# Spray Drying of Food Flavors—V

## Factors influencing shelf-life of encapsulated orange peel oil

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It is well documented in the literature (Westing, et al., 1988; Inglett, et al., 1988; Anandaraman and Reineccius, 1986) that flavor stability is very dependent upon the carrier material used in encapsulation. While encapsulated flavorings may be stabilized against oxidation through the use of antioxidants, market demands for "all natural" or "no preservatives added" make this route unattractive. It is desirable to obtain at least one year shelf-life of encapsulated flavorings without the use of any food additives.

Anandaraman and Reineccius (1986) have demonstrated that excellent stability of spray dried orange peel oil can be obtained using high dextrose equivalent (DE) corn syrups as the carrier matrix. However, high DE corn syrups lack any emulsification properties, may become caked during storage and provide poor flavor retention in the drying operation. It is desirable to determine the properties of the flavor carrier that influence shelf-life so that better carriers can be developed.

This study investigated the influence of trace pro-oxidants (e.g., copper and iron), surface oil, entrapped air and absolute density on the shelf-life of spray dried single fold orange peel oil.

### Materials and Methods

Gum Arabic (Colloides Naturels, Far Hill, NJ), Capsul (tradename of product from National Starch and Chemical Corp., Bridgewater, NJ), M100 and M365 (DE of 10 and 36.5, respectively from Grain Processing Corp., Muscatine, IA) were used as carriers. The carriers were rehydrated in water with some heating required. The carriers were prepared both with and without orange oil. The infeed solids are shown in Table I. Single-fold orange peel oil (Sunkist Growers, Inc., Ontraio, CA) without any antioxidants was added to the carrier solution to give a carrier to flavor ratio of 4:1.

**Table I. Infeed Solids Levels of Different Carriers**

| | With Oil | Without Oil |
|---|---|---|
| Gum Arabic | 25% | 30% |
| Capsul | 36% | 40% |
| M100 | 41% | 45% |
| M365 | 60% | 70% |

The solutions were homogenized immediately prior to spray drying using a Greerco laboratory high sheer mixer. The infeed solids levels were selected so that the viscosities were approximately the same (approx. 300 cps.). The samples were spray dried in a Niro Utility drier with the inlet temperature at 200°C and the outlet at 100°C. The dried samples were analyzed for total oil, surface oil, and


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moisture. The samples dried without oil were analyzed for prooxidants and were also used for the density measurements. The samples with oil were stored at 37°C and sampled every other day for shelf life determination.

*Total Oil.* Total oil was determined by using a Clevenger apparatus. Twenty grams of sample were added to 150 ml of water in a 500 ml flat bottom flask. The samples were mixed until dissolved and then boiling stones and an antifoaming agent were added. The mixture was distilled for three hours and the volume of oil was read directly from the sidearm of the Clevenger apparatus after it cooled to room temperature. The volume of oil was converted to grams by multiplying by the density of orange oil (0.83 g/ml).

*Surface Oil.* The amount of extractable oil on the dried powder was determined by Soxhlet extraction. Twenty grams of powder were weighed into an extraction thimble and covered with glass wool. The powder was extracted with 200 ml of pentane for four hours. An internal standard (2.5 mg/ml 2-octanone) was added to the extract prior to evaporation under nitrogen. Each extract was evaporated to a volume of approximately 1 ml. The amount of oil in the concentrated extract was determined by gas chromatography (Anandaraman and Reineccius, 1987). The instrument parameters were the same as those described later for the shelf life study.

*Moisture.* Moisture was determined by the toluene distillation method (Anandaraman and Reineccius, 1987). Forty grams of sample were weighed into a 500 ml flat bottom flask with 175 ml toluene. Boiling stones and antifoam were added. The flask was fitted with a Bidwell-Sterling trap and the sample brought to a boil on a hot plate. The distillation was carried out for three hours after which time the sample was allowed to cool to room temperature. The volume of water was read directly from the trap.

*Mineral Testing.* The samples dried without oil were submitted to the Soil Science Department at the University of Minnesota for mineral testing. The amount of copper and iron in each of the carriers was determined by Inductively Coupled Plasma (ICP).

*Absolute Density.* The absolute density of the bulk powders was determined using a volume displacement method (Buma, 1966). A 100 ml volumetric flask was weighed and then ten grams of spray dried carrier was added. Heptane was added and a partial vacuum was pulled to remove any air bubbles. The flask was filled carefully to the 100 ml volume line with more heptane, taking care not to add air bubbles. The full flask was weighed again and the density of the particles calculated based on the weight (volume) of heptane added to the flask.

*Shelf Life.* Approximately 200 grams of each powder were stored in screw cap test tubes in a 37°C incubator. Approximately two grams were removed every other day and stored in a freezer (−20°C) until analysis by gas chromatography (GC). The products were monitored for the formation of limonene-1,2-epoxide, an oxidation product of d-limonene (Anandaraman, 1984). Briefly, this involved dissolving 0.15 g of powder in 0.85 g $H_2O$. Four ml acetone, containing .25 mg/ml 2-octanone, was then added slowly with agitation. The sample was allowed to settle and a 1 ul aliquot of the liquid phase was injected into the GC. A Hewlett Packard model 5880 gas chromatograph was used. The following conditions were used:

Column: 12 m x .2 mm x .33 um HP-1 (Hewlett Packard, Avondale, PA)
Carrier gas: Hydrogen
Column head pressure: 12.5 psig
Split ratio: 1:30
Oven temperature profile:

| | |
|---|---|
| Initial temperature: | 70 C |
| Initial time: | 0 minutes |
| Program rate: | 10 C/min. |
| Final temperature: | 190 C |
| Final time: | 7 minutes |

Detector: FID

*Scanning Electron Microscope (SEM).* A Philips 500 SEM was used to view particle structure. This was accomplished by imbedding the capsules in an epoxy resin, allowing the resin to cure, and then cutting a fine edge using a microtome. The resins then were mounted on stubs using double stick tape and a carbon paint. The sample was made conductive by applying a thin layer of gold to its surface. The samples were examined in the secondary electron imaging mode at an acceleration voltage of 25 kV. All photographs were taken at a magnification of 1250X.

## Results and Discussion

The results of the shelf life test on the spray dried orange oil in the different carriers are shown in Figure 1. It has been shown from sensory analysis by Anandaraman (1984) that the shelf life of encapsulated orange peel oil is over when limonene oxide, an oxidation product of orange oil, reaches the level of approximately 2 mg/g oil. An interesting point to note is that Capsul, a modified starch sold

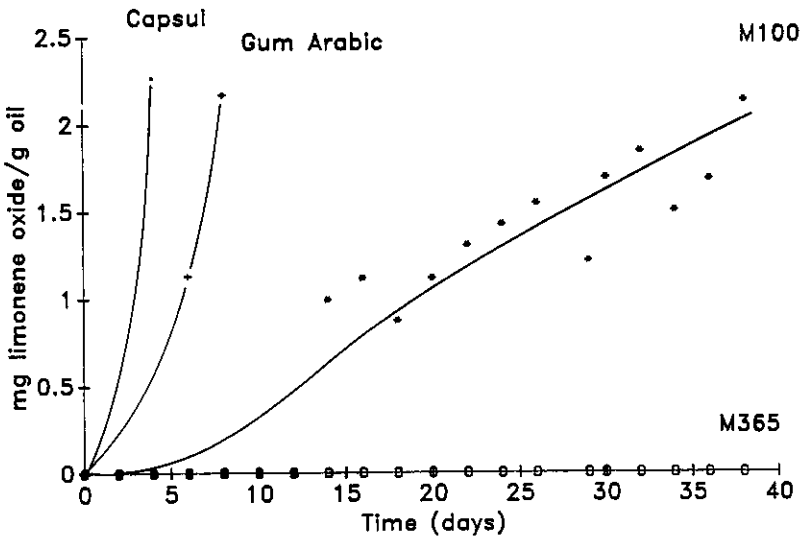


**Figure 1. The formation of limonene oxide in orange oil which has been spray dried in various encapsulating matrices (stored at 37°C).**

for the purpose of encapsulation, reaches the level of unacceptability after only four days at 37°C while M365, a corn syrup solid, showed no limonene oxide after nearly 40 days under the same conditions. The explanation of this shelf life data was the goal of this research. If a definite cause of the ending of shelf life could be determined, the challenge of finding an improved carrier system would be greatly reduced. Generally there are five different factors that are considered to influence the oxidation rate of orange peel oil; prooxidants like copper and iron, moisture content or more appropriately water activity, surface oil, entrapped air, and oxygen diffusion into the dried particle due to matrix porosity.

Copper and iron are commonly known as effective catalysts in promoting oxidation (Newhall and Kesterson, 1961). The prooxidant content of the carriers are shown in Table II. A substantial range is observed with gum arabic having the highest levels of both copper and iron.

While there appears to be somewhat of a relationship between copper content and shelf life, the very low copper levels and outlying point at .17 ppm make this relationship very questionable. The apparent relationship for the first three points is more than likely coincidental rather than valid.

While one could suggest that samples with lower iron content have a longer shelf life, it is obvious that this relationship is also very weak and factors other than iron content are playing a much greater role in determining shelf life.

Anker and Reineccius (1988) have shown that water activity influences the oxidation rate of encapsulated orange peel oil. They found that the higher the water activities (up to 0.51) gave a longer shelf life. While we have not determined water activities for our samples, moisture contents are shown in Table II. There is no relationship observed between moisture content and shelf life in this study.

Surface oil has long been believed to be the determining factor for the shelf life of spray dried flowers (Brenner. 1983). The current data do not support this theory. The results presented in Table II show that gum arabic has over 4X the surface oil

**Table II. Results of analysis on encapsulated orange oils**

| | Encapsulating Matrix | | | |
|---|---|---|---|---|
| | Gum Arabic | Capsul | M100 | M365 |
| Copper (ppm) | 1.52 | .81 | .55 | .17 |
| Iron (ppm) | 8.11 | 5.51 | .92 | 1.38 |
| Moisture content (%) | 4.55 | 2.64 | 3.36 | 1.97 |
| Surface oil (mg/100 g powder) | 397.50 | 123.40 | 36.60 | 11.00 |
| Absolute density (g/ml) | 1.06 | .93 | 1.28 | 1.36 |
| Shelf life (days)[a] | 24 | 4 | 38 | >42[b] |

[a] Sampling period where limonene-1,2-epoxide first exceeded 2 mg/g limonene.

[b] After 42 days of accelerated shelf life testing there was no limonene-1,2-expoxide detected.

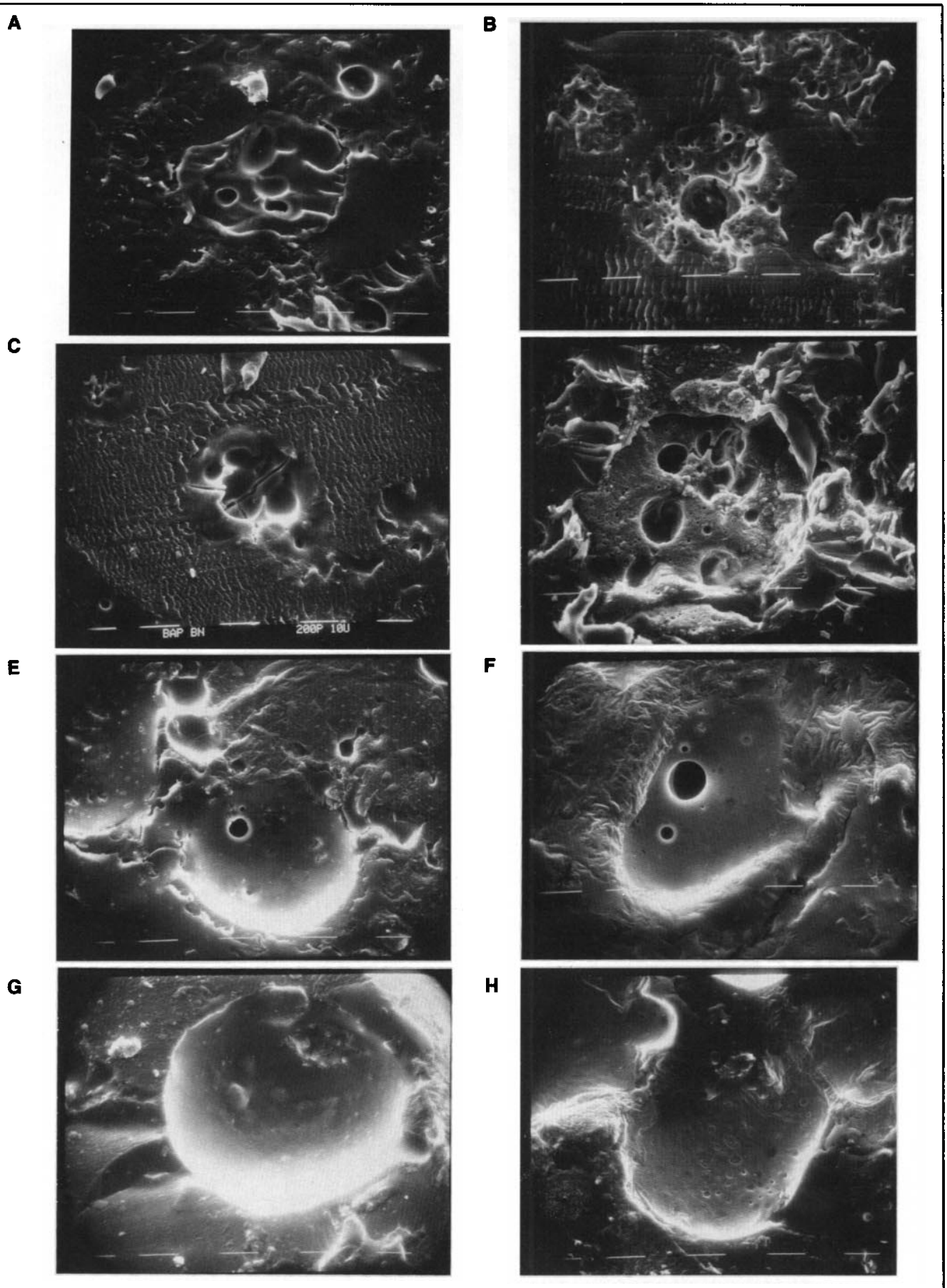


**Figure 2. Scanning electron micrographs of the encapsulated orange oils and encapsulating materials. A. Gum arabic; B. Gum arabic with orange oil; C. Capsul; D. Capsul with orange oil; E. Maltrin M100; F. Maltrin M-100 with orange oil; G. Maltrin M-365; H. Maltrin M-365 with orange oil.**

of Capsul. If this were the determining factor, one would expect that gum arabic would have ¼ the shelf life of Capsul and that is definitely not the case. Therefore, it does not appear that surface oil is playing a significant role in determining the shelf life of the encapsulated orange oil.

The next factor to consider is oxygen availability for oxidation. Air may be incorporated into the dry product in two ways: it may come from air being incorporated into the infeed matrix, e.g. via foaming during reconstitution of the dry matrix (we do not vacuum treat the infeed material), or it can be incorporated into the droplet at the time of atomization. This air could theoretically be the cause of oxidation of the encapsulated flavor. The amount of entrapped air was calculated by absolute density measurements and was observed visually by Scanning Electron Microscope (SEM) observation. As shown in Table II, there is a difference in absolute densities between the spray dried carriers. The SEM photographs verify the varying amounts of entrapped air with the different carriers (see Figure 2). When the shelf life was plotted against the absolute density (see Figure 3) a relationship was observed. This raised the question of whether the difference in absolute densities was a factor because of the entrapped air or because the density differences meant there were differing degrees of porosity between the carriers.

A calculation was made to answer this question. From the work of Anandaraman (1984), we know that approximately 3.5 ml of $O_2$ is needed per gram of oil to permit sufficient oxidation to end shelf life. From this current research, the volume of oxygen that is entrapped in the particle was calculated. The values were .33 ml $O_2$/g oil for Capsul, .27 ml $O_2$/g oil for gum arabic, and 0.077 ml $O_2$/g oil for M100. The M365 had virtually no entrapped air. Therefore, the amount of oxygen entrapped in the matrix during drying is not sufficient to cause the oxidation of the encapsulated oil.

We hypothesize that the diffusion of oxygen through the matrix of the spray dried particle is an important variable influencing the oxidative stability of spray dried citrus oils. Since there is no relationship between surface oil content and shelf life (within limits of good drying practice), oxygen must reach the oil which is enclosed within the dry particle. Also since our calculations show there is not sufficient entrapped oxygen to cause oxidation, oxygen must diffuse through the dry matrix to reach the citrus oil. We feel it is this variation in oxygen permeability which accounts for the differences in shelf life that we observed in this study.

Future work on this project will attempt to measure oxygen diffusion rates in different encapsulation matrices.

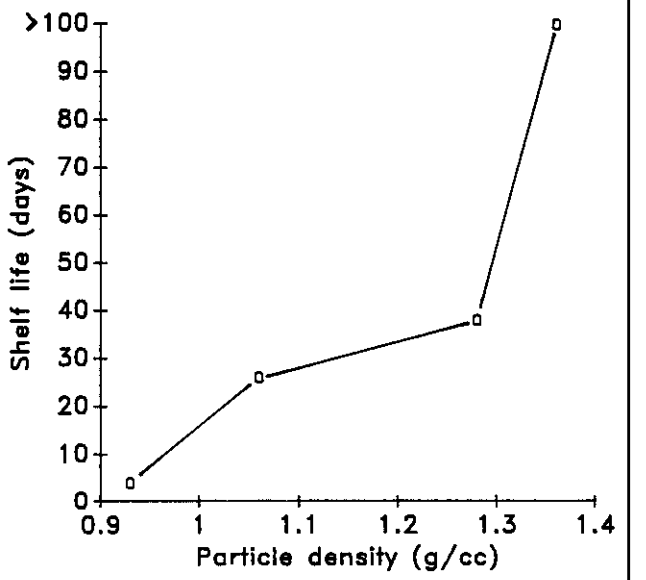


**Figure 3. The relationship between shelf-life of encapsulated orange peel oil and absolute density.**

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