Two Challenging Flavor Systems: Citrus Oils and Vanilla Extracts

Delivery options in-use.

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A flavor's composition and physical properties are key determinates when considering a delivery vehicle for its application. Some immediate considerations include customer requirements, competitive costing, any unusual manufacturing requirements as well as product environments the flavor system must meet. Experience with previous, similar technical requests with their development approaches are usually drawn upon to rapidly move toward a best possible flavor and delivery system. Here we will explore two very basic but distinct flavor systems, citrus oils and vanilla extracts, with some delivery options in their use.

A critical issue arising from the presence of the limonene in citrus oils is its susceptibility to oxidation and the formation of limonene oxide (epoxide).

Citrus Oils

Citrus oils are of major continuing importance and interest to flavorists.[1] Orange, grapefruit, lemon, lime, mandarin, blood orange and tangerine citrus oils are obtained in the form of cold-pressed single or folded oils. A key component of these flavor oils is the terpene limonene, which can constitute 40–90% of an individual cold-pressed oil. A critical issue arising from the presence of the limonene is its susceptibility to oxidation and the formation of limonene oxide (epoxide). When the limonene epoxide reaches levels of >2.0 mg epoxide/g limonene, an unacceptable off-flavor sensory threshold level is reached. Serendipitously, the ability to monitor citrus oil deterioration by GLC or HPLC analyses of the epoxide levels has been employed in a number of spray-drying encapsulation studies of cold-pressed orange oils.

Orange oil spray drying variables such as carriers, total emulsion solids, emulsion droplet particle size distributions, and dryer operational conditions were evaluated by G. Reineccius.[2, 3] His summary from these studies was:

> "… generally there are five different factors that are considered to influence the oxidation rate of orange peel oil; pro-oxidants like copper and iron, moisture content or more appropriately water activity [of the spray-dried product], surface oil, entrapped air, and oxygen diffusion into the dried particle due to matrix porosity."[4]

While these initial studies were informative and useful regarding the encapsulation of orange oil by spray-drying, this work did not take into consideration formation of the glassy state as a function of the carrier matrix and process, or in the identification and optimization of specific carrier formulations to increase the glass transition temperature, Tg, of the spray-dried product. The earlier experimental studies used an accelerated storage model at 50°C. However, this test procedure negated any protective function of the gassy state by converting the spray-dried citrus oil powders into the less desirable, more reactive rubbery state. Other spray-dried orange oil stability studies by the author used a lower storage temperature of 37°C.[5] This temperature was still likely to fall into the Tg zone. Without concomitant differential scanning calorimetry (DSC) analyses characterizing both the initial spray-dried powder and storage sample states as related to their glass transition temperatures, only semi-qualitative information on orange peel oil stability as a function of spray-drying carriers and conditions was possible.

Several simple procedures can improve the shelf life of spray-dried citrus oils. The M^{++} and M^{+++} pro-oxidant metals in the carrier aqueous phase can be inactivated by complexing with Na^2 ethylenediaminetetraacetic acid (EDTA). Also, carrier formulations can be designed to produce an increased Tg glassy state using a general formula consisting of a food polymer (gum arabic or octenylsuccinic acid anhydride [OSAN] starch), intermediate weight oligomers (maltodextrins) and lower molecular weight "packing" carbohydrates (maltose, high maltose corn syrups, trehalose). The absence of exposure to UVA and UVB light is also recommended. Significant extension of citrus oil stability by encapsulation with either melt extrusion, melt injection, spray-drying, or freeze-drying can be generated by a sophisticated use of antioxidant systems. Gaseous oxygen, which is dissolved in the emulsion aqueous phase, in the spray-dryer hot air stream, and adsorbed by the dried particles, contributes to the deteriorative process.

The reactivities of each 0_2 molecular form—i.e., the singlet, doublet and triplet states—must be addressed. Each oxygen state requires specific antioxidant agents to prevent the initial molecular reactions leading to limonene epoxide formation. To extend protection, an antioxidant cocktail can be identified and added to the cold-pressed oil before emulsification and spray-drying. Using these techniques, extension of citrus oil storage stability times can be increased by a factor of 5–10x versus untreated, similarly processed oil.

The industry standard for high stability, encapsulated citrus oils employs the melt-injection process originally developed by Sunkist and is now sold by Firmenich under the trade name Durarome. This batch process requires preparing a sugar carbohydrate syrup, boiling off significant levels of moisture, emulsifying the citrus oil into the melt under pressure, injecting fine threads of the oil-melt emulsion into a cold isopropanol solvent bath, recovering the solid flavor and removing residual solvent by filtration and then heating. These products are well-suited for consumer products such as powdered drink mixes and flavored teas. All the original patents of the formulas and process have been in the public domain for many years. However, the inefficient batch process and requirements for handling solvents discourages in-house production by most flavor houses.

A much more efficient process for encapsulating a wide variety of flavor oils involves the melt-extrusion technology.[6] This system can be run continuously to yield much lower operational processing costs. Melt extrusion can generate a glassy matrix for either water-soluble or lipophilic flavor systems. One major issue with melt extrusion of citrus oils is the residual surface oil resulting from the milling and sieving steps of the bulk extrudate preceding packaging. By selecting specific gelatin or hydrolyzed gelatin matrix formulas, surface oil can be reduced significantly.[7] However, the gelatin matrix can also unbalance citrus flavors by interacting with aldehydic or ketonal components of a flavor component such as citral.

Coupling a solvent wash with the melt extrusion process would be a simple route to prepare long shelf life citrus oils. However, modification of the current production process would add semi-batch steps into a continuous system. This would negate the reduced operational costs and decrease production efficiency as well as requiring attendant solvent handling issues. For this reason entry into the somewhat limited product market for citrus oils already established by the Durarome ingredients was not considered.

Some melt-injection processes are well suited for consumer products such as powdered drink mixes and flavored teas; however, the inefficient batch process and requirements for handling solvents discourages in-house production by most flavor houses.

An intermediate approach to inhibiting oxidation of spray-dried orange oil, in which the spray-dried, low-moisture powder is sealed within a gas impermeable polymer pouch, was disclosed by Popplewell et al.[8] Ultimately, though, when this spray-dried powder is placed in a product application, the oxidative deterioration process recommences. In a similar approach carbon dioxide gas can be employed to flush many powders; dried agricultural items; and processed, expanded foods like puffed cereals to exclude air and then sealed in a moisture- and gas-impermeable polymer pouch. That pouch will then shrink fit as a reduced internal pressure results by the mechanism of capillary condensation. This packaging system can also protect a spray-dried citrus oil in a similar manner as noted.

One unusual product request for a citrus oil was in a line of flavored vinegars to complement a food service line of flavored oils. This citrus flavored product was achieved by identifying lemon oil-vinegar-ethanol-surfactant formulas that spontaneously formed a microemulsion (or more correctly a nanodispersion) generating a clear, colored lemon oil "solution." Surprisingly, formation of ethyl acetate by interesterfication of the ethanol and acetic acid was not immediately noted by sensory testing after sitting at ambient conditions. These formulations were disclosed in U.S. Patent 6,077,559.[a]

Other citrus oil encapsulating systems have been evaluated at different times. These include complex coacervation, spray-chilling, and cyclodextrin complexation. The latter system would normally protect the limonene by complex formation while at the same time complexing the oxygenated flavor volatiles within the citrus oil. One approach to complexation by the β-cyclodextrin would employ terpeneless citrus oils to increase the load of flavor actives in the complex.

Vanilla Extracts

One flavor with almost universal appeal is vanilla (extract). Available to the consumer and used in most baked sweet goods, chocolate drinks, ice creams and desserts, its flavor is subtle but most importantly functions as a flavor-enhancing agent with other sensory stimuli. It can also be a base component in many compounded flavor systems.

Several product applications employing vanilla extract and vanillin have resulted in unusual requirements. One customer requested a formulation of a compounded peanut butter flavor emulsion with significant enhanced "vanilla" character. The developed formulas yielded the desired flavor character along with a level of vanillin component. However, vanillin then started to crystallize out of the flavor emulsion. The technical hurdle now became controlling the vanillin state. This problem was not solved in a timely manner to satisfy the customer deadlines and the work discontinued.

Shortly afterward two sophisticated research papers were

[a] SS Logan et al., *Flavored oil-in-vinegar microemulsion concentrates, method for preparing the same, and flavored vinegars prepared from the same*.

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uncovered discussing the solubility and partitioning response of vanillin in the four component system: vanillin-soybean oil-water-surfactant.[9, 10] Multiple three-component phase diagrams were developed, the phases separated and the location and compositions containing vanillin determined. A liquid crystal lamellar phase developed with lecithin acting as the surfactant. The emulsion, made up at 67.8% water, 27.1% oil and 5.1% lecithin, had equal amounts of vanillin in the water, the oil and liquid crystalline phases. This emulsion was characterized with the liquid crystalline phase showing a maximum vanillin solubility of the emulsifier phase 8.0%, the aqueous phase 1.0% and the oil phase 3%. The partition of vanillin between different phases reflected those maximum solubilities before additional vanillin was added or water removed to initiate crystallization. With this model information, the origin of vanillin solubility and crystallization in the peanut butter flavor could have been understood. However, any changes in that formula due to other flavor agents, alternate surfactants, dissolved solutes in the aqueous phase, and the type and properties of the oil phase would all have profound effects on this polydispersed system.

While the physical chemistry of this polydispersed system gave key insights to the partitioning of vanillin in the emulsion, there was no equivalent sensory characterization of the total emulsion or the isolated water, oil and liquid crystalline phases for vanillin character and intensity. In the Friberg studies crystalline vanillin was employed.[10] If a vanilla extract were to be substituted in this study, the ethanol (EtOH) of the extract would alter the interfacial forces within the mixture, most probably leading to a microemulsion (nanodispersion) phase. One obvious alternative in this system would be substitution of folded vanilla extracts to increase vanillin levels while decreasing the EtOH component. The most critical component in terms of sensory effects is the selected emulsifier(s). These surfactants can sometimes contribute significant off flavors, as well as masking or, in unique cases, enhancing effects upon flavor character.

Another request for an "oil-soluble" vanilla was received for use in a flavored lipstick product line. Here again time did not allow adequate research to determine the best delivery system for this request. On the basis of the Friberg papers, a practical approach to render a vanilla extract into a hydrophobic form would be to prepare a hexagonal II (H_{II}) liquid crystal phase. In this mesophase the emulsifier acyl chains form the outer side of cylindrical-shaped aggregates with the inside polar groups surrounding the continuous interior aqueous region (vanilla extract). A starting formula for preparing the preferred H_{II} (or alternately the cubic) liquid crystalline phase might consist of 65% oil, 28% water and 7% of low hydrophilic-lipophilic balance (HLB) emulsifier(s). Once the formula was optimized for the preferred liquid crystalline phase, crystalline vanillin would be added until near saturation of flavorant in all phases was reached.

A major, international consumer products company had a unique issue with a vanillin-containing chocolate drink powder. Samples of bottles stored for extended times had crystals of vanillin forming on the interior of the lid. This response results from the phenomena of sublimation by vanillin molecules. In the same way dry ice goes from a solid to a gas, vanillin molecules, even in an amorphous solid state, can exhibit significant vapor pressure to allow gaseous transport. This dynamic was apparently acting within the product container. The customer placed a request for a delivery vehicle to eliminate this response. Melt-extrusion was employed utilizing a carbohydrate matrix to encapsulate the vanilla flavor. Tests of the encapsulated samples by the customer indicated that the recrystallization phenomena was significantly reduced but still did not meet their product long-term storage specifications.

After flavorists complete their formulations, there are still many issues to be identified as the flavor goes through processing into a delivery vehicle and then ultimately in the final product. Some of these responses are totally unexpected events that can lead to new discoveries and methods for flavor delivery.

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