

# Optimization of Gum Acacia/ Modified Starch/Maltodextrin Blends for the Spray Drying of Flavors

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**E**ncapsulation is the process by which one material or mixture of materials is coated with or entrapped within another material or system. The encapsulation of flavors serves to retain the aroma in a food product during storage, protect the flavor from undesirable interactions with food, minimize flavor/flavor interactions, guard against either light-induced reactions or oxidation, and to effect a controlled release. This occurs at a later state during processing, storage or final preparation prior to consumption.<sup>18</sup>

Spray drying largely dominates the market for the encapsulation of flavors. Carbohydrates, such as hydrolyzed starches, emulsifying starches and gums (essentially gum acacia), serve as the most common carrier materials.<sup>16,17</sup> Hydrolyzed starches include maltodextrins and corn-syrup solids. These materials are inexpensive, bland in flavor, very soluble (up to 75%), and exhibit low viscosity in solution.<sup>6,7</sup> Their major shortcomings are a virtual lack of emulsifying capacity and marginal retention of volatiles.<sup>16</sup> Hydrolyzed starches vary greatly in protecting encapsulated flavors from oxidation. There is a strong dependence of oxidative stability on the dextrose equivalent (DE) of the product. Because of this, oxygen uptake decreases as DE increases.<sup>2</sup> They may be labeled natural only if produced via enzymatic hydrolysis.<sup>18</sup>

Emulsifying starches have been partially hydrolyzed and derivatized to impart lipophilic properties. The lipophilic group added to the starch backbone comes from the reaction with 1-octenyl succinic anhydride at a 0.02 degree of substitution.<sup>12,5</sup> These modified starches provide excellent volatile retention and emulsification properties.<sup>8,27</sup> Their main drawbacks include potential off-flavors, higher

cost, and poor flavor protection against oxidation.<sup>16</sup> In addition, modified starches are not considered natural and may not be permitted for food use in some countries.<sup>18</sup>

Gum arabic (gum acacia) has been the standard of excellence as a flavor encapsulating material for many years. It is an excellent emulsifier, bland in flavor, and provides good retention of volatiles during the drying process.<sup>25,26</sup> While in past years cost and availability of gum acacia have been important concerns, these issues are less important today due to systematic cultivation.<sup>19</sup> The gum also has the advantage of being considered natural in most countries.<sup>18</sup>

It is evident from the above discussion that gum acacia represents a good compromise among encapsulating materials in terms of the desirable attributes expected in the resulting powder. However, blends of gum acacia with maltodextrins and/or modified starches may represent an encapsulating matrix with improved properties regarding flavor retention, emulsion stability and protection against oxidation. Although previous researchers have already investigated blends of gum acacia with maltodextrins and/or modified starches,<sup>23,26,20</sup> none of them undertook a systematic, statistically rigorous approach in order to define optimum combinations among the blends. This study is original in contemplating this key aspect through the utilization of a mixture-experimental design. In addition, this study evaluates a commercial modified starch, Hi-Cap,<sup>a</sup> as an encapsulation agent for the first time.

<sup>a</sup> Hi-Cap, National Starch & Chemical Co., Bridge-water, NJ

## Materials

A commercial spray-dried gum acacia ([RD 436] (Acacia senegal)<sup>b</sup> was provided. Hi-Cap 100, a modified food starch, and Maltrin-200,<sup>c</sup> a 20 DE maltodextrin, were also supplied. The encapsulated material was cold-pressed orange oil; Valencia (Florida).<sup>d</sup> Pentane, hexane and

<sup>b</sup> RD436, Colloïdes Naturels International (Bridge-water, NJ)

<sup>c</sup> Maltrin-200, Grain Processing Corp., Muscatine, IA

<sup>d</sup> Cold-pressed Valencia orange oil, Robertet Flavors, Piscataway, NJ

acetone,<sup>e</sup> and limonene and 2-octanone,<sup>f</sup> were used as either solvents or standards, as mentioned above.

## Proximate Analysis

Gum acacia, modified starch and maltodextrin were analyzed for moisture and mineral content. Moisture was determined in triplicate by the Karl Fisher titration (as described by Bradley and Labuza)<sup>4,10</sup> using hot extraction and an Aquatest CMA Seradyn titration unit. Qualitative/quantitative analysis of minerals was performed by atomic emission spectroscopy (AES) according to the AOAC method, 985.01<sup>3</sup> using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) apparatus.<sup>g</sup> Samples were run in duplicate.

## Emulsion Preparation and Spray Drying

Carriers were separately rehydrated overnight and then gently heated at 60°C in a water bath<sup>h</sup> to allow complete dissolution. Blends of carriers, described in the experimental design below, were prepared by directly mixing the components at the corresponding concentrations. Solutions were allowed to cool to room temperature before storing under refrigeration (4°C) until emulsion preparation. Orange oil was emulsified into the hydrated carrier blends immediately before spray drying, using a bench-top high-speed mixer<sup>i</sup> connected to a rheostat at 60% of full power for 7 min. Emulsions were then spray-dried with a Niro Atomizer Utility model drier.<sup>j</sup> Inlet and exit air temperatures were 200 and 100°C, respectively. Powders were stored at 4°C until analysis. Moisture content of carriers was taken into consideration to prepare the carrier solutions so to get an accurate concentration.

## Experimental Design

An augmented simplex-centroid mixture design was chosen to evaluate the blends of gum acacia, modified starch and maltodextrin as encapsulation carriers.

<sup>e</sup> Pentane, hexane and acetone, Fischer Scientific, Pittsburgh, PA

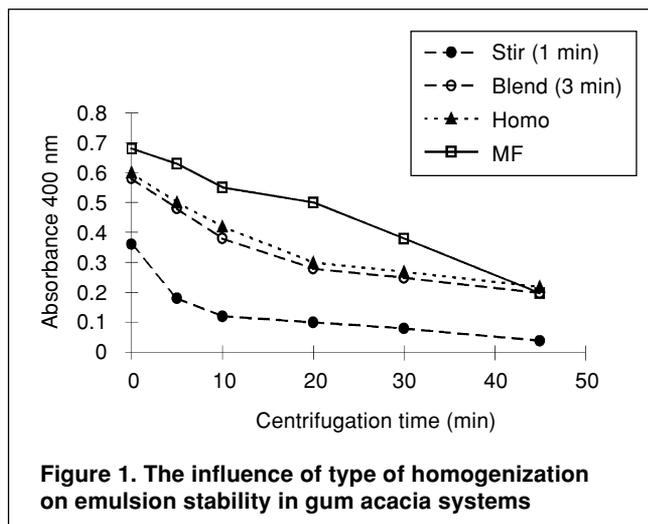
<sup>f</sup> Limonene and 2-octanone, Sigma Chemical, St Louis, MO

<sup>g</sup> Inductively coupled plasma atomic emission spectroscopy, Applied Research Laboratories Inc., Dearborn, MI

<sup>h</sup> water bath, Precision Scientific Co., Chicago, IL

<sup>i</sup> Grifford-Wood mixer, Greerco Corp., Hudson, NH

<sup>j</sup> Niro Atomizer, Ramsey, NJ



Mixture experiments are a special case of response-surface experiments in which the response depends only on the proportion of the various components rather than on their absolute amounts (Oehlert, 1997).

If  $x_1$ ,  $x_2$ , and  $x_k$  are the variables representing the proportions of the  $k$  ingredients or

$$\sum_{i=1}^k x_i = x_1 + x_2 + \dots + x_k = 1$$

components of the mixture, the values of the  $x_i$  are constrained such that,  $0 \leq x_i \leq 1$ , with  $i = 1, 2, k$ , and the proportions of the  $k$  ingredients in the mixture sum to unity. A three-component augmented simplex-centroid design with its corresponding coded values (i.e., the proportions of the components in each blend over the triangle) is shown in Figure 1.<sup>9</sup>

In addition, many mixtures require some or all components to be present in at least minimum proportions. Lower bounds  $L_i$  on component proportions impose the constraint:

$$0 \leq L_i \leq x_i \leq 1$$

To simplify the construction of the design coordinates, a set of pseudo components are constructed by coding the original component variables to a simplex coordinate system for the pseudo component's variables  $X_i$ , with constraints  $0 \leq X_i \leq 1$ . If the lower bound for component  $i$  is  $L_i$  and  $L = \sum L_i$ , then the pseudo-component  $X_i$  is computed as:

$$X_i = \frac{x_i - L_i}{1 - L}$$

The proportions of the original components required for mixtures in the experiment can be derived by the reverse transformation once the  $L$  boundaries have been established.<sup>9</sup>

$$x_i = L_i + X_i(1 - L)$$

Because the main objective of this study was to investigate a potential replacement of gum acacia with other carriers, a lower bound  $L = 25\%$  was established for gum acacia (25-100% range), whereas modified starch and maltodextrin were given a lower bound  $L = 0\%$  (0-75% range). The complete design for the experiment is shown in Table 1 with values for the pseudo-component coordinates and the resulting components in the sub-region of the original simplex-centroid. Design points in the delimited periphery of the triangle were replicated once, and those in the centrum, twice.

### Determination of Optimum Infeed Solids

Based on the fact that carrier blends throughout the mixture design would have different viscosities depending upon components, it was decided that all mixtures would be formulated to have a viscosity of 250 cp. In order to define the concentration that would give this viscosity value for each combination, a preliminary experiment was run in which the viscosity of each blend was measured at least five times within a concentration range of 20-50% after homogenization, using a bench-top high-speed mixer at 50% of full power for 10 min. A first-order model, being the best match for all data points, was then fit using the water analyzer series-reaction kinetics program,<sup>11</sup> and the

**Table 1. Resulting Coordinates of Mixture Experiment in the Sub-Region defined by Pseudo-Components**

Coordinates	Gum Acacia (%)	Modified Starch (%)	Maltodextrin (%)
<b>Periphery</b>			
(1, 0, 0)	100	0	0
(0, 1, 0)	25	0	75
(0, 0, 1)	25	75	
(1/2, 1/2, 0)	62.5	0	37.5
(1/2, 0, 1/2)	62.5	37.5	0
(0, 1/2, 1/2)	25	37.5	37.5
<b>Centrum</b>			
(1/3, 1/3, 1/3)	49.75	25.125	25.125
(4/6, 1/6, 1/6)	74.50	12.75	12.75
(1/6, 4/6, 1/6)	36.25	51	12.75
(1/6, 1/6, 4/6)	36.25	12.75	51

concentration at viscosity = 250 cp computed from the corresponding fitting equation. The first-order model for viscosity was characterized by the following equation:

$$\ln \eta = k_1 C$$

where  $C$  is concentration (%),  $\eta$  viscosity, and  $k_1$  the first-order rate constant. Obviously, the viscosity is that of deionized water ( $\cong 1$  cp) at  $C = 0$ . Viscosity measurements were performed using a rotational viscometer.<sup>k</sup> Concentrations of orange oil in the emulsions were pre-defined as 1/4 of the corresponding carrier blend concentration in the starting solution (carrier-to-flavor ratio 4:1).

### Measurements and Computation: Flavor Retention

Total oil in the spray-dried powders was determined by Clevenger distillation. Twenty grams of powder were dissolved in 150 ml of deionized water in a 500 ml round-bottomed flask. Sonication was applied for 5 min in order to break powder clumps and facilitate dissolution. Boiling chips and approximately 0.5 ml of anti-foam solution<sup>l</sup> were added. The Clevenger apparatus was fit to the top of the flask with an ice water-cooled condenser on top of it. The solution was distilled for 3 h. The volume of the oil, read directly from the oil collection arm, was converted to grams of oil by multiplying by the density of the oil, 0.85 g/ml.<sup>20</sup>

Flavor retention was computed according to the expression:

$$\text{FlRet}(\%) = \frac{W_{\text{oil}}}{\text{ThRet}} \div 100$$

<sup>k</sup>Rotovisco, Haake Inc., Saddle Brook, NJ

<sup>l</sup>Antifoam solution, Fisher Scientific, Pittsburgh, PA

Where  $FlRet$  is the flavor retention,  $W_{oil}$  the actual weight of orange oil in the powder and  $ThRet$  the theoretical quantity of oil in the powder (i.e., 4 g of oil in 20 g of powder).

### Surface Oil

To determine the amount of extractable oil on the surface of the dried powders, 20 g of sample, 150 ml of pentane and 1 ml of a stock solution of 2-octanone in pentane (2 mg/ml) as an internal standard were placed in a volumetric flask and shaken overnight to extract the oil.<sup>m</sup> The extract was filtered<sup>n</sup> to separate the powder and evaporated to 1 ml under nitrogen. The amount of oil in the sample was determined by gas chromatography using a Hewlett Packard HP 6890 chromatograph<sup>o</sup> under the following conditions: column: HP-5<sup>p</sup> (Crosslinked 5% Ph Me Silicone); carrier gas: helium; column head pressure: 15 psi; split ratio: 1/60; oven temperature profile: initial temperature: 50°C, initial time: 0 min, program rate: 10°C/min, final temperature: 190°C, final time: 2 min; detector: flame ionization detector; injection volume: 1  $\mu$ l.

Determination was based on the detection of limonene, by far the most abundant component of orange oil, according to the following formula:

$$Lim = \frac{IS_{am}}{IS_{area}} \div ArLim \div RRF$$

Where  $Lim$  is the amount of limonene,  $IS_{am}$  the amount of internal standard,  $IS_{area}$  the area of internal standard,  $ArLim$  the area of limonene peak and  $RRF$  the relative response factor of limonene to 2-octanone as the internal standard. Surface-oil values were expressed as mg of surface oil per 100 g of spray-dried powder.<sup>22,19</sup>

### Moisture

Moisture of the powders was determined by the Karl Fisher titration method as described by Bradley and Labuza,<sup>4,10</sup> using hot extraction and an Aquatest CMA Seradyn titration unit (Japan). Samples were run in triplicate.

### Absolute Density

Absolute density of powders was determined following gas displacement principles<sup>15</sup> with a multi-pycnometer.<sup>q</sup>

### Emulsion Stability

A 0.2% solution of each spray-dried powder was prepared in deionized water and its stability monitored by absorbance at 500 nm, as measured using a Beckman DU 530

spectrophotometer.<sup>r</sup> Readings were taken until disappearance of 90% of initial absorbance, or until a week from first reading (time = 0), whichever happened first. A 0.16% solution of carrier (gum acacia) was used as a blank for absorbance measurements, based on a carrier-to-flavor ratio of 4:1. Absorbance-vs-time data for each sample was fit to a first-order model using the water analyzer series-reaction kinetics program. The first-order model was characterized by the following equation:

$$\ln A = \ln A_0 - k_1 t$$

Where  $t$  is time,  $A$  absorbance at time =  $t$ ,  $A_0$  absorbance at time = 0 and  $k_1$  the first-order rate constant.<sup>24</sup> Emulsion stability end-point or, time to breakage, was computed from the above fitting equation at  $A = 0.1A_0$ . In order to differentiate statistically between zero and first order, it is imperative to go beyond 50% of disappearance of the monitoring parameter.<sup>24</sup> This was in fact the fundamental criterion to evaluate emulsion shelf life. Absorbance values were the average of two consecutive readings. Single determinations of emulsion shelf life were conducted across samples.

### Shelf-Life Study

Samples of each powder were stored in screw-cap test tubes in an incubator at 37°C and withdrawn at days 0, 2, 4, 7, 12, 19 and 30. Pulled samples were stored at -20°C until analysis by gas chromatography for limonene-1,2-epoxide, a typical oxidation product of d-limonene.<sup>1</sup> A 0.15 g sample of powder was dissolved in 0.85 g deionized water. Then 4 ml of an acetone solution containing 0.25mg/ml 2-octanone was added slowly with agitation. The sample was allowed to settle and a 3 $\mu$ l aliquot of the liquid phase was injected into the gas chromatograph<sup>s</sup> under the conditions aforementioned for surface-oil determination, with the exception of the split-ratio (1/30).

End of shelf life was taken as the point at which limonene-1, 2-epoxide was greater than 2.0 mg/g limonene.<sup>1</sup> For each sample of carrier-blend combinations, the ratio between limonene epoxide and limonene was obtained by dividing the corresponding chromatographic peak areas and multiplying by 1000. A zero-order reaction model, considered the best match for all data points, was fit using the water analyzer series-reaction kinetics program, and the end of shelf life computed from the corresponding equation. Zero-order reaction was characterized as:

$$A - A_0 = k_0 t$$

<sup>m</sup> Orbit Shaker No. 3590, Lab-Line Instruments Inc., Melrose Park, IL

<sup>n</sup> Whatman filter paper #3, W&R Balston Ltd., England

<sup>o</sup> Hewlett Packard HP 6890 chromatograph, Hewlett Packard, Wilmington, DE

<sup>p</sup> HP-5, Hewlett Packard, Wilmington, DE

<sup>q</sup> Multi-pycnometer, QuantaChrome Corp., Boynton Beach, FL

<sup>r</sup> Beckman DU 530 spectrophotometer, Beckman Instruments, Schaumburg, IL

<sup>s</sup> Gas chromatograph, Hewlett Packard HP 6890, Hewlett Packard, Wilmington, DE

Where  $t$  is time,  $A_0$  shelf-life at time = 0 (mg limonene epoxide per g limonene),  $A$  shelf-life at time =  $t$ , and  $k_0$  the zero-order rate constant.

### Statistical Analysis

If the three components  $x_1$ ,  $x_2$  and  $x_3$  of a mixture experiment were mutually independent, the equation to approximate a quadratic response surface would be:

$$y = x_1 + x_2 + x_3 + x_1^2 + x_2^2 + x_3^2 + x_1x_2 + x_1x_3 + x_2x_3$$

However, based on the restriction:

$$x_1^2 + x_2^2 + x_3^2 = 1$$

the above equation is reduced to:

$$y = x_1 + x_2 + x_3 + x_1x_2 + x_1x_3 + x_2x_3 - 1$$

which is still a quadratic model subjected to a specific restriction.

Regression analysis was run for this model against all six responses (moisture of powders, density of powders, flavor retention, surface oil, emulsion stability and shelf life) to evaluate its overall fitness ( $r^2$  value) as well as analysis of variance to assess the significance of individual terms (p-value). Mixture components acacia, starch and maltodextrin ( $x_1$ ,  $x_2$  and  $x_3$ , respectively) were introduced in the model through their coded, rather than absolute, values. Location of the stationary point in the quadratic surface was achieved by canonical correlation for which two components of the mixture, acacia and starch, were run against all responses. The third component, maltodextrin, was essentially defined in terms of the first two components, as aforementioned.

The absolute stationary point, a maximum, minimum or saddle point, could fall inside or outside the experimental range defined by the periphery of the triangle. Nevertheless, the ultimate objective was to find maximum and minimum responses within the triangle. In other words, local points in the specific region of the overall surface delimited by the mixture triangle. From the coded values for acacia and starch at the location of maximum and minimum points, coded maltodextrin was evidently computed as:

$$\text{coded maltodextrin} = 1 - \text{coded acacia} - \text{coded starch}$$

Finally, all coded values were converted back to their actual values, and the response at maximum and minimum points computed from the corresponding regression equation. Statistical analyses were performed with the MacAnova statistical package (Oehlert and Bingham, 1997).

### Results and Discussion: Moisture

Although all linear terms were highly significant in the regression equation, only one cross-product, acacia \* maltodextrin, showed a marginal significance at the 90% confidence level (Table 2). Canonical correlation indicated the existence of an overall saddle point with coordinates (2.16, -2.08, 0.92), only of theoretical value but not feasible physical existence due to the negative coefficient for starch. Within the experimental range, the quadratic surface predicted a maximum at coordinates (1, 0, 0), that is, 100% gum acacia and 0% modified starch and maltodextrin, and a minimum at coordinates (0, 0.57, 0.43), corresponding to 25% gum acacia, 42.75% modified starch and 32.25% maltodextrin. Predicted response values for the maximum and minimum points were 5.00% and 1.85%, respectively (Figure 2). In general, those combinations richer in gum acacia had a higher moisture content after spray drying. Beyond the experimental fact that gum

acacia showed twice as high initial moisture content as any other mixture component (Table 3), it is speculated that the open, highly branched structure of the gum was capable of retaining more water molecules through hydrogen bonds established by its numerous free-negative groups ( $\text{COO}^-$ ). There was a significant positive correlation ( $r = 0.68$ ) between moisture and emulsion stability (Table 4), for which no satisfactory explanation could be found beyond the mere consideration of similar trends in the data for both variables according to mixture composition

(which therefore became the link between the two responses).

### Density

No cross product was significant in the equation associated to the quadratic surface indicating that the response was dependent on a linear combination of the three mixture components (all linear terms were highly significant). Therefore, it was irrelevant to run a canonical correlation for an unfeasible quadratic surface. There was no clear influence of matrix composition on particle density because no apparent trend in the data could be discerned from the location of density values over the mixture triangle (Figure 3).

### Flavor Retention

All linear terms and one cross product, starch \* maltodextrin, were significant in the characterizing equation for the quadratic surface. Canonical correlation gave a saddle point just outside the triangle at coordinates (0.76, 0.28, -0.04), of theoretical significance but not physical existence because of the negative coefficient for maltodextrin. The location of

maximum and minimum points restricted to the mixture triangle were (0, 0.68, 0.32) and

(0, 0, 1), for blends of 25% gum acacia, 51% modified starch and 24% maltodextrin, and 25% gum acacia, 0% modified starch and 75% maltodextrin, respectively. The corresponding predicted values of flavor retention were 98.21% and 67% for maximum and minimum, respectively (Figure 4). There was a clear trend in the data: the more modified starch and the less maltodextrin in the blend, the higher the oil retention. These results confirmed reports in the literature<sup>16,18</sup> that regard modified starches as excellent carriers for volatile retention and characterize maltodextrins as having a marginal retention.

### Surface Oil

Because surface oil increased sharply towards the maltodextrin axis, a logarithmic transformation of the response was necessary. The quadratic surface was validated by the significance of one cross product, starch \* maltodextrin. Canonical correlation showed a saddle point

**Table 2. Statistical Analysis (p-values) of Mixture Responses**

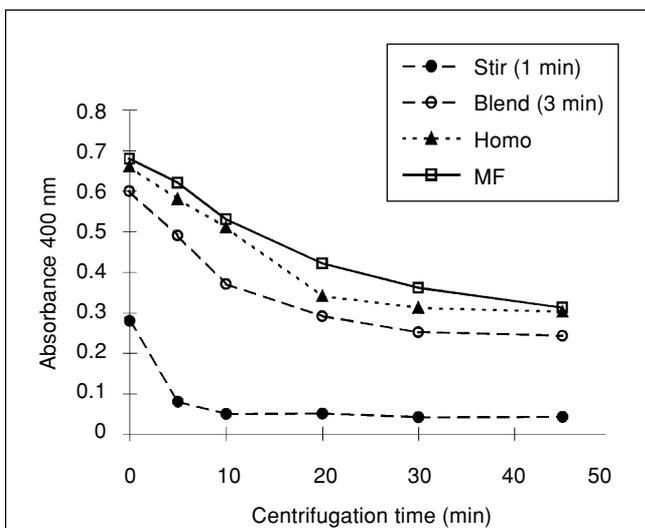
	Moisture	Density	Oil Retention	Surface Oil	Emulsion Stability	Shelf-Life
Acacia	1.55 x 10 <sup>-8</sup>	1.18 x 10 <sup>-6</sup>	1.20 x 10 <sup>-10</sup>	1.39 x 10 <sup>-5</sup>	1.45 x 10 <sup>-8</sup>	2.43 x 10 <sup>-8</sup>
Starch	7.97 x 10 <sup>-6</sup>	5.65 x 10 <sup>-5</sup>	1.01 x 10 <sup>-9</sup>	2.65 x 10 <sup>-5</sup>	3.75 x 10 <sup>-6</sup>	1.06 x 10 <sup>-8</sup>
Maltodextrin	6.87 x 10 <sup>-5</sup>	1.33 x 10 <sup>-4</sup>	5.05 x 10 <sup>-8</sup>	3.10 x 10 <sup>-6</sup>	1.98 x 10 <sup>-5</sup>	1.02 x 10 <sup>-8</sup>
Acacia * Starch	0.993	0.241	0.835	0.640	0.025**	0.018**
Starch * Maltodex	0.152	0.636	0.023**	0.031**	0.151	0.582
Acacia * Maltodex	0.076*	0.952	0.834	0.667	0.161	0.651

All linear terms were highly significant (p < 0.01) in all responses.

For cross-product terms:

\* Significant at p < 0.10

\*\* Significant at p < 0.05



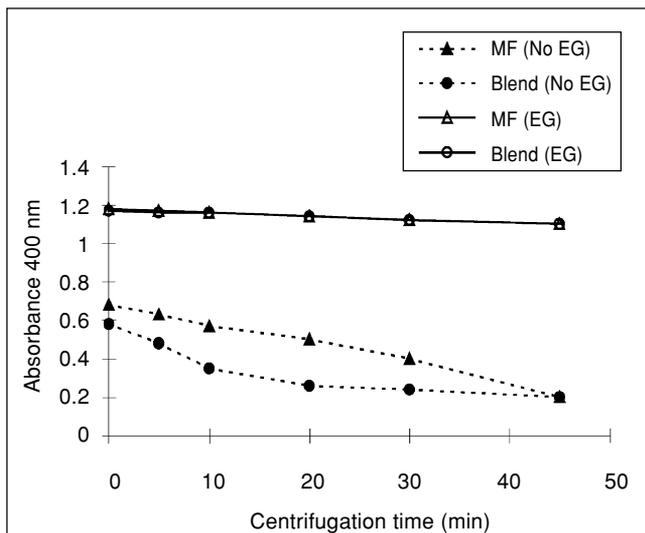
**Figure 2. The influence of type of homogenization on emulsion stability in modified starch systems**

**Table 3. Moisture and Qualitative/Quantitative Mineral Analysis of Carriers**

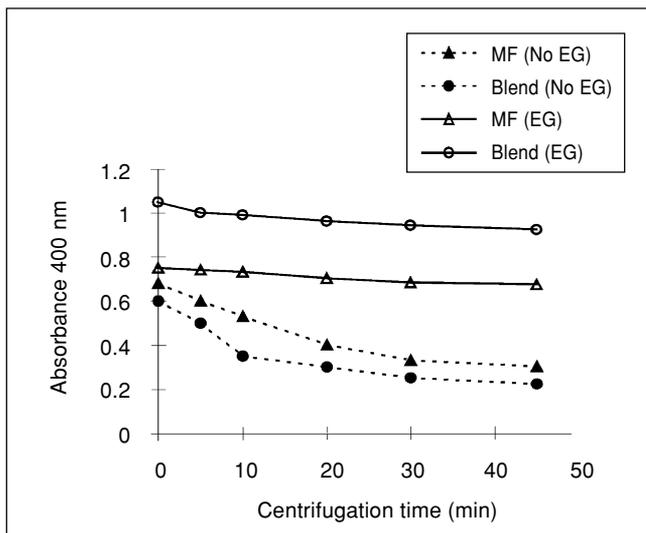
	Gum Acacia	Modified Starch	Maltodextrin
Moisture	9.48%	5.71%	4.77%
Minerals			
K	7636	211	76
Na	447	2371	930
Ca	5799	314	232
Mg	2358	111	83
Fe	5.56	0.94	1.96
Cu	1.48	< 0.52	< 0.52
Zn	0.44	0.40	< 0.14
Al	8.04	< 3.58	< 3.58

Moisture values are expressed as dry basis.

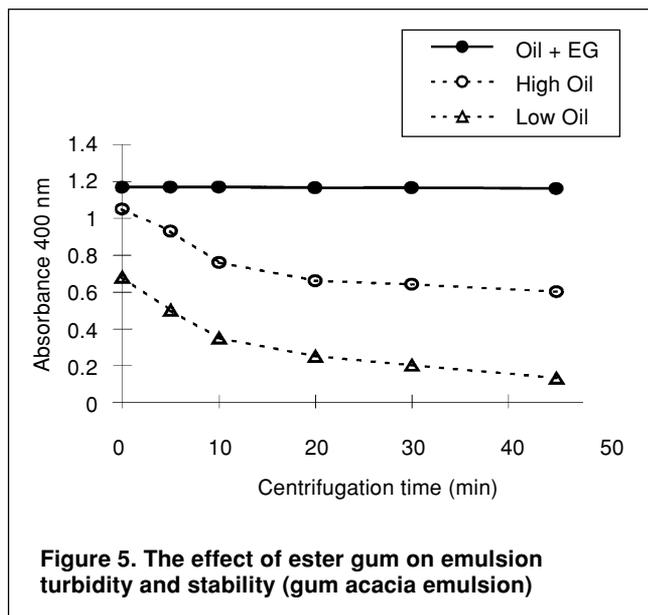
All Mineral Content values are expressed in ppm.



**Figure 3. The influence of adding weighing agents to promote emulsion stability (gum acacia emulsion)**



**Figure 4. The influence of adding weighing agents to promote emulsion stability (modified starch emulsion)**



outside the limits of the mixture triangle at coordinates (0.72, 0.39, -0.11), again of theoretical validity but not feasible physical existence because of the negative coefficient for maltodextrin. Within the experimental range, a maximum existed at (0, 0, 1), that is, 25% gum acacia, 0% modified starch and 75% maltodextrin, and a minimum at (0, 0.62, 0.38), corresponding to 25% gum acacia, 46.5% modified starch and 28.5% maltodextrin. Responses were 242 and 27 mg/100 g powder, respectively (Figure 5). The higher the maltodextrin content in the blend, the higher the amount of surface oil, which was obviously related to the poor volatile retention characteristics of maltodextrin. In addition, surface oil was highly negatively correlated ( $r = -0.95$ ) to oil retention (Table 4) confirming the above trend. No significant correlation existed between surface oil and shelf life. The industry has been prone to use surface oil as an indicator of shelf life, which is not a valid assumption. Other researchers reached similar conclusions.<sup>20</sup> Although it is evident that unprotected oil will undergo rapid oxidation, the effective amount of oxidized products formed at the surface of the powder does not seem to be significant enough to govern shelf life.

### Emulsion Stability

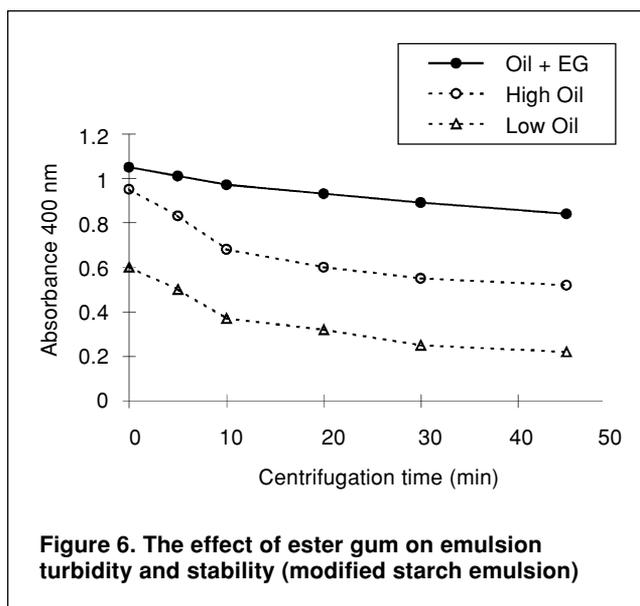
All linear terms in the quadratic surface equation were highly significant. One cross product, acacia \* starch, showed statistical significance at the 95% confidence level. Canonical correlation gave a saddle point in the surface at coordinates (0.29, 0.60, 0.11), translated as 46.75% gum acacia, 45% modified starch and 8.25% maltodextrin. A maximum in the surface was located at coordinates (0.81, 0, 0.19), equivalent to 85.75% gum acacia, 0% modified starch and 14.25% maltodextrin, with a breakage time of 683.8 h. A minimum in the surface was located at coordi-

**Table 4. Correlation Coefficients among Response Variables from Mixture Experiment**

	Moisture	Density	Oil Ret.	Surf. Oil	Em. Stb.	Shelf-Life
Moisture	1					
Density	0.23	1				
Oil Rec.	-0.18	0.01	1			
Surf.Oil	0.08	-0.18	-0.95**	1		
Em.Stb.	0.68*	0.18	-0.15	0.18	1	
Shelf-Life	-0.29	-0.64*	-0.27	0.35	-0.17	1

\* Significant at  $p < 0.05$

\*\* Significant at  $p < 0.01$



nates (0, 0.37, 0.63), equivalent to 25% gum acacia, 27.75% modified starch and 47.25% maltodextrin, with a breakage time of 330.0 h (Figure 6). Poor emulsifying properties of maltodextrin were evident: the more maltodextrin in the blend, the lower the emulsion stability. Gum acacia alone gave better emulsion stability than those blends in which it was partially replaced by modified starch. Considering that the emulsifying ability of a modified starch is significantly improved over that of the native form, it is assumed that a negative interaction occurred between the two carriers with respect to their emulsifying abilities. Speculatively, a competition between the gum and modified starch for adsorption sites on the oil droplets may have taken place.

### Shelf Life

A sharp increase in data points over the axis towards the lower right corner required a logarithmic transformation of the response to improve the model. Besides the expected high significance associated with all linear terms, one cross product, acacia \* starch, proved to be highly significant as well. Canonical correlation indicated a saddle point in the quadratic surface at coordinates (-1.00, -1.07, 3.07), of theoretical importance but evidently of no physical existence. The portion of the surface over the mixture triangle presented local maximum and minimum points at coordinates (0, 0, 1), that is, 25% gum acacia,

0% modified starch and 75% maltodextrin, and (0.59, 0.41, 0), that is, 69.25% gum acacia, 30.75% modified starch and 0% maltodextrin, respectively. Shelf-life values at those locations were 426.2 h and 125.3 h. Replacement of gum acacia by either modified starch or maltodextrin translated into longer shelf life for the corresponding blends: the more the gum replaced, the longer the shelf life. The particular gum acacia used in this study had significant levels of trace metals and this likely accounted for its poorer shelf life (Table 3). One would expect a natural variability of metal contamination in gum acacias; much greater than one would expect in the modified starch or maltodextrin due to the level of processing required for

the latter products. There was a significant negative correlation ( $r = -0.65$ ) between shelf life and density of spray-dried powders (Table 4). This relationship appears contradictory: a denser, more compact powder would be expected to have a lower oxygen permeability and, therefore, a longer shelf-life. However, density is only one factor influencing the permeability of a matrix to oxygen and ultimately the product shelf life.

### Conclusions

According to the results of this study, there is a trade-off in what can be achieved as advantageous or not when replacing gum acacia with modified starch and/or maltodextrin for spray drying purposes. A combination of 25% gum acacia, 50% modified starch and 25% maltodextrin will yield a spray-dried powder with greater flavor retention, less surface oil and lower moisture content than 100% gum acacia, but also lower emulsion stability when reconstituted in water. Shelf-life will be improved by adding either the modified starch (Hi Cap) or 20 DE maltodextrin to gum acacia but one must keep in mind that this may not be true of other gum acacias because they vary greatly in their ability to protect flavors from oxidation. If one uses a very good gum acacia, the addition of Hi Cap or maltodextrin may not have a beneficial effect on shelf life.

It is of interest that Hi Cap performed very well in this study. Its inclusion in the spray-drying formulation with gum acacia was generally very positive. Historically, modified starches have not provided good protection to oxidizable flavorings and we have not recommend them for the encapsulation of oxidizable flavorings. However, this product performed quite favorably in all respects except emulsion stability. Emulsion stability was slightly poorer on incorporating Hi Cap into the gum acacia system. This does not mean that the modified starch is a poor emulsifier but that its use in combination with gum acacia does not give improved emulsion stability. Higher percentages of maltodextrin are not recommended because of a dramatic drop in flavor retention, an exponential increase in surface oil and poorer emulsion stability.

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