product. They key is to choose materials that are anhydrous, otherwise stability problems will occur.

Botanical materials such as freeze-dried aloe, chamomile extract in oil, and even dried flower buds and bulk herbs have been used in effervescent products. Levels used are generally less than 1 or 2%.

Emollient materials such as squalane, vitamin E, almond oil and many cosmetic esters are frequently incorporated, again, generally at 0.1% to 2%.

Surfactants are used both as fragrance emulsifiers and as foamers. When used as emulsifiers, surfactants prevent the perfume oil from floating on the water’s surface. Many consumers prefer this since floating oil systems tend to be messy and hard to clean up. Typical emulsifiers are PEG-30 castor oil, Polysorbate 80 or 85 and Laureth 4. The precise choice will depend on the HLB of the perfume oil.

If surfactants are going to be used to create foam, special formulations are required to achieve consumer acceptable performance. This will be discussed later in this article.

Polymers can also be added to help modify skin feel and the feel of the bath water. Commonly used materials include Polyquaternium 10 and PEG. Levels are typically 0.2% to 3 or 4%.

Binders are almost always needed to make good, solid effervescent tablets. Sorbitol, lactose and maltodextrin are usually used at levels ranging from 10-20%.

Process aides are materials that are added to help the powders flow more efficiently and to prevent sticking on the production equipment. The most frequently used of these materials are fumed silica, calcium silicate, corn starch, and sometimes talc. In general, these materials are work well when incorporated at only a few tenths of a percent.

Production Methods

There are four major methods used to make effervescent products.

Direct compression is the most commonly used method for manufacturing effervescent tablets. It is the simplest and most cost effective of the methods. In this technique, dry materials are blended and then compressed directly on a tablet press or other compression machinery.

Wet granulation requires that some or all of the formula's components be wet with a small amount of a solvent, generally either water or alcohol, during the mixing process. The solvent causes powdery material to aggregate into granules that can be efficiently processed on compression equipment. Since solvent addition can actually start the effervescent reaction, it must be done under very carefully controlled conditions and then the solvent must be completely removed from the mixture. This is done either by oven drying or by vacuum treatment. A secondary benefit of processing effervescent materials this way is that dyes can be used in place of lakes or pigments to color the product itself. The addition of the solvent solubilizes the dye, spreading it evenly in the bulk mixture. Bright product colors can be achieved this way.

Dry molding is the favorite process of the homemade bath bomb producers. In this process, the dry components are mixed with oils, pressed into molds, and then oven dried to bind everything together.

Wet molding, like wet granulation, requires the addition of a solvent. After the solvent is added, the mixture is formed in molds and then allowed to dry either in ambient conditions or in ovens. Both wet and dry molding processes are much like forming wet sand into a sand castle…elegant results are possible, but noticeable flaws occur easily.

Figure 4 compares some key attributes of products produced using the various manufacturing methods. (INSERT FIGURE 4)

Product Forms

Since compression processes are the most economical way to manufacture effervescent products, tableted marbles and disks have become the most common shapes for today's effervescent bath items. Generally, these tablets weigh between 3 to 50 grams. The consumer will use from 1 to perhaps 5 or 6 per bath depending on the size of the tablet and the product concept. Shapes other than disks and spheres are possible with the use of appropriate tooling. Tableted shapes, however, are usually symmetrical and they always have a vertical band around their equators.

Molded shapes are larger than tablets. They can range anywhere from about 75 grams up to 400 grams. The consumer generally uses only one piece per bath. So-called bath bombs, bath balls and bath fizzies are molded shapes. Hearts, flowers, eggs, and other shapes can be molded.

Granules are small pieces of fully formulated product that have been compacted and sized. The advantage to granular products is that it is easy for the consumer to measure and use as much product per bath as she wants. Granules can be easily scooped or poured into the bath where tablets and bath balls are difficult to break into smaller units.

Effervescent bath powders are usually simple raw material blends. Like granules, powder dosage is easy to control. However, since non-compacted powders have high surface areas, they tend to be highly reactive. This makes product stability difficult to achieve with effervescent powders.

Multi-Sensory Stimulation

As mentioned at the beginning of this article, everyone who has spent even a little time working on product formulation and development has learned that the more senses a product is able to stimulate, the more interesting it is to the consumer. And when a product is more interesting to the consumer, it will generate more sales and more loyalty.

One of the beauties of effervescent products is that they are able to stimulate up to 4 senses--scent, sight, touch, and sound-- at one time. Taste can certainly also be stimulated, but that sense is usually beyond the scope of our industry.

Olfactory Stimuli

Scent is the most important of the senses in the cosmetics and toiletries industry. All product developers and marketers have learned that fragrance selection can make or break a product. A well-designed perfume can provide the sensory cue needed to drive a product with marginal technical performance to marketplace success. Conversely, even a product with vastly superior technical performance cannot succeed in the real world if its fragrance does not support its positioning. It is critical that product developers work very closely with their fragrance suppliers to assure that the perfume is excellent fit for the product concept. Otherwise they will not have done justice to all of their technical development efforts.

In the case of bath products, the fragrance has the opportunity to perform several times: it can make the bath water smell nice; it can scent the entire room; it can leave a lingering scent on the skin; and in the case of aromatherapy fragrances, it can provide specific benefits such as calming or invigorating.

Effervescent products are excellent delivery vehicles for fragrances. The CO_2 gas evolved by the effervescent reaction helps lift and disperse aromatic compounds in and around the areas where the product is being used. There are also ways, which will be discussed later, to increase the fragrance lift of effervescent products even further.

Figure 5 (INSERT FIGURE 5) summarizes the fundamental fragrance performance of the various effervescent product forms. Tableted forms like disks and marbles are high density, so they will sit on the bottom of the bathtub as they react. This means that fragrance will be released relatively slowly, perhaps over 2-7 minutes depending on their size. If the product contains an emulsifier, the fragrance will be distributed throughout the bath water. This maximizes the scent of the water itself and provides a product that is not a mess to clean up. If there is no emulsifier, the perfume oil will float on the water's surface. This maximizes its release into the air and the room. It will also maximize the amount of fragrance that remains on the skin. This is because as the bather gets out of the tub, she will pull her body through the layer of perfume oil, leaving a thin film of it on her skin. This is not to say that a non-emulsified perfume oil is required to deliver excellent fragrance performance to the air, room and skin. These performances can be delivered with non-messy emulsified perfumes if they are designed well.

Molded products react much more quickly than tableted products. They also tend to float. This means that the fragrance will be released very rapidly on the surface of the water. A lot of the fragrance will go directly into the air, scenting the entire area. Some of the perfume, will, of course, remain in or on the water, depending on whether an emulsifier is included in the formula.

Granules act a lot like tablets in that they are dense and sink while they are effervescing. However, since they are small, the granules will be pretty much dissolved by the time they hit the bottom of the tub. At most, they will last on the bottom for 30 or 40 seconds. This means that the fragrance release from granules will be very quick. Another important point about fragrance release from granules is that this form allows consumers to easily measure out the amount of product being used. Thus they can control the amount of perfume being used to their personal preference.

Effervescent powders are low density. They basically flash as they hit the water's surface. This gives a very quick burst of fragrance. Like granules, powders are easy for the consumer to vary the amount used.

<u>Maximizing Fragrance Impact</u>

As mentioned earlier, the effervescent reaction, via its generation of CO_2 gas helps propel fragrances into the air and water. This performance can be maximized via a new technology that improves fragrance volatilization from these products.

This formulation approach is called Effervescent/Exothermic technology. It combines an effervescent matrix with a material that gets warm when it gets wet. The resulting combination of fizzing and warmth synergistically boosts the release of volatile materials.

Figure 6 (INSERT FIGURE 6) illustrates how this technology works. Formula 1 is an effervescent/exothermic product. It contains an acid, a carbonate and a material that has an exothermic heat of hydration or solution. In this case the exothermic material is magnesium chloride. It has a heat of solution of about 36 kcal/g-mole. When a 30-gram tablet of this composition was placed in 50 ml of 25^{o}C water, a 29^{o}C temperature rise was observed. This formula's dissolution time was very reasonable at about 7 minutes and the subjective evaluation of the fragrance lift was very good.

In comparison, formula 2 is a standard effervescent product. Here the temperature actually decreased $5^{o}C$. This is not surprising given that the effervescent reaction is endothermic and the release of carbon dioxide gas has a cooling effect. While the 10-minute dissolution time may be a bit long, it should be reiterated that this experiment was conducted at $25^{o}C$, quite a bit cooler than typical bath water temperature (usually around $40^{o}C$). So 10 minutes is not a surprisingly long dissolution time for a 30-gram tablet in cool water. The fragrance lift generated by this product was poor compared to exothermic/effervescent combination.

Formulas 3 and 4 show products that are not effervescent. They simply have the exothermic material in combination with either the carbonate (formula 3) or acid (formula 4). Here the temperature rises, but dissolution times that are so long that the fragrance lift is dramatically diminished. Thus one can see that the combination of effervescence and warming creates a product with improved lift of volatile materials.

Products that utilize this technology should be produced as tablets since they are the easiest form to keep dry. It is even more important to maintain dryness with the exothermic material present than it is with conventional effervescent products since premature hydration of this material will render it unable to perform its function in use.

This technology opens the door for some unique products. For example, it can be used to create effervescent products for the shower. These products would be fragrance tablets that are placed on the floor of the shower which are activated by the constant stream of water that would hit them.. These tablets could be used to deliver aromatherapy oils or room freshening benefits.

Another idea would be to put small tablets into a vase or goblet and use them to fragrance an area. US Patent No. 5,993,854 covers this technology.

Another new technology for improving fragrance delivery from effervescent products takes advantage of the low density of molded effervescent products in combination with a surfactant. It is well known that surfactants' natural tendency to migrate to water/oil, air/water and air/oil interfaces allow them to form lathers or foams. These foams are thin films of surfactant and oil rich water that have large surface areas in contact with air. When surfactants carry fragrance into foam, the perfume oils have large surface areas off of which they can diffuse into the surrounding air. Thus, the foam bubbles help deliver fragrances.

Since molded effervescent products react turbulently on the surface of the water, they can help whip up a foam. Tableted products cannot do this since they react on the bottom of the tub.

Figure 7 (INSERT FIGURE 7) illustrates this effect. As you see, the molded product has a density less than 1, so it will float. It also has a high dissolution rate, greater than a gram per second. The result is a consumer-acceptable foam layer. A tablet made with the same formula as the molded ball has a much higher density and a much lower dissolution rate. It does not create a nice bubble bath.

US Patent No. 6,121,215 covers this technology and International patent applications have been filed.

<u>Visual Stimuli</u>

At the store shelf, product shape, color and texture all contribute to the message that is sent to the potential consumer. In use, many visual performance signals are possible. For instance, water color can be changed, the degree of turbulence that the product has can be chosen, foam can included, and lingering color flecks can be added.

As mentioned previously, coloring effervescent products is straightforward. Dyes, lakes and pigments can be added without trouble. Use of sophisticated manufacturing equipment and techniques can create products that contain multiple colors. For instance, a tablet press that is fed by hoppers of different colored materials can produce striped products. Bilayer tablets can be manufactured in much the same way. Speckled or variegated products can be manufactured by mixing colored granules into the unpressed or unmolded powder. Tablets and molded shapes can be manufactured using these techniques.

Glitter can be added to effervescent products. Metallic glitter gives a sophisticated look to the product, but since it does not dissolve, leaves quite a mess in and around the bathtub. Kids, particularly teenage girls love it; their moms are not so keen on the idea. A solution to this is to use water-soluble glitter. This material is available in many colors. It imparts a sparkly look to the product and does not cause a mess in the tub.

Bulk herbs, botanicals and even dried flowers can be added to molded products. These give an interesting natural look to the product and they create a kind “tea” in the bath water. One concern is that they can create quite a mess. However, if the materials have large enough pieces, they can be cleaned up fairly easily.

Product shape, of course, is easily modified by choosing appropriate tooling. Hearts, eggs, balls, and disks are all common shapes. Shapes as complex as flowers, snowmen and angels have been produced.

In use, there are several ways of enhancing visual appeal. Obviously, as discussed before, dyes can be included to change the color of the bath water.

Foaming products, like the one just discussed, can add to the visual experience. Everyone who has seen a picture of a woman, sitting in the tub, sipping champagne, understands that bubble baths are one of the most well known looks of luxury.

Soluble glitter also provides an interesting in-use look when it is incorporated in the foaming molded product. When used in this product, the colored flecks tend to float on the foam's surface, giving it a speckled appearance. As they dissolve, their color spreads out a bit, giving a "melting" look. Of course, they eventually completely disappear, leaving no mess behind.

Tactile Stimuli

When it comes to bath products, the sense of touch focuses on 2 areas: the feel of the water and the feel of the skin, both during and after product use.

Water effects center on three main areas: foam, emolliency or slip, and the massage feeling of the effervescent reaction. Skin effects include the use of emollients and polymers and the incorporation of materials that can cause the skin to tingle.

In the water, approaches for creating an acceptable foaming product and for adjusting the reactivity of effervescent systems have been covered above. Effervescent product formulators have learned that the feel of the effervescent CO_2 bubbles rising from the product creates a very relaxing environment. Consumers who use effervescent foot and nail soak products particularly appreciate this effect. It is like a mini-massage.

Emollients, humectants and polymers are frequently added to effervescent bathing products. However, developers must remember when any of these materials are added they must be in virtually anhydrous forms. Usage levels for these materials range from 0.5-5%. Commonly added emollients include vegetable oils such as sunflower oil, jojoba oil and almond oil and esters such as IPM and the various benzoate esters. Humectant polymers such as PEG and polyquaternium 10 have been used successfully.

Materials that cause skin tingling sensations are also interesting. Menthol is the most common of these materials. However, one must very careful not to use too much menthol in bath products. The tingling effect might be just a bit too localized. In foot and nail soaks though, menthol provides a very stimulating effect.

For effects on the skin, the materials used are much the same as those used to modify the feel of the water. An additional type of material to consider here is a vasodilator. There is a great deal of published literature that indicates that dissolved CO_2 can act to dilate the skin's surface capillaries. This should provide a feeling of warmth. Literature references regarding this effect are easy to find.

Auditory Stimuli

Hearing is not a sense that is normally aroused by cosmetic products. However, effervescent products have the ability to stimulate this sense. The fizzing sound of these products is an essential part of the experience of using them. Tailoring the effervescent reaction to be fast or slow will affect the audible effect of the product. The sound is part of the fun.

Another type of auditory stimulation can be achieved by utilizing crackling granules. Crackling granules are not effervescent in the sense that they use the acid/carbonate reaction to generate carbon dioxide. However, they are the direct result of carbonation. Crackling granules are created by entrapping pressurized CO_2 in a solid, water-soluble matrix. The matrix is usually composed of an amorphous sugar blend that actually encapsulates the gas. When these granules contact water, the sugar dissolves, releasing the tiny pockets of gas with a lot of noise.

An interesting audible product is a blooming bath oil that incorporates crackling granules. This type of product will disperse a self-emulsifying bath oil that crackles for several minutes. The duration of the sound will depend on the size and quantity of the granules and, of course, the water temperature. Durations of 2-3 minutes are not uncommon, but it can go on for 5-7 minutes. In order to stimulate other senses, the granules and/or the oil can be colored to give interesting effects. A US patent application for this technology has been allowed.

Conclusion

As you can see, effervescent technology opens the door to many multi-sensory product possibilities. New formulation approaches such as exothermic effervescent shower tablets, floating/foaming molded fizz balls and blooming bath oils with encapsulated carbonated granules add multi sensory stimuli to this product category. These technologies can simultaneously arouse the olfactory, visual, tactile and auditory senses to new levels. Thus product formulators and developers now have novel options for creating new product concepts that increase consumer involvement with their creations. The more involvement consumers have, the more delighted they will be.

FIGURE 1

The Effervescent Reaction

Acid + Carbonate Salt → CO_2↑ + Acid Salt + H_20

Ex: Citric Acid + 3NaHCO3 → $3CO_2$↑ + Na_3Citrate + $3H_20$

FIGURE 2

Commonly Used Carbonate Salts

	Na_2CO_3	$NaHCO_3$
Molecular Weight	106	84
Eq. Of Acid to Neutralize	2	1
% CO_2	41.5	52.4

FIGURE 3

Commonly Used Acids

	Citric	Fumaric	Adipic	Malic
Molecular Weight	192.1	116.1	146.1	134.1
Moles of Acidity	3	2	2	2
Eq. Weight	64.05	58.05	73.05	67.05
Solubility (%)	68.6	1.1	1.4	55.8

FIGURE 4

Production Method Comparison

	Direct Compression	Wet Granulation	Dry Molding	Wet Molding
Cost	Lowest	Low	High	High
Product Density	1.6-1.8 g/cc	1.6-1.8 g/cc	0.9-1.1 g/cc	0.9-1.1 g/cc
Dissolution Time	2-7 minutes	2-7 minutes	1-3 minutes	1-2 minutes
Stability	Moisture proof wrap and/or desiccant required	Moisture proof wrap and/or desiccant required	Relatively stable to ambient humidity	Relatively stable to ambient humidity

FIGURE 5

Olfactory Performance by Product Form

Product Form	Performance
Compressed Products	• High Density-Effervesce at Bottom of Tub • Slow Fragrance Release
Molded Products	• Low Density-Effervesce on Water Surface • Rapid Fragrance Release
Granules	• High Density, Small Particle Size Releases Fragrance Quickly while Product Sinks
Powders	• Low Density, Small Particle Size Flashes Fragrance at Water's Surface

FIGURE 6

Exothermic-Effervescent Technology to Improve Olfactory Stimulation

Formula	1	2	3	4
Acid	✓	✓		✓
Carbonate	✓	✓	✓	
Exothermic Material	✓		✓	✓
Temp. Rise (^{o}C)	29	-5	19	9
Dissolution Time	6:57	10:03	29:45	40:32
Fragrance Lift	Very Good	Poor	Poor	Poor

FIGURE 7

Foaming-Floating Technology to Improve Olfactory Stimulation

Process	Density (g/cc)	Dissolution Rate (g/sec)	Foam Acceptability
Molding	0.90	>1.0	Excellent
Tableting	1.43	<0.5	Fair

Possible Sidebar (For insertion near section on olfactory stimuli?)

I learned an important lesson about the power of fragrance early in my career. My first project as a fresh-out-of-college product development engineer involved a possible perfume change for a popular dishwashing liquid. The immediate task was to assess which of two fragrance candidates would be preferred by consumers. I marched out to the pilot plant and mixed up a drum of unfragranced product. I split this batch in two and added perfume A to one half and perfume B to the other half. This way I was sure that both products were identical except for the perfume. My team placed these products in a paired comparison product test. When the results came back a few weeks later, we found that one product was preferred. Not just for fragrance quality, but also for cleaning dishes, cutting grease, foaming enough, on and on--right down the line for all of the important product performance attributes.

The lesson was clear: the choice of the proper perfume has a significant effect on how consumers perceive a product. It can make a marginally performing product a big winner. Or, on the flip side, even a product with excellent technical performance can be hurt in the marketplace if the fragrance doesn't communicate properly. Even with the tight product introduction schedules that all developers face, it is critical to spend significant effort making sure that fragrance screening and selection is truly optimized for the product concept.