

# Flavor Encapsulation



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# **Flavor Encapsulation**

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## Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

# Preface

**F**LAVORS REPRESENT A SMALL BUT SIGNIFICANT SEGMENT of the food industry. The flavor of a food is the most important reason for repeat sales. Consumers will buy a product again only if it has good flavor. Flavors are volatile, labile compounds that are prone to evaporation and degradation.

Encapsulation processes are means by which liquid flavor compounds are enclosed in a carrier matrix to provide dry, free-flowing materials. Encapsulation facilitates the addition of flavors to dry products such as instant beverages and bakery mixes. It can also provide protection against oxidation and other degradative reactions. The term *encapsulation* describes a variety of processes, including spray-drying, extrusion, coacervation, and molecular inclusion. However, none of these processes provides the ultimate product, which would combine correct particle size, the desired flavor load, and complete protection against oxidation. Researchers are studying all aspects of encapsulation and improving existing procedures.

This symposium was developed to provide an overview of existing processes and to investigate new developments. The speakers came from industry and academia to provide two perspectives: applied research with immediate product benefits and basic research, which can contribute information for long-term improvements. Whereas many people are involved in the manufacture and use of encapsulated flavors, there is little published information on how encapsulation is accomplished and what factors affect encapsulation processes. This book represents the compilation of the information presented at the symposium. We hope it will serve as a reference for the people who work in all aspects of the food and flavor industry who are interested in the encapsulation of flavors. We are sincerely grateful to all of the authors who were willing to present information at the symposium and who cooperated by preparing manuscripts. We appreciate all of your efforts.

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March 1, 1988

# Chapter 1

## Flavor Encapsulation

### An Overview

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The encapsulation of foods, flavors, fragrances and the like has been attempted and commercialized by many different methods. A comprehensive overview is given of these many methods. The overview describes each method in terms of the basic chemical and/or physical principles involved. The basic literature references, particularly fundamental or basic patents, are included. Each method was generally developed to solve a particular problem encountered by a product development or formulation chemist. The relationships among problems, capabilities, and encapsulation methods are shown. The overview concludes with a list of reasons for encapsulation, such as prevention of oxidation, conversion of liquids to solids and detackification.

The use of microcapsules in food is generally that of an additive. By regulatory definition, a food additive is any substance which becomes added to food either intentionally or unintentionally other than food itself. This includes both compounds added directly and those that are added indirectly such as migrating from packaging materials. We will limit our discussion here to direct, intentional additives. This means, for example, that the Vitamin C in orange juice is not an additive but the Vitamin C added to orange juice is.

There are several hundred types of microcapsules being used as a food additive in the U.S. today. Most of these are used in the development and production of artificial flavors or natural flavors and spices. Microcapsules as food additives may be added to enhance or alter appearance. Food is not only consumed for its calories or nutrients. It is also part of our cultural experience and it must be appealing in all of its aspects. It is not just a biological necessity, its consumption is a social activity, an aesthetic experience and an expression of cultural and personal experiences. This means that food must not only taste good but it also must have the right color, texture and aroma.



The use of microcapsules can improve or enhance nutrition. The processing required to produce many of the food products used today and the long shelf needed to provide a variety of foods available far from the place where they were grown often results in the loss of nutritional value. The products are often restored to their natural nutritional values through the addition of vitamins, minerals and in some cases, proteins.

Microcapsules can be used as preservatives. Most food preservation originally was accomplished by curing, smoking or pickling which were primarily effective in changing the moisture content or water activity in foods. Then came canning, pasteurization, freezing and chemical preservatives. Microcapsules can also enhance the convenience of food products. Changing lifestyles and the limited time available for food preparation require an increasing variety of high quality, nutritious and convenient food products today.

#### Microencapsulation Terminology

Microcapsules represent an extra degree of freedom in the formulation or development of these food products. Many of the reasons or causes for the use of microcapsules are covered in a previous symposium (1) and a continued updated review on this subject (2). The use of microcapsules is one means of achieving controlled release of the core or inner material. The term controlled release actually covers a wide range of technologies and microencapsulation is one way of achieving controlled release. In fact, microencapsulation is the dominant means for achieving controlled release both in product volume and dollar value.

One particular example of controlled release is sustained release. In this form the desired material is continuously released over a period of time at a constant rate. Two timely publications (3)(4) cover the general area of controlled release, which can also include the controlled release of agricultural materials and biological materials, for example, pheromones. In using the term microencapsulation in this article, the author intends to refer to capsules in the size range of 1 micron to 1000 microns. Capsules below 1 micron in size are frequently referred to as nanocapsules and they are made by one or more very specialized methods (5). The term capsule refers to macro objects in the order of 1 millimeter or larger. This term of capsule is frequently used in the delivery of pharmaceuticals.

The simplest way of looking at a microcapsule is that of imagining a hen's egg reduced in size. The shell has a number of names depending on the industry and company with which one works. This shell can be referred to as a membrane, a wall, a covering or a coating. The internal core material also goes by a number of terms such as payload, core, encapsulant, fill, active ingredient, internal phase, IP or internal ingredient. For the purposes of the article here we will refer to the terms wall and core. Often in the making of microcapsules by a chemical process known as coacervation, there is the additional use of the terms external phase or continuous phase.

### Microcapsule Design

The architecture of microcapsules is generally divided into several arbitrary and overlapping classifications. One such design is known as matrix encapsulation. In this design the matrix particle resembles that of a peanut cluster. The core material is buried to varying depths inside of the wall material. The most common or well known type of microcapsule is that of a spherical or reservoir design. It is this design that most approaches a hen's egg. It is also possible to design other microcapsules that have multiple cores where the multiple cores may actually be an agglomerate of several different types of microcapsules.

If the core material is an irregular material, such as occurs with a ground particle, then the wall will somewhat follow the contour of the irregular particle and one achieves an irregular microcapsule. The last well known design for a microcapsule is that of a multiple wall. In this case the multiple walls are placed around a core to achieve multiple purposes related to the manufacture of the capsules, their subsequent storage and controlled release.

In a discussion of microencapsulation technology, particularly when one is talking quantities and cost, it is necessary to understand that encapsulation is a volume process, independent of the density or value of the core material. Thus microencapsulators frequently state that it is just as expensive on a volume basis to encapsulate diamond as graphite. Likewise, on a volume basis it is just as expensive to encapsulate paraffin wax as tungsten metal. When experimenting with or acquiring microcapsules, it should be emphasized that it is necessary to use common terminology because preference to discuss microcapsules in terms of the core material, particularly when one is discussing the cost of production.

One should also keep in view that the total process of microencapsulation actually covers three separate processes on a time scale. The first process consists of forming a wall around the core material. The second process involves keeping the core inside the wall material so that it does not release. Also, the wall material must prevent the entrance of undesirable materials that may harm the core. And finally, it is necessary to get the core material out beginning at the right time and at the right rate. There is a good reference material covering the current work in the area of microencapsulation (6) and a review article that is continually updated (7).

### Microcapsule Uses

The uses of microcapsules since the initial coacervation work in the 1940's are many and varied. A good early review of these uses that also includes pharmaceuticals and agricultural materials is contained in reference (8). The uses of microcapsules that are of interest here include the following:

1. Reduce the reactivity of the core with regard to the outside environment, for example oxygen and water;
2. Decrease the evaporation or transfer rate of the core material to the outside environment;

3. Promote the ease of handling of the core material;
  - a. Prevent lumping;
  - b. Position the core material more uniformly through a mix by giving it a size and outside surface like the remainder of the materials in the mix;
  - c. Convert a liquid to a solid form; and,
  - d. Promote the easy mixing of the core material.
4. Control the release of the core material so as to achieve the proper delay until the right stimulus;
5. Taste mask the core; and,
6. Dilute the core material when it is only used in very small amounts; but, achieve uniform dispersion in the host material.

#### Release Mechanisms

A variety of release mechanisms have been proposed for microcapsules; but in fact, the number that have actually been achieved and are of interest here are rather limited. These are as follows:

1. A compressive force in terms of a 2 point or a 12 point force breaks open the capsule by mechanical means;
2. The capsule is broken open in a shear mode such as that in a Waring blender or a Z-blade type mixer;
3. The wall is dissolved away from around the core such as when a liquid flavoring oil is used in a dry powdered beverage mix;
4. The wall melts away from the core releasing the core in an environment such as that occurring during baking; and,
5. The core diffuses through the wall at a slow rate due to the influence of an exterior fluid such as water or by an elevated temperature.

#### Release Rates

The release rates that are achievable from a single microcapsule are generally "0" order, 1/2 order or 1st order. "0" order occurs when the core is a pure material and releases through the wall of a reservoir microcapsule as a pure material. Half order release generally occurs with matrix particles. 1st order release occurs when the core material is actually a solution. As the solute material releases from the capsule the concentration of solute material in the solvent decreases and a 1st order release is achieved. Please note that these types of release rates occur from a given single microcapsule. A mixture of microcapsules will include a distribution of capsules varying in size and wall thickness. The effect, therefore, is to produce a release rate different from "0", "1/2" or "1" because of the ensemble of microcapsules. It is therefore very desirable to carefully examine on an experimental basis the release rate from an ensemble of microcapsules and to recognize that the deviation from theory is due to the distribution in size and wall thickness.

#### Microcapsule Formation

The general technology for forming microcapsules is divided into two classifications known as physical methods and chemical

methods. The physical methods are generally divided into the following:

1. Spray coating.
  - a. Pan coating. This is a mature, well established technology intially patented by a pharmacist in the 19th century by the name of Upjohn. It generally requires large core particles and produces the coated tablets that we are familiar with;
  - b. Fluid bed coating. One version of this coating is known as Wurster coating and was developed in the 1950's and 60's (9). The Wurster coater relies upon a bottom positioned nozzle spraying the wall material up into a fluidized bed of core particles. Another version sprays the wall material down into the core particles.
2. Annular jet. This technology was developed by the Southwest Research Institute and has not been extensively used in the food industry (10). It relies upon two concentric jets. The inner jet contains the liquid core material. The outer jet contains the liquid wall material, generally molten, that solidifies upon exiting the jet. This dual fluid stream breaks into droplets much as water does upon exiting a spray nozzle;
3. Spinning disk. A new method was developed by Professor Robert E. Sparks at Washington University in St. Louis. This method relies upon a spinning disk and the simultaneous motion of core material and wall material exiting from that disk in droplet form (11). The capsules and particles of wall material are collected below the disk. The capsules are separated from the wall particles (chaff) by a sizing operation;
4. Spray cooling. It is a method of spray cooling a molten matrix material containing minute droplets of the core materials (12). This method is well known because of its practice by the Sunkist Company;
5. Spray drying. It is a method to be discussed at length in the following papers; and,
6. Spray chilling. It is a process of spray chilling the wall around an atomized core (13). The resulting capsules move countercurrent to a flow of tempered air and are collected in a large container below the spray nozzle. It is practiced currently by the Durkee Company.

The number of methods for chemical encapsulation is actually far less. They are necessary because they are very effective in encapsulating liquids and small core sizes. In particular, it is possible to encapsulate flavors and fragrances down to 10 microns in size. Two methods are known as water-in-oil and oil-in-water. The oil-in-water process is known as complex coacervation. This process relies, for example, upon a solution of gelatin and the complex it forms with a solution of gum arabic. Complex coacervation will be described in a later paper by the author. The other method of encapsulating water soluble cores within an oil medium is generally not used in the food industry.

### Conclusion

In looking at the need for encapsulation in a product it should be emphasized that microcapsules are rarely sold and consumed by themselves. Microcapsules are generally additives to a larger system and must function within that system. Consequently there are a number of performance requirements placed on microcapsules when a limited number of encapsulating materials and methods exist. Consequently it is necessary to make a number of trade-offs and compromises to incorporate microcapsules into a food product as an additive. In contrast to this, though, there is the continual development of new materials for encapsulation, particularly in the Wurster method. Fortunately a number of the patents have now expired and so it is possible for the encapsulator to use a number of methods without fear of patent infringement.

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## Chapter 2

# Maltodextrins and Low-Dextrose-Equivalence Corn Syrup Solids

## Production and Technology for the Flavor Industry

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Maltodextrins are nonsweet soluble carbohydrates that are used in flavor encapsulation and throughout the food industry. This paper presents information on how maltodextrins are produced, their chemical and physical properties, and the functional characteristics that make maltodextrins useful to the flavor industry.

Encapsulation and drying of flavors are dependent on the performance of encapsulating agents. These agents should:

1. Protect the active ingredient from oxidation, caused by heat, light, humidity, and other substances over a long shelf life.
2. Prevent the evaporation of volatile components.
3. Provide the ability to put the active ingredient into a free-flowing powder for ease of handling and incorporation into dry food systems (King, T. et al., 1976).

To provide these functions, the encapsulating agent should have the following properties (King et al., 1976): emulsion stabilizing capabilities; film-forming ability; low hygroscopicity; low viscosity; and the ability to release the active ingredient upon hydration as well as be of relatively low cost and in reliable supply.

Maltodextrins and low DE corn syrup solids can be an important part of the matrix system for the encapsulation and drying of flavors.

### Definition of Maltodextrins and Corn Syrup Solids

The FDA defines maltodextrin  $(C_6H_{12}O_5)_n H_2O$  (CAS. Reg. No. 9050-36-6) as nonsweet, nutritive saccharide polymers that consist of D-glucose units linked primarily by alpha-1-4 bonds and that have dextrose equivalence (DE) less than 20. They are prepared as white powders or concentrated solutions by partial hydrolysis of corn starch with safe and suitable acids and/or enzymes (48FR51911, Nov. 15, 1983).

Maltodextrins are generally recognized as safe (GRAS) as a direct human food ingredient at levels consistent with current good manufacturing practices (21 CFR 184.1444).

Corn syrup solids  $(C_6H_{12}O_5)_n H_2O$  (CAS. Reg. No. 68131-37-3) are defined by the FDA as dried glucose syrups (21 CFR 168.121) in which the reducing sugar content (DE) is 20.0 or higher. Corn syrup solids are presently under GRAS review along with other sweeteners and table syrups.

#### Production of Maltodextrins and Corn Syrup Solids

Maltodextrins and corn syrup solids are produced from starch, usually corn. The starch, which is almost pure carbohydrate, is cooked or pasted to open the granule and then hydrolyzed. Products can be made by hydrolyzing with acid or enzymes or with a combination of acid and enzymes. After the desired amount of hydrolysis has occurred, the reaction is stopped, and the product is filtered to remove insoluble materials and then dried.

Maltodextrins and corn syrup solids are most often defined by their dextrose equivalence (DE). DE is a measure of the degree of hydrolysis of the starch molecule which compares the reducing power of the sugar groups as compared to the reducing power of an equal weight of glucose present.

Other methods that are used to characterize maltodextrins and corn syrup solids include liquid chromatography which can be used to quantify the relative amounts of shorter chain polymers found in a particular DE product. Maltodextrins and corn syrup solids are made up of polymers of anhydroglucose units having varied chain lengths rather than one particular polymer size (Table I).

Table I. Typical Carbohydrate Profile  
(Carbohydrate analysis by HPLC, % by weight )

Degree of Polymerization, DP	Maltodextrins and Corn Syrup Solids			
	5 DE	10 DE	15 DE	20 DE
1	0.2	0.5	0.7	2.3
2	0.3	2.7	4.5	7.9
3	0.6	4.3	6.6	9.6
4	0.6	3.7	5.3	6.2
5	0.6	3.1	4.4	5.5
6	1.0	5.7	8.6	12.7
7	1.2	7.1	9.8	9.8
8	0.8	4.5	4.9	2.5
9	0.5	3.1	2.9	0.2
10	0.3	1.6	0.3	0.1
Above 10	93.9	63.7	52.0	43.2

The average molecular weight decreases as the DE of a maltodextrin increases, but even at low DE's, it is much smaller than the original starch: 5 DE - 3600; 10 DE - 1800; 15 DE - 1200; 20 DE - 900.

This relative molecular size difference between starch and the hydrolysis sugars gives maltodextrins and corn syrup solids their valuable functional properties for the flavor industry.

### Functional Properties

Emulsion Stabilization. Emulsion droplet size and stability are critical for the production of encapsulated flavor oils. Maltodextrins and corn syrup solids do not have "true" emulsifying capabilities (lipophyllic/hydrophyllic properties). They are made up of glucose units, but the average chain length is also too small to stabilize normal levels of citrus oils or other oil carried flavors by viscosity. For these reasons, maltodextrins are usually combined with other true emulsifying matrix materials such as gum arabic or specially modified starches to achieve the necessary emulsion stability. The amount of the emulsifying agent necessary will vary depending on its ability to emulsify, the level of oil to be encapsulated, the production system used, and the desired stability when the encapsulated oil is used.

Film-Forming Properties. In the encapsulation of flavors, the quality of the end product is affected by both how quickly the matrix material forms a film or selective membrane around the flavoring agent, and by the quality of the matrix film and its ability to protect the flavoring agent.

Menting and Hoogstad (1967) studied the effect of increasing matrix concentrations on volatiles retention using one maltodextrin. They reported an increase in solids increased the rate at which a selective film formed to capture the volatiles. Bangs and Reineccius (1981) studied the influence of maltodextrin DE on the retention of volatile flavor compounds; they found that the average retention of combined volatile components decreased with an increase in the DE of the maltodextrin. Reineccius and Bangs (1985) also reported that an optimum feed solids content may vary depending on the composition of the solids and the characteristics of the flavor components. Subramaniam (1984) reported an increase in protection of encapsulated orange oil during storage with an increase in DE of the matrix solids. These references and others point to a need for further study to relate the properties of maltodextrins and corn syrup solids films to their abilities as flavor encapsulating agents.

Hygroscopicity. Maltodextrins and low DE corn syrup solids are very nonhygroscopic. Therefore, flavors dried with these products are free-flowing powders. Hygroscopicity does increase with higher DE's. Figure 1 shows the physical changes in several DE products that had equilibrated at various relative humidities.

Viscosity. Viscosity and solubility may be the two most important characteristics of an encapsulation matrix ingredient. The increase in solids to the dryer at a constant solids/flavor ratio can greatly increase the economic efficiency of an operation. Most processing systems have a maximum viscosity at which they can operate. Proper atomization may also affect the flavor retention (Reineccius and Bangs 1985). The low viscosity of maltodextrins and corn syrup solids is shown in Figure 2. The viscosity of these products



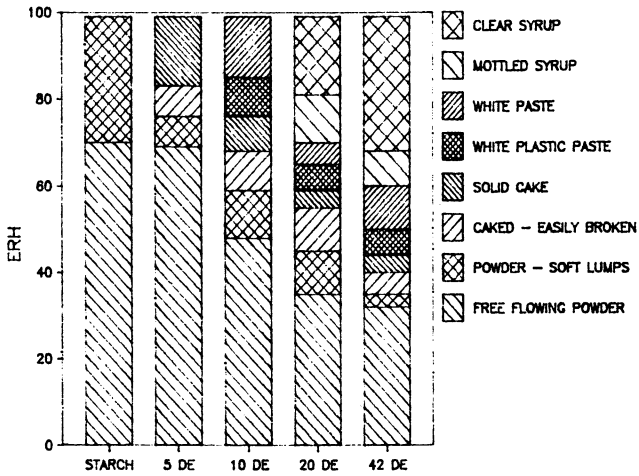


Figure 1. Effect of Relative Humidity on Physical Characteristics.

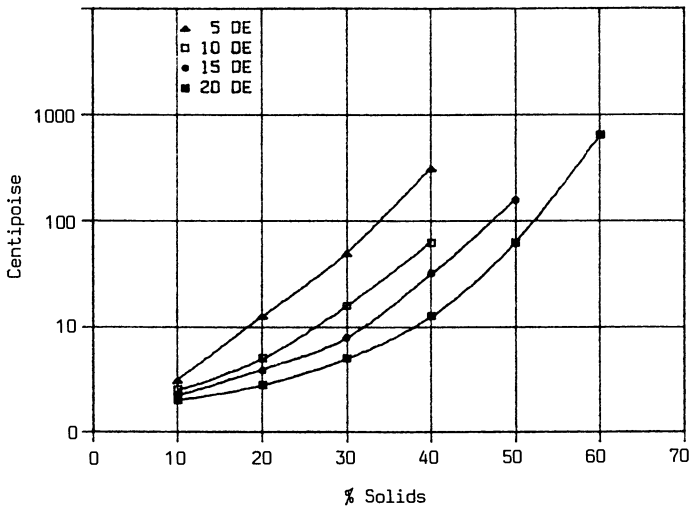


Figure 2. Viscosity of Maltodextrin and Corn Syrup Solids Solutions at Varied Percent Solids.

decreases with increasing DE's. Maltodextrins and corn syrup solids also exhibit Newtonian viscosity, decreasing in viscosity as they are heated. Maximum solids levels for encapsulation may also be reached at the solubility limits of the matrix ingredients. Above these limits, the level of flavor compound may be out of ratio with the active matrix polymers, so the retention of flavor decreases (Reineccius and Bangs 1985). Insoluble materials may also affect the quality of encapsulating film by interfering with the continuous film matrix. Maltodextrins and corn syrup solids will demonstrate good solubility in the following solids range: 5 DE - 30-45%; 10 DE - 45-55%; 15 DE - 50-65%; 20 DE 60-75%.

Flavor Release. Encapsulated flavors find uses throughout the food industry. One major example would be beverage dry mixes. Maltodextrins and corn syrup solids have excellent cold water solubility, so their use in encapsulated flavors will provide a rapid release of flavors used in beverage applications. Maltodextrins and low DE corn syrup solids also have very little flavor or sweetness of their own, form clear solutions, and virtually disappear once in an application.

Low Cost-Reliable Supply. Maltodextrins and corn syrup solids carry a much lower cost than almost all other encapsulating matrix ingredients. They are produced both in the U.S. and in foreign countries by several suppliers, so they are readily available. When used alone or as one of a combination of encapsulation matrix ingredients, maltodextrins and corn syrup solids are an effective part of the encapsulating system.

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## Chapter 3

# Corn Starch Derivatives

### Possible Wall Materials for Spray-Dried Flavor Manufacture

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One of the primary variables which influences the recoveries of volatile flavor and aroma chemicals during spray drying is the wall material. Utilization of spray dried flavors in food systems presents further constraints on the wall material selection process. Of the food grade polymers available to the manufacturer of spray dried flavorings (i.e., gum acacia, lipophilic starches, maltodextrins, corn syrup solids), no single wall material exhibits the ideal traits deemed necessary for this economically important process.

The focus of this work was to determine if a glycopeptide or a simple dextrinized, oxidized starch could be produced which would enhance the behavior of a starch-based polymer for spray dried flavoring production. Enhancement of a starch's lipophilic/hydrophilic balance was anticipated to maintain the polymer's "film forming" and cohesive wall development during the spray drying process while improving its emulsifying/interfacial activity capabilities.

Of the myriad of modified starch systems tested, ranging from simple enzymically dextrinized starches to covalently attached amino acids and peptides onto dextrinized and/or oxidized (hypochlorite or periodate) corn starch bases, two polymers were selected as holding promise. The first system was a low dextrose equivalent (DE 5.7) enzyme-modified corn starch. The second starch-based polymer developed was a periodate-oxidized, amylase-dextrinized, covalently-attached phenylalanine glycoamine.

<sup>1</sup>Current address: Campbell Soup Company, Camden, NJ 08101

Possibly the most important, and least understood, aspect of spray-dried flavorings manufacture is the role the wall material plays in this process. The polymers utilized for this product are controlled by FDA constraints, cost, finished product labelling considerations and compatability, functionality and historical usage. Given these considerations, polymers selected for the retention and maintenance of labile flavors and aromas in industrial spray dried, food grade systems include both carbohydrate (hydrolyzed starches, "lipophilic" starches, plant exudates) and protein. The importance of these wall materials should not be underestimated.

Protein-based materials previously considered for flavor "microencapsulation" via spray drying include gelatin and gelatin derivatives (1-3), polypeptone (4), soy protein (5) and bovine milk-derived proteins (5-8). Although protein-based polymers do exhibit excellent aqueous emulsion stability for many flavoring "oils" and result in good retentions of the volatile flavoring materials following drying, specific attributes limit their usefulness. These deleterious properties include poor cold water solubility, chemical reactivity (especially with carbonyls) and high cost.

Carbohydrate-derived polymers may overcome these negative attributes (9). Previously published work (10-13) demonstrated the potential for improved functional characteristics of dextrinized, oxidized and native starches by simple intermolecular casein linkage via aldol condensation reactions. Gelation potential and emulsion stabilization characteristics were improved by this polymeric condensation of protein and polysaccharide.

Simple starch hydrolyzates have been used extensively to produce dried flavoring materials (14-17). Inexpensive, functional dextrinized starches unfortunately exhibit one major deficiency: the inability to form stable aqueous emulsions following flavor incorporation. With no physical adsorption of the added flavoring material in stabilized micelles and low aqueous viscosities, the Stokes law-governed emulsion destabilization is extremely rapid. Retention of volatiles resulting from the drying process subsequently suffers.

This deficiency has been overcome by the development of "lipophilic" starches (18,19); starch hydrolyzates incorporating a covalently bound lipophilic species, 1-octenyl succinate. In this manner, a lipophilic polymer is produced which allows for excellent aqueous flavor emulsion stability, good water solubility (40% w/w), excellent retentions of the volatile flavoring material following drying and minimal "extractable" oil in the finished product (9), functional properties only exhibited by gum arabic prior to their development.

Gum acacia, a natural plant exudate polysaccharide, has historically been used as the wall material of choice. Due to fluctuations in availability and increasing costs of this natural polymer, alternate choices have been examined (9). Worth noting at this point is the 1.5% to 3% protein content associated with this polysaccharide (20).

None of the aforementioned polymers presently enjoys universal appeal as carrier solids for dried flavorings. Proteins suffer due to cost and chemical reactivity, malto-dextrins and corn syrup solids due to a dearth of interfacial function, lipophilic starches due to labelling constraints (a marketing decision), and gum arabic due to cost, as well as intermittent supply deficiencies. An inexpensive, "natural", strongly surface active polymer with excellent water solubility and chemical inertness clearly has vast economic potential. Oxidized, hydrolyzed and/or glycoamine starch-based derivatives were examined as possible avenues for delivering this polymer.

Dried flavoring wall material development conducted in this study was completed in two separate phases. Firstly, a water-dispersible starch polymer which; 1) exhibited good flavor retention potential during spray drying and 2) was able to form a stable flavor-incorporated aqueous emulsion was examined. Further derivation of this starch polymer with amino acids, peptides or protein followed, in order to further enhance the base material for the task of flavor encapsulation.

#### MATERIALS AND METHODS

**Polymer Selection.** The selection of corn starch as the starting material was made due to its low cost, ready availability, multitude of previous derivatization literature work and favorable chemical and physical properties (i.e., inert, readily derivatized homopolysaccharide capable of forming high solids content aqueous dispersions with relatively low viscosities). The corn starch used in this study was purchased in bulk from a local food cooperative. Table I gives the proximate analysis of a typical corn starch.

Table I. Corn starch proximate analysis<sup>a</sup>

Starch %	88
% amylose	28
% amylopectin	72
Moisture %	11
Protein %	0.35
Ash %	0.1
Fat %	0.04
Total Lipids %	0.87
SO <sub>2</sub> (mg/Kg)	49
Crude Fiber %	0.1
pH	5
Gel Temperature Range	62-72 C
Average Molecular Weight	50-60 x 10 <sup>6</sup>

<sup>a</sup>Data from reference 23.

In some of the preliminary work, dextrinized corn starches varying in dextrose equivalency (DE) from 5 to 36 (Grain Processing Corp., Muscatine, IA) were used.

Starch Oxidation. In order to produce starch derivatives with improved water dispersibilities and reduced retrogradation potential (22,23), two oxidative reagents were tested; sodium hypochlorite (MW 74.44) and sodium periodate (MW 213.91). Sodium hypochlorite was purchased as bleach from a local supermarket. Sodium periodate was purchased as the pure reagent from Sigma Chemical Company (St. Louis, MO).

Due to inherent variability of natural polymer (i.e., corn starch) molecular size and difficulties associated with ascertaining the average molecular weight value for such large polymers, the addition of both oxidizing agents to corn starch was expressed on a weight basis. This value ranged from 0% to 20% (w/w) for hypochlorite addition and 0% to 28% (w/w) for periodate addition.

The hypochlorite/water solutions were pretitrated to pH 8.5 with 1.0 N HCl in order to neutralize the presence of inherent sodium hydroxide. Leaching out of non-crystalline amylose from the native starch granules has been previously described in systems with pH values greater than 9.0 (24).

Quenching of the oxidative reaction was completed by the use of ethylene glycol (25), along with sample filtering, retentate washing and dialysis.

All oxidative reactions were completed at ambient temperature (ca. 26°C) in 1 L stainless steel beakers. The reactor vessel systems were constantly mixed by the use of magnetic stirring plates (Model 4812; Cole-Parmer, Chicago, IL) with teflon-coated stir bar incorporation.

Molecular Weight Reduction. A partial hydrolysis of both reacted and unreacted corn starches was necessary in order to result in the aqueous dispersion concentrations required of a flavor-encapsulating agent. This polysaccharide molecular weight reduction was completed by the use of an alpha-amylase enzyme (Novo Ban 120L; Novo Laboratories, Inc., Wilton, CT). Temperature (65 C) and pH (6.0) optimums for amylase activity were controlled, along with the addition of 0.5 g/L CaCl<sub>2</sub>, an enzyme cofactor. Although amylase reaction times varied according to end-product requirements, a constant amylase activity of 100 KNU (Kilo Novo Units) per liter was maintained.

Dialysis. Some of the oxidized, gelatinized starches were dialyzed against distilled water for 24 hours in MW cut-off 6-8 X 1000 dialysis tubing (Spectra/Por 1; Fisher Scientific, Pittsburg, PA). Glycoamine derivatives of the starch-base materials were also dialyzed against distilled water for 40 hours in MW cut-off 3.5 X 1000 dialysis tubing (Spectra/Por 3; Fisher Scientific, Pittsburg, PA).

Water Removal. The base materials were spray dried in a Niro Utility Model spray dryer (Niro Atomizer Ltd, Columbia, MD) following oxidation, gelatinization, amylase treatment and/or dialysis. A dryer inlet air temperature of 250 C and outlet air temperature of 110 C was used, along with a sample infeed temperature of 60-70 C. Utilizing these conditions of operation, a

water removal rate of about 35 Kg per hour was achieved. Yields of finished product obtained were in the range of 75% to 90% of the starting material, based on a final moisture content of 5%.

Oxidized Starch Production Methods. Multiple methodologies were utilized to produce the corn starch products of hypochlorite and periodate oxidation. Ultimately only three of these procedures were selected as yielding functional product and will, therefore, be the only methods to be outlined here.

Method A. The desired amount of oxidizing agent (hypochlorite or periodate) was added to 400 mL of distilled water in a 1 L stainless steel beaker and mixed with a magnetic stirring device to ensure proper dissolution. One-hundred grams of corn starch (25% w/v) was added slowly into the vortex of this sample. Following a predetermined time table of events, the oxidizing agent was quenched and the entire starch suspension was filtered, using Whatman #4 filter paper placed on a Buchner funnel. Four volumes of distilled water were used to wash the starch retentate.

Following oxidation, filtering and washing, the starch was resuspended in one volume of distilled water and was again mixed on a magnetic stir plate. Five per cent (v/v) 8.0 N NaOH was added to the starch suspension, resulting in a rapid gelatinization process. Fifteen minutes after base addition, an appropriate amount of 2.0 N HCl was added to reduce the starch dispersion pH to 4.5. The sample was heated to 95 C for 30 minutes to ensure complete starch gelatinization had occurred.

The finished gelatinized, oxidized starch was cooled to 30 C in a water bath, dialyzed and spray dried.

Method B. Proceed as described in Method A but eliminate the use of base for starch gelatinization. Dilution of the starch suspension to 5% (w/v) was necessary to allow proper heat transfer and mixing when using heat alone to perform the gelatinization process.

Both a pre- and post-gelatinization alpha-amylase treatment were given to this derivatized starch. The pre-gelatinization dextrinization with amylase was completed at room temperature for two hours in a 25% (w/v) suspension, followed by filtering and washing of the retentate with one volume of distilled water. The suspended corn starch (20% w/v) was heated to 70 C on a heated stirring plate to initiate gelatinization. The slurry was subsequently cooled to 65 C and amylase was added for the appropriate time interval. The completion of gelatinization and amylase denaturation was satisfied by finally heating the starch dispersion to 95 C for one hour, after adjusting the pH to 4.5.

Method C. Proceed as Method B using the pregelatinized amylase treatment only.

Dextrose Equivalency. Corn starch dextrose equivalent values (DE) were used to measure the carbonyl groups present in both dialdehyde, oxidized starch production and the production of dextrinized starches (26).

Saccharide Analysis. The analysis of low DE starch hydrolyzates for their degree of polymerization (DP) saccharide profile was completed by a high performance liquid chromatographic method (27).

Titrateable Acidity. The possibility of carboxylic acid group generation from excessive oxidation of corn starch was monitored by titrateable acidity (TA). A 0.01 N NaOH solution was used to titrate a dilute aqueous starch suspension (20 mL of a 5% w/v sample) for the presence of acidic functional groups, using phenolphthalein as the indicator dye. An unreacted starch sample was also titrated to yield a sample blank value. TA values were expressed as mL of base required to reach the colorimetric phenolphthalein and end-point.

Molecular Weight Determination. A number average molecular weight term for the oxidized starch polymers was determined by the colligative property of freezing point depression (28) using the cryoscope technique (Advanced Digimatic Osmometer Model 3DII; Advanced Instruments, Inc., Needham Heights, MA).

Dipeptide Synthesis. The synthesis of tyrosyl-tyrosine and phenylalanine dimer was performed (29) using a modified liquid phase technique.

Glycoamine Synthesis. The covalent coupling of amino acid monomers and polypeptide fractions to carbohydrate backbones, previously described (30), was completed using a stationary pH modification (31) of a previously published method (32).

Calfskin gelatin (60 bloom strength), bovine casein and the amino acids tested (phenylalanine, leucine, tyrosine, tryptophan) were all purchased from Sigma Chemical Company (St. Louis, MO).

Amino Acid/Dimer Analysis. The analysis of dipeptides and the covalent attachment of peptides to carbohydrate was monitored by a high performance liquid chromatographic method (33).

Viability of Starch Derivatives as Flavoring Encapsulants. The capillary GC vapor phase flux term (defined by a percent external standard or %ESTD flux) previously described (34) was used to screen starch derivatives (oxidized, dextrinized and/or covalent amino acid linkage) as to their flavor encapsulation potential. The samples were prepared as previously described (34) with the exception of an added reduced pressure deaeration step, thus allowing the use of the headspace diffusivity versus retention standard curves to predict volatile lemon oil retention following spray drying.

Evaluation of Encapsulation Efficiency of Synthesized Wall Materials. Wall materials developed from this work were analyzed for their ability to "encapsulate" lemon oil (20% db) by the standard procedures set forth in (34). Both the mini-spray dryer and Niro spray dryer were used when appropriate, depending on sample size constraints.



A capillary GC-acetone precipitation method (35) was used to analyze the spray dried samples for lemon oil encapsulation efficiency.

## RESULTS AND DISCUSSION

Starch (amylose and amylopectin) hydrolysis along with esterification, etherification or oxidation have been previously discussed as available methods for producing starch derivatives with improved water dispersibilities and reduced retrogradation potential (21, 22). Since oxidative and hydrolytic reactions are simple, easily controlled chemical modifications, starch-derived polymers made by hydrolysis alone or oxidative and hydrolytic processes were developed and tested.

Due to potential benefits associated with maintaining some undefined concentration of oligomer (e.g., DP > 8; 5), oligosaccharides of a DE of 10 or less were produced. Initially, a further constraint was desired for the development of a starch-based wall material, Food ad Drug Administration acceptability. Therefore, sodium hypochlorite was the oxidizing agent of choice for the early oxidation attempts (36).

Following preliminary hypochlorite treatments, a coherent process path was identified and implemented. Corn starch was oxidized with 6.4% (w/w) hypochlorite for two hours and given a combined base-heat gelatinization process (Method A). This base material exhibited excellent physical characteristics (i.e., stable emulsion with 20% db lemon oil incorporation into an aqueous dispersion, low lemon oil vapor phase flux (low headspace content), lack of inherent flavor and aroma) and when finally tested for spray dried lemon oil (20% db) retention efficiency in a lab-scale mini-dryer, the viability of this polymer was ascertained. Nearly 70% of the added lemon oil was retained following the drying of this DE 1.45 starch, a measure of functionality matched only by gum arabic (34).

Further starch base material development would have ceased at this point but unfortunately this material could not be readily duplicated. The oxidation of primary and secondary alcohols to carbonyls and, further, to carboxylic acids was seemingly detrimental to the potential encapsulation of lemon oil via spray drying. As previously discussed (24, 37) about 25% of consumed hypochlorite cleaves the C-2:C-3 glucopyranosyl linkage by forming an enediol followed by dicarboxylation. The remainder of the consumed hypochlorite either oxidizes the -1,4- bonds (i.e., depolymerization) or primary alcohol groups (24). Proper selection of the oxidizing agent, its level of use and processing times and temperatures were necessary in order to avoid starch oxidation to carboxylic acid formation. An inability to maintain the required low levels of acidic group formation was apparently the problem associated with hypochlorite utilization (Figure 1).

Although starch oxidation was still deemed worthy of investigation due to its ability to deter aqueous starch retrogradation, no starch oxidizing agent approved for food use was apparently specific enough for the production of the desired dialdehyde

starch. Sodium periodate was selected for its ability to specifically oxidize 1,2 glycols to dialdehydes in nearly stoichiometric ratios (21).

Again, preliminary work was conducted to determine process conditions yielding a functional understanding of periodate and its effect on corn starch polysaccharide fractions. A stoichiometric linear increase in starch DE (a measure of total reducing groups) with increasing levels of periodate addition was achieved (Figure 2). Titratable acidities were well within pre-determined constraints (<3 mL 0.01N NaOH per gram). Periodate-oxidized starch appeared to yield starch bases with good reproducibility and of desirable end-products (i.e., dialdehyde starch).

Starch base material development was completed by producing a periodate-oxidized, amylase-hydrolyzed material (Method C; Oxidized). The process flowsheet for the production of this material and a corresponding amylase-treated Control (i) starch is given in Figure 3.

Characterization of both the Control and Oxidized starches was completed by examining emulsion stability, vapor phase flux, dryer retention values of added lemon oil (Table II),

Table II. Lemon oil retentions (20%<sub>db</sub>) of spray-dried base starches

Sample	Polymer Content (% w/v)	Headspace Content (%EStd) <sup>b</sup>	Mini-Dryer Retention (%)	Niro Dryer Retention (%)
Control (no NaIO <sub>4</sub> )	49.0	33	50.4	NA <sup>a</sup>
Oxidized	59.05 59.25	33 67	37.8 NA	NA 87.6

<sup>a</sup>not attempted

<sup>b</sup>Reference 34

oligosaccharide DP content (Figure 4) and number average molecular weight estimation. The saccharide degree of polymerization (DP) of these polymers exhibited large concentrations of DP 3, 6, 7 and 8 oligosaccharides; glucose polymers typical of amylase-treated corn starches (28). As expected (39), the Control starch hydrolyzed more readily than the periodate-treated Oxidized starch (percentage of starch polymers greater than DP 10 of 32.2% and 58.6%, respectively). The Oxidized polymer was determined to have a number average molecular weight of 2080. Retrogradation problems hindered molecular weight determination of the non-oxidized Control starch using the cryoscopic technique. An estimate of between 1200 and 1400 was the best that could be ascertained.

Given the excellent lemon oil-incorporated emulsion stabilities of both polymers, the excellent dryer retention performance of the Control material and good lemon oil retentions using the Oxidized starch, scaled-up systems were prepared and dried. One

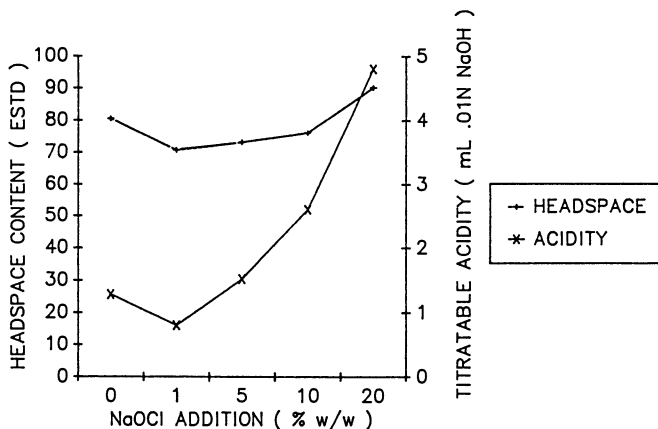


Figure 1. Effect of hypochlorite addition on starch titratable acidity and lemon oil headspace content values.

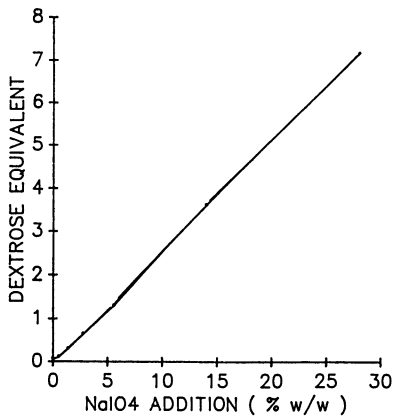


Figure 2. Influence of periodate addition on dextrose equivalent.

- 1) 400 mL distilled water (d-H<sub>2</sub>O)
- 2) + 100 grams corn starch (25% w/v)  
Control
- 2) + 2.80 grams NaIO<sub>4</sub>  
+ 100 grams corn starch (25% w/v)  
30 minute oxidation  
Oxidized
- 3) filter and wash retentate with four volumes of d-H<sub>2</sub>O
- 4) resuspend retentate in one volume d-H<sub>2</sub>O
- 5) + 0.5 g/L CaCl<sub>2</sub>; adjust pH to 6.0
- 6) + 100 KNU Novo Ban 120L α-amylase (2 hours at room temperature)
- 7) filter and wash with 4 volumes d-H<sub>2</sub>O
- 8) suspend retentate in 1 volume d-H<sub>2</sub>O + 4 volumes of 80 C d-H<sub>2</sub>O
- 9) heat to 70 C
- 10) cool to 65 C and add 100 KNU Novo Ban 120L α-amylase (65 C for 30 minutes)
- 11) heat to 95 C for 60 minutes
- 12) spray dry

Figure 3. Process flowsheet for corn starch wall material production.

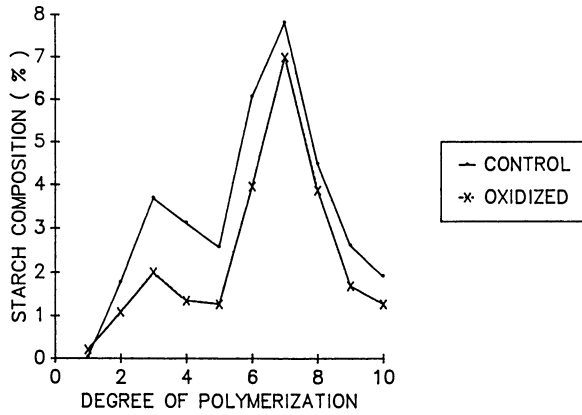


Figure 4. Degree of polymerization of control and oxidized starches.

kilogram of the Control and 2.5 Kg of the Oxidized starch polymers were produced for further derivatization, encapsulation and characterization work.

#### Starch-Amine Derivatives

Covalent linkage of amino acid, peptide or protein moieties onto the hydrolyzed and/or oxidized polymers (Control and Oxidized starches) was examined for its ability to improve the potential for microregion lipophilicity within the carbohydrate polymer. Proteinaceous materials are often strongly surface active (39) and may, if carefully selected, contribute positively to wall material characteristics. This selection process was carried-out using maltodextrins (DE 10 and/or 25) as the carbohydrate framework and various amino acid-derived materials as the function-altering accessory, ranging from gelatin and casein proteins to simple amino acids.

The finished polymer was to act as an "improved" wall material and, therefore, the ability of this polymer to reduce the vapor-phase flux of lemon oil (from an aqueous sample) was the preselected flagging procedure.

Protein attachment (i.e., casein and gelatin) to a DE 10 maltodextrin base failed to yield any substantial improvement in hindering lemon oil vapor phase flux using mole ratios of 0, 0.005 and 0.01 of protein to each "mole" of maltodextrin (92.6%, 78.6% and 83.1% ESTD, respectively). The cyanogen bromide attachment procedure being used (31) most likely allowed for multiple peptide linkages for each protein molecule and would, therefore, inhibit the protein species from residing in a perpendicular manner relative to the carbohydrate base, the perceived desirable location for this substitution. This peptide attachment work was followed by covalently bonding a number of lipophilic amino acids (phenylalanine, tyrosine, leucine, tryptophan) to the DE 10 and DE 25 maltodextrins. Table III gives the lemon oil vapor phase flux (expressed as Headspace content) data which resulted from this work. None of these amino acid-attached polymers resulted in substantial improvement over the control maltodextrin data, within the levels of substitution used.

Phenylalanine was chosen for further glycoamine synthesis work.

Attention was also given to developing tyrosine and phenylalanine dimers. Although these dimers were produced, yields were poor (less than 10%) and sample clean-up presented major obstacles. Solid-phase production of these dipeptides (29) appeared much more feasible but was deemed unworthy of the necessary time expenditure. Aspartame (L-aspartyl-L-phenylalanine methyl ester) was used instead for the evaluation of a dipeptide.

The addition of phenylalanine to the previously described starch base materials (Control and Oxidized starches) was done on a 10% (w/w) level for covalent attachment. The Oxidized starch was apparently more conductive to cyanogen bromide activation for amino acid attachment than was the Control starch (92% attachment versus 67%, respectively). The addition of aspartame was also completed for the Oxidized (ii) starch polymer on a level of

Table III. Influence of Binding Amino Acids to Maltodextrins on Lemon Oil Vapor Phase Flux

Sample	Mole Ratio (Amino Acid to Maltodextrin)	Headspace Content <sup>a</sup> (% EStd)
Phenylalanine/ DE 10	0.5:1	96.2
	1:1	81.8
	3:1	74.9
Phenylalanine/ DE 25	0.5:1	100.8
	1:1	96.6
Tyrosine/ DE 10	0.5:1	92.8
	1:1	91.8
	3:1	90.3
Tyrosine/ DE 25	0.5:1	89.3
	1:1	84.8
Leucine/ DE 10	0.5:1	94.4
	1:1	82.2
Leucine/ DE 25	0.5:1	96.0
	1:1	90.3
Tryptophan/ DE 10	0.5:1	85.3
	1:1	78.3
Tryptophan/ DE 25	0.5:1	91.9
	1:1	88.5
DE 10	---	92.6
DE 25	---	90.6

<sup>a</sup>Reference 34, 33% w/v

molar equivalency to phenylalanine addition. Vapor phase flux and dryer retention data for lemon oil are given in Table IV for these systems.

Table IV. Vapor phase flux and dryer retentions of lemon oil incorporation (20%<sub>db</sub>) into selected glycoamine polymers and their base materials

Sample	Polymer Content (% w/v)	Headspace Content (% EStd) <sup>c</sup>	Retention	
			mini-	Niro
Control	33	49.0	50.4	NA <sup>a</sup>
Control/ Phenylalanine	33	52.6	48.7	NA
Oxidized	33	59.05	37.8	NA
	67	59.25	NA	87.6
Oxidized/ Phenylalanine	33	40.9	55.1	NA
Oxidized/Aspartame	33	50.7	46.4	NA
Oxidized + Phenylalanine <sup>b</sup>	33	71.5	NA	NA
Capsul <sup>c</sup>	33	41.5	53.0	97.3
	67	35.55	NA	93.8
Gum Arabic <sup>c</sup>	33	21.4	71.5	98.9

<sup>a</sup>not attempted

<sup>b</sup>dry-blended (no cyanogen bromide treatment)

<sup>c</sup>Reference 34

Substantial improvement (about 50%) of lemon oil encapsulation efficiency was attained for the covalently-linked phenylalanine-Oxidized starch wall material over the Oxidized starch control. In fact, this particular glycoamine resulted in lemon oil retentions following drying in the mini-spray dryer which surpassed both the Control and lipophilic starches (See Table IV). Dry blending phenylalanine with the Oxidized starch base exhibited the benefits associated with covalently linked glycoamine production via lemon oil vapor phase flux analysis.

The other two glycoamine derivatives failed to substantially improve polymer performance. Aspartame linkage to the Oxidized starch resulted in improved lemon oil encapsulation efficiency over the Oxidized material, alone, but not to the extent of the phenylalanine glycoamine polymer. Covalent attachment of phenylalanine to the Control starch was actually a slight detriment to lemon oil retention versus the control starch (48.7% retention in the mini-dryer versus 50.4%, respectively), although this difference was not deemed significant.



CONCLUSIONS

The efficacy of hydrolyzed, oxidized and/or amino acid-substituted corn starch derivatives as wall materials for matrix-encapsulating flavoring materials was determined. Amino acid/peptide attachment would ultimately appear to warrant the most attention if further work was focused in this area. Further learnings into gum arabic physical/chemical attributes should allow the development of a naturally-derived starch polymer which behaves in a positive, controllable manner and at a competitive price.

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## Chapter 4

# Encapsulation of Orange Oil

### Use of Oligosaccharides from $\alpha$ -Amylase Modified Starches of Maize, Rice, Cassava, and Potato

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Oligosaccharides were prepared by the action of alpha-amylase on ordinary corn, waxy corn, amylo maize VII corn, rice, wheat, cassava and potato starches; their compositions, were measured by HPLC on a HPX-42A column. The oligosaccharides were used to encapsulate single-fold orange oil at an optimum infeed concentration and to achieve maximum flavor retention during spray drying. All the oligosaccharides provided ideal viscosity for the infeed mixtures. The spray-dried samples were analyzed for total oil, surface oil, moisture content, shelf life and for emulsion stability by observing optical density changes with time on a centrifuged aqueous mixture. Retention of orange oil during spray drying was best with wheat and amylo maize VII oligosaccharides, whereas waxy corn and cassava oligomers appear to be best for shelf life.

Numerous materials are commercially available for use as flavor encapsulating agents via spray drying (4). However, each of these materials has one or more limitations. Chemically-modified starches (i.e., having emulsifying properties) have been shown to yield excellent retention of volatiles during drying (4), but provide poor protection to oxidation (7). The partially hydrolyzed starches (e.g., maltodextrins and glucose syrup solids) provide excellent protection against oxidation of the encapsulated flavor but give no emulsification and yield poor retention of volatiles (1). Gum arabic provides excellent emulsification and good retention of volatiles but provides limited protection against oxidation (7). In recent years, cost and availability have also been deterrents to the use of gum arabic. While select blends of commercially available carriers may provide acceptable retention and shelf-life, the search continues to develop a superior flavor carrier at an acceptable cost. To this end, we have enzymatically hydrolyzed various starches and evaluated their potential for use as flavor encapsulating materials.

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### Materials and Methods

Preparation of oligosaccharides. Waxy corn (Frodex 25, American-Maize Products Co., Hammond, IN), ordinary corn (Maltrin M-250, Grain Processing Corp., Muscatine, IA) and potato (Avebe America Inc., Hopelawn, NJ) hydrolysates were obtained commercially. Wheat, cassava, rice, and amylo maize VII starches were enzymatically hydrolyzed using a thermally stable alpha-amylase from Bacillus licheniformis (E.C.3.2.1.1; 1,4-alpha-D-glucan glucanohydrolase; Taka-Therm L-340 from Biotech Products Division of Miles Laboratories, Inc., Elkhart, IN). While the procedure for hydrolysis was detailed previously (3), a brief outline follows.

Glucose syrup solids from wheat, rice, and cassava starches. A starch suspension was prepared by mixing 250 g of the starch with 580 mL of distilled water (30% w/w). The water contained 87 ppm of calcium (0.32 g per L  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ). The pH of the slurry was adjusted to 6.0 with 1.0 N NaOH. Thermally stable alpha-amylase from Bacillus licheniformis was added to the stirred suspension (0.20 mL, 68,000 Modified Wohlgemuth Units (MWU), per 250 g of starch) at 50°C; the suspension was heated to 95°C in a 2-L round-bottomed flask with continuous stirring in a bath containing ethylene glycol. The conversion was allowed to proceed for 1 hr or until the desired degree of hydrolysis was obtained. After the desired conversion time, 0.1% of Darco G-60 and 2% of J.M. Hyflo Filter Cel (based on solution weight) were mixed into the solution with continuous stirring. The pH was adjusted to 3.5-4.0 with 0.2 N sulfuric acid and the mixture was heated at 95°C for 10 min to inactivate the remaining enzyme. The pH was raised to 6.5 with 1 N NaOH, and the mixture was filtered hot through a bed of filter-aid on Whatman No. 1 paper in a Buchner funnel under vacuum. The resulting filtrates were dried in a Model GA-31 Pulvis Mini Spray Dryer (Yamato, Northbrook, IL).

Maltodextrin from high-amylose corn starch. A suspension of high-amylose corn starch (Amylo maize VII, a product of American Maize Products Co., Hammond, IN) was prepared by mixing 250 g (20% w/w) with 1000 mL of water containing 87 ppm of calcium (0.32 g per L  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ). The starch was gelatinized in a jet-cooker at 280-290°F (30-40 lb of steam pressure). The gelatinized starch slurry was collected in a Dewar flask, and the pH was adjusted to 6.0 with 1.0 N NaOH. Alpha-amylase (Taka-Therm L-340, 0.2 mL per 250 g of starch at 90-95°C) was added to the stirred suspension, and then heated to 95°C in a 3-L round-bottomed flask with continuous stirring in a bath containing ethylene glycol. The conversion was allowed to proceed for 1 hr or until the desired degree of hydrolysis was obtained. The malto-oligosaccharides were processed as described earlier (3).

HPLC analysis of starch hydrolysates. The oligosaccharide compositions of the various starch hydrolysates used in this study were determined by high performance liquid chromatography (HPLC). An automated liquid chromatographic system used in this study

consisted of a Spectra Physics (San Jose, CA) Model 8700XR pump controller and an organizer (SP8750S) for the solvent delivery system; a Model 410 differential refractometer (Waters Associates, Milford, MA); and a Spectra Physics computing integrator (SP4270). The column was an Aminex HPX-42A (300 x 7.8 mm) from Bio-Rad Laboratories (Richmond, CA), held at 85°C in a column heater (Bio-Rad Laboratories, No. 125-0425). The method and quantitation has been detailed by Inglett (3).

Oligosaccharide compositions of the various starch hydrolysates are shown in Table I. The reducing sugar contents (expressed as dextrose equivalents, DE) were estimated from the hydrolysate compositions by dividing the content of each oligomer by its DP and adding the eight numbers. The following are the estimated DE values: ordinary corn, 25; waxy corn, 24; amylo maize, 17; wheat, 26; rice, 27; potato, 18; and cassava, 24. Maltodextrins are defined by the FDA as having DE less than 20; syrup solids are defined as dried glucose syrups in which the DE is 20 or higher.

Spray drying. Single fold valencia peel oil without antioxidant was provided by Fries and Fries (Cincinnati, OH). A quantity of orange oil corresponding to 25% (by weight) of the carrier solids was added to a 50% solids aqueous solution of each enzyme-modified starch. The orange oil emulsion was homogenized using a Greer Co. (Hudson, NH) laboratory high shear mixer for 3 min immediately prior to spray drying.

A Niro Utility Dryer (Columbia, MD) equipped with a 12 cm diameter radial vane centrifugal atomizer (24,000 rpm) was used for spray drying. Drying conditions were standardized at an inlet air temperature of 200 ± 5°C and an exit air temperature of 100 ± 3°C using cocurrent flow. Under these conditions, the dryer was evaporating about 12 Kg water per hour.

Analysis of Spray Dried Samples. Moisture content was determined in duplicate via toluene distillation and total volatile oil by Clevenger (1). Surface oil was measured by Soxhlet extraction (2). Shelf-life was determined by gas chromatography (6); the end of shelf-life was the time taken (at 37°C storage) to reach a limonene epoxide concentration of 2 mg/g oil.

### Results and Discussion

All hydrolyzed starches readily went into solution at 50% solids. The viscosities of all solutions were quite low (<100 cps); higher solids solutions could have been used for spray drying. Higher solids solutions would have resulted in improved flavor retention during spray drying (5). All of the starches dried very well, yielding good product recoveries. Moisture contents of the products (1.8 to 3%) are acceptable for spray dried flavorings (See Figure 1). The retentions of orange oil varied from 42 to 72% (Figure 2). The amylo maize, wheat, cassava, and rice provided better oil retentions than the other enzyme-modified starches and would probably be quite acceptable if higher infeed solids had been used. It is questionable if the corn, waxy corn or potato starch would yield acceptable oil retention even at higher infeed solids. There is no obvious relationship between oligosaccharide

Table I. Oligosaccharide Compositions Prepared from Starches by Thermal Stable Alpha-Amylase Actions<sup>1</sup>

8&>	Degree of Polymerization, DP						1
	7	6	5	4	3	2	
Ordinary Corn							
33.6	0.2	19.2	10.5	8.1	12.0	12.3	4.2
Waxy Corn							
42.0	1.8	16.0	9.5	7.1	10.0	9.9	3.6
Amylomaize VII							
54.2	7.0	11.2	8.5	6.8	7.5	4.0	0.5
Wheat							
31.1	3.0	11.8	15.8	9.0	13.9	12.1	3.3
Rice							
35.1	0.1	13.1	15.0	8.6	13.9	11.4	3.0
Potato							
45.3	8.2	17.9	7.2	6.3	9.5	4.6	0.7
Cassava							
34.8	2.0	15.4	13.2	8.6	13.1	10.3	2.2

<sup>1</sup>Carbohydrate composition, determined by HPLC, are expressed as % by weight. All values are averages of two separate determinations.

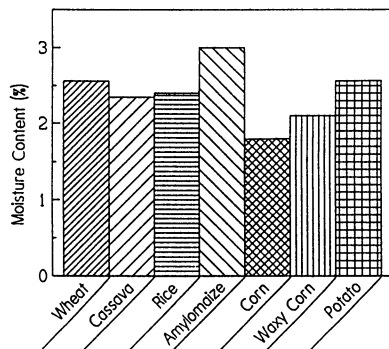


Fig. 1. Moisture contents of orange oil encapsulated with wheat, cassava, rice, amylomaize, corn, waxy corn, and potato malto-oligosaccharides.

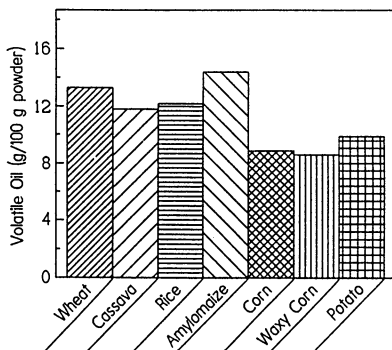


Fig. 2. Retentions of orange oil after spray drying with wheat, cassava, rice, amylomaize, corn, waxy corn, and potato malto-oligosaccharides.



composition and the retention of orange oil. One would expect the maltodextrin with the highest proportion of large oligosaccharides to yield the best retention. This hypothesis is in general not supported by most of our data. It does appear that amylo maize does support the higher oil retention property; the potato data does not.

Surface oil contents of the dried products ranged from 4 to 304 mg oil/100 grams powder. As can be seen in Figure 3, the potato starch product had the lowest surface oil while the amylo maize had the highest surface oil. It has generally been accepted that shelf-life is related to surface oil. The logic being that the surface oil is not protected from oxygen and readily undergoes oxidation during storage. One would, therefore, expect the potato starch to have the longest shelf-life during storage and the amylo maize the shortest. Our results on the shelf-life properties do not support this belief (Figure 4). While the amylo maize product did have the shortest shelf-life, as expected, the potato starch product exhibited similar instability to oxidation. The potato starch product should have been the most stable, based on its surface oil content. Thus, it appears that surface oil is not the primary determinant of oxidative stability. This observation supports the work of Anandaraman and Reineccius (1) who found that encapsulated orange oil oxidized at approximately the same rate as the equivalent product which had been washed with solvent to remove any surface oil.

Shelf-life data appears to be related to starch oligosaccharide composition. Amylo maize (17 DE) has the highest proportion of large oligosaccharides, and the lowest proportion of small oligosaccharides (Table I); this maltodextrin has the poorest shelf-life. Potato maltodextrin (18 DE) has a similar composition and exhibits a similar shelf-life. The other glucose syrup solids have very similar oligosaccharide composition (and DE's) and shelf-lives similar to each other, but different from the amylo maize and potato products. The presence of small oligosaccharides (high DE) may promote oxidative stability by forming a more effective oxygen barrier.

The shelf-life of virtually all the encapsulated orange oils was quite good. Assuming a  $Q_{10}$  of 2.4 (1), one would predict a shelf-life of about 7 months at 70°F for the worst product (amylo maize) and at least 14 months for the better products (corn, wheat, rice, waxy corn, and cassava). Considering that there was no antioxidant in these encapsulated products, the shelf-lives are very good. This work supports the observations of Anandaraman and Reineccius (1) that high DE maltodextrin or glucose syrup solids provide excellent barrier properties and produce encapsulated citrus oils with excellent shelf-life.

The problem of emulsion stability remains. While no data are presented here, the orange oil separated quite rapidly once the powdered products were reconstituted. While wheat, amylo maize and rice encapsulated products appeared more stable, their emulsion stabilities were still unacceptable.

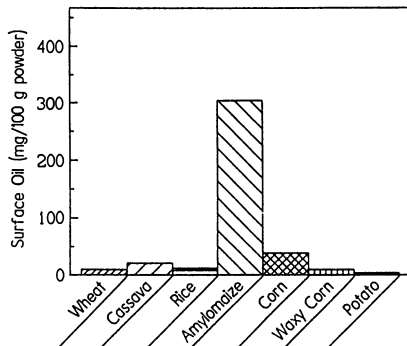


Fig. 3. Surface oil contents of encapsulated orange oil with wheat, cassava, rice, amylomaize, corn, waxy corn, and potato malto-oligosaccharides.

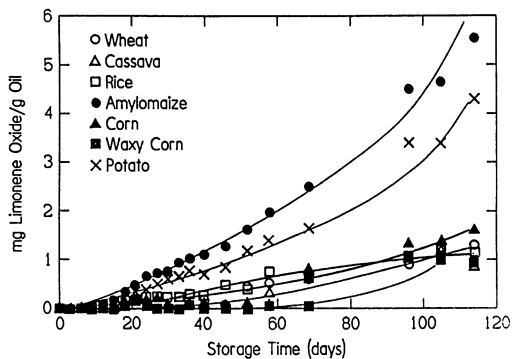


Fig. 4. Shelf-life of encapsulated orange oil samples, as measured by limonene oxide formation at 37°C.

### Conclusions

This study supports the hypothesis that high DE maltodextrins and syrup solids permit the formation of encapsulated products with excellent stability to oxidation. Different enzyme-hydrolyzed starches yielded encapsulated orange oils which varied in stability: amylo maize and potato maltodextrins exhibited the poorest stabilities while normal corn, waxy corn, cassava, rice, and wheat glucose syrup solids yielded the best and approximately equivalent shelf-lives. Based on oil retention during drying, amylo maize, wheat, rice, and cassava yielded satisfactory products.

Overall, it appears that syrup solids from wheat, cassava, and rice could be used for flavor encapsulation. However, an effort is needed to provide some emulsification for these carbohydrates.

### Acknowledgments

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## Chapter 5

### Acacia Gums

#### Stabilizers for Flavor Encapsulation

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Acacia gum's unique structure makes it an excellent carrier for flavor encapsulation. A natural product - traditionally collected in the bush by nomads - it is now possible to rationalize, through many plantations, the harvest and quality of the gum. Starting from tissues, *in-vitro* cultivation has already begun in our laboratories preparing the Third Generation Acacia gums. A few examples will underline how far this research has advanced. This paper will also cover the association of acacia gums which are now filling in for traditional gum arabic in the aromatic industry. Different formulations will be studied for making flavors in powder form using acacia gums as protective colloids. Organoleptic character and shelf-life will be verified according to the type and concentration of the gum.

Acacia gums, commonly called gum arabic, are natural vegetable colloids obtained by exudations from the trunk and branches of leguminous plants of the family of Acacia. There are several hundred species of Acacia; only a few of which are able to produce gum and these are mainly concentrated in the sub-desert region of the African continent: the SAHEL. The main producing countries of gum arabic are the Sudan, Senegal, Mali and Nigeria. The world market for this gum, which is used as an ingredient and additive, is around 60,000 metric tons.

Kordofan, a Sudanese region producing gum arabic, has given its name as a tradename to the gum which comes from the Acacia senegal. The Acacia senegal has been used on occasions as a reference for pharmacopoeias and different standards regulating gum arabic but increasingly the related species of Acacia are being sold in the market.

The gum arabic is collected during the dry season which runs from November to May. The trees are first tapped by the villagers and then the exudation begins. After exudation and drying the gum forms nodules which are then collected by hand and later sold in

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markets where they are bought by wholesalers. The gum is then sorted by hand to standardize the product, baged and exported. Despite two harvests per year (December and April), the quantity of gum obtained from each tree generally does not exceed 300 g.

Even though the question is still being studied, the production of gum seems to be a response to some type of aggression upon the Acacia tree: injury of tissues or infection by micro-organisms. Encouraging research is now being conducted on experimental plantations to study the influences that various treatments (spraying, fertilizers) exert on gum production.

Some production comes from "wild" trees but increasingly the gum is harvested in organized gum tree plantations.

A traditional method of cultivation is being used. First the seeds are selected and are placed in a hothouse and watered regularly to assist germination. The young seedling is then transplanted in a carefully prepared plot of land at the start of the rainy season. Four years later the Acacia tree can be tapped to produce gum. Acacia gum tree plantation programs involving thousands of hectares are being carried out in different African countries with the technical assistance of specific gum development associations. It must be noted that in addition to providing gum, Acacia plantations carry numerous advantages in these desert regions. They are an efficient means of combatting desertification by fixing soils, improving fertilization of the crop growing land (nitrogen, enrichment (a legume)) and a permanent source of income which settles nomadic peoples.

In addition to these village plantations, we at our Marseilles Research Center are developing a generation of Acacia plants by in vitro cultivation. Production of Acacia plants by seed germination does not allow all the properties of the donor to be genetically reproduced. On the contrary, biotechnology allows us through micro-propagation to multiply and clone specimens which are all genetically identical to the initial specimen.

The advantages of this method applied to Acacia cultivation are immediately apparent: perfect selection of species, consistent gum yields, increased gum output, improved standardization of exudates.

For this technique, a cutting is taken from a rich gum producing adult specimen. This cutting will be decontaminated and then inserted into a multiplication medium containing hormones needed to form new buds.

Some of the desirable specimens that result from this budding are inserted into an inducement medium to root. From one bud, four buds take root each month.

The incubation stage in phytotron lasts 15 days and is followed by a further 15 days of rooting in a tube in the presence of hormones maintained at a controlled temperature and humidity. After two weeks of transplanting and growth in a hothouse, the growth is then completed by 2 months in a conventional nursery.

We lack the experience to accurately evaluate the output gain obtained from micro-propagation, but compared to the development of rose bushes, 800,000 new rose bush plants are obtained in 11 months from 3 donors; the traditional seedling method required 3 years from 10,000 donors.

In crude form (exported from Africa) Acacia gum contains a percentage of impurities comprising mineral and vegetable matter

inherent in the system of collection. To eliminate these impurities, the old method treated the product by a dry process using different stages: crushing, pulverization, selection and sifting. Increasingly Acacia gums are sold in spray dried form. Before spray drying, the gum is placed in a water solution and is then filtered and centrifuged. This ensures levels of impurities less than 0.04%. In addition bacteriological quality is improved since the solution undergoes pasteurization and the production batches are standardized to be perfectly uniform.

All these Acacia gums and/or synergistic combinations of Acacia are sold with guarantees of color, viscosity and levels of impurities. Further treatment such as sterilization by gamma or beta radiation are applicable to Acacia gums without altering the products functional properties.

Acacia gums belong to the group of complex acid polysaccharides of primarily uronic acid type and occurring as a mixed salt (sodium, calcium, magnesium and potassium). Owing to the complex character of this polymer, the stereochemical organization of the molecule is not completely known even though the qualitative and quantitative analysis of the sugars is.

Nevertheless, hydrolysis of a gum arabic solution in an acid medium and analysis of the sugars by paper chromatography reveals the presence of the following sugars:

D Galactose, L Arabinose, L Rhamnose, D partially methylated glucuronic acids.

Certain authors also find traces of glucose. In the case of Acacia senegal exudate, the percentage of the constituent sugars are quantitatively 40% for galactose, 24% for arabinose, 13% for rhamnose and 23% for glucuronic acids. The molecular structure may be represented by the Figure 1; it is important to note that the main skeleton comprises galactopuranose units with 1-3 bonds with the other sugars connected by 1-6 bonds. It is also worth noting that the acid patterns are at the periphery of the molecule and are therefore very active in creating an anionic environment.

The molecular weight is not very high: 500,000 daltons. However by gel exclusion chromatography it is easy to highlight the presence of high molecular weight polymers as well as polymers with lower molecular weight and the same sugar composition. Only the degree of polymerization is different; differences in properties may result. This globular and highly branched structure of gum arabic is responsible for the virtual absence of the development of high viscosity when compared with other colloids containing similar sugars in their molecular structures and comparable molecular weights.

The major difference between colloids such as Guar, Tragacanth and Carrageens is the linear molecular organization which will form more rigid structures with high viscosity (or gelified structures) through bridges of hydrogen bonds between the different linear chains and water. (See Table I)

The ash content, protein concentration, maximum intrinsic viscosity, equivalent weight and rotatory capacity are some of the features specific to each species of Acacia exudate.

The physical properties of gum arabic are due to its high solubility in water (up to 50%), stability in an acid medium (up to pH3), binding and adhesive properties, affects upon crystal growth, film forming and surface active features. The last two functional

Table I. COMPARATIVE VISCOSITIES BETWEEN VARIOUS COLLOIDS  
 Solution at 1% concentration in water  
 Brookfield RVT 20 rpm

Guar gum .....	3500 cps
Locust Bean Gum .....	3000 cps
Tragacanth .....	700 cps
Carrageens (Lambda) .....	500 cps
Gum Arabic .....	5 cps

properties will now be discussed since they are the prime reasons for the application of gum arabic in the flavor industry.

In the aromatic industry Acacia gums are used as stabilizers and emulsifiers to prepare concentrates for beverages and as an encapsulating agent to produce aromas in powder form. More generally they render all liposoluble substances (vitamins, fats, coloring agents) hydrodispersable and ensure their effective protection against oxidation, hydrolysis and other more subtle chemical reactions induced by temperature, pH, etc. The preparation of concentrates for beverages entails the following standard stages:

- manufacture of the aqueous phase by dissolving Acacia gums in water (stabilizing-emulsifying agents) with other additives (preservatives, coloring agents),
- preparation of the oil phase by dissolving the weighting-clouding agent in the aromatic composition (purified and desodorized Damar gum, esterified colophony, SAIB, brominated oils).

The next step is to mix the oil phase with the aqueous phase and succeed in reducing the oil phase into globules with a diameter of 1 micron. Experience shows that the narrower the distribution around 1 micron, the greater the stability. The oil globules will then remain perfectly stable in the concentrate and in the beverage. Following poor stabilization, coalescence of the poorly dispersed oil phase will occur and this will produce a white or colored ring at the top of the bottle or a loss of turbidity at the bottom of the bottle. To achieve this reduction in size, the aqueous/oil phase mixture is subjected to pre-homogenization using a high shearing mixer to reduce the size of oil globules to 5 microns followed by homogenization at several stages up to 250 kg/cm<sup>2</sup>. The size of the globules under microscopic examination must be 1 micron. For the purpose of fine analysis it is possible to study the weighted distribution of the particle size by use of the Coulter Counter method (Figure 2).

The traditional concentrate formula for beverages (type 1%) is as follows:

Aromatic composition	:	6 to 8%
Resin (weighting agent)	:	3 to 8%
Spray dried Acacia gum	:	15 to 20%
Water	:	q.s. 100%

Synergistic combinations of Acacia gums (Emulgum type R) exist on the market which are specially formulated to develop emulsifying

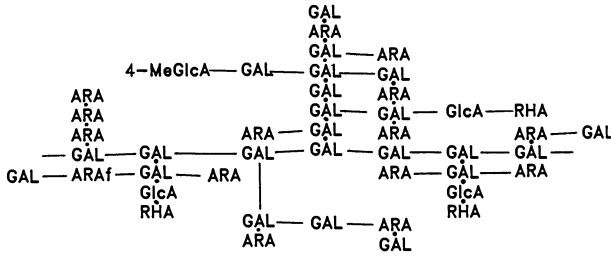


Figure 1. Proposed structure for gum arabic (Stephen 1982).

Formulation :            6,5 % orange oil  
                                   3,5 % Emulgum (Acacia gums)  
                                   6,0 % Esterified colophany  
                                   q.s. 100% water

Percentage in Differential Weights

<u>Range</u>	<u>Diameters microns</u>	<u>Diff. Weights %</u>
1	0.50	25.7
2	0.63	18.9
3	0.79	12.2
4	1.00	8.1
5	1.26	6.7
6	1.59	5.8
7	2.00	4.2
8	2.52	3.2
9	3.17	2.6
10	4.00	2.8
11	5.04	1.7
12	6.35	2.2
13	8.00	1.3
14	10.08	1.4
15	12.70	1.0
16	16.00	1.9

Differential Weights (%)

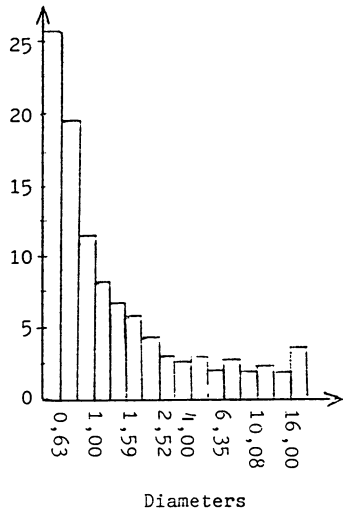


Figure 2. Typical distribution of oil phase in an oil/water emulsion for soft drinks (Coulter Counter).



capacity 4 to 5 times greater than that of traditional Acacia gum, a mere 3 to 5% of these blended controlled Acacia gums are used.

This formulated concentrate is diluted with 1% sugar syrup at 65 Brix in the presence of citric acid to obtain the syrup. This syrup will then be diluted 5 times with carbonated water to obtain the final drink at 10 Brix.

Because of the natural differences in oils, the general formula must be adjusted for each oil composition and each type of resin employed.

Various parameters must be controlled to ensure good emulsion stability:

- the oil phase must have a density as close as possible to that of the aqueous phase (d-1.03). The level of weighting agent will be calculated according to density of the resin used (from 1.04 for Damar resin to 1.33 for the brominated oils).
- Owing to its film forming properties Acacia gum must cover perfectly each oil globule with a colloidal film. As Acacia gum emits negative charges around the circumference of its molecule, electric repulsion will occur between each oil globule so that coalescence is prevented. The oil globule must be neither too small as this would cause the globules to agglomerate nor too large (immediate rise).
- Finally the viscosity of the aqueous phase induced by the Acacia gum slows internal agitation and stabilizes the system.

The use of Acacia gum as an encapsulation agent is governed by the same principles as the preparation of a stable liquid emulsion.

In the aqueous phase the colloidal agents are made soluble. These agents are atomized carriers which when dissolved in water provide a uniform and flexible film around each fat globule. This coating will ensure the stability of the aroma in powder. The film must protect the aroma against oxidation by the air or light and prevent evaporation of volatile matter.

The most efficient colloids are pure Acacia gums. For reasons of economy, mixtures of Acacia gums and dextrin may be used. As in the preparation of concentrates for beverages, the oil phase to be protected will be added to the aqueous phase and the coating will be formed during homogenization. The emulsion will then be dried by atomization with air temperature at the inlet of 160 or 180°C and a powder temperature at the outlet of 85 to 90°C.

A typical emulsion formula for encapsulation on pure gum may be expressed as follows:

Aromatic composition	:	7%
Spray dried Acacia gum	:	28%
Water	:	q.s. 100%

The dry substance content is 35% and the flavor content on the powder 20%. When mixing a medium as with gums and malto-dextrins, the formula becomes:

Aromatic composition	:	10%
Spray dried Acacia gums	:	15%
Malto-dextrins	:	25%
Water	:	q.s. 100%

The solid content of the emulsion is then 50% and the final dried powder will contain 20% of aroma. Once the aroma is obtained as a powder at the outlet of the tower, it is necessary to determine the quantity of aroma effectively fixed on the support. This is done by steam distillation of the powder. In the case of encapsulation on pure Acacia gum, the atomization efficiency (ratio between the quantity of oil recovered afterwards by steam distillation and the theoretical fixed quantity) is 98%.

The quantity of surface oil must also be tested.

If the oil is not properly encapsulated, it will be quickly oxidised. The quantity of surface oil may be determined by cold washing the powder with hexane.

Stability during storage may be tested by chromatographic analysis of a powder subjected to accelerated ageing in an oven. The most practical method remains taste evaluation of the atomized product by a panel (Table II).

Table II. ENCAPSULATION OF ORANGE OIL USING ACACIA GUMS  
Comparative composition of oil before and after spray drying

Components	Orange oil	Spray dried orange oil
Alpha Pinène	0,31	0,30
Sabinène	0,347	0,333
Beta Pinène	0,055	0,10
Myrène	1,488	1,469
Octanal	0,129	0,129
Limonène	97,77	94,05
Linalcol	1,059	1,039
Monanal	0,062	0,061
Decanal	0,216	0,517
Neral	0,139	0,139
Géranial	0,252	0,22
Valencène	0,174	0,162

If the liposoluble coloring agents are encapsulated (carotene etc.), the absorption spectrum, i.e. color evolution must be followed by spectrophotometry.

If the quantity of oil to be fixed in a dried powder is a parameter dependent on the end use, the formulator can choose between different Acacia gums. With a traditional Acacia gum (exudate of Acacia senegal), a dry substance value of 35% represents a maximum value before spray drying. Beyond this value the emulsion viscosity is too high and drying inside the atomization tower does not take place satisfactorily.

On the other hand, using a synergistic combination of Acacia gums with a high emulsifying capacity (Emulgum BV) and low viscosity in mixture with malto-dextrins, a dry substance of 50% and quite acceptable atomization may be obtained. By this process the spray drying cost is greatly reduced. A 4 month storage study of a powder containing 20% of orange aroma shows, using chromatography in the steam phase, that encapsulation on a mixture of Emulgum BV and malto-dextrin with 50% solids into the dryer is as efficient as encapsulation as pure Acacia gum with 35% of dry solids into the dryer.

A recent study has been performed on various spray dried orange flavors (20% oil fixed in the powder) encapsulated on various Acacia gums and on mixtures of Acacia gums and malto-dextrins. The aromas in powder were tested by chromatography and then examined by electronic microscopy. This clearly shows the regular and uniform film covering each particle 10 to 40 microns in diameter. Prints of broken particles reveal numerous oil droplets (1 micron in diameter) spread in a gum nucleus. Protection of the oil phase then becomes fully effective.

These natural vegetable exudates of Acacia trees have been known and used in the food industry for many years.

The greater knowledge of botanical species and in-depth study of the exudates have made it possible to extend the range of usage Acacia gums. Growing by micro-propagation now permits reliable and organized production of these selected species. In the aromatic industry, the emulsifying, stabilizing and encapsulating properties of Acacia gums make them the most effective medium for the stabilization of liquid emulsions or the encapsulation by atomization of liposoluble compounds sensitive to oxidation.

With the previously mentioned developments in farming and knowledge of structure, it is now possible to eliminate problems of pricing and availability. This in turn allows the flavorist to prepare encapsulated products (spray dried and emulsions) which are of the highest gum arabic quality and less expensive than other chemically derivatized substitutes.

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## Chapter 6

# Emulsion-Stabilizing Starches

## Use in Flavor Encapsulation

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In recent years the importance and utilization of powdered or encapsulated flavors has grown tremendously. Large quantities of encapsulated flavors are used by the food industry in dry packaged goods such as beverages, puddings, cake mixes and other desert products where shelf-life and flavor stability are important. The key to optimum encapsulation of fats and flavors is the performance of the encapsulating agent (1). For an agent to perform at its optimum, it should provide the following functions (2):

1. Protect the active ingredient from oxidation, light, evaporation, humidity and other substance in the food system.
2. Mask taste, flavor or odors until needed.
3. Delay release of an active ingredient.
4. Provide the ability to put the active ingredient into a free flowing powder for ease of handling.

In order to provide these functions the encapsulating agent should have the following properties:

Emulsion Stabilization  
Good Film Forming  
Low Hygroscopicity  
Low Viscosity  
Bland Taste - No Odor  
Release Flavor On Hydration  
Low Cost

Gum arabic has been the encapsulating agent of choice for many years. Gum arabic has all the properties mentioned above which has helped expand its use in the Food Industry.

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• 1988 American Chemical Society

In the early 1970's and mid 1980's gum arabic has suffered from supply shortages due to drought conditions in the major producing regions (i.e., Sudan). These severe shortages have reduced the available output of gum arabic and caused the price to reach \$2.50 per pound (3). To make up the differences in supplies, due to crop loss, poorer quality gum arabic has been used with increased regularity. The poorer quality gum arabic is higher in dirt content and more susceptible to heat degradation during the pasteurization process which reduces its encapsulating performance. The supply shortages have forced many flavor manufacturers to look for substitutes for gum arabic.

Initial work began with testing various starches for encapsulation properties. Low viscosity, stable starch dextrins were first evaluated versus gum arabic for encapsulation efficiencies. Dispersions of corn and tapioca dextrins were used to encapsulate single fold orange oil. The spray-dried powders were evaluated for surface and encapsulated oil. The data is presented in Table 1 (2).

TABLE 1

ENCAPSULATION PERFORMANCE OF GUM ARABIC vs. STANDARD STARCH  
DEXTRINS

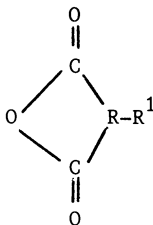
<u>Encapsul- ating Agent</u>	<u>Starting Oil Level %</u>	<u>Total Oil Retained After Spray- Drying %</u>	<u>Surface Oil %</u>	<u>Encapsul- ated Oil, %</u>	<u>Encapsul- ated Efficiency,%</u>
Gum Arabic	20.0	18.1	1.4	16.7	83.5
Corn Dextrin	20.0	16.9	4.1	12.8	64.0
Tapioca Dextrin	20.0	17.9	2.9	15.0	75.0

One sees from the data, presented in TABLE 1, that the starch dextrins have the ability to encapsulate the orange oil, but does not encapsulate as much oil as gum arabic. The starch dextrins match the viscosity and stability of the gum arabic when placed in solution, however; other properties such as emulsifying and emulsion stabilizing properties are poorer in the dextrins. We believe that the emulsifying properties inherent in gum arabic are partially responsible for its encapsulating abilities.

Emulsions made with a fine oil droplet particle size, usually less than one micron, are more stable with the oil droplets less likely to coalesce and separate. The encapsulation of a good quality emulsion is generally more efficient with less surface oil on the spray-dried powder. We wanted to build surfactant properties into the starch backbone to improve encapsulation efficiencies. Studies of the mechanism by which surfactants stabilize emulsions were made in order to accomplish this.

Conventional surface active agents are characterized by the presence in the molecule of a hydrophilic group and a hydrophobic group. These molecules orient themselves at the oil/water interface when the oil is dispersed in water under high agitation. The hydrophobic portion of the molecule dissolves in the oil phase and the hydrophilic group dissolves in the water phase. A monolayer of the surfactant molecule surrounds the oil droplet and prevents reagglomeration. These monolayer films are weak and can easily be disrupted causing the emulsions to break. In the past, starches have been used to add viscosity to the emulsions thus preventing coalescing by the nature of their hydrophilic chains. When starches are treated with lipophilic reagents so that they contain hydrophobic and hydrophilic groups, the starch molecules are attracted to the interface of the water and oil droplets in an emulsion. The resulting film surrounding the oil droplet is much stronger and more continuous making the emulsion more stable. The starch derivatives with balanced hydrophobic and hydrophilic groups are superior to unmodified starches in stabilizing emulsions.

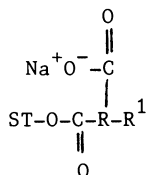
A very successful approach to the preparation of starch-based emulsion stabilizers has been the development of polysaccharide derivatives of substituted dicarboxylic acids by Caldwell and Wurzburg (4). The invention involves the treatment of starch with substituted cyclic dicarboxylic acid anhydrides having the following structural formula:



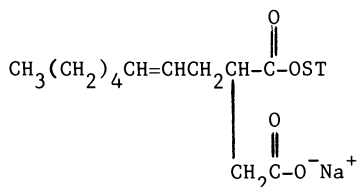
where R represents a dimethylene or trimethylene radical and R<sup>1</sup> is the substituent group, ordinarily a long hydrocarbon chain. An example of these types of reagents are the

substituted succinic acid anhydrides in which the substituent hydrophobic chain is an alkyl or alkenyl group containing from 5 to 18 carbon atoms.

The starch derivative is prepared by a standard esterification reaction where the reagent and the starch suspended in water are mixed under alkaline conditions. The acid ester may be represented by the following structural formula:



wherein R is the dimethylene or trimethylene radical and R<sup>1</sup> is the substituent hydrophobic group. The most important derivative cleared for food use by the FDA and having applications in the pharmaceutical and industrial areas as well, is octenylsuccinic acid anhydride (5). The FDA has set a maximum level of treatment for octenylsuccinic acid anhydride on the starch at 3% which corresponds to a degree of substitution of 0.02 (6). This treatment can be conducted on a wide variety of starch bases, acid hydrolyzed starches and dextrans. The structure of the starch octenylsuccinate is shown below:



## Materials and Methods

### Carrier

Gum arabic, standard starch dextrans and laboratory prepared low viscosity starch octenylsuccinates were used for all encapsulation work.

### Flavor Oils

Orange terpenes, lemon oil and single fold orange oil obtained from Naarden Inc., were used for encapsulation studies.

### Emulsification and Spray-Drying

Two hundred grams of carrier was dispersed in distilled water at the desired levels (solution viscosities similar to gum arabic) and flavor oil emulsions were made using a Waring blender at high speed for two minutes. The emulsion was spray-dried using an inlet temperature of 200°C and an outlet temperature of 90°C. Atomization was achieved using centrifugal wheel atomization.

### Oil Retentions

A 10 gram sample was placed in a 200 ml round bottom flask and 100 ml of distilled water added. A Dean-Stark trap and condenser were used and the mixture was brought to a boil. The steam distilled oil was measured after four hours versus control mixtures. In order to measure surface oil on the spray-dried powders, the powder was first washed with a solvent (ethyl ether or hexane) then oil retentions were run by the steam distillation method illustrated above. Differences in oil volume for solvent washed versus non-washed were attributed to surface oil on the spray-dried powders.

### GC Analysis to Measure Carrier's Ability to Protect Orange Terpenes from Oxidation

Orange terpenes were emulsified in various carrier's and spray-dried. The spray-dried powders were aged for 3 days at 80°C in a draft oven. Beta-pinene is an oxidation product in orange terpenes which can be measured by GC. The beta-pinene level is proportional to the degree of oxidation of the orange terpenes. High levels of beta-pinene content in the spray-dried powders indicate poor oxidation resistance imparted to the encapsulated terpenes by the carrier.

A Beckman Model 4 GC was equipped with a carbowax column, temperature 180°C (inlet). A microliter injection was made and the oxidized beta-pinene peak was measured. The retention time for the oxidized beta-pinene peak is 5.5 minutes. The encapsulated orange terpenes were first dissolved in water before injection.

### Emulsion Particle Size

Particle size of the oil droplets after emulsification was determined by microscopy. This was accomplished prior to spray-drying. A typical good emulsion would have an oil particle size of less than 2 microns (um).



### Overnight Emulsion Stability

This is a subjective test to determine the storage stability of an emulsion. A sample of the liquid emulsion before spray-drying is used to fill a 16 oz. tall glass jar. The jar is capped and stored in an oven for 16 hours at 50°C. When storage is complete, the jar is removed from the oven and evaluated. Surface oil layers on the emulsion indicate poor emulsion stability performance by the carrier.

### Results and Discussion

An example of the improved emulsion stabilizing properties imparted by treatment of starch with octenylsuccinic acid anhydride can be seen in TABLE 2 (5):

TABLE 2 EMULSION STABILITY OF GUM ARABIC vs. STARCH CARRIERS

<u>Encapsulating Agent</u>	<u>Percent Solids</u>	<u>% Lemon Oil</u>	<u>Emulsion Particle Size (um)</u>	<u>Overnight Emulsion Stability 50°C</u>
Gum Arabic	30	30	< 3	Some Surface Oil
Conventional Dextrin	40	30	2 - 10	Oil Layer
Low Viscosity Starch Octenylsuccinate	40	30	< 2	Excellent

The octenylsuccinic acid anhydride treated starches give on the average smaller oil droplet particle sizes and better emulsion storage stability than both gum arabic and a starch dextrin.

Emulsions of lemon oil stabilized with gum arabic, a conventional starch dextrin and a low viscosity starch octenylsuccinate were spray-dried and evaluated for encapsulating efficiencies. Oil retentions and surface oil determinations were made according to the Materials and Methods section. TABLE 3 demonstrates the superiority of the starch octenylsuccinate in flavor retention and surface oil to gum arabic and a starch dextrin (5):

TABLE 3

COMPARISON OF ENCAPSULATING EFFICIENCIES OF GUM ARABIC vs. STARCH CARRIERS

Encapsulating Agent	Amount of Flavor In Powder (%)		Flavor Lost On Drying (%)	Retained Flavor On Surface (%)	Truly Encapsulated Flavor (%)
	Initial	Retained			
Gum Arabic	30.5	28.7	5.9	16.5	23.9
Conventional Dextrin	30.7	23.5	23.6	25.6	17.4
Low Viscosity Starch Octenylsuccinate	30.1	30.0	0.3	1.0	29.4

The data show that when spray-drying a 30% lemon oil level on the weight of the carrier, the starch octenylsuccinate only loses 0.3% of the oil during the spray-drying process. Surface flavor oil was also lower for the starch octenylsuccinates which indicates excellent encapsulation efficiencies.

In order to further demonstrate the superior encapsulation efficiencies of starch octenylsuccinates, comparison studies of surface oil versus oil level were made against gum arabic (2). The data is presented in TABLE 4:

TABLE 4

SURFACE OIL COMPARISON OF GUM ARABIC vs. STARCH OCTENYLSUCCINATE

Oil Level On Spray-Dried Powders (%)	% Oil On Surface of Powders	
	Gum Arabic	Low Viscosity Starch Octenylsuccinate
20	1	1
30	8	1
40	23	7
50	71	14

At lower oil usage levels (20% - 30%) gum arabic and starch octenylsuccinates performed equally. High oil levels (greater than 40%) showed marked differences in surface oil content of the powders, with the starch octenylsuccinates out performing gum arabic. Less flavor oil on the surface of the powder will help improve overall shelf-life stability.

Another important aspect of encapsulation efficiency is the resistance to oxidation that the carrier imparts to the flavor oils. The oxidation resistance properties are critical to shelf-life stability of the encapsulated product. Oxidation properties can be measured organoleptically by a taste panel or by gas chromatograph of the recovered oil. Peaks related to oxidation products of orange terpenes obtained from GC analysis can be monitored as the powders are aged for three days at 80°C. The GC was used to measure beta-pinene, an oxidation product of orange terpenes. The results are reported in square inches. The greater the area for the beta-pinene peak, the poorer the oxidation resistance of carrier towards the orange terpenes. The data is presented in TABLE 5:

TABLE 5

OXIDATION RESISTANCE OF ORANGE TERPENES vs. CARRIER TYPE

<u>Encapsulation Agent</u>	<u>Orange Terpene Level (%)</u>	<u>GC<sub>2</sub> (in<sup>2</sup>)</u>	<u>Taste Panel</u>
Gum Arabic	20	1.04	Excellent
Tapioca Dextrin	20	1.77	Good
Low Viscosity Starch Octenyl-succinate	20	0.95	Excellent

As can be seen from the data in TABLE 5 the low viscosity starch octenyl-succinate closely matches the oxidation resistance of gum arabic. This product would offer improved shelf-life over a standard starch dextrin and similar stability to a gum arabic encapsulated flavor.

Spray-drying costs are always a factor in determining the economics of an encapsulated product. Drying costs are related to the amount of water that must be removed in the spray-drying process. It is therefore advantageous to enter the drier at the highest possible solids that still gives

low enough viscosity to provide for efficient atomization as well as good oil retention. A comparison of solids versus Brookfield viscosity for gum arabic and a low viscosity starch octenylsuccinate demonstrate the starches' ability to be used at higher solids (TABLE 6). This improves spray-drying rates and lowers cost (8).

TABLE 6

BROOKFIELD VISCOSITY OF GUM ARABIC vs. STARCH  
OCTENYLSUCCINATE  
AS A FUNCTION OF CONCENTRATION

<u>% Solids</u>	<u>Gum Arabic</u>	<u>Starch Octenylsuccinate</u>
30	200	100
35	380	200
40	1,000	200

Conclusions

Starch octenylsuccinates offer excellent emulsifying properties, flavor oil retention and good oxidation resistance versus gum arabic. They can be made on a variety of starch bases, dextrans or fluidities which provide versatility and improved spray-drying costs. Starch octenylsuccinate are low in cost, domestically produced and are not subject to the market fluctuations that gum arabic encounters.

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## Chapter 7

# Spray-Drying of Food Flavors

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Spray drying is the most commonly used technique for the production of dry flavorings. In spray drying, an aqueous infeed material (water, carrier, and flavor) is atomized into a stream of hot air. The atomized particles dry very rapidly, trapping volatile flavor constituents inside the droplets. The powder is recovered via cyclone collectors. Flavor retention is quite satisfactory if dryer operating parameters are properly chosen. Flavor retention is maximized by using a high infeed solids level, high viscosity infeed, optimum inlet (160-210 C) and high exit (>100 C) air temperatures and high molecular weight flavor molecules. The shelf-life of oxidizable flavor compounds is strongly influenced by the flavor carrier.

Spray drying is the major process employed to produce dry flavorings. The popularity of this process is partially historic, i.e., it was the first process used in the flavor industry to produce an "encapsulated" flavoring. However, the merits of the process have ensured its continued dominance in the flavor area. These merits include availability of equipment, low process cost, wide choice of carrier solids, good retention of volatiles, and good stability of the finished flavoring.

The initial step in spray drying of a flavor is the selection of a suitable carrier material. One can divide the major flavor carriers into three classes (and blends thereof): hydrolyzed starches, emulsifying starches, and gums (essentially gum arabic).

The hydrolyzed starches are inexpensive, bland in flavor, very soluble (up to 75%), and exhibit low viscosity in solution. The major shortcomings of these products are a virtual lack of emulsifying capacity and marginal retention of volatiles.

The emulsifying starches have been partially hydrolyzed and then derivatized to impart lipophilic properties. The lipophilic

group added to the starch backbone comes from the reaction with 1-octenyl succinic anhydride (1, 2). These starches provide excellent volatile retention during spray drying and emulsification properties (3, 4). Their principle drawbacks include off-flavors, cost, and poor protection of the flavoring to oxidation.

Gum arabic has been the standard of excellence as a flavor encapsulating material. It is an excellent emulsifier, bland in flavor, and provides very good retention of volatiles during the drying process (4). The major shortcomings of gum arabic have related to high cost and limited availability.

Once a carrier choice has been made, the carrier is hydrated (sometimes with heating) to the optimum solids level. While most work (5) has shown that increasing the solids level of the dryer infeed matrix not only greatly improves flavor retention during drying but has an added advantage of increasing dryer throughput, there is an optimum infeed solids level for each carrier material (5). This is the solids level at which maximum solubility of the carrier is achieved.

The hydrated carrier is then mixed with the chosen flavoring material, a coarse emulsion formed via high shear mixing and then it is homogenized prior to going into the spray dryer. While there is considerable variation from company to company on the level of homogenization given the infeed material, it has been suggested that there is a significant advantage to efficient homogenization (6).

There are many different types of spray dryers used in the flavor industry. They differ in size, shape and type of atomization. Atomization is typically accomplished by either a single-fluid high-pressure spray nozzle or centrifugal wheel. While the two-fluid nozzle is used in some applications, it is not commonly used in the flavor industry. Centrifugal wheel atomizers have an advantage of handling very viscous and abrasive infeed materials while the pressure spray systems offer greater flexibility in producing larger particle size powder. Approximately 80% of the industry utilizes centrifugal wheel atomization. Virtually all spray dryers used in the flavor industry are cocurrent in design, i.e., product enters the dryer flowing in the same direction as the drying air. This results in very rapid drying and does not subject the flavoring to as much heat as would a counter current system. In the cocurrent dryer, the flavoring never exceeds the exit air temperature of the dryer. The atomized product is cooled by water evaporation and the powder temperature is normally 35 to 40 C below the dryer exit temperature.

Drying chamber shape predominantly is either conical or flat-bottomed. The flat-bottomed dryers remove the powder as it falls to the floor of the dryer by use of a rotating pneumatic powder discharger that functions as a vacuum cleaner. These dryers subject the product to significantly more heat than do the cone-bottomed dryers. While for many types of dry flavorings this additional heat is insignificant, thermally labile materials (e.g., natural flavorings - tomato, cheese, and numerous fruit juice based products) may suffer from the additional heat.

The dry product is primarily collected in cyclone collectors (a few bag houses still remain), sieved, and finally packaged in moisture barrier containers. The exit air from the dryer often has to be treated to meet local pollution control laws. While many of the older dryers use gas incineration, as energy costs have increased these incineration systems have become quite costly to operate. New dryer installations use scrubbing systems (e.g., aqueous/chemical sprays) to remove entrained solids and gaseous volatile flavors.

At first glance one might be surprised that volatile flavor compounds are retained during spray drying. The major volatile constituent in the infeed matrix is water. During this drying process, at least 90% of the water is evaporated but yet the more volatile flavor constituents (e.g., diacetyl, ethylacetate, ethyl butyrate) are nearly completely retained when optimum drying conditions are followed. One would expect the flavor constituents to be lost to a large extent during the drying process.

The reason for the surprisingly good retention of volatiles has been the subject of substantial research (7-35). The accepted explanation for this phenomenon relates to the fact that as an atomized droplet of infeed material contacts the hot dryer air, it starts to dry on the outside. The surface of the drying droplet decreases very rapidly in moisture content. When this surface reaches a moisture content ranging from 7 to 23 percent, it is no longer permeable to most flavor compounds but remains quite permeable to the relatively smaller, soluble water molecules. Therefore, this dry ( $a_w < 0.90$ ) surface acts as a semipermeable membrane permitting the continued loss (or diffusion) of water but efficiently retaining (or stopping diffusion) flavor molecules. A study by Menting et al. (20, 21) showed that between 40 and 100% moisture, diffusion coefficients of water and organic flavorants varied by less than a factor of 10. However, once the carrier material attained  $< 7\%$  moisture, the diffusion constants of water to organic flavorant differed very greatly. As an example, the diffusion coefficient of acetone was 300 times less than that of water. The vastly reduced diffusion coefficient of acetone effectively prohibits its movement through the dry matrix and it cannot reach the surface to undergo evaporation.

In order then to determine what influences flavor retention during drying, one must focus attention on the very early stages of dehydration. In fact, it has been shown that the major fraction of total volatiles lost during nozzle-atomized spray drying occurs within ten centimeters of the pressure nozzle (17, 33, 35).

The process parameters which have been stated as influencing the retention of volatile flavor compounds during spray drying are (36):

1. Solids content of the infeed material.
2. Molecular weight and vapor pressure of flavor compounds.
3. Type and molecular weight of the carrier used.
4. Concentration of the flavor components.
5. Viscosity of the dryer infeed material.



6. Drying air velocity.
7. Dryer inlet and exit air temperatures.
8. Percent humidity of the dryer inlet air.
9. Particle size of the atomized droplet.
10. Dryer feed temperature.

The primary factor determining the retention of volatiles during drying is infeed solids content (14, 20, 21, 23, 24, 37). High infeed solids dryer feeds increase retentions during drying by reducing the time necessary to form a semipermeable membrane at the drying particle surface. The very strong dependence of flavor retention on infeed solids content is readily apparent from Figure 1. A study by Leahy et al. (4) has shown that infeed solids content is even more important in determining flavor retention during drying than is the type of carrier. While previous data has suggested that one should use the highest infeed solids possible, recent work has shown that there is an optimum infeed solids content for the drying of flavoring materials (5). An optimum solids level exists since one generally uses a constant ratio of flavoring materials to carrier solids. At some solids content, solubility is exceeded by adding more carrier. While it may be possible to pump and atomize this higher solids matrix, the undissolved carrier does not provide any effective encapsulating effect and poorer flavor retention is noted during the drying process (Fig. 2). It is apparent that each carrier material has its own optimum infeed solids for flavor retention which is based on solubility.

The fact that both molecular weight and vapor pressure of the flavor compounds have an influence on their retention during spray drying is both obvious and well documented in the literature (4, 8, 10, 24). Molecular weight is a reasonable representation of molecular size which actually is the primary factor determining diffusion. For flavor molecules of increasing molecular size, diffusion rate slows and the flavor molecules do not reach the particle surface as readily. A second factor promoting the retention of larger flavor molecules is that the drying surface becomes impermeable more quickly during drying. Diffusion is effectively stopped at a higher moisture content. Both of these factors favor the retention of larger molecular weight (molecular size) flavorants. Vapor pressure or volatility plays a secondary role in determining flavor retention due to its influence in controlling flavor loss until the drying droplet surface becomes semipermeable. The end result is that small, very volatile flavor compounds are lost to a greater extent than the larger less volatile flavor compounds (Fig 3).

While the infeed solids content of the infeed material has an unquestionably greater influence on the retention of volatile flavors than does the type of carrier used, carrier type does influence flavor retention during spray drying (4, 16, 31, 37, 38). This influence can be indirect in the sense that some carrier materials become very viscous at relatively low solids contents. Low solids means poor flavor retention. The effect of type of carrier on flavor retention can also be direct. Carriers

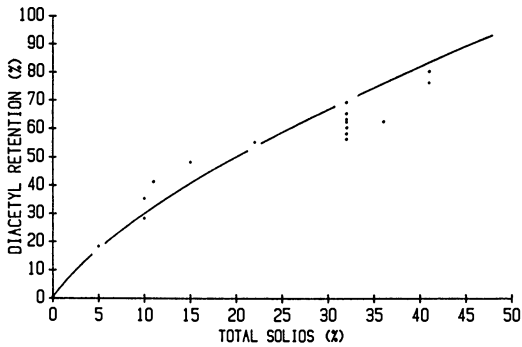


Fig. 1. Effect on solids level on the retention of volatiles during spray drying. (Reproduced with permission from ref. 37. Copyright 1969 American Dairy Science Association.)

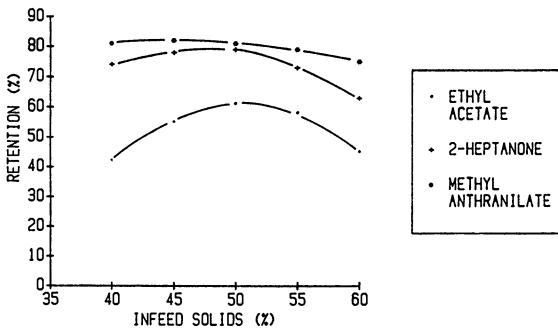


Fig. 2. Optimization of solids levels for the retention of volatiles during spray drying. (Reproduced with permission from ref. 5. Copyright 1982 Allured Publishing Corporation.)

which are good emulsifiers and/or good film formers typically yield better flavor retention than do carriers which lack these properties.

Higher flavor loads generally result in poorer flavor retention (7, 9, 23, 37). Due to this phenomenon, most products to be spray dried are dried at a solids to flavor ratio of 4 to 1. One of the few exceptions to the 4:1 ratio limit is the patent of Brenner (39). Brenner advocates the use of a plasticizing carrier component which reportedly permits the effective encapsulation of flavoring at up to 1:4 ratios (carrier:flavor). While this patent has been in existence for about 11 years, this author knows of no commercial products using this high loading.

Infeed viscosity exerts an effect on flavor retention during drying by influencing circulation currents within the drying droplet. If viscosity is low, internal mixing may occur during drying which delays formation of the semipermeable surface. This delay permits greater flavor losses. Therefore, at the same infed solids content, one would expect greater flavor retention for a high viscosity infed vs. a low viscosity infed material.

High dryer air velocity (relative to the atomized particle) is known to improve the retention of flavorants. This effect is due to a more rapid heat and mass transfer associated with the drying process. This factor is largely controlled by dryer design and cannot be changed to a significant degree as a dryer operating variable.

The influence of dryer inlet and exit air temperatures has received considerable study (7, 8, 9, 23, 37, 40, 41). It is desirable that a high enough inlet air temperature be used to allow rapid formation of a semipermeable membrane on the droplet surface but yet not so high as to cause heat damage to the dry product or "ballooning" of the drying droplet. Inlet air temperatures of 160-210 C are reported as giving optimum flavor retention during drying (7, 8, 23, 37). Inlet air temperatures above 210 C have been found to decrease flavor retention for some types of carriers. This decrease in flavor retention is due to ballooning during drying. Ballooning occurs when sufficiently high inlet air temperatures are used that steam is formed in the interior of the drying droplet. Steam formation causes the droplet to puff-up (or balloon) thereby producing a thin-walled hollow particle. This particle will not retain flavor compounds as well as the non-ballooned counterpart. The ballooning temperature is primarily a function of carrier material and dryer design. Spray dried flavorings have been successfully produced using inlet air temperatures from 280-350 C (36, 41).

The influence of dryer exit air temperature on flavor retention is not as well documented. Reineccius and Coulter (37) have shown that flavor retention increases with increasing exit air temperatures. This is presumably due to the higher exit air temperatures (at a fixed inlet air temperature) giving the dryer air a lower humidity. Low humidity results in more rapid drying and, therefore, better flavor retention. There are other concerns for using high exit air temperatures, however. High exit air temperatures may result in heat damage to some flavoring materials

(e.g. cheese, tomato, and natural fruit juices) and also result in decreased dryer throughput. Therefore, in practice, dryer exit air temperatures usually range from 80-90 C.

Dryer air humidity can be controlled by dehumidifying the inlet air. This would favor rapid drying and flavor retention. Dehumidification typically is cost prohibitive and, therefore, is seldom done.

Infeed temperature has also been studied by numerous workers (8, 23, 24, 27, 28, 33). Sivetz and Foote (24) have noted that chilling the dryer infeed (30% coffee solids extract) before drying markedly improved the flavor of the spray dried coffee. Cooling the infeed material would increase the feed viscosity which, in turn, would affect circulation currents within the atomized droplets and size of these droplets, along with the vapor pressure and diffusivity of the flavor compounds. Thijssen's work tends to disagree with these findings (8, 23, 27, 28). Thijssen stated that dryer infeed temperature should be elevated such that higher infeed solids (i.e. greater solubility) may be used. The higher infeed solids would result in better flavor retention.

The role of particle size of the atomized droplets in determining flavor retention is also controversial. Several workers have reported that larger particle sizes result in improved flavor retentions (7, 9, 23, 24, 42, 43). To the contrary, Reineccius and Coulter (37) could find no effect of particle size on retention. This controversy has been partially cleared up by work showing that particle size is not significant if high infeed solids are used (8). Reineccius and Coulter (37) did their study at a high infeed solids content. While there may not be a relationship between flavor retention and particle size, it often is desirable to produce large particles to facilitate rehydration. Small particles tend to disperse very poorly, especially in cold water and instead form lumps on the liquid surface. Large particles can be obtained through judicious choice of dryer operating conditions (e.g., high infeed viscosity and solids, low-pressure large-orifice if using a pressure spray atomizer or low wheel speed if using a centrifugal atomizer) or the use of agglomeration techniques.

The final subject of this review will consider the shelf-life of spray dried flavorings. This discussion will be brief since there are several other papers on this subject as part of this symposium. A large portion of the dry flavorings produced include some citrus oils. These citrus oils are prone to oxidation during storage (45). In the past, the citrus oils have been stabilized via the use of antioxidants (BHA). However, today's market is demanding preservative-free flavorings. This creates a very significant shelf-life problem. As is shown in other work presented at this symposium (41, 44), the shelf-life of dried orange oil (no antioxidant) may be only a few weeks at room temperature. The industry requires at least a year shelf-life.

In order to improve upon shelf-life, the encapsulated flavoring must be protected from oxidation. This brings up con-

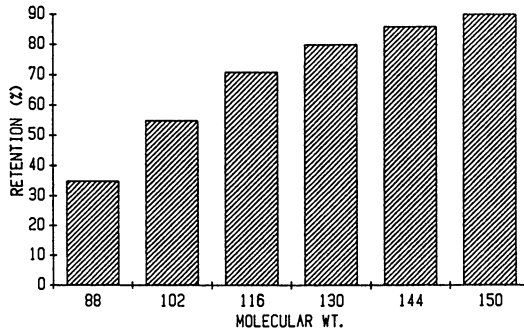


Fig. 3. Effect of molecular weight of volatiles on their retention during drying.

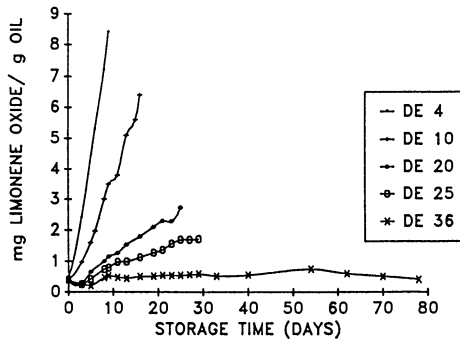


Fig. 4. Shelf-life of orange oils (as measured by limonene epoxide formation) as influenced by flavor carrier. (Reproduced with permission from ref. 46. Copyright 1986 Institute of Food Technology.)

sideration for the presence of antioxidants (natural), trace metals (e.g., copper and iron), entrained air and oxygen barrier properties of the final spray dried particle.

Anandaraman (45, 46) has shown that there is a very strong protective effect of higher dextrose equivalent (DE) starches (corn syrup solids) against oxidative deterioration (Fig. 4). The higher DE products have a greater number of free reducing groups. It is possible that some of the stability observed by Anandaraman (45, 46) is due to the high reducing environment provided by the encapsulating matrix. One might consider the matrix itself to be acting as an antioxidant.

One must be very cautious about using flavor carriers which contain trace minerals that are pro-oxidants. There is no question that copper and iron will catalyze the oxidation of citrus oils. One will find a significant variation in trace mineral content of commercial flavor carriers.

The role of entrained air (i.e., air included or trapped within the particle) in determining shelf-life of spray dried flavorings has not been studied. It would appear logical that one should minimize the entrained air since any air contact will promote oxidation.

Probably the major determinant of shelf-life of spray dried flavorings is the porosity of the dried particle to oxygen. While there is no direct data to support this statement, we have found vastly different shelf-lives for products which contain essentially similar trace metal levels, surface oils, and absolute densities. We can find no other explanation for the differences in shelf-life other than matrix porosity. This area needs to be further studied in order to confirm this hypothesis and then take advantage of it to improve the shelf-life of spray dried flavorings.

In closing, spray drying has been the traditional means of producing encapsulated flavorings. If adequate care is used in selection of spray dryer operating conditions, a very high quality product can be obtained at relatively low cost. Recent marked trends (i.e., "natural") as well as competitive processes for encapsulation are putting demands on the spray drying process for improvement of shelf-life characteristics. Work currently is in progress to enhance the shelf-life of spray dried flavorings.

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## Chapter 8

# Spray-Dried Orange Oil

### Effect of Emulsion Size on Flavor Retention and Shelf Stability

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The effect of emulsion size on the retention and shelf-life of spray dried orange oil were investigated. Orange peel oil was spray dried using either gum arabic or Amiogum 23 as a carrier. Five different emulsion sizes were created by mixing to various extents, homogenization and Microfluidization. Microfluidization is a new technique for making small uniform emulsions and is detailed in the paper. The spray dried powders were tested for oil retention, moisture content and extractable surface oil. Samples were stored at elevated temperatures and monitored by gas chromatography for the formation of limonene-1,2-epoxide to determine the shelf-life. Rehydrated powders were analyzed for particle size to confirm that different emulsion sizes were prepared. A smaller emulsion size yielded a higher percent retention of orange oil with a smaller amount of surface oil but did not give a longer shelf-life. Sensory analysis of reconstituted powders from the smallest and largest emulsion size indicated that the emulsion size did not have a significant affect on the perceived intensity of the orange flavor.

Spray drying is one of the most cost effective and widely used methods of flavor encapsulation. While the process of spray drying is fairly straight forward, there are many variables relative to both sample preparation and actual drying conditions. Many of these variables have been outlined and discussed by Reineccius et al (1). One problem that is of concern when encapsulating citrus oils is the extent to which the flavor is incorporated into the carrier solution before drying. The solution can be mixed just enough to disperse the flavor, creating a coarse emulsion or it can be homogenized to create a fine

emulsion. The emulsion size may be important not only in determining the properties of the spray dried powder, but may also be important in products such as beverages where the powder is used as a flavoring agent.

An emulsion can be defined as a system in which an immiscible liquid (e.g., citrus oil) is dispersed as droplets in another immiscible liquid (water) by mechanical agitation (2). Maintaining the emulsion is a difficult task which usually requires the use of an emulsifying agent. The emulsifying agent lowers surface tension of the droplets and forms a barrier to help prevent coalescence of the droplets. Gum arabic is an excellent emulsifying agent which can also serve as a carrier in spray drying. Modified starches which act as both an emulsifying agent and a carrier are also available. While these emulsifying agents help prevent destabilization of an emulsion by coalescence, emulsions also undergo separation with dispersed droplets either rising or settling. This is dependent on whether they are more or less dense than the continuous phase. The rate of separation of an emulsion is predicted by Stokes law:

$$v = \frac{2r^2g(d_1-d_2)}{9n}$$

Where  $V$  = velocity of rise (or fall) of droplets,  $r$  = droplet radius,  $g$  = acceleration due to gravity,  $d_1$  and  $d_2$  = densities of the two phases and  $n$  = viscosity of the continuous phase. In the equation,  $g$ , is fixed. The densities of the two phases are also fixed, citrus oils having a density of approximately 0.83 g/mL and water 1.00 g/mL. Weighing agents such as glyceryl abietate, glycerol tribenzoate and brominated vegetable oil can be added to increase the density of the oil, and lessen the difference in densities; however, legal limits and limited solubility of these agents prevents the addition of enough to bring the density of the oil up to that of a typical beverage that the spray dried powder might be used in. When preparing an emulsion for spray drying, the viscosity of the solution can be increased by increasing the solids or carrier level in the solution. This is effective in stabilizing the infeed material but does essentially nothing if the finished powder is used in a liquid beverage application where the usage level is typically 0.1 to 0.2%. The only variable left that can be changed is the radius of the droplets that are dispersed.

The dispersed droplet size, referred to as emulsion or particle size, can be reduced in the spray drier infeed matrix by more vigorous mixing or homogenization. There is also a new technique for creating small emulsions termed microfluidization which will be discussed later. This research was designed to determine whether the size of emulsion in the infeed solution will affect the characteristics of the final spray dried powder.

#### Materials and Methods

Gum arabic (Colloides Naturels, Far Hill, NJ) and Amiogum 23, a modified food starch (American Maize, Hammond, IN) were used as

carriers. The carriers were rehydrated in warm water (ca. 80°C) in a proportion of 625 mL H<sub>2</sub>O to 300 g carrier. The solution was mixed thoroughly and allowed to sit overnight.

Four emulsion sizes were prepared immediately prior to spray drying the first two sets of samples. Five emulsions were prepared for the third set of samples. Gum arabic was used as the carrier for the first and third sets and Amiogum 23 for the second set. Single-fold orange oil without any antioxidants was added to the carrier solution to give a carrier to flavor ratio of 4:1. The orange oil was stirred in with a whisk just until no oil was left on the surface to create the coarsest emulsion. The medium coarse emulsion was made by blending the oil into the carrier solution with a Greerco high shear mixer at medium speed for 2 minutes. The medium fine emulsion was also prepared using the Greerco mixer with 5 minutes of blending on high speed. The fine emulsion was prepared by homogenizing with one pass through a single stage Gaulin homogenizer operating at a pressure of 2500 psig. For the third set of samples, the fifth emulsion was prepared in a Microfluidizer model 110T (Microfluidics Corp., Newton, MA). Microfluidization based on patented technology in which a split feed stream flows into an interaction chamber at ultrahigh velocities and pressures (up to 1500 ft and 16,000 psi respectively). The two streams collide head-on and exit the chamber at a right angle to the collision. The force of the collision creates cavitation and shear forces to decrease the particle size. The feed stream was prepared in a manner similar to the coarse emulsion in which the orange oil was blended into the carrier solution with a whisk. The Microfluidizer was operated at a pressure of 11,000 psi and the sample was collected after one pass through the interaction chamber.

The samples (ca. 2500 g for each sample) were spray dried in a Niro Utility drier with the inlet temperature at 200 C and outlet at 100 C. The drier temperatures were allowed to stabilize before samples were collected for analysis. The dried samples were analyzed for total oil, surface oil, moisture, emulsion size and emulsion stability. Samples were also stored at an elevated temperature for shelf-life determination. Sensory analysis of rehydrated powder from the coarse and Microfluidized emulsions was performed to determine if differences in emulsion size affects the perceived flavor intensity.

Total Oil. Total oil was determined using a Clevenger apparatus. Twenty g powder was dissolved in 150 mL water in a 500 mL flask. A few boiling chips and ca. 0.5 mL antifoam emulsion were added. The Clevenger apparatus was fitted into the top of the flask with a water cooled condenser on top of the Clevenger. The solution was slowly brought to a boil and allowed to distill for 3 hr. The volume of oil, read directly from the oil collection arm, was converted to g oil by multiplying by the density of the oil (0.83 g/mL).

Surface Oil. The amount of extractable surface oil of the dried powder was determined by Soxhlet extraction. Twenty g of powder was put in an extraction thimble and covered with glass wool.

The powder was extracted with 150 mL pentane for 4 hr. 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 final volume of approximately 1 mL. The amount of oil in the sample was determined by gas chromatography. The instrument parameters were the same as those described below for monitoring for oxidation products during the shelf-life study.

Moisture. Moisture was determined by the toluene distillation method. A 40 g sample of powder was added to 250 mL toluene in a 500 mL flask. 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 2½ hr. The distillate was allowed to cool to room temperature before the volume of water was read directly from the trap.

Emulsion Size. The determination of particle size was accomplished using a Leeds and Northrup model 7991-4 Microtrac. A 1% solution of spray dried powder in water was prepared and gently stirred with a magnetic stir bar until the powder was completely dispersed. The absence of any clumps when the solution was viewed under a microscope was used as an indicator of complete dispersion. A few mL of solution were placed in the chamber of the Microtrac. In the instrument, the solution flows past a laser beam in an optically clear cell. The angle of diffraction of the laser beam is measured and the size of the emulsion calculated. The calculation is based on the principle that the smaller the emulsion size, the larger the angle of diffraction. The instrument gives results on emulsion size and size distribution as well as calculating the surface area of the emulsion. The entire analysis is computerized.

Emulsion Stability. The stability of the emulsions was determined by measuring optical density of the solutions following centrifugation. A 0.2% solution of each spray dried powder was prepared in water and the optical density read at 400 nm in a Coleman spectrophotometer. A 0.16% solution of carrier (gum arabic) was used as a blank. This is based on a carrier to flavor ratio of 4:1. The initial optical density of each solution was read and then the solutions were centrifuged in an IEC International Centrifuge at 500 x g for 5, 10, 15, 30, 45 and 60 min. The optical density was read after each time period.

Shelf-life. Samples of each powder were stored in screw cap test tubes in an incubator. Product from the first two spray drying runs was held at 45 + 2 C. Product from the last run was held at 37 + 2 C. Samples were withdrawn every two days from the samples stored at 45 C and every three days from the samples stored at 37 C. Pulled samples were stored in screw cap vials at 0 C until analysis by gas chromatography (GC). The products were monitored for the formation of limonene-1,2-epoxide and L-carvone, both oxidation products of d-limonene (3).

A 0.15 g sample of powder was dissolved in 0.85 g H<sub>2</sub>O. Then 4 mL acetone, containing 0.25 mg/mL 2-octanone, was added slowly

with agitation. The sample was allowed to settle and a 1  $\mu$ l aliquot of the liquid phase was injected into the GC. A Hewlett Packard model 5880 gas chromatograph was used. The analysis was run under the following conditions:

Column: 30 m SE 54 x 0.25 mm fused silica, J & W Scientific  
(Rancho Cordoba, CA)  
Carrier gas: Hydrogen  
Column head pressure: 15 psig.  
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: FID

Sensory Analysis. A paired comparison test was run to determine if the difference in oil droplet size in the emulsion changed the perceived intensity of the orange flavor. The coarsest emulsion (3.87  $\mu$ M) and the Microfluidized sample (0.90  $\mu$ M) from the third set of spray dried samples were compared. The solutions were prepared using 200 ppm flavor in a 10% (w/v) sucrose solution with 0.30% of a 50% citric acid solution added. The amount of each powder required to attain 200 ppm orange oil was calculated on the basis of percent oil in each powder (determined by Clevenger analysis). A pair of samples at approximately 10 C was given to each of 24 untrained panelists. The samples were coded with random numbers. Half the panelists were asked to taste the coarsest sample first while the other half tasted the Microfluidized sample first. This was done to determine whether or not adaptation was a factor. The panelists were asked to indicate which sample had the most intense orange flavor.

### Results and Discussion

The test for emulsion size in the finished powders was run to confirm that different oil droplet sizes were created by the different processing conditions. The average particle sizes are listed in Table I. An important point to note is that as particle size decreased, the range of particle sizes also decreased. The smaller the emulsion, the more uniform the particle size. This is illustrated in Figure 1.

The results for total oil are listed in Table II. Higher retention resulted as the emulsion size decreased. An average of 13.8 g oil/100 g powder (69% of the starting weight of oil) was retained in the coarse emulsion and 19.1 g oil/100 g powder (95% of the starting weight of oil) in the homogenized or fine emulsion. In the Microfluidized sample, 100% of the starting weight of oil was retained.

Table I. Emulsion Size of Spray Dried Orange Powders

Sample	Trial <sup>a,b</sup>			Average
	1	3		
Coarse	4.18	3.87		4.03
Medium Coarse	2.28	2.77		2.53
Medium Fine	1.62	2.08		1.85
Homogenized	1.40	2.12		1.76
Microfluidized	<sup>c</sup>	0.90		0.90

<sup>a</sup>All values given in microns

<sup>b</sup>Emulsion sizes determined only on first and third trials

<sup>c</sup>Microfluidized sample not prepared for first trial

Table II. Influence of Emulsion Size on the Retention of Orange Oil During Spray Drying

Sample	Total Oil Content <sup>a</sup>			
	Trial <sup>a</sup>			Average
	1	2	3	
Coarse	12.3	16.1	13.0	13.8
Medium Coarse	16.5	17.1	18.3	17.3
Medium Fine	17.4	19.1	19.2	18.6
Homogenized	19.3	19.1	19.0	19.1
Microfluidized	<sup>b</sup>	<sup>b</sup>	20.0	20.0

<sup>a</sup>All values given in g oil/100 g powder

<sup>b</sup>Microfluidized sample not prepared for first two trials

The results of the shelf-life study are illustrated in Figures 2-4. The end of shelf-life was taken as the point at which the limonene-1,2-epoxide was greater than 2.0 mg/g oil. Subramaniam (3) reported that a trained sensory panel determined that products were unacceptable (oxidized) in a range from 1.42 to 7.48 mg limonene-1,2-epoxide/g oil. Most samples were between 2 and 4 mg/g oil. The end of shelf-life from all three sets of samples is compiled in Table III. There is no consistent or apparent correlation between emulsion size and length of shelf-life. At 45 C, the medium coarse sample lasted longest in one set while the homogenized sample lasted longest in the other set. The coarse sample was the most stable in the third set of samples. Between the two sets of the samples stored at 45 C, the second set showed a shorter shelf-life. The oil used for the second set did not taste oxidized, but had initial levels of limonene-1,2-epoxide and L-carvone greater than zero. The oil had started to oxidize before spray drying and resulted in a

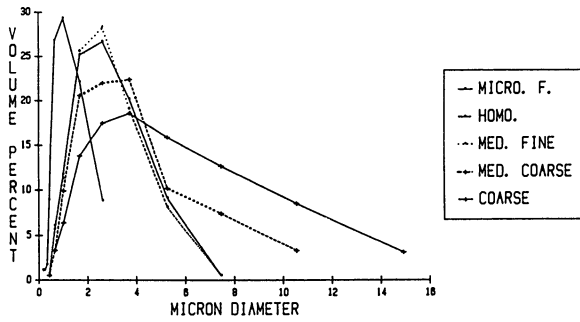


Figure 1. The effect of emulsification method on particle size distribution.

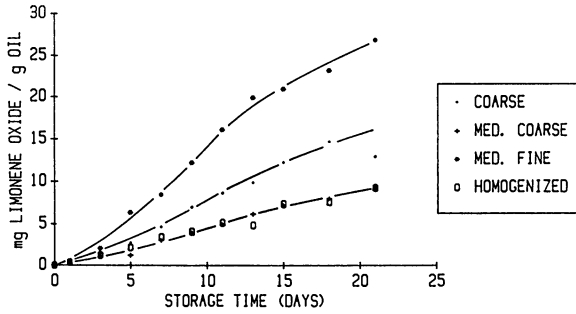


Figure 2. Influence of emulsion size on shelf life (45 C) of spray dried orange oil with gum arabic as carrier.

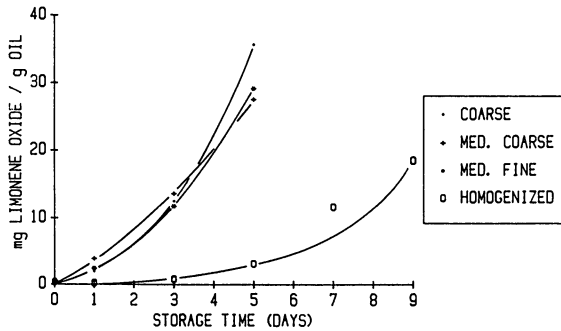


Figure 3. Influence of emulsion size on shelf life (45 C) of spray dried orange oil with Amiogum 23 as carrier.



shorter shelf-life. This points to the importance of using fresh orange oil for spray drying to achieve the longest possible shelf-life.

Table III. The Influence of Emulsion Size on the Shelf-life of Encapsulated Orange Oil

Sample	Days to End of Shelf-life		
	1 <sup>a</sup>	Trial 2 <sup>b</sup>	3 <sup>c</sup>
Coarse	5	3	24
Medium Coarse	7	1	16
Medium Fine	3	1	16
Homogenized	5	5	16
Microfluidized	a	a	16

<sup>a</sup>Stored at 45 C

<sup>b</sup>Stored at 37 C

<sup>c</sup>Microfluidized sample was not prepared for first two sets of samples.

The extractable surface oil results of the spray dried powders are listed in Table IV. The extractable surface oil decreased as the emulsion size decreased. Based on previous knowledge, one would anticipate that less surface oil would result in a better shelf-life. The results of this study do not support that theory especially when you consider the third set of samples in which the coarse emulsion had the greatest amount of extractable surface oil yet also had the longest shelf-life. There may be competing factors between emulsion size and extractable surface oil that produce these results. While the finer emulsions have less extractable surface oil which should improve shelf-stability, the total surface area of the oil droplets in these powders is greater (Table V). The lower amount of surface oil provides less oil that is openly exposed to oxidation but the greater surface area of the droplets in the carrier matrix provides greater possibility for oxidation once oxygen has permeated the spray dried particles.

Table IV. Influence of Emulsion Size on the Surface Oil Content of Spray Dried Orange Oil

Sample	Surface Oil <sup>a</sup>		
	2	Trial <sup>b</sup> 3	Average
Coarse	76.6	74.1	75.3
Medium Coarse	33.5	69.8	51.7
Medium Fine	37.7	41.7	39.7
Homogenized	23.0	32.1	27.5
Microfluidized	c	33.5	33.0

<sup>a</sup>All values given in mg oil/100 g powder

<sup>b</sup>Determined only on trials 2 and 3

<sup>c</sup>Microfluidized sample not prepared for second trial

Table V. Influence of Emulsion Size on Surface Area of Oil Droplets

Sample	Total Surface Area <sup>a, b</sup>		
	Trail		Average
	1	3	
Coarse	2.47	2.72	2.60
Medium Coarse	4.34	3.40	3.87
Medium Fine	5.24	4.06	4.65
Homogenized	6.07	4.01	5.04
Microfluidized	<sup>c</sup>	8.91	8.91

<sup>a</sup>All values listed in m<sup>2</sup>/cc of powder

<sup>b</sup>Values determined only for first and third trials

<sup>c</sup>Microfluidized sample prepared only for third trial

Moisture content of the samples is listed in Table VI. The percent moisture in the samples ranged from an average of 4.7 to 5.8. While the moisture content tended to drop as the emulsion size decreased, there was not a significant difference ( $\alpha = .05$ ) between any two samples.

Table VI. Moisture Content of Spray Dried Products

Sample	Moisture (%)			Average
	Set			
	1	2	3	
Coarse	<sup>a</sup>	6.6	5.0	5.8
Medium Coarse	3.1	5.8	5.2	4.7
Medium Fine	<sup>a</sup>	5.2	4.7	5.0
Homogenized	4.2	5.4	4.4	4.7
Microfluidized	<sup>a</sup>	<sup>a</sup>	4.7	4.7

<sup>a</sup>Powder was not available to analyze for moisture content.

The emulsion stability is illustrated in Figure 5. The results agreed with what could be predicted by Stokes law; i.e., that a smaller particle radius will yield a more stable emulsion. The rate of decrease in optical density was greatest in the least stable emulsions. The decrease in optical density was from the creaming phenomenon which is the orange oil rising to the top of the solution. This point is most important in beverage applications where the solution must remain stable for weeks or even months.

The results from sensory analysis of the coarse and Microfluidized powders revealed that there was no significant difference ( $\alpha = 0.5$ ) in flavor intensity between the two powders. Of the 24 panelists, 14 selected the Microfluidized sample as having a more intense orange flavor. The reason for testing for a difference in flavor intensity was based on the possibility that a larger number of particles, even though smaller, striking the taste buds on the tongue would create the sensation of more flavor. A possible explanation for no difference between the two

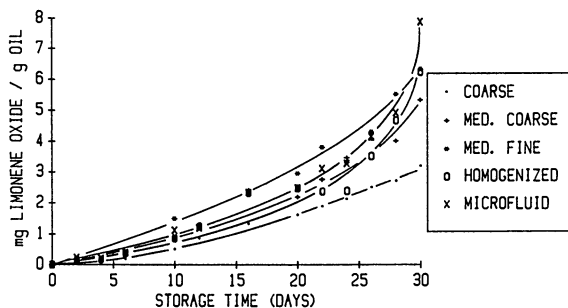


Figure 4. Influence of emulsion size on shelf life (37 C) of spray dried orange oil with gum arabic as carrier.

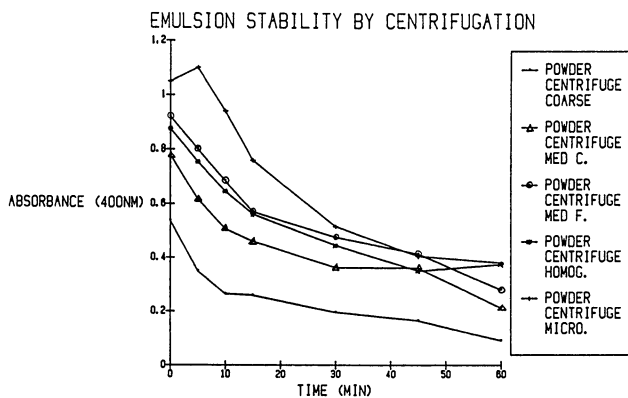


Figure 5. Influence of particle size on emulsion stability.

powders with different emulsion sizes is that the surface tension of the smaller droplets is greater which could reduce the impact on the tongue.

The results of this study indicate that there are advantages to creating smaller emulsions when preparing solutions for spray drying even though larger or coarser emulsions are much easier to prepare and require less sophisticated equipment. The main advantage of smaller emulsions is a better retention of citrus oil in the spray dried powder. This results in a direct economic benefit to the manufacturer and user of the product. Less citrus oil is lost during drying and less powder, therefore, is needed in the finished product to achieve the same flavor level. A second advantage is that smaller emulsions also yield dried powders which have less extractable surface oil. While this did not result in better shelf-stability or resistance to oxidation in the product, it may contribute to the aroma of the product remaining acceptable for a longer period of time. As mentioned earlier, the oil on the surface has no protection from oxidation. A larger amount of extractable surface oil that can readily oxidize could give a dry product, such as an instant beverage, an off-aroma; however, once rehydrated the product might still be acceptable from a sensory standpoint. A third advantage of producing a finer emulsion is that the emulsion is more stable. This is particularly important in beverage applications where viscosity cannot be increased to help stabilize the flavor emulsion. These are the three distinct advantages of creating finer emulsions for spray drying citrus oils. While the emulsion size is only one factor which can influence the stability of spray-dried citrus oils, it may be possible to use this information in conjunction with other data and information to manufacture a product with an extended shelf-life, better emulsion stability, and higher flavor load.

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## Chapter 9

# Encapsulated Orange Oil

## Influence of Spray-Dryer Air Temperatures on Retention and Shelf Life

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Single fold orange oil was encapsulated with gum arabic via spray drying using inlet and exit air temperatures ranging from 160 to 280 C and 80 to 130 C respectively. The resultant powders were analyzed for moisture content (toluene distillation), surface oil (Soxhlet extraction), and total oil (Clevenger distillation) prior to shelf-life testing. The powders were then adjusted to a water activity ( $a_w$ ) of ca. 0.54 over  $Mg(NO_3)_2$  for shelf-life testing. A preliminary drying run was done at 200 C inlet and 100 C exit air temperatures. The  $a_w$  of the resultant powder was adjusted from ca. 0.03 to ca. 0.54. Maximum shelf-life was observed at the highest  $a_w$  tested. Shelf-life testing was done at 37 C monitoring for the formation of limonene oxidation products (limonene oxide). The powder dried at the highest operating temperature (280 C inlet air) was found to have the maximum shelf-life.

In 1985 worldwide sales of flavors and fragrances were 5.26 billion dollars (1). In the United States, which accounts for ca. 28% of total worldwide sales, the sale of dry flavors is estimated to be nearly 50% of the total flavor sales (2). Dried flavors, and specifically spray dried flavors, are an important segment of the flavor industry and their stability is critical to this industry. The stability of encapsulated orange peel oil has been investigated with attention directed to the oxidation of limonene, one of its major constituents. The formation of limonene oxide has been shown to be a good indicator of the shelf-life of encapsulated orange peel oil (3). Various parameters (encapsulating agent, solids concentration, feed temperature and air inlet temperatures) have been studied with respect to their effect on volatile retention (4, 5, 6). The purpose of this study was to determine the effect of spray dryer

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operating temperatures on shelf-life, while eliminating the effect of other variables (such as encapsulating agent, solids concentration, and powder moisture content) on shelf-life.

#### Materials and Methods

Materials. Gum arabic was obtained from Colloides Naturels Inc. (Far Hills, NJ) and Meer Corp. (Bergen, NJ). Single strength cold pressed orange oil was obtained from Sunkist Growers Inc. (Ontario, CA) The inorganic and organic chemicals used in the analyses were ACS certified grade.

Water Activity Study. A 30% (w/w) solids gum arabic solution was heated to and held at 82 C with constant stirring for 45 minutes. The solution was covered and left to stand overnight at room temperature. Single fold orange peel oil (25% w/w of gum solids) was added to the hydrated gum arabic solution and homogenized using a Greerco Corp. laboratory high shear mixer. The emulsion was fed into a Niro Utility Dryer equipped with a centrifugal atomizer. Inside chamber dimensions of this spray drier are 150 cm. height and 120 cm. diameter. The inlet air temperature was 200+5 C and exit air temperature was 100+3 C.

Following drying, 40g samples were placed in each of six desiccators containing either Drierite or saturated salt solutions of LiCl,  $K_2H_3O_2$ ,  $MgCl_2$ ,  $K_2CO_3$ , or  $Mg(NO_3)_2$ . At 25 C the water activities ( $a_w$ 's) of these desiccants are 0.001, 0.115, 0.234, 0.329, 0.443, and 0.536 respectively. A vacuum was pulled on each desiccator and the  $a_w$  of the powder samples equilibrated at room temperature for 72 hours. The resulting powders were placed in a 37 C walk-in incubator and samples were removed every two days for gas chromatographic analysis to determine the amount of oxidation products.

Dryer Temperature Study. An orange peel oil/gum arabic emulsion was prepared and spray dried as previously described. Six runs were made varying both the inlet and exit air temperatures (Table I).

Table I. Spray Dryer Operating Temperatures

Inlet T ( C )	Exit T ( C )
200 $\pm$ 5	80 $\pm$ 3
200	105
200	130
160	105
240	105
280	105

A 100g sample of each powder was placed in a desiccator over a saturated solution of  $Mg(NO_3)_2$ . A vacuum was pulled and the  $a_w$  of the powders was allowed to equilibrate at room temperature for 72 hours. The desiccator was then placed in a 37 C walk-in incubator where the temperature was allowed to equilibrate for 24 hours before shelf-life sampling began. At a storage time of

zero, excess sample was removed and air was admitted to the desiccator. The remainder of each powder was placed in glass containers and stored at 4 C for further analyses.

Moisture Determination. Sample moisture was determined by using a modified A.O.A.C. toluene distillation method (7) for both the powders stored at 37 C ( $a_w$  adjusted over  $Mg(NO_3)_2$ ) and the powders stored at 4 C ( $a_w$  unadjusted). Toluene (175mL) was added to 40g of unadjusted powder or 20g of adjusted powder in a 500 mL flat bottomed flask fitted with a Bidwell-Sterling trap and water cooled condenser. Samples distilled for 3 hours and then the volume of water collected was recorded.

Surface Oil Determination. Surface oil was extracted from a 12-15g sample of each powder using a Soxhlet apparatus (7). The sample was placed in a Whatman cellulose extraction thimble (33mm x 80mm) and covered with glass wool. The thimble was placed in the Soxhlet extraction chamber, fitted with a water cooled condenser, and attached to a 250 mL flat bottomed flask containing 125mL of petane. After refluxing over steam for 4 hours, 1mL of pentane containing 2.04mg/mL of 2-octanone as internal standard was added to the flask. The volume was reduced to ca. 2mL under  $N_2$ . The amount of surface oil present was determined by the internal standard method after gas chromatographic analysis. The gas chromatographic conditions were as follows:

Column: 0.25mm i.d. x 30m WCOT fused silica  
Stationary phase: DB-5 (J & W Scientific, Rancho Cordova, CA)  
Carrier gas: Hydrogen  
Split ratio: 1:40  
Column temperature: 50 C to 200 C programmed at 10 C/minute  
Detector temperature: 200 C  
Sample size: 2uL

Total Oil Determination. Total oil was determined by Clevenger hydrodistillation (8). A 20g sample of powder was mixed with 150mL of deionized water in a 250mL flat bottomed flask. Boiling stones and antifoam (silicone oil, Aldrich Chemical Company) were added. A Clevenger oil trap and water cooled condenser were attached. The sample was distilled for three hours. The volume of oil collected was multiplied by the oil density (0.833g/mL) to give the weight of oil present in the sample.

Storage Stability. Samples were prepared for gas chromatographic analysis by dissolving 0.15g powder in 0.85g distilled water in a 3-dram screw cap vial and mixing well using a vortex mixer (Scientific Products deluxe mixer). Acetone (4mL) containing 0.25mg/mL of 2-octanone as internal standard was added slowly while mixing. Anhydrous  $MgSO_4$  (0.10g) was added to the vial contents. The resulting supernatant was injected without further preparation into a Hewlett-Packard Model 5840 gas chromatograph

(flame ionization detector). The amount of limonene oxide present was determined by the internal standard method (7).

The gas chromatographic conditions were as follows:

Column: 0.25mm i.d. x 25m WCOT fused silica  
Stationary phase: OV-1 (J & W Scientific, Rancho Cordova, CA)  
Carrier Gas: Helium (18psig)  
Split ratio: 1:40  
Column temperature: 50 C to 250 C programmed at 10 C/minute  
Detector temperature: 275 C  
Injection port: 200 C  
Sample size: 2uL

### Results and Discussion

Effect of Water Activity. A preliminary study was done to determine the  $a_w$  at which encapsulated orange peel oil was the most stable to oxidation. Figure 1 summarizes the results of this study. The formation of the limonene oxidation product, limonene oxide, was the slowest for the powder adjusted over  $Mg(NO_3)_2$  ( $a_w = 0.536$ ). While the levels of oxidation product do not follow in exact order of  $a_w$ , it is evident that better storage stability correlates with a higher  $a_w$  of the powder. This relationship was not anticipated. Literature on lipid oxidation (7, 8, 9) indicates that there is an optimum  $a_w$  for product shelf-life which corresponds to the monolayer region. For typical dry products, the monolayer region corresponds to an  $a_w$  ranging from ca. 0.2 to 0.35. Our higher  $a_w$ 's are definitely above the monolayer region and we would have expected the rate of oxidation to have increased. While it is possible that the rate of oxidation would have increased had we gone to higher  $a_w$ 's, the moisture content was already well over what is common for commercial products. Therefore, the study of higher  $a_w$ 's is impractical since the products of commerce would never be manufactured at  $a_w$ 's higher than used in our study.

Once we had determined the optimum practical  $a_w$  for the storage of encapsulated orange peel oil, we initiated a study on the influence of spray dryer inlet and exit air temperature on product shelf-life.

Moisture. As anticipated, moisture contents of the powder samples decreased with decreasing temperature differentials between inlet and exit air temperatures when either inlet or exit air temperature was held constant (Figure 2). The sample with the highest temperature differential (  $T=120$  C) and lowest exit air temperature ( $T=80$  C) had the highest moisture content (7.8%) of all the powder samples. The role of temperature differential on product moisture content is apparent from either data series in Figure 2. While the sample dried at 280 C inlet and 105 C exit air temperatures had the greatest temperature differential, the



dryer air at 105 C could hold substantially more water than the 80 C exit air on the 200/80 C product. This resulted in a lower moisture content despite a greater temperature differential.

The unadjusted powder samples had a sample standard deviation of 1.62% moisture compared to 0.69% moisture for the powder samples adjusted over  $Mg(NO_3)_2$  (Figure 3). The moisture content of the samples adjusted of  $Mg(NO_3)_2$  ranged from 7.59% to 9.20%.

Surface Oil. Surface oil increased with decreasing inlet and exit air temperature differential for samples dried at an inlet air temperature of 200 C (Figure 4). This was also observed for the samples dried at a constant exit air temperature of 105 C, with the exception of the sample dried at an inlet air temperature of 160 C which may have been in error since we would not expect a deviation in the relationship between surface oil and temperature differential. This sample should be reproduced and analyzed again.

One might expect the drying droplet to balloon with increasing inlet air temperature creating a greater surface area and, therefore, a greater surface oil content. We did not observe this in our study. The higher moisture of the powders with greater temperature differentials could have interfered with the surface oil extraction procedure yielding erroneous values. Further studies should be done in this area to determine if indeed the surface oil content of spray dried orange peel oil does decrease with increasing temperature differential.

Total Oil. The results of the total oil analysis are summarized in Figure 5. Total oil varied by less than one standard deviation for all samples (i.e., 0.86%). Therefore, it appears that inlet and exit air operating temperatures did not have a significant effect on the total oil content of the powder samples.

Previous work has shown that flavor retention increases with increasing inlet air temperature until internal steam is formed in the drying droplet (12). The higher inlet air temperatures produce a more rapid drying which thereby results in a shorter time until the formation of a high solids "skin" around the drying droplet. This "skin" acts as a semipermeable membrane which retains the larger (relative to water) flavor molecules. At some inlet air temperature, however, internal steam formation will cause "ballooning" of the drying droplet. Ballooning results in a very high surface to volume ratio for the powder and, therefore, greater flavor losses. Apparently 280 C is not adequate to produce ballooning.

Previous work (12) has also demonstrated that higher exit air temperatures result in improved flavor retention. It has been postulated that higher exit air temperatures result in more rapid drying, thereby providing better retention of volatiles. We do not observe this relationship in this study.

In this study, we have not observed a relationship between dryer operating temperatures and the retention of orange peel oil. The effect of dryer operating temperatures on oil retention may be partially negated due to the inherently small losses of flavor

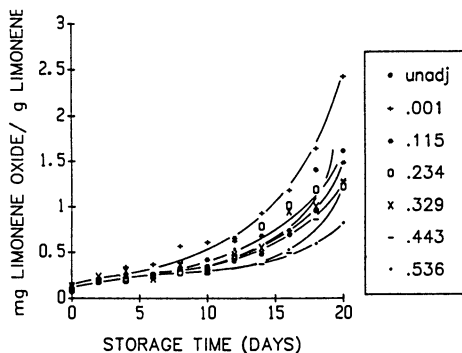


Figure 1. Effect of water activity on shelf life of encapsulated orange peel oil.

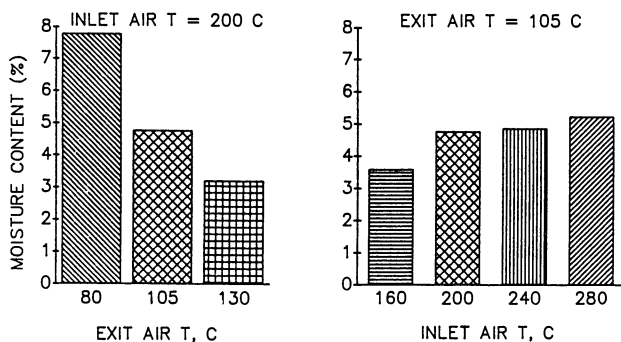


Figure 2. Influence of inlet and exit air temperatures on the moisture content of spray dried orange peel oil.

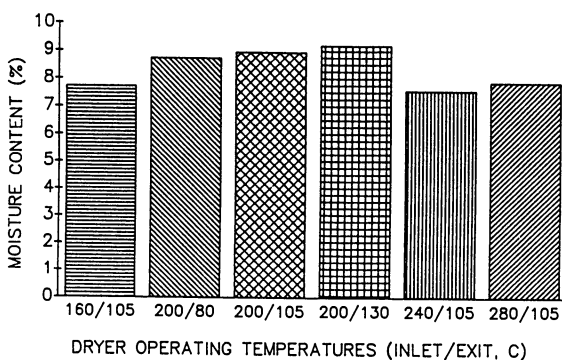


Figure 3. Moisture contents of spray dried orange peel oil which had been adjusted in water activity over  $Mg(NO_3)_2$ .

during drying. Flavor losses, at most, were only 15%. Previous studies have looked at the losses of more volatile substances (e.g., diacetyl, butanol, acetone) which were present from parts per million up to 1-2% (13). Volatile losses in these studies have often been up to 70-80%. When losses are greater, smaller effects may more readily be ascertained.

Storage Stability. The formation of limonene oxide at 37 C was measured as a function of time to determine shelf-life of the encapsulated orange peel oil samples. Figure 6 shows the shelf-life results. A value of 2mg limonene oxide/g limonene was used as the end of shelf-life for oxidized encapsulated oil samples (3). The sample dried at 160 C and 105 C inlet and exit air temperatures respectively and the smallest temperature differential (55 C). This sample formed limonene oxide much faster than the other five samples. By 23 days, this powder had reached a value of 2mg limonene oxide/g limonene. The sample dried at 280 C and 105 C inlet and exit temperatures respectively did not reach 2 mg limonene oxide/g limonene until after 34 days of storage at 37 C. This sample also had the largest inlet and exit air temperature differential (175 C). The remaining four samples had reached 2mg limonene oxide/g limonene after about 30 days of storage at 37 C.

Previous work has theorized that storage stability is enhanced when the surface oil is lower (2, 7). For this study the opposite effect was observed: the sample with the lowest surface oil (107mg surface oil/100g powder; drying conditions of 160 C inlet and 105 C exit air temperatures) had the shortest shelf-life. However, the sample with the longest shelf-life (drying condition of 280 C inlet and 105 C exit air temperatures) had a surface oil content nearly the same (110mg surface oil/100g powder). It appears that surface oil is not an important determinant of shelf-life. This is supported by the recent work of Anandaraman and Reineccius (4) where an encapsulated orange peel oil was washed with organic solvent to remove surface oil prior to shelf-life testing. The product with no surface oil exhibited a shelf-life very similar to the product with surface oil. Other factors such as matrix porosity (to oxygen), absolute density, trace mineral level (copper and iron) and presence of antioxidants are most likely more significant in determining the rate of oxidation of encapsulated orange peel oil.

In summary, we have found that the optimum (within the limits of this study)  $a_w$  for shelf-life is 0.54. In addition, the dryer inlet and exit air temperatures had no effect upon oil retention and perhaps only a minor effect upon shelf-life. If there is a significant effect it is that the higher inlet air temperature actually yielded a better shelf-life. A higher temperature differential means that dryer throughput also is increased and operating costs are cut. The more product that can be produced per hour, the lower the production costs. A larger temperature differential also results in a higher final product moisture. This is good for shelf-life since a higher  $a_w$  means a longer shelf-life. If we had not adjusted the  $a_w$ 's of all our products to be the same  $a_w$ , we would have seen even greater effects of operating temperature on shelf-life.

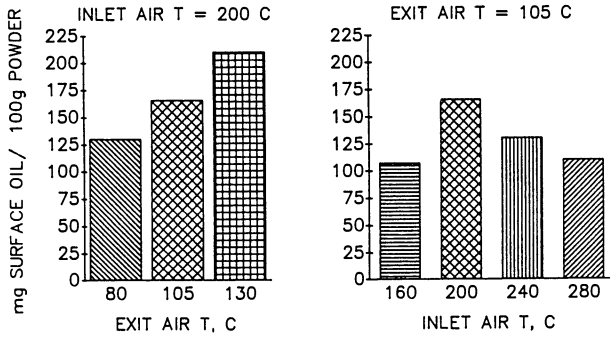


Figure 4. Influence of dryer inlet and exit air temperatures on the surface oil content of spray dried orange peel oil.

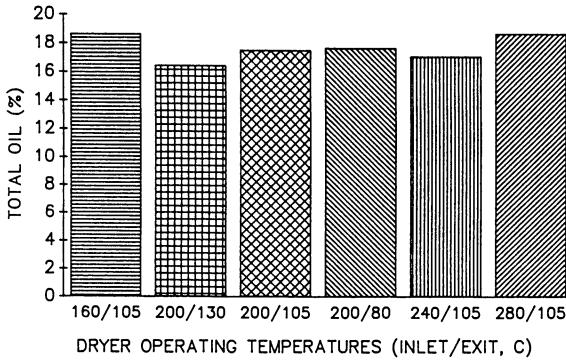


Figure 5. Influence of inlet and exit air temperatures on the retention of orange peel oil during spray drying.

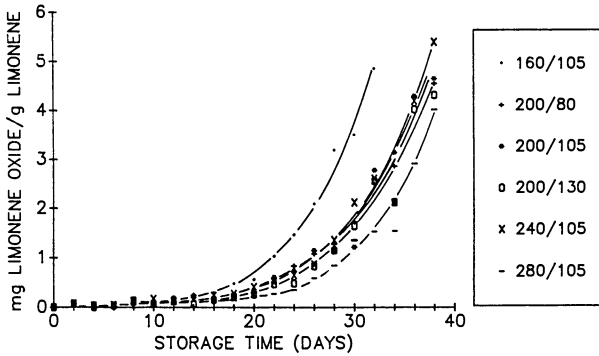


Figure 6. Influence of dryer inlet and exit air temperatures on the shelf life (37 C) of spray dried orange peel oil.

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## Chapter 10

# Effect of Particle Size and Microstructure Properties on Encapsulated Orange Oil

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The change of particle size distribution of encapsulated orange oil was achieved by varying the voltage supply of a centrifugal wheel atomizer during spray drying. Mean particle diameter of the encapsulated oil increased with the decrease in voltage supply. Moisture content, moisture sorption characteristics and bulk density were found to be independent of particle size distribution, whereas oil retention and surface oil content were significantly affected. The examination of surface morphology by scanning electron microscopy revealed that there was an observable increase in surface imperfections for large particles. Powders with large particles generally exhibited a more protective effect against oil oxidation than small particles.

There are three major purposes for encapsulating flavors. The primary reason is to convert liquid flavors into a dry and free flowing powder form. This is commonly encountered in the application of convenience foods and beverages. Flavor compounds are rather volatile and generally thermally or chemically labile in nature. They undergo oxidation, isomerization, and polymerization with facility and interact easily with other flavor constituents, food components and packaging materials. This will lead to a decrease in flavor strength and even the development of off-flavor. Encapsulation is an effective way to provide a barrier against the undesirable environmental factors and thereby minimize the changes. Lastly, the control of release properties of flavors through the encapsulation technique has intrigued many researchers.

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A specific mode or rate of release of the flavor into the matrix is sometimes highly desirable. Chewing gum with slow release flavors is one of the increasing applications (1).

Spray drying is the most widely used, least expensive and favored route among the methods available for encapsulation (2). Various theories of volatile retention in spray drying have been proposed and reviewed (3). In addition to the nature of flavor compounds, flavor retention is governed by type of carriers, infeed composition, solids concentration (4), dryer inlet/exit air temperature, air velocity and humidity, feeding rate and atomization characteristics. In addition to flavor retention, the stability of the encapsulated product, as mentioned earlier, is also of importance and is governed by nearly the same parameters. However, the effect and mechanics of each individual factor are much less understood. Recently, it was reported that when maltodextrins were used as the encapsulating agent, increasing the dextrose equivalent by 10 could result in a three to six fold enhancement in shelf life (5). The reduction in emulsion size of feed emulsion also improved the shelf stability (Risch, S. J., University of Minnesota, personal communication, 1986). However, the influence of particle size distribution on the stability of encapsulated flavors has not been clearly addressed in the literature.

Via a specially designed tall column, a stream of controlled uniform size particles were generated from a nozzle atomizer. The effect of drop-size distribution on the volatile loss in the nozzle zone (6) and on the particle morphology (7-8) were examined. Another novel droplet generator using a vibrating - orifice was designed and used to study particle surface morphology (9). Feed concentration, feed composition, initial drop diameter and air temperature history were shown to determine surface morphology (e.g. expansion, cratering, fold formation) of the dried particles.

The purpose of this study was to investigate the effect of particle size on encapsulated orange oil, a widely used flavor which is highly susceptible to oxidation, using a readily available laboratory scale spray dryer. A close examination of the surface morphology was also attempted.

### Experimental

Spray Drying of Orange Oil. Capsul, a modified food starch (National Starch and Chemical Corp., Bridgewater, NJ), was used as the encapsulation agent. Capsul solution with 30% (w/w) solids content in deionized water was prepared. Orange oil (Florida Valencia), 20% (w/w) of solids, was emulsified into

the carrier solution using a trihomo-mixer (Gifford-Wood Model 1L77, Greerco Corp., Hudson, NH) for 3 minutes. The emulsion was fed to an AnhydroLab.S1 Spray Dryer (APV Anhydro, Inc., Attleboro Falls, MA) via a Varistaltic pump (Manostat, New York, NY). Air inlet and outlet temperatures employed were 200–210 °C and 80–90 °C, respectively. A centrifugal wheel atomizer was used to accomplish the atomization. The voltage of the atomizer was varied via a variostat to change the particle size distribution. Three voltages were used in this study, viz., 200, 150 and 75 v and the finished powders were coded A, B and C in this order. A typical feed composition was 1000 g capsul, 2334 g deionized water and 200 g orange oil. The finished powders were stored in amber bottles at -25 °C prior to accelerated storage study and relevant analyses.

Particle Size Analysis. To ascertain the effect of atomizer voltage on the particle size, the particle size distributions of three powders were first determined. The Microtrac laser light particle size analyzer (Medallion Laboratories, Minneapolis, MN) was used in this study. The volume percent data over particle diameter ranging 2.8  $\mu$  to 176  $\mu$  was recorded. Mean value of the volume percent distribution and calculated surface area were also obtained.

Total Oil Determination. The conventional Clevenger hydrodistillation method was used. A 20 g sample was used and the distillation was continued for 16 hours. Oil density (0.844 g/ml) was used to convert the volumetric estimate to gravimetric estimate.

Moisture Determination. There are many methods available for moisture determination. The commonly used toluene distillation method is still regarded as adequate and accurate for quality control situations by Anandaraman and Reineccius (10). This method was employed in this study. A 10.0 gm sample was used and the distillation was continued for 4–5 hours.

Surface Oil Determination. The Soxhlet extraction method recommended for extracting the surface oil from the encapsulated powders (10) was slightly modified. Powder (12–15g) was weighed into a predried and cooled Whatman cellulose extraction thimble (33 mm x 80 mm, single thickness), covered with glass wool and placed in the extraction chamber. HPLC grade pentane (160 ml) was employed as the extracting solvent. The extraction was done for 7 hours. Pentane (1 ml) containing 0.2 mg ethyl heptanoate was added to the extraction flask and pentane was evaporated in a 30 °C water bath under a stream of nitrogen to a final volume of ca. 0.2 ml. Quantitation of the extractable oil was accomplished by gas chromatographic quantitation of limonene, the major component of orange oil, by the internal standard method.



A calibration standard was prepared by concentrating the solution containing 60 mg oil, 0.2 mg ethyl heptanoate and 160 ml pentane to the equivalent volume (ca. 0.2 ml). A Perkin - Elmer Sigma 2B gas chromatograph equipped with a flame ionization detector was used for analysis. The gas chromatographic conditions were as follows:  
Column: 0.32 mm i.d. x 30 m Carbowax bonded phase capillary column  
Split: 1 to 50  
Carrier Gas: Helium at 29 cm/sec  
Column Temperature: 60 °C to 120 °C, programmed at 5 °C/min; to 230 °C programmed at 8 °C/min; final hold for 15 min  
Injection Size: 0.24 µl  
Injection Port and Detector Temperatures: 220 °C and 280 °C

Scanning Electron Microscopy. An ISI model Super II (International Scientific Instruments Inc., Milpitas, CA) scanning electron microscope was used for morphology study (Labtech, Fairfield, NJ). Powder was properly loaded on specimen stub via a double stick tape. Samples were coated with 60% gold and 40% palladium for 6 min at 100 to 200 mtorr in a sputter coater.

The conditions of electron microscope were as follows:  
Objective Aperture: 50 µ  
Sample Distance: 18 mm  
Accelerating Voltage: 15 Kv  
Tilt Angle: 0  
The samples were examined at 120x, 600 x and 1800 x magnifications.

Bulk Density. Bulk density was determined by the tapping method. Powder (30 gm) was loosely weighed into a 100 ml graduated cylinder. Cylinder with the powder was tapped on a flat surface to a constant volume. The final volume was recorded. Bulk density was calculated by dividing the sample weight by the volume.

Moisture Sorption Isotherm. Moisture sorption isotherms of the encapsulated orange oils were determined by the moisture equilibration method. Sample powders were dried in a vacuum oven at 60 °C for 7 hours and cooled to minimize the hysteresis effect prior to storage in the dessicators of various water activities. In addition to Drierite, five saturated salt solutions were used in dessicators. These salt solutions were lithium chloride, magnesium chloride, potassium carbonate, sodium nitrite and potassium chloride. Their water activities were 0.110, 0.330, 0.440, 0.650 and 0.850, respectively, at 20 °C. Each sample contained 1.2 to 1.5 g powder and four-week equilibration time was employed. The percentage of

moisture content change (g H<sub>2</sub>O/100 g solids) was determined.

Accelerated Storage Study. Each of the three powders (20g) were transferred to amber glass bottles (2 oz.). These bottles were stored in a constant temperature oven (45 ± 1°C). Samples (1g) were taken after 0, 3, 5, 7 and 10 days of storage for gas chromatographic analysis and sensory evaluation against respective control samples stored at -25°C.

Gas Chromatographic Analysis. The contribution of limonene-1, 2-epoxides and carvone to the development of oxidized flavor of encapsulated orange oil has been investigated (5). The concentrations of these two compounds were reported to provide a reliable index of the stability of the encapsulated orange oil. Therefore, a gas chromatographic internal standard method was employed to quantify these two index compounds in the storage study.

The encapsulated orange oil (0.1 g) was rehydrated in 7.5 ml distilled water via the use of a vortex mixer for 30 sec. Acetone (50 µl) containing 100 µg ethyl heptanoate (internal standard) was added and mixed for another 30 sec. This solution was forced through a preconditioned Sep-pak C18 reverse phase cartridge. The cartridge was then flushed with 5 ml distilled water. The oil was recovered by 3 ml methylene chloride and dried over anhydrous sodium sulfate. The eluant was concentrated down to 10 µl under a stream of nitrogen. A Hewlett Packard Model 5840A gas chromatograph equipped with a flame ionization detector was used for analysis. The gas chromatographic conditions were as follows:

Column: 0.53 mm i.d. x 30 m Carbowax bonded phase column

Injection: 2 µl on - column injection

Carrier Gas: Helium at 112 cm/sec.

Column Temperature: 60°C, initial hold for 2 min; to 129°C programmed at 3°C/min; to 210°C programmed at 8°C/min; final hold for another 15 min.

Injection Port and Detector Temperatures: 220°C and 280°C.

The identification of limonene-1,2-epoxides and carvone was accomplished by retention indices and mass spectra, obtained separately by GC-MS, in comparison to authentic reference compounds.

Sensory Evaluation. The organoleptic evaluation of the samples was conducted by a paired comparison test. The expert panel consisted of six to eight members. The encapsulated samples (stored at 45°C) were evaluated against the control samples at 0.1% (w/w) in spring water.

The judges were asked to choose the sample having the oxidized flavor. When 100% of the panelists detected

the oxidized flavor for the samples, it was chosen as the end of shelf life.

### Results and Discussion

**Particle Size Distribution.** The particle size distributions of three encapsulated orange oils at three different voltages of centrifugal wheel atomizer are presented in Figure 1. The volume percent data were plotted against the particle diameter in microns. Within the measuring particle diameter range (2.8 to 176  $\mu$ ), the decrease in voltage supply of centrifugal wheel during spray drying, when other variables were maintained constant, shifted the overall particle size distribution to the right, toward the larger diameters. For instance, the two most predominant diameters for powder A were 62  $\mu$  (26.4%) and 44  $\mu$  (22.5%) while for powder B were 88  $\mu$  (23.5%) and 62  $\mu$  (26.3%) and for powder C were 88  $\mu$  (27.5%) and 62  $\mu$  (25.1%). It is worth noting that powder C had an especially high percent (18.4%) of particles in the 125  $\mu$  range. From the distribution plot, mean particle diameter and surface area were subsequently calculated and are presented in Table I.

Table I. Mean particle diameter and calculated surface area of encapsulated orange oils

Powder Code	Voltage Used (v)	Mean particle Diameter ( $\mu$ )	Calculated Surface Area ( $M^2/cm^3$ )
A	200	42.48	0.21
B	150	53.21	0.16
C	75	66.64	0.12

The mean particle diameter of powder A was 42.48  $\mu$  which fell in the range of common spray dried powders (11). The mean particle diameters of powders B and C were 53.21  $\mu$  and 66.64  $\mu$ , respectively, which were 25.3% and 56.9% larger than powder A. The data verified that the particle size distribution could be changed via the control of voltage supply of centrifugal wheel during spray drying. This approach was, therefore, adopted in this study. The value of the calculated surface area showed an opposite trend in contrast to the change in particle diameter. The lower voltage was used, the less surface area was obtained

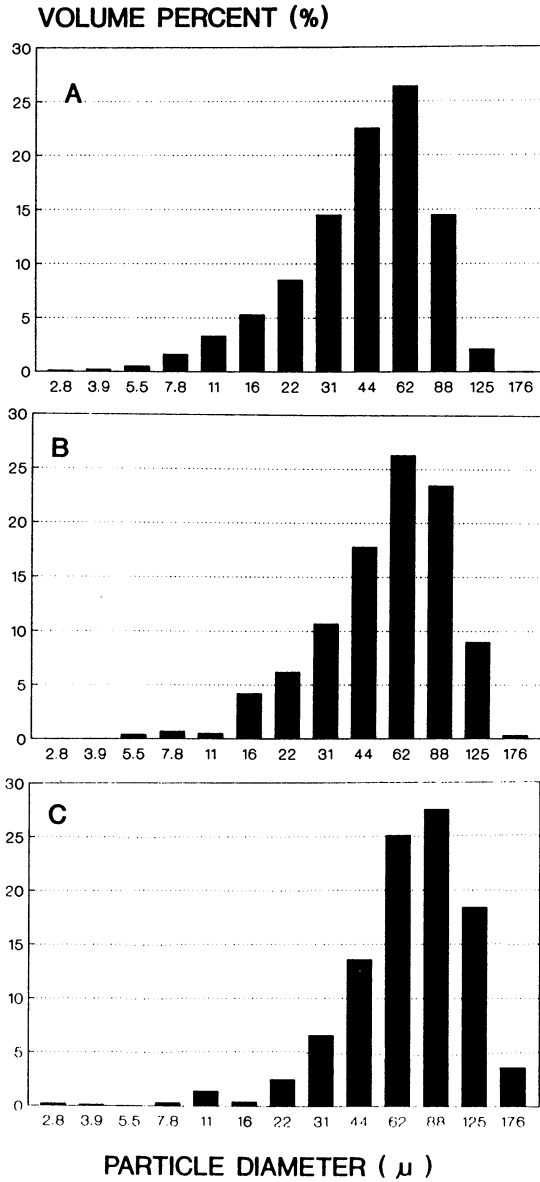


FIGURE 1. PARTICLE SIZE DISTRIBUTION OF THREE ENCAPSULATED ORANGE OILS SPRAY DRIED AT DIFFERENT VOLTAGES, A: 200 v; B:150 v; C:75 v.

for the powders. The result is logically expected since the increase in particle diameter will reduce the surface area per unit volume.

Analysis of Encapsulated Orange Oil. The influence of particle size on the chemical properties was first examined. The chemical data of three powders are presented in Table II. The moisture content of all powders was quite comparable.

Table II. Moisture, total oil and surface oil contents of encapsulated orange oil

Powder Code	Moisture (% Powder)	Total Oil (% Powder)	Surface Oil (mg/100g Powder)	Surface Oil (% Oil)
A	3.0	15.2	102	0.67
B	3.2	15.9	267	1.68
C	3.0	12.8	909	7.10

It ranged from 3.0 to 3.2%. However, there were observable differences in total oil and surface oil contents among powders. The total oil content was highest (15.9%, equivalent to 95% retention) for powder B with intermediate particles while it was lowest (12.8%, equivalent to 77% retention) for powder C with largest particles. This unique finding may aid in explaining the role of particle size in determining flavor retention in spray drying, which has challenged many researchers. The published findings have not been universally agreed upon, mainly due to the variation in drying design or means to achieve varied particle size distributions (3). The data as shown in Table II indicated that flavor retention increased first with the increase in particle size, probably reached a maximum point and subsequently decreased significantly. This can be logically explained. While large particles have reduced surface area to volume ratio, which would result in better flavor retention, it also takes longer time for film formation around the larger drying droplets in the drying process. The longer the time necessary for film formation, the greater the loss of volatile flavors.

These two competing factors will determine the overall effect of particle size on oil retention. The overall effect can be significant as shown by the difference (18%) in flavor retention between powders B and C.

The surface oil content of the three encapsulated orange oils ranged from 102 (powder A) to 909 (powder C) mg/100 g powder, which corresponded to 0.67 (powder A) and 7.10 (powder C) %oil. Powders B and C had about 2 1/2 and 9 times surface oil as compared to powder A. This was not expected since powders with larger diameters had less calculated surface area as shown in Table I. It is therefore speculated that other powder characteristics, e.g. surface morphology, may play an important role on the oil retention properties and should be further studied.

Scanning Electron Microscopy. In order to examine surface morphology of the powders, scanning electron microscopy was used, which has been widely used in food development (12). The investigation was done at 15 Kv. The electron micrographs of powders are presented at 120 x, 600 x and 1800 x magnifications in Figures 2 to 4. At 120 x magnification, very small particles were found to adhere to large particles for all three powders. The difference in particle size distributions could not be easily determined from the electron micrographs since they appeared to be very similar. At 600 x magnification, the surface features were more clearly revealed.

Powder C had particles with more and deeper folds or shrinkages and had frequently, as shown in Figure 5, broken hollow particles, possibly due to ballooning effect, as compared to powders A and B. The observed change is further magnified (1800 x) in Figure 4. This kind of surface imperfections (fissures, shrinkages etc.) damaged the surface integrity of the spheres and may have resulted in the increase in actual surface area as compared to calculated value in Table I and subsequently have increased the surface oil content for large particles. Surface imperfections have been well documented in the literature when slow process of film formation of drying droplets is encountered.

Bulk Density. The bulk densities determined by the tapping method for three powders were 0.424, 0.426 and 0.425 g/ml. From a theoretical viewpoint, particles with a smaller diameter should contribute to a tighter packing and thus lead to an increase in bulk density. This difference was not noted. Again, this could result from the difference in particle morphology. The increased tendency to expand or form internal voids in small size fractions (8) may have offset the expected effect of particle size itself. Therefore, no significant difference was observed.

Moisture Sorption Characteristics. Moisture sorption isotherms for the encapsulated orange oils are illustrated in Figure 6. Except at low (0.001) and high (0.850) water activities, powder A absorbed

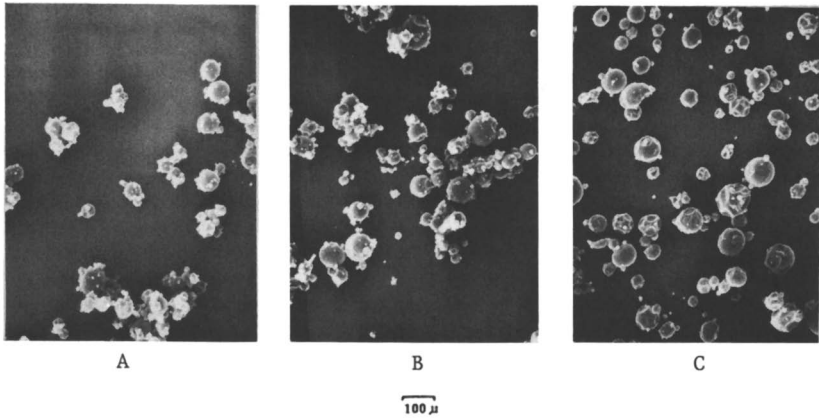


FIGURE 2. SCANNING ELECTRON MICROGRAPHS (120X MAGNIFICATION) OF THREE ENCAPSULATED ORANGE OILS SPRAY DRIED AT DIFFERENT VOLTAGES, A: 200 V; B:150 V; C:75 V.

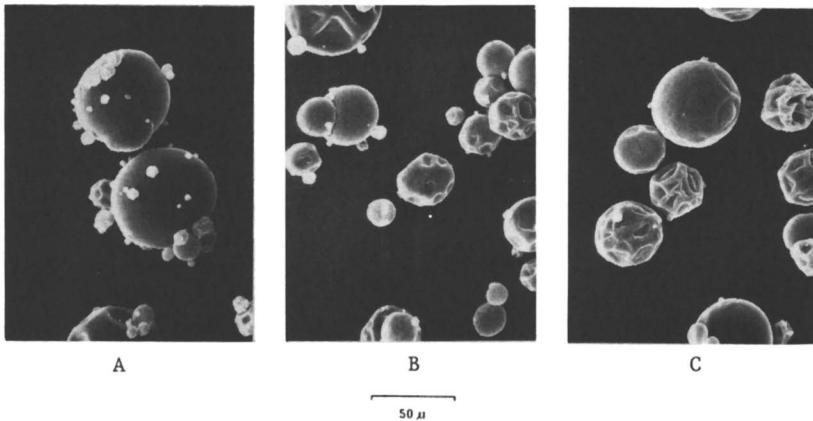


FIGURE 3. SCANNING ELECTRON MICROGRAPHS (600X MAGNIFICATION) OF THREE ENCAPSULATED ORANGE OILS SPRAY DRIED AT DIFFERENT VOLTAGES, A: 200 V; B:150 V; C:75 V.

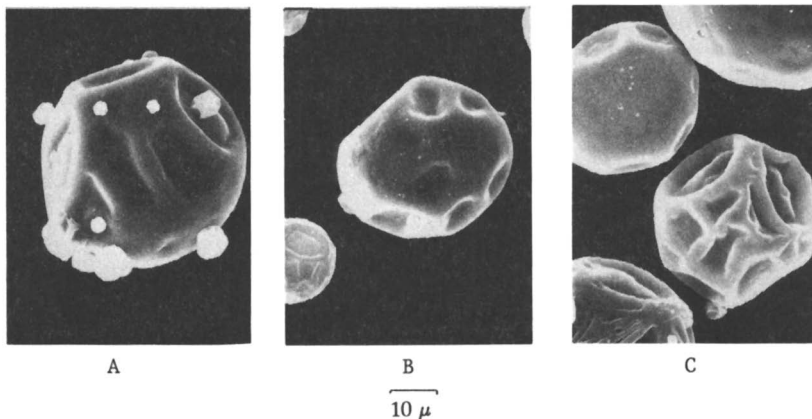


FIGURE 4. SCANNING ELECTRON MICROGRAPHS (1800X MAGNIFICATION) OF THREE ENCAPSULATED OILS SPRAY DRIED AT DIFFERENT VOLTAGES, A: 200 v; B:150 v; c:75 v.

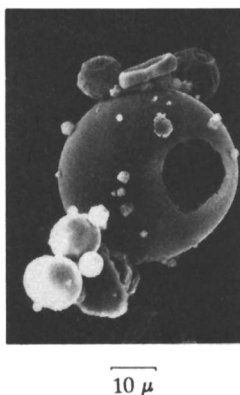


FIGURE 5. A BROKEN, HOLLOW SPRAY DRIED PARTICLE DEPICTED BY SCANNING ELECTRON MICROGRAPH AT 15 KV AND 1800X MAGNIFICATION.



slightly more moisture (average value: 0.6 g/100 g solids) than the other two powders.

However, this observed difference is only marginal. Powders B and C had almost identical sorption isotherms.

Accelerated Shelf Stability Study. A typical gas chromatogram showing the increase of two oxidation index compounds, limonene-1,2-epoxides and carvone during storage is represented in Figure 7. The concentrations of limonene-1,2-epoxides and carvone of three encapsulated oils at different times during storage at 45 °C are presented in Figures 8 and 9. The epoxide concentration was found to increase linearly after the induction period with storage time, irrespective of the particle diameter. It followed pseudo zero order kinetics for all three powders after a 3 day induction period. The formation of carvone in the powders exhibited a similar trend as changes in epoxide formation. It also conformed to pseudo zero order kinetics. Data of simple linear regression for zero order fit for epoxide and carvone formations in three powders are presented in Table III.

Table III. Linear regression for limonene - 1,2 - epoxides and carvone concentrations (mg/g oil) as a function of storage time (days) at 45 °C

Index Compound	Powder Code	Rate Constant (mg/g oil/day)	r
Limonene - 1,2 - Epoxides	A	4.04	0.99
	B	2.36	0.97
	C	3.36	0.99
Carvone	A	1.65	0.91
	B	0.72	0.99
	C	1.44	0.97

Overall, powder B with intermediate particle diameter was found to provide best protection against the oxidation of orange oil. The rate of limonene-1,2-epoxide formation of powder A was 4.04 mg/g oil/day. This rate was decreased to 60% and 80% for powders B and C, respectively. The decrease in protective effect of powder C could have been caused by the increase in particle surface imperfections as discussed earlier. The second stability index compound, carvone, had a slower formation rate which was 30-40% of limonene-1,2-

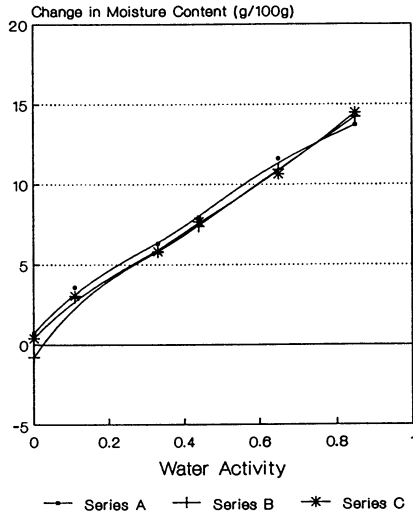


FIGURE 6. MOISTURE SORPTION ISOTHERMS OF THREE ENCAPSULATED ORANGE OILS SPRAY DRIED AT DIFFERENT VOLTAGES, A:200v; B: 150v; c: 75v.

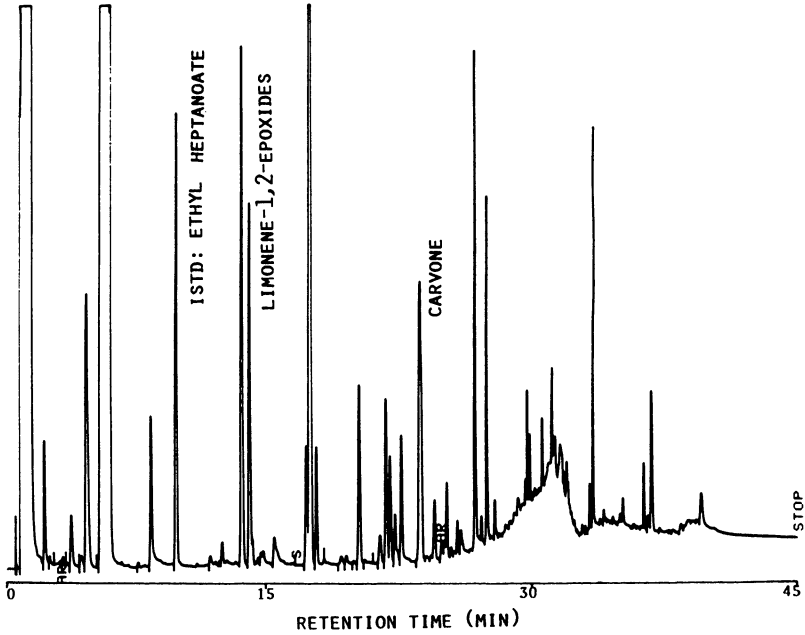


FIGURE 7. GAS CHROMATOGRAM OF OXIDIZED ORANGE OIL RECOVERED FROM SPRAY DRIED OIL.

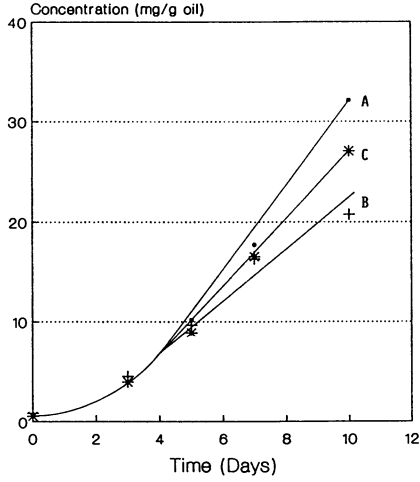


FIGURE 8. CHANGE IN LIMONENE-1,2-EPOXIDES CONCENTRATION STORED AT 45°C OF THREE ENCAPSULATED OILS SPRAY DRIED AT DIFFERENT VOLTAGES, A: 200V; B: 150V; C: 75V.

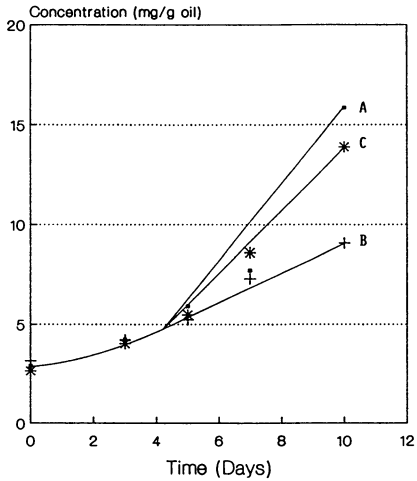


FIGURE 9. CHANGE IN CARVONE CONCENTRATION STORED AT 45°C OF THREE ENCAPSULATED OILS SPRAY DRIED AT DIFFERENT VOLTAGES, A: 200V; B: 150V; C: 75V.

epoxides. As with the case of limonene-1,2-epoxides, a similar particle diameter effect was observed. The formation rate of carvone was decreased to, probably, the lowest point and increased again with the increase in particle diameter.

Powder with large particles was shown to exhibit better protection against oxidation for encapsulated orange oils. However, the effect of particle size may have been slightly offset by the degree of surface imperfection of powders. Except for the morphological imperfections, the protective effect of powders B and C should have been greater than observed.

Sensory Evaluation. Results on the sensory evaluation of the three encapsulated powders showed that all three powders developed oxidized flavor even at first sampling time (3 days). Since an expert trained panel was used, the recognition threshold of members for oxidized flavor was far below the expected value. In addition, since oven stored samples were evaluated against freezer stored samples in the pair comparison test, panelists could not characterize the degree of difference in oxidized flavor between various powders. It is therefore suggested that lower storage temperature (<45°C) or much earlier sampling time, and more frequent samplings should be used in the future to obtain meaningful sensory data. And a more discriminating sensory test, e.g. category scaling or magnitude estimation, can be employed to quantify the sensory properties of encapsulated orange oils.

#### Conclusions

In spray drying, particle size distribution of encapsulated orange oil could be effectively controlled by changing the voltage supply of a centrifugal wheel atomizer. The decrease in voltage supply resulted in increase in mean particle diameter of powders. Surface morphological imperfections were more significantly observed for larger particles. Moisture content, moisture sorption characteristics and bulk density were not affected by particle size distributions. The increase in surface oil content was noted for larger diameter powders. There was an optimal particle diameter to achieve maximal oil retention and shelf stability.

#### Acknowledgements

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# Chapter 11

## Encapsulation of Flavors by Extrusion

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The encapsulation of flavoring materials by extrusion is a relatively new process compared to spray drying. This process starts by forming a low moisture (5-10%) carbohydrate melt (110-130 C). This melt is composed of a low DE maltodextrin, simple sugar and perhaps a modified food starch. An emulsifier is added to the melt and then the flavoring material is added with vigorous agitation. This molten emulsion is forced through a die (ca. 1/64 inch holes) into a cold isopropanol bath. Here the melt solidifies into an amorphous structure which is broken into small rod shaped pieces by mechanical agitation. The flavor pieces are recovered by centrifugation, dried under a vacuum, mixed with a free flowing agent and packaged for sale. The product of this process contains 8-20% flavor load and is exceptionally stable to deterioration by oxidation.

Encapsulation of flavors via extrusion is a relatively new process compared to spray drying. The first patent on flavor encapsulation by extrusion was issued to Swisher (1) in 1957. The primary benefit claimed in this patent was the maintenance of fresh flavor in encapsulated citrus oils which otherwise would readily oxidize during storage, yielding objectionable off-flavors. While spray dried flavorings have continued to dominate the dry flavor market, encapsulated products have been gaining market share. Initial studies that led to the work of Swisher (1) were done by Schultz et al (2). This work involved the addition of citrus oils to a molten solution of sucrose and dextrose, cooling the solution to form a hard slab similar to rock candy and then grinding the solid to the desired size.

The extrusion process of Swisher (1) has formed the basis of the current commercial processes which exist today. Swisher (1) added an essential oil (e.g., orange peel oil), which contained antioxidant and a dispersing agent, to an aqueous melt of corn

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syrup (42 DE). The corn syrup melt contained from 3 to 8½% moisture and was held at a temperature ranging from 85 to 125 C (typically about 120 C). The flavor/corn syrup mixture was agitated violently while blanketed with nitrogen to form an oxygen free emulsion. This emulsion was extruded into pellets or into a hot immiscible liquid (e.g., vegetable or mineral oils) which was then rapidly cooled to form solid emulsion globules. The hardened pellets or solid globules were ground to the desired particle size, washed with solvent (e.g., isopropanol) to remove surface essential oil and then dried under vacuum to yield a free-flowing granular flavoring material containing 8-10% flavoring.

The antioxidants suggested by Swisher (1) were 4-methyl-2,6-ditertiary butylphenol, butylated hydroxyanisole or any other oil soluble, heat stable antioxidant. Antioxidants (0.05% of the essential oil) were considered to be necessary since the heat of the molten corn syrup might otherwise result in oxidation of the citrus oils.

Swisher (1) found that a dispersing agent (i.e., emulsifier) was also essential to the process. Without an emulsifier, it was impossible to form a fine emulsion. A coarse emulsion resulted in poor oil retention during encapsulation and would rapidly destabilize when the flavoring was reconstituted in beverage applications. He recommended the use of diacetyl tartaric acid ester of a mono-di-glyceride, monoglyceride sodium sulfo-acetate, polymeric alkyaryl polyether alcohol polyethylene glycol fatty acid esters, sodium lauryl sulfate, vegetable oils, glyceryl monostearate, acetylated monoglycerides, citrus stearoptene, lecithin, gum arabic, locust bean gum, guar gum, tragacanth gum, pectin, pectin albedo, agar or algin as emulsifiers. The emulsification system used in the patent examples was a blend of monoglyceride sodium sulfoacetate and mono-diglyceride at about a 1% level (based on total emulsion weight).

Swisher (1) conducted an accelerated spoilage test on the product (encapsulated orange peel oil) he obtained via this process and estimated shelf-life at about 1 year.

A second patent was awarded to Swisher (3) which made several improvements upon his basic process. He advocated adding glycerol to the corn syrup solids (4-9% of total weight of corn syrup/water mixture) and then cooking this mixture to 110 to 130 C. The glycerol provided a liquid medium in which the corn syrup solids were soluble and had adequate heat transfer properties to permit melting of the corn syrup solids. This had the benefit of requiring less water addition to solubilize the corn syrup solids (which ultimately had to be removed in cooking prior to the addition of the flavoring) and provided a plasticizing effect on the finished product (i.e., developed less cracks and fissures which permitted oxygen to enter the dry matrix). The hot glycerol/corn syrup solution was cooled to about 110 C prior to the addition of the flavoring material.

The second major modification added by Swisher (3) was the extrusion of his molten flavor emulsion through a die (1/64" holes) into a cold (down to -18 C) isopropanol bath. While his patent included the use of other solvents (i.e., kerosene, petro-

leum ether, methanol, acetone, methyl ethyl ketone, limonene, benzene and toluene), isopropanol was the solvent of choice. This solvent served three functions. First, the cold solvent rapidly solidified the molten matrix producing an amorphous structure which was very impermeable to oxygen. Second, the solvent removed any remaining surface oil which would otherwise become oxidized during storage. Third, the isopropanol would extract a substantial proportion of the water present in the extruded matrix without removing the encapsulated flavoring. It was possible to reduce moisture content down to 1/2 to 2% by permitting the extruded material to remain in the isopropanol for a significant time. Times given in the patent ranged from 36 to 144 hours.

Agitation of the spaghetti-like extruded emulsion in the isopropanol bath reduced the particle size to the desired dimensions. The practical limit to particle size was when the length was reduced to equal the diameter.

Following the solvent storage step, the particles were removed from the solvent by filtration or centrifugation, further dried to remove residual isopropanol, mixed with anticaking agent (e.g., 2% tricalcium phosphate) and then packaged. It should be noted that this product was quite hygroscopic due to the combination of the high DE corn syrup and glycerol which were used as the primary matrix material.

Beck (4) received a patent in which he advocated the use of sucrose and hydrolyzed cereal solids as the encapsulation matrix materials. The hydrolyzed cereal solids were defined as having a DE below 20, typically 10 to 15 being preferred. This sucrose/maltodextrin matrix was considerably less hygroscopic than the 42 DE corn syrup advocated by Swisher (1, 3). A typical formulation of the carbohydrate melt prior to cooking was 400 ml water (3.2%), 6840 g sucrose (about 0.1% moisture, 55.3% of formulation) and 5160 g hydrolyzed cereal solids (10-13 DE, 41.3% of formulation). A second modification advocated by Beck (4) was the use of pyrogenic silica as a free flowing agent.

Barnes and Steinke (5) used essentially the same process as that developed by Swisher (3) but chose to use a matrix of maltodextrin and modified food starch. The modified food starch suggested was either Capsul (tradename of product from National Starch) or Amiogum (tradename of product from American Maize). These modified starches are produced via a derivatization of waxy maize with octenylbutanedioate which provides emulsification properties to the starch (6). The authors stated that the primary role of the modified starch was to "absorb" the flavor oil into the matrix. They claimed that the use of an emulsifying starch in place of sucrose (as had been earlier advocated by Beck (4)) had several advantages. An initial advantage is that the product can be made "sugar-free" which may have some labeling advantages. A second advantage claimed was that inversion of sucrose results in hygroscopicity in the finished product. The presence of sucrose in the encapsulation system, therefore, limits cook time, extrusion time and cook temperature since each of these parameters influences sucrose inversion. The use of a modified starch then provides flexibility in the process which can yield a



superior product. A third advantage claimed for the use of modified starch is a high loading potential. Previous extrusion processes yielded low load flavorings (8-10%) while Barnes and Steinke (5) claimed up to 40% loadings were possible.

Barnes and Steinke (5) have also suggested that it is possible to encapsulate orange juice solids, propylene glycol and fruit essences via their process. The orange juice solids can be encapsulated up to 10-15% loading levels starting with 58°Brix orange concentrate. In the case of fruit essences, they suggested that the water and low molecular weight alcohols should be removed prior to encapsulation. Encapsulation of the purified essence is further enhanced by the addition of an edible oil and/or emulsifying agent.

A formulation given for the carbohydrate matrix used in the encapsulation of orange oil is as follows\*:

Maltodextrin	1940 g
Capsul®	485 g
C <sub>6</sub> -C <sub>10</sub> fatty acids (emulsifying agents)	150 g
Water	1880 g

\*Barnes and Steinke (5) - Example 1.

Miller and Mutka (7) have also outlined a process for the encapsulation of juice solids. They found it necessary to clarify the juice and then concentrate it to about 85°Brix prior to encapsulation. Clarification was accomplished by ultrafiltration or enzymatic treatment and was required in order to avoid viscosity problems during concentration. The high solids level was desirable since lower solids juices would need to be cooked longer to achieve acceptable moisture levels for extrusion and would, therefore, suffer heat damage.

The matrix used for the encapsulation of juice solids was a mixture of low DE maltodextrin (DE 10) and lactose. A typical formulation prior to cooking would be 23% water, 26% lactose and 51% maltodextrin. This material was cooked to the desired temperature (ca. 110 C), mixed with 85°Brix juice solids and optionally, peel oil, extruded, washed and dried. The extrusion process is essentially the same as used by Swisher (3). A product containing up to 40% juice solids may be produced via this process. This loading of juice solids is substantially greater than the 10-15% juice solids loading claimed by Barnes and Steinke (5).

A patent has been recently issued on extrusion encapsulation to Miller and Mutka (8). This patent contains no new formulation or process innovations but rather a refinement of the existing art (1, 3). A flow chart of the overall process is presented in Figure 1 with a view of the extrusion process presented in Figure 2. The carbohydrate matrix consists of a high DE maltodextrin and sugar, e.g., 6025 g of 20 DE maltodextrin solution (70% solids) plus 4125 g sugar (Example 1 in patent). This carbohydrate matrix is heated to promote solubility and then cooked to 120 to 124 C to reduce moisture content. They found a

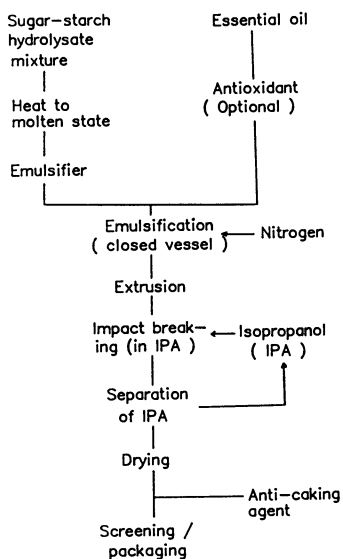


Figure 1. Process flow diagram for the encapsulation of flavorings via extrusion.

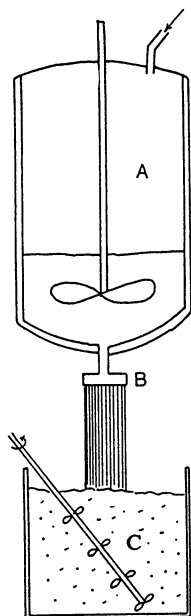


Figure 2. Diagram of extrusion process. A) Pressurized reactor; B) Die; C) Isopropanol bath.

cook temperature of 123 C to be the optimum for oil levels above 22%. (See Table I.) At oil levels below 20%, higher cook tem-

Table I. The influence of cook temperature on encapsulation efficiency (8)

% Oil Encapsulated	% Encapsulation Efficiency	Cook Temperature (C)
20.5	63.5	118
22.9	70.9	122
21.1	65.3	126
19.3	59.8	130
19.2	59.4	134

1. Composition of system: 6025 g of 20 DE maltodextrin (70% solids), 4125 g sugar, 240 g EMARGOL KL (tradename of sulfoacetates of mono & diglycerides by Witco Company) and 4200 g cold pressed orange oil.

peratures were not detrimental to encapsulation efficiency. Cook temperatures above 123 C were found to have a negative effect on encapsulation efficiency of high oil loads which was postulated to be due to too little moisture in the melt to facilitate oil emulsification. At least 5% moisture was considered essential for adequate emulsification.

Prior to oil addition, an emulsifier is added to the carbohydrate melt. While Miller and Mutka (8) suggested 0.5 to 5% emulsifier (based on total weight of aqueous melt), optimization of this parameter was critical for obtaining high flavor loadings. They found encapsulation efficiency was the best using sulfoacetates of mono and diglycerides, polyglycerol esters or lecithins at about 1.9%.

Once the emulsifier is well blended into the carbohydrate melt, the flavoring material is added. An emulsion is formed using a flat bladed turbine type agitator (about 4½ inches in diameter). The time of agitation is typically about 5 min. The next step involves pressurization of the extrusion vessel with either nitrogen or carbon dioxide. While others have mentioned pressurization of the vessel for extrusion, Miller and Mutka (8) have optimized this parameter for encapsulation efficiency. They found 7-50 psi most suitable for improving encapsulation efficiency. At pressures above 100 psi, they found some emulsions broke and encapsulation efficiency was very poor.

The extrusion into a cold isopropanol bath, recovery by centrifugation, drying in a vacuum oven, addition of a free flowing agent and packaging are essentially unchanged from the recommendations of Swisher (3).

In summarizing the work of Miller and Mutka (8), they have found that optimizing the cook temperature, emulsifier level and extrusion vessel pressurization permits the production of encapsulated flavoring of high flavor load. While the patent claims loadings up to 35%, the practical limit appears to be 16-20%. While this is comparable to the flavor loading typically

accomplished via spray drying, the encapsulation efficiency is only about 70%. Encapsulation efficiency during spray drying of similar materials is 90-95%.

The evolution of this process from forming a "rock" candy and then grinding it up as a flavoring material to a very competitive commercial process has occurred over a period of about 30 years. This process offers exceptional protection of the flavor to oxidative deterioration. It is quite superior in this respect to the traditional method of spray drying. Flavorings extremely prone to oxidation (e.g., citrus oils) can be encapsulated via extrusion without antioxidants and still have shelf-lives measured in years. Recent refinements in the process have permitted the production of high load products which makes the process more cost competitive with spray drying, although the poor encapsulation efficiency is still a drawback. The major problem still facing this process is related to emulsion stability. It is exceptionally difficult to form a stable emulsion in extremely viscous carbohydrate melts. Work needs to be continued in this area.

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## Chapter 12

### Shelf Life of Orange Oil

#### Effects of Encapsulation by Spray-Drying, Extrusion, and Molecular Inclusion

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A shelf life investigation of different processes for encapsulation of orange peel oil was conducted at storage temperatures of 25, 37, and 50 C. Gum Arabic, modified food starch, and a 25 D.E. corn syrup were selected as spray drying agents. Regular Durarome (trade name of extrusion product) containing sucrose and a sucrose-free Durarome represented the extrusion products. Beta-cyclodextrin was used for the molecular inclusion of orange oil. The quantity of limonene-1,2-epoxide produced during storage was measured by gas chromatography. A concentration of 2 mg epoxide per gram of orange peel oil was designated to be the end of shelf life. The encapsulated orange oil samples were also analyzed for total oil, surface oil, moisture, emulsion stability, and flavor. The extrusion and beta-cyclodextrin products yielded the best shelf life during storage.

The encapsulation of food flavors presents a very unique and challenging area of investigation. Commercial production of encapsulated flavors is accomplished by a variety of methods. Spray drying, extrusion, coacervation and adsorption techniques are among the more widely used (1). A relatively new method is the molecular inclusion of flavor in beta-cyclodextrin (2, 3). This process has not yet attained commercial use in foods in the United States.

There are a wide variety of encapsulating agents available on the market. Modified food starches, maltodextrins, gums, proteins, corn syrups and sugars are popular choices (4-7). The selection of an encapsulating agent depends upon the chemical composition of the flavor, the encapsulation method, the desired properties of the final microcapsule and its end uses. Other considerations include cost and availability.

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Chemically active flavors require the proper selection of encapsulating agent and processing method to provide protection against oxidation. Citrus essential oils are an example. Consisting largely of mono- and sesquiterpene hydrocarbons, these flavors have a tendency to degrade rapidly, resulting in the development of off-flavors and aromas (8).

Cold pressed orange oil contains over 95% by weight monoterpene hydrocarbons. The principal constituent, d-limonene, ranges from 83-97 percent (9). Limonene degradation has been well documented in the literature (10, 11). Anandaraman identified limonene-1,2-epoxide and carvone as two of the earliest degradation products of d-limonene (12, 13).

Little work has been published comparing the shelf life of flavors encapsulated by different processes. The purpose of this investigation was to determine the shelf life of cold pressed orange oil encapsulated by spray drying, extrusion, and molecular inclusion. Limonene-1,2-epoxide concentration was used to monitor oxidation.

### Materials and Methods

**Materials.** Spray dried gum arabic was obtained from the Meer Corporation (North Bergen, NJ). A low D.E. modified food starch (Amiogum 23) and beta-cyclodextrin samples were obtained from the American Maize-Products Company (Hammond, IN). A 25 D.E. corn syrup, M250, was obtained from the Grain Processing Corporation (Muscatine, IA). The extrusion encapsulated products, regular (containing sucrose) and sucrose-free (SF) Duraromes, were supplied by MCP Foods, Incorporated (Anaheim, CA). The cold pressed orange peel oil was also supplied by MCP Foods. All organic compounds or solvents and inorganic chemicals used in the analyses were ACS certified grade.

**Encapsulation of Orange Peel Oil.** Solutions of gum arabic, Amiogum 23, and M250 each containing 35 percent (w/w) solids dispersed in deionized water were gently heated (60 C) over a steam bath to facilitate solubilization. The solutions were allowed to cool to room temperature before storing under refrigeration overnight (4 C). Orange peel oil (25% w/w of solids) was emulsified into the hydrated carriers using a Greerco lab homogenizer. Each emulsion was immediately spray dried using a Niro Utility Dryer equipped with a centrifugal wheel atomizer. Drying conditions were controlled using inlet and exit air temperatures of  $200 \pm 3$  C and  $100 \pm 3$  C, respectively.

The molecular inclusion of orange peel oil in beta-cyclodextrin was accomplished by applying the method of Reineccius and Risch (3). Beta-cyclodextrin (500 g) was dissolved in 5,000 ml of an ethanol:water solution (1:2) at 55 C. Orange peel oil (50 g) was combined with 500 ml ethanol, and this flavor mixture was added slowly to the beta-cyclodextrin solution. During the addition of the flavor, the solution of beta-cyclodextrin was continuously agitated and the temperature maintained at 55 C. The final solution was cooled gradually to room temperature and refrigerated overnight at 4 C. The

beta-cyclodextrin flavor complex was recovered by filtration. This complex was placed in a gravity oven and allowed to dry at 55 C for sixteen hours. The complex was removed from the oven and allowed to air dry for an additional 16 hours at room temperature (25 C).

Two extrusion products, regular and sucrose-free (abbreviated Reg and SF) Duraromes, were encapsulated at MCP Foods using patented processing parameters (14). The SF matrix was composed of maltodextrin, polyhydric alcohols and emulsifiers, while the Reg matrix consisted of maltodextrin, sucrose and emulsifiers. In brief, the extrusion process involved emulsification of orange peel oil into a melt of the ingredients described above. The molten products were then extruded under pressure through a die template into a chilled isopropyl alcohol bath. Subsequently, the products were broken into small, rod-shaped particles and dried to remove the alcohol.

Determination of Total Oil. The Clevenger hydrodistillation method was used for total oil determination (15). Forty gram samples were distilled for 3½ hours. However, due to limited availability, some sample sizes were restricted to 20 grams. Volumetric readings were multiplied by the oil density to arrive at the gravimetric values. All samples were analyzed in duplicate.

Simultaneous steam distillation and solvent extraction was used to approximate the orange oil content of the beta-cyclodextrin inclusion complex (3). Diethyl ether served as the extracting solvent. One gram samples were refluxed for 1 hour. Upon cooling, the ether phase was recovered and a known quantity of internal standard (2-octanone) was added. Orange oil (100 mg) was subjected to the same process described above in order to provide recovery data. GC analyses of the recovered ether phases were performed in the manner outlined in the Determination of Shelf Life section of this paper. A comparison of the data provided an estimate of % limonene (w/w) in the beta-cyclodextrin inclusion complex. Correction of this value using the limonene content in the starting oil (92%) yielded an approximation of orange oil content.

Determination of Surface Oil. A Soxhlet continuous extraction apparatus was used for removing the surface oil from the encapsulated samples. The procedures used were similar to those described previously by Anandaraman and Reineccius (16). Modifications included a reduced extraction time of 4½ hours and the selection of 2-octanone as the internal standard.

Determination of Moisture. A modified AOAC method for ground spices was used for moisture determination of encapsulated orange oil (17). Twenty and 40 gram samples were refluxed in 150 ml anhydrous toluene for 3½ hours. All samples were analyzed in duplicate.

Determination of Emulsion Stability and Oil Droplet Size. A combination of centrifugation and spectrophotometric techniques was used for the evaluation of emulsion stability. Solutions

(0.1%) of each sample were prepared using distilled water, and centrifuged in an IEC International centrifuge at 500 x G. They were evaluated at 0, 5, 10, 20 and 30 minute intervals using a Coleman spectrophotometer at a wavelength of 400 nm. Absorbance readings were measured immediately following centrifugation.

Particle size distribution (oil droplets) using a light scattering technique was measured on a Leeds and Northrop Microtrak particle size analyzer as described by Weiss and Frock (18). Replicate samples of the encapsulated products were dissolved in water. The beta-cyclodextrin sample was only partially soluble; therefore, the insolubles were allowed to separate out before removing the supernatant for evaluation.

Sensory Evaluation. All encapsulated orange oil samples were compared to the starting orange oil using the Triangle Difference test (19). The samples and orange oil were maintained in a freezer prior to analysis. The triangle tests were conducted at the MCP Foods facility using 12-14 panelists. The samples were evaluated in duplicate in a beverage base consisting of distilled water, sucrose, and citric acid, and were presented in random order at room temperature. Due to color and cloud differences, the samples were evaluated in masked containers.

Determination of Shelf-Life. Encapsulated orange oil samples were placed in glass culture tubes (50 ml). Samples were stored at room temperature (25 C), in a walk-in incubator (37 C), and in a gravity oven (50 C). Samples were analyzed by gas chromatography (GC) on a weekly basis for 25 C, every third day for 37 C, and daily for 50 C. Samples were evaluated until degradation resulted in a level of 2 mg limonene-1,2-epoxide per g of orange oil was attained or until 6 months had elapsed, whichever came first. Samples attaining the 2 mg/g concentration were tasted to verify the presence of off-flavor before sampling was terminated.

Encapsulated orange oil samples (150 mg) were weighed into 10 ml vials and dissolved in 850 mg distilled water. Four ml of acetone containing 0.25 mg/ml 2-octanone as an internal standard were added dropwise to the dissolved samples. The samples were continuously agitated throughout the addition of the internal standard solution using a vortex mixer.

The GC was calibrated using a mixture of known quantities of d-limonene, d-limonene oxide (cis and trans), 2-octanone, and carvone. GC analyses were performed by injecting 1  $\mu$ l samples with 1:40 split (column flow:split flow), into a Hewlett-Packard 5840A GC equipped with a flame ionization detector. A fused silica capillary column 50m x 0.25 mm i.d., coated with OV-101 as a liquid phase was used. Column temperature was programmed from 50-250 C at 10 C/min, and helium was used as the carrier gas. The injection port temperature was 200 C and the detector temperature was 275 C.



### Results and Discussion

All samples were evaluated at time zero for total oil, surface oil, moisture, emulsion stability and sensory properties to provide background information for subsequent shelf life testing. Most of the methods were selected based on previous findings (3, 16, 20). The results of the total oil, surface oil, moisture, and oil droplet mean volume diameter are presented in Table I. All values represent means of two or more samples.

Table I. Comparison of Total Oil, Surface Oil, Moisture and Oil Droplet Volume Mean Diameter

Encapsulation Process/Agent	Test Results			
	Total Oil (% w/w)	Surface Oil (mg oil/ 100 g pwd)	Moisture (% w/w)	Oil Droplet Volume Mean Diameter ( $\mu$ )
<u>SPRAY DRYING</u>				
Gum Arabic	17.5	107	4.6	2.19
M250	11.4	15	2.1	6.62
Amiogum	19.5	15	5.2	1.35
<u>MOLECULAR INCLUSION</u>				
Beta-cyclodextrin	8.2	431	5.5	1.58
<u>EXTRUSION</u>				
Reg Durarome	8.6	2	4.3	3.31
SF Durarome	8.7	2	3.8	6.02

Total Oil. When compared to the other encapsulation processes, the spray dried products contained the highest amounts of volatile oil. Spray drying typically yields product with volatile oil contents ranging from 15-20% w/w. The extrusion products, Reg and SF Duraromes, contained volatile oil contents in the range of 8-10% w/w which was expected with this process (14). The beta-cyclodextrin complex had a lower volatile oil content than a previously reported value of 9.2% w/w (21).

The oil value shown for beta-cyclodextrin was an approximation. Clevenger hydrodistillation failed to recover any volatiles from the inclusion complex. An alternate method was attempted using simultaneous steam distillation and solvent extraction. GC quantitation of the recovered volatiles did not yield reproducible results.

The M250 sample had the lowest volatile oil content of the spray dried products. At 35% infeed solids concentration, the M250 emulsion was difficult to stabilize even with continuous agitation throughout the drying process. The 35% infeed concentration was chosen as the basis for preparing all spray dried samples. While this solids level was appropriate for gum arabic and Amiogum, it may not have been the optimum level for M250. It was previously determined by Leahy et al. that higher infeed solids improved oil retentions (5).

Surface Oil. The surface oil content by Soxhlet extraction ranged from 2 to 431 mg/100 g dry sample. The lowest values were obtained from the extrusion products which had undergone a solvent washing step in the manufacturing process that removed most of the surface oil. The highest value was seen for the beta-cyclodextrin complex. Insufficient mixing time during the preparation stage may have resulted in incomplete flavor inclusion.

Emulsion Stability. The samples were examined for emulsion stability using centrifugation and light scattering techniques (oil droplet volume mean diameter). In general, these tests were used to determine stability of the emulsions to creaming effects. The results of the analyses are presented in Table I and Figure 1. With the exception of beta-cyclodextrin, the data showed good correlation. The emulsion stability was highest for samples having oil droplet volume mean diameters closest to 1 micron. In contrast, the beta-cyclodextrin showed rapid emulsion destabilization with time, although the oil droplet volume mean diameter was 1.52 microns.

Moisture. The moisture contents as determined by toluene distillation ranged from 2.1-5.5% w/w. The lowest value was obtained for the SD M250 sample while the highest value was seen with the beta-cyclodextrin complex.

Sensory Evaluation. Sensory evaluation of the encapsulated samples was conducted to determine whether or not the encapsulation processes had perceptibly changed the orange peel flavor. Triangle difference tests were used to compare each sample to the starting orange peel oil. The results of these tests showed no significant differences in flavor between the encapsulated samples and the starting orange peel oil.

Shelf Life. Encapsulated orange oil samples were subjected to accelerated shelf life testing at 37 and 50 C. Control samples were stored at 25 C. The samples were evaluated until degradation was sufficient to produce a level of 2 mg limonene-1,2-epoxide per gram orange oil by GC analysis. Previous work established that similar concentrations of limonene-1,2-epoxide could be used as an index for measuring oil oxidation, although the direct contribution of this compound to off-flavor development was marginal (12).

The gas chromatograms of fresh and oxidized cold pressed orange oil are presented in Figure 2. The compound, 2-octanone, was used as the internal standard.

The number of days required to attain 2 mg epoxide/g orange oil is shown in Table II. The values obtained for the gum arabic, M250-, and Amiogum were determined using linear equations derived from the graphs of the natural log of shelf life (days) versus the storage temperature (C). For gum arabic,  $\ln(\text{days}) = -0.083(\text{temp., C}) + 6.67$ ,  $r^2 = 0.99$ . Similarly, for M250 and Amiogum,  $\ln(\text{days}) = -0.051(\text{temp., C}) + 6.36$ ,  $r^2 = 0.87$  and  $\ln(\text{days}) = -0.097(\text{temp., C}) + 6.48$ ,  $r^2 = 0.99$ , respectively.

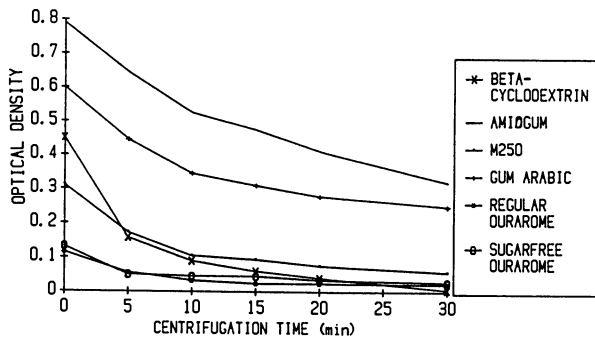


Figure 1. Emulsion stability of encapsulated orange oil samples.

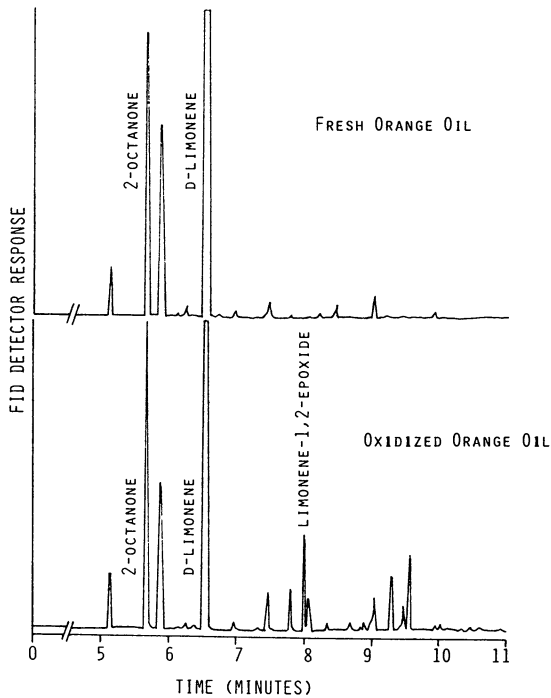


Figure 2. Gas chromatograms of fresh and oxidized orange peel oil - zero time and 6 months storage.

Table II. Shelf Life of Encapsulated Orange Peel Oil

Encapsulation Process/Agent	Shelf Life (Days)		
	Storage Temperature, C		
	25	37	50
<u>SPRAY DRYING</u>			
Gum Arabic	99	37	12
M250	162	88	45
Amiogum	57	18	5
<u>MOLECULAR INCLUSION</u>			
Beta-cyclodextrin	1604	562	180
<u>EXTRUSION</u>			
Reg Durarome	1604	562	180
SF Durarome	1604	562	180

Shelf life values for the beta-cyclodextrin, Reg, and SF Duraromes at 50 C were arbitrarily assigned at 180 days (i.e., termination of study) even though the epoxide values had not reached the 2 mg/g oil level. Shelf life values were then estimated for 25 and 37 C using an average  $Q_{10}$  value = 2.4, obtained from an earlier shelf life investigation by Anandaraman (12, 13). These values represent rough approximations.

The graphs of limonene-1,2-epoxide as a function of storage time at 25, 37 and 50 C are presented in Figures 3, 4 and 5. Limonene-1,2-epoxide appeared to have an induction period where little or no epoxide formation occurs. Beyond the induction period, limonene-1,2-epoxide formation followed first order kinetics for the spray dried products. Gum arabic, M250, and Amiogum consistently showed the fastest rates of epoxide formation at the three storage temperatures.

Graphs of the natural log of the epoxide concentration as a function of storage time at 25, 37 and 50 C revealed linear relationships for the spray dried samples ( $r^2 = 0.87-0.99$ ). The relationship for M250 at 37 C was somewhat lower ( $r^2 = 0.78$ ) due to difficulty in determining where the induction period ended and the first order kinetics began.

The rate of epoxide formation and shelf life may have been influenced by the starting oil. The shelf life of spray dried orange oil using M250 was previously investigated at storage temperatures of 32, 45 and 60 C by Anandaraman (12, 13). Interpolation of this data provided shelf life estimates of 44 and 16 days for storage temperatures of 37 and 50 C, respectively. These values were much lower than the M250 values shown in Table II. In the previous investigation, the limonene-1,2-epoxide concentration of the encapsulated orange oil at time zero was 0.41 mg/g oil (12). In this investigation, the epoxide concentration at time zero was 0 mg/g oil.

Calculation of surface oil as a percent of the total oil produced values of 0.61, 0.13, and 0.08% for gum arabic, M250, and Amiogum, respectively. Higher surface oil values did not correspond to lower shelf lives. The shelf lives of gum arabic

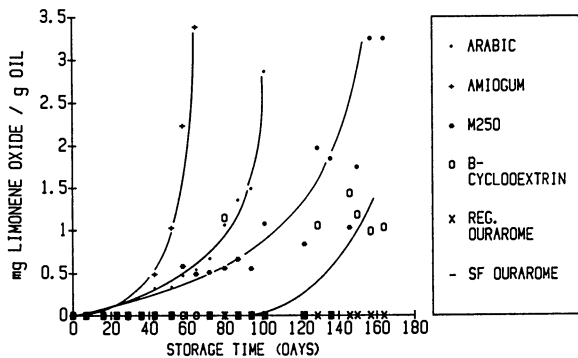


Figure 3. Shelf life of encapsulated orange oil samples stored at 25 C.

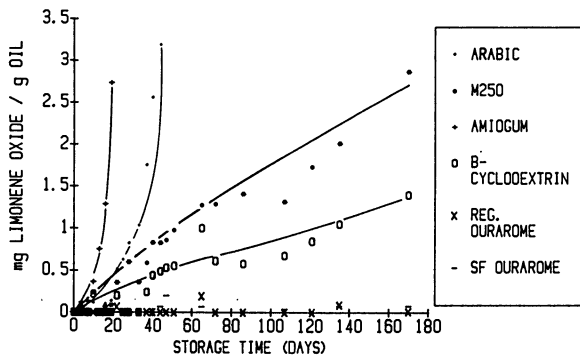


Figure 4. Shelf life of encapsulated orange oil samples stored at 37 C.

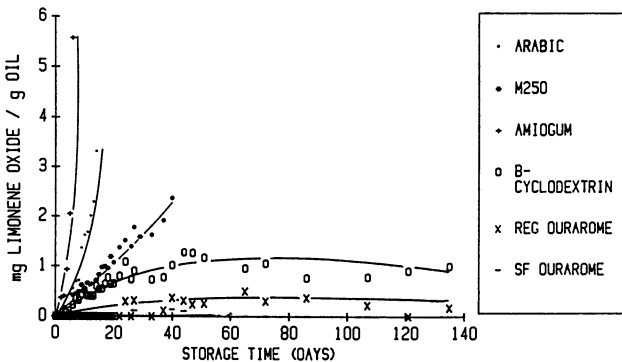


Figure 5. Shelf life of encapsulated orange oil samples stored at 50 C.

and M250 exceeded those of Amiogum at all storage temperatures. This suggested that surface oil less than 1% by weight of the total oil did not adversely affect shelf life of encapsulated orange oil. These results were in agreement with a previous investigation that showed that the presence of low levels of surface oil in encapsulated orange oil samples yielded only slightly higher oxygen absorption rates as compared to the same samples in which the surface oil had been removed (12, 13).

The beta-cyclodextrin inclusion complex reached a level of 1 mg limonene-1,2-epoxide per gram orange oil after 129, 65 and 40 days at 25, 37 and 50 C, respectively. Upon attaining this concentration, the level of epoxide remained constant or began decreasing with time (Figures 3, 4, 5). This suggested that appreciable degradation of the epoxide had begun. Due to the slow rate at which the lionene-1,2-epoxide formed, a level of 2 mg lionene-1,2-epoxide as not attained during the 6 month test period.

The two extrusion products, Reg and SF Duraromes, exhibited the lowest rates of limonene-1,2-epoxide formation. After 6 months storage at temperatures of 25 and 37 C, these products contained epoxide levels of < 0.20 mg/g orange oil. At 50 C, the Reg Durarome showed levels < 0.50 mg/g orange oil. Epoxide degradation may also have been a factor similar to that seen with beta-cyclodextrin.

### Summary

The stability of orange peel oil depends on the selection of the encapsulation process and the encapsulating agent. The results of this study indicated that the differences in shelf life were greatly accentuated at higher temperatures. The shelf life of the spray dried products ranged from 5-35 days compared to the extrusion and beta-cyclodextrin products which were still acceptable after 180 days at 50 C.

Overall, extrusion encapsulation provided superior protection of orange peel oil as measured by epoxide formation. The molecular inclusion of orange oil via beta-cyclodextrin also provided very good protection although the limonene-1,2-epoxide concentrations were consistently higher than for the extrusion products.

Spray drying provided the least protection to orange peel oil. Of the three spray drying agents evaluated, M250 provided the best protection to orange oil. This is in agreement with a previous investigation which showed that hydrolyzed starches with increasing DE provided better protection to encapsulated orange oil (12, 13). The presence of pro-oxidants, trace metals, or other compounds as well as differences in oxygen permeability may have contributed to the differences in the rates of epoxide formation seen between these carriers.

### Acknowledgments

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## Chapter 13

# Flavor Encapsulation with Alginates

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Alginates, unique hydrocolloids extracted from selected species of brown seaweed (kelp), interact with calcium ions to produce thermally stable gels. Using this interaction, flavor oils may be encapsulated or entrapped in the algin gel matrix. Encapsulation is accomplished at ambient temperatures. Products may be used "as is" (wet) or subsequently dried. This technique offers the potential for novel flavor effects, flavor protection, and new food products.

Because of their ability to react with calcium ions at ambient temperatures to form thermally stable gels or fibers, alginates can provide a useful encapsulating or entrapping system for oil soluble flavor compounds.

Algin is the structural polysaccharide of the brown seaweeds. One of the most abundant and useful species of these marine plants is Macrocystis pyrifera, also called giant kelp. This plant grows in water as deep as 100 ft., and under optimum conditions can grow one inch/hour! Giant kelp is harvested with mechanical harvesters which cut only the top portion of the plant, about three feet below the water's surface. Algin is then extracted from the kelp plant through an ion exchange process and converted to various salt forms. The most common salt is sodium alginate, sold as a water soluble powder. During manufacturing, properties such as viscosity, clarity and calcium content are controlled to achieve proprietary products of specified functionality.

Alginates are composed of two monomeric sugar acids; D-Mannuronic acid and L-Guluronic acid. These two monomers are connected by 1-->4 glycosidic linkages. Commercially available polymers range from molecular weights (M.W.s) of 12,000 - 180,000 Daltons (1). The proportions of the two monomers vary from one species to another, but in all species studied there are homogeneous blocks of each type of residue, polymannuronic (M-blocks),

polyguluronic (G-blocks), or continuously alternating residues (MG-blocks). A single algin molecule will contain all three segments. For example, the giant kelp, *Macrocystis pyrifera*, contains ca. 40% M-blocks, ca. 18% G-blocks, and ca. 42% M/G-blocks, while algin from *Laminaria hyperborea* contains 13% M-blocks, ca. 60% G-blocks, and ca. 27% M/G-blocks (2).

The geometries of these segments are considerably different. The M-blocks have an "extended ribbon"-type conformation, while the G-blocks are much more buckled. When two G-block regions align side by side, diamond shaped holes are formed, having dimensions ideally suited for the cooperative binding of calcium ions. The calcium ions are bound between two algin chains like eggs in an egg box. Therefore, the calcium reactivity of algin is the result of calcium induced dimeric association of the G-block regions (3-4).

Depending on the amount of calcium added to a 0.5% high M.W. (high viscosity) alginate sol, and the method of addition, high viscosity "solutions", free standing gels, or insoluble, fibrous precipitates may be produced. Because of the ionic nature of the calcium/alginate reaction, gels so formed possess thermal stability and do not melt upon heating. Although the gels are not reversible by heating, they can be reversed or weakened through ion exchange with chelating agents (sequestrants) or extended treatment with Na, K, Mg or ammonium salts.

Diffusion setting is one of several methods used to form alginate gels. This method requires hydration of the alginate separately from the calcium source. When the alginate sol contacts a calcium salt solution (such as 3-5% calcium chloride, acetate, or lactate), a gel forms instantly at the interface. Calcium ions continue to diffuse into the alginate, causing the gel to strengthen with time. This reaction can be easily demonstrated by simply pouring a 2% sodium alginate sol into a 5% calcium chloride solution. A gel forms instantly, and can be removed from the calcium chloride and handled as a solid.

Many extruded, reformed food products presently use this gelation method to bind food particles into specific shapes. Often the gelation reaction not only performs a binding function but also acts as a processing aid. Algin is hydrated by mixing it with the comminuted food, the mixture is extruded in a specific shape and sprayed with, or dipped in, the calcium solution to produce the instant surface gel. The food products are usually battered, breaded, and fried prior to packaging and freezing. The application of an algin film, by first coating a food product such as oysters or fish fillets with an algin sol, followed by a calcium solution spray, forms an effective coating to minimize freezer burn during prolonged storage. Application of this coating to foods normally fried (onion rings, for example) provides an effective fat barrier, and the gel does not melt.

It is important to realize that an algin/calcium gel or film is permeable to water soluble molecules with molecular weights of less than 5,000 Daltons. Molecules of higher molecular weight may also slowly diffuse through the gel, but those with molecular weights of 10,000 and higher will not diffuse (5). For example, sugar and soluble colors will diffuse out of a gel placed in water, and water itself can be lost from algin gels in dry environments. Lipid

materials will be held in the gel matrix even though they are of low molecular size, however. Consequently, although water soluble flavor compounds will not be held by algin gels, oil soluble compounds can be encapsulated or trapped in algin/calcium matrices. An interesting example of encapsulation and diffusion is the production of ethanol by yeast cells (*Saccharomyces cerevisiae*) encapsulated in an alginate gel. The cells are immobilized in the algin gel, sugar diffuses into the gel where the yeast converts it to alcohol, which then diffuses out of the gel. Alcohol can thus be produced continuously by passing a glucose solution through a column of the encapsulated cells (5). In a similar fashion, the algin/calcium gel has been used to immobilize various enzymes. Even viable, insulin producing cells (islets), have been encapsulated. Injection of these encapsulated cells into rats with induced diabetes corrected the diabetic state for two to three weeks (6).

In order to encapsulate or entrap oil soluble flavors with alginates, it is first necessary to form an emulsion, using standard emulsion technology. Once the emulsion is formed, the alginate sol/emulsion is added dropwise, or atomized, into a calcium chloride solution (5% or higher). Gel beads will form instantly, with the oil soluble material trapped inside the beads. The diameter of the beads can be varied from 200 - 5000 microns, depending on formulation and mechanical equipment used. The gel beads may be kept in the hydrated gel state or dehydrated, depending on needs. The use of high calcium chloride concentrations (> 20%) helps to dehydrate the beads, but the bitter chloride flavor may persist. Rinsing off excess  $\text{CaCl}_2$  helps or calcium lactate may be substituted (solubility limits the concentration to < 5%, however). Encapsulation of heat sensitive materials in this manner helps reduce heat degradation.

A second method for entrapping oil soluble flavors involves reversing the above procedure. By the addition of a calcium salt solution to an efficiently mixed alginate flavor oil emulsion, insoluble calcium alginate fibers are formed which also entrap flavor oils, although not quite as efficiently as the previous method. These highly reacted calcium alginate fibers are very stable to heat, acid, and further mixing, retaining their integrity and serving as useful texturizing ingredients under conditions free of significant ion exchange. This fibrous-like material may also have a texture very similar to fruit pulp, and serve a texture function as well as that of a flavor carrier, especially for fruit, vegetable, or meat products. By the proper addition of various ingredients prior to the reaction with calcium (e.g., other gums, starch, fats, proteins, fruit or vegetable fiber, dextrans, etc.), the texture of the final fibers can be modified within broad limits (7).

Using this method, extremely high viscosity develops as the calcium salt is introduced to the alginate emulsion; consequently efficient mixing, such as that obtained with a Hobart mixer is required. The alginate fiber size may be controlled by the type of mixing used during the calcium/alginate reaction period and the few minutes immediately following calcium salt addition. The higher the shear rate, the smaller the fibers will be. This method has potential for flavor entrapment in such products as fruit- or vegetable-like pulp for beverages, hard candy, bakery fillings, and ice cream toppings.

Although alginate encapsulation or entrapment of oil soluble flavors is quite different from traditional encapsulation methods, it could serve as a valuable tool for liquid systems where a protective effect, delayed release, or combination texture/flavor effect is needed.

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## Chapter 14

# Coacervation for Flavor Encapsulation

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Coacervation is a term borrowed from colloid chemistry to describe the basic process of capsule wall formation. The encapsulation process was discovered and developed by Barrett K. Green of the National Cash Register Corporation (NCR) in the 1940's and 1950's. Actually, coacervative encapsulation (or microencapsulation) is a three part process: particle or droplet formation; coacervative wall formation; and, capsule isolation. Each step involves a distinct technology in the area of physical chemistry. The first coacervative capsules were made using gelatin as a wall in an "oil-in-water" system. Later developments produced "water-in-oil" systems for highly polar and water soluble cores. The capabilities and limitations of coacervative encapsulation are presented along with the basic literature references. There is some discussion on the art of coacervation.

The basic process for using one form of coacervation, also known as aqueous phase separation, was described in an early patent by B.K. Green and L. Schleicher (1). The patent relates to oil-containing microcapsules of a complex hydrophilic colloid wall material and a method of making them. B.K. Green's attempts began in a Dayton, Ohio laboratory. In the late 1930's B.K. Green, a young chemist just out of school, was intrigued by the dearth of information in the colloid field of liquids dispersed in solids. He had earlier recognized the usefulness of such disperse systems in photographic applications. When his company needed a product that would give multiple paper copies without carbon paper. B.K. Green turned to his ideas on dispersions. By 1940, the first working No-Carbon-Required (NCR) paper was prepared, but this was only the beginning. His breakthrough came in 1942 when he was investigating Bungenberg de Jong's coacervation studies (2). One paper mentioned the preparation of solid gelatin spheres, while another dealt with the inclusion of an oil phase within a gelatin coacervate. B.K. Green used both concepts and prepared the first gelatin microcapsules. From this beginning it was nine long years

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to the development of a marketable product. The new printing system was triggered by including a colorless dye-base in the oil droplets (coated back, CB) and coating the second sheet of paper (coated front, CF) with acidic clay which could react with the dye-base to produce a color.

#### Coacervation and Microencapsulation

Coacervation is a colloid phenomenon. If one starts with a solution of a colloid in an appropriate solvent, then according to the nature of the colloid, various changes can bring about a reduction of the solubility of the colloid. As a result of this reduction a large part of the colloid can be separated out into a new phase. The original one phase system becomes two phases. One is rich and the other is poor in colloid concentration. The colloid-rich phase in a dispersed state appears as amorphous liquid droplets called coacervate droplets. Upon standing these coalesce into one clear homogenous colloid-rich liquid layer, known as the coacervate layer which can be deposited so as to produce the wall material of the resultant capsules.

Coacervation may be initiated in a number of different ways. Examples are changing the temperature, changing the pH or adding a second substance such as a concentrated aqueous ionic salt solution or a non-solvent.

As the coacervate forms, it must wet the suspended core particles or core droplets and coalesce into a continuous coating for the process of microencapsulation to occur. The final step for microencapsulation is the hardening of the coacervate wall and the isolation of the microcapsules, usually the most difficult step in the total process.

#### Simple Coacervation

Simple coacervation involves the use of either a second more-water soluble polymer or an aqueous non-solvent for the gelatin. This produces the partial dehydration/desolvation of the gelatin molecules at a temperature above the gelling point. This results in the separation of a liquid gelatin-rich phase in association with an equilibrium liquid (gelatin-poor) which under optimum separation conditions can be almost completely devoid of gelatin.

Simple coacervation can be effected either by mixing two colloidal dispersions, one having a high affinity for water, or it can be induced by adding a strongly hydrophilic substance such as alcohol or sodium sulfate. The water soluble polymer is concentrated in water by the action of a water miscible, non-solvent for the emerging polymer (gelatin) phase. Ethanol, acetone, dioxane, isopropanol and propanol have been used to cause separation of coacervates of gelatin, polyvinyl alcohol and methylcellulose. Phase separation can be effected by the addition of an electrolyte such as an inorganic salt to an aqueous solution of a polymer such as gelatin, polyvinyl alcohol or carboxymethyl cellulose.

A typical simple coacervation using gelatin colloid is as follows: to a 10 percent dispersion of gelatin in water, the core material is added with continuous stirring and at a temperature of 40° C. Then a 20 percent sodium sulfate solution or ethanol is added at 50 to 60 percent by final total volume, in order to induce the coacervation. This system is cooled to 5°C; then, it is necessary to insolubilize the coacervate capsules suspended in the equilibrium liquid by the addition of a hardening agent such as glutaraldehyde and adjusting the pH. The resulting microcapsules are washed, dried and collected.

#### Complex Coacervation

Complex coacervation (3) can be induced in systems having two dispersed hydrophilic colloids of opposite electric charges. Neutralization of the overall positive charges on one of the colloids by the negative charge on the other is used to bring about separation of the polymer-rich complex coacervate phase.

The gelatin-gum arabic (gum acacia) system is the most studied complex coacervation system. Complex coacervation is possible only at pH values below the isoelectric point of gelatin. It is at these pH values that gelatin becomes positively charged, but gum arabic continues to be negatively charged. A typical complex coacervation process using gelatin and gum arabic colloids is as follows: The core material is emulsified or suspended either in the gelatin or gum arabic solution. The aqueous solution of both the gelatin and gum arabic should each be below 3 percent by weight. Then, the gelatin or the gum arabic solution (whichever was not previously used to suspend the core material) is added into the system. The temperature of the system must be higher than the gel point of an aqueous gelatin solution (greater than 35 C). The pH is adjusted to 3.8-4.3 and continuous mixing is maintained throughout the whole process. The system is cooled to 5° C and the gelled coacervate capsule walls are insolubilized by either adding glutaraldehyde or another hardening agent and adjusting the pH. The microcapsules are washed, dried and collected.

#### Aqueous Phase Separation

The term aqueous phase separation is often more simply described as "oil-in-water" microencapsulation. The two encapsulation processes described above are examples of this "oil-in-water" encapsulation. In this process the core material is the oil and it should be immiscible in the continuous phase, namely water. A commercial example of aqueous phase separation would be the microencapsulation of an oily flavor such as sour cream with a gelatin wall. These microcapsules would then be dispersed in a dry cake mix. The mechanism of release would be during the moist baking cycle of the cake, moist-heat causing the capsule walls to first swell and then rupture.

#### Organic Phase Separation

The term organic phase separation (4) is sometimes more simply referred to as "water-in-oil" microencapsulation. In this case the polar core is dispersed into an oily or non-polar continuous medium. The wall material is then dissolved in this continuous medium. A simple technique for encapsulation consists of dissolving ethylcellulose in cyclohexane at a temperature of 50°C with continuing mixing. Only one phase is present. The cyclohexane is the oily, continuous phase and the ethylcellulose will later form the coacervative wall. The temperature is elevated to 70°C over a period of 20 to 30 minutes. The core material is added and the temperature raised to 80°C over a period of time and is held at that temperature for one hour. The system is allowed to cool rapidly to 20-40°C. Upon cooling, the ethylcellulose will gradually emerge as a separated coacervate phase which will then gradually solidify by the time 20°C is reached (unlike hot cyclohexane, the cold material is a non-solvent). The capsules are washed, filtered and air dried. It should be noted that ethylcellulose is generally approved for use in the pharmaceutical industry. However, for its use in the food industry the "Code of Federal Regulations" should be consulted under the categories of both microencapsulation and ethylcellulose.

Another ethylcellulose wall encapsulation system involves the addition of polyisobutylene to the ethylcellulose/cyclohexane. The procedure begins with the addition of ethylcellulose to a mixture of cyclohexane and polyisobutylene at room temperature. Polyisobutylene, which is more soluble in cyclohexane than is ethylcellulose, is more effective in causing the latter to emerge as a separate liquid coacervate than would be the case with merely cooling the cyclohexane. The solution is then heated to 80°C and the core material added. The system is cooled to 40°C in 60 minutes and cooled quickly to 20-25°C. Microcapsules are filtered, washed and dried. A modification of this system involves the following procedure: The polyisobutylene is dissolved in cyclohexane at a temperature of 70°C and with continuous stirring. After cooling the system to 40°C, ethylcellulose is added and dissolved. The core is dispersed in this solution and the system again heated to 78°C and held for 10 minutes at this temperature. Then it is slowly cooled to room temperature followed by cooling to 10°C over two hours. Besides polyisobutylene, other coacervation inducing agents have been used such as polyethylene and butyl rubber.

#### Designing the Process--Process and Material Selection

Coacervation is a very complicated physical phenomenon. And, many factors affect the properties of the resulting microcapsules. Coacervation and phase separation from organic and aqueous media involve many properties, materials and processes such as: phase inducing agents, stirring rates, core to wall ratios, polymer characteristics, core characteristics (wettability, solubility), cooling rates and rates of addition.



The basic production of microcapsules actually involves three distinct steps as discussed above. The hardening of the microcapsules sufficient for isolation of them into a dry free-flowing powder remains as a persistent problem. One of the earliest attempts is the gelatin-tannin reaction (5). Tannic acid is recognized as a means for "hardening" gelatin-walled capsules. It should be noted that a particular encapsulation system, such as would be described in any one of the patents in the literature, is not necessarily effective in encapsulating a given flavor. Consequently it is often necessary to develop or modify an encapsulation system for each flavor. This is particularly true when one looks at the multitude of requirements related to storage and release of the microcapsule core.

In developing or modifying an encapsulation system, it is very helpful to look at the available wall materials that one may have for use. A reasonably comprehensive list is available (6). This list should be used in conjunction with materials also listed in the "Code of Federal Regulations", Title 21, particularly parts 1 to 199 (7). The following materials should be useful in developing a microencapsulation system using coacervation:

Acacia (Gum Arabic)	Polyethylene Glycols
Butadiene-Styrene 75/25 Rubber	Polyisobutylene
Butadiene-Styrene 50/50 Rubber	Polyvinyl Acetate
Butyl Rubber	Polyvinylpyrrolidone
Carob Bean Gum	Potassium Alginate
Carrageenan	Potassium Citrate
Citric Acid	Potassium Polymetaphosphate
Dextrin	Potassium Tripolyphosphate
Dimethylpolysiloxane	Povidone
Dimethyl Silicone	PVP
Ethylcellulose	Refined Paraffin Wax
Food Starch, Modified	Shellac, Bleached
Guar Gum	Sodium Alginate
Hydroxypropyl Cellulose	Sodium Carboxymethylcellulose
Hydroxypropyl Methylcellulose	Sodium Citrate
Isobutylene-Isoprene Copolymer	Sodium Ferrocyanide
Locust Bean Gum	Sodium Polyphosphates, Glassy (Sodium hexametaphosphate)
Methylcellulose	Sodium Trimetaphosphate
Methyl Ethyl Cellulose	Sodium Tripolyphosphate
Microcrystalline Wax	Synthetic Wax (Ethylene Polymer)
Paraffin, Synthetic	Tannic Acid
Petroleum Wax	Terpene Resin, Natural
Petroleum Wax, Synthetic	Tragacanth
Poloxamer	White Shellac
Polyethylene	Xanthan Gum

Conclusions

A number of encapsulation systems such as spray drying appear to be superior to coacervation because of cost and availability of materials. There are times, however, when coacervation is absolutely necessary. This generally occurs when reservoir microcapsules of a small size, say 10 to 70 microns, are needed or when the core material is a polar liquid and capsules can only be made by organic phase separation. With oily cores it is generally best to start with a gelatin system and modify it accordingly. The gluteraldehyde hardening of gelatin should be judiciously used in accordance with the restrictions stated in the "Code of Federal Regulations".

There yet remains considerable amounts of art to coacervative microencapsulation. Here art is best described as a phenomenon awaiting a scientific explanation. In coacervation the kind of addition and the rate of and order of addition are extremely critical. In general, the slower the process the better it is for coacervative encapsulation. It is the intuitive feel that encapsulators practice that it frequently termed "art."

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## Interfacial Tension Behavior of Citrus Oils Against Phases Formed by Complex Coacervation of Gelatin

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The Wilhelmy plate technique has been used to characterize the interfacial tension (IFT) of four citrus oils against aqueous coacervate and supernatant phases formed by complex coacervation of gelatin. Three complex coacervate systems have been investigated: gelatin/gum arabic, gelatin/polyphosphate and gelatin/alginate. Initial IFT values for all interfaces examined were below  $8\text{mJ/m}^2$ . The IFT of all interfaces decreased as age of the interface increased. Complex coacervate phases at 40 to 50°C, gave an IFT that aged within 6 hours to a value too low to measure by the Wilhelmy plate method. The rate of aging decreases markedly when the temperature decreases to 1.2°C.

The encapsulation of various essential oils has intrigued the food, cosmetic, and pharmaceutical industries for some time. Several encapsulation systems based on the complex coacervation of gelatin have been used to encapsulate a range of essential oils. However, variable results have been obtained, especially with citrus oils. In order to characterize the behavior of such oils, their interfacial behavior against water and the aqueous phases that exist in several gelatin-based complex coacervation systems has been studied. This report summarizes the interfacial tension (IFT) data obtained and is an extension of a preliminary study (1).

### EXPERIMENTAL

**Materials.** Acid precursor gelatin samples of 227 and 283 bloom strength were supplied by Rousselot, Paris, France. They had isoelectric pH values of 8.4 and 8.6 respectively. Their ash contents (800°C) were 0.17 percent. Gum arabic in powder form was purchased from Laboris, Paris France. Sodium Alginate was supplied by MRS, Carentan, France. The polyphosphate (Calgon 209) was purchased from the Calgon Division of Merck, Pittsburgh, PA. Four citrus oils were supplied by MRS, Grasse, France. Orange oil 1 was a mixture of mandarin, tangerine, and California cold pressed

orange oils. Orange oil 2 was California cold pressed orange oil. Lemon oil 1 was Ivory Coast lemon oil fortified with citral. Lemon oil 2 was Ivory Coast lemon oil. All citrus oils were stored in the dark in closed containers at 4°C until used.

Complex Coacervation Procedures. Gelatin/alginate (G/A), gelatin/polyphosphate (G/P), and gelatin/gum arabic (G/GA) complex coacervate and supernatant phases were used in this study. G/A complex coacervate and supernatant phases were formed at pH 4.2 with a 3.7:1 (w/w) mixture of gelatin (227 bloom) and sodium alginate (total solids: 1.8 wt. percent). G/P complex coacervate and supernatant phases were formed at pH 4.4 with a 9:1 (w/w) mixture of gelatin (283 bloom) and polyphosphate (total solids: 3.3 wt. percent). G/GA complex coacervate and supernatant phases were formed at pH 4.0 with a 1:1 (w/w) mixture of gelatin (283 bloom) and gum arabic (total solids: 3.3 wt. percent).

All complex coacervate and supernatant phases were formed at 50°C and then adjusted to the temperature at which IFT was to be measured. During 20-30 min. equilibrium at this temperature, the two phases were separated by gravitational settling and were isolated. Each phase was centrifuged at 2000 RPM for 2 min. in a centrifuge heated to the temperature at which IFT was to be measured. This assured complete separation of the coacervate and supernatant phases. The clarified phases were used in the IFT determinations. Solids content of each supernatant and coacervate phase used was determined by drying an aliquot at 110°C to constant weight. The total elapsed time between formation of a complex coacervate system and initiation of IFT measurements was kept below one hour. The IFT aging behavior of the complex coacervate phase was characterized first. This took 0.25 to 6 hrs. and was normally terminated because the IFT aged to a value too low to measure by the Wilhelmy plate method. The IFT aging behavior of the citrus oil/supernatant phase was then determined. This was followed for up to 22 hrs. in cases where IFT of interfaces formed by a supernatant phase aged slowly. All IFT runs were made on separate coacervate systems formed under identical conditions.

Interfacial Tension Procedure. IFT measurements were made by the Wilhelmy plate method. The apparatus was the same as that described previously (2). A standard protocol was followed for all IFT determinations. The desired interface was formed at a specified temperature by partially filling a thermostatted sample holder with the desired aqueous phase. This phase, distilled water (mono; triple) or a supernatant aqueous phase isolated from a complex coacervate system, completely covered the Wilhelmy plate (roughened platinum). The desired citrus oil was carefully layered onto the aqueous phase. It had been preheated (or cooled) to the same temperature as the aqueous phase. Once the citrus oil/aqueous phase interface was formed, the Wilhelmy plate was drawn completely through the interface and into the oil phase where it was zeroed. The plate was then placed at the citrus oil/aqueous phase interface. The force on this plate was monitored continuously and converted into IFT data.

The above experimental protocol could not be used to measure the IFT of most citrus oil/complex coacervate interfaces. When the Wilhelmy plate was placed in a complex coacervate phase before an oil phase was layered on the coacervate phase, a thick coating of coacervate phase was carried into the oil phase as the plate was drawn into the oil phase and subsequently placed at the oil/coacervate phase interface. This coating would slowly drain off the plate once it was placed at the interface. Many air bubbles often appeared on the plate as drainage progressed. These phenomena created such erratic force measurements that it was essentially impossible to determine meaningful IFT values. Accordingly, the plate was kept out of both the complex coacervate and citrus oil phases when the interface was formed. An effort was made to place the plate at such interfaces by simply lowering it through the oil phase to the interface. The plate was repulsed by the interface and would not stay there. Thus, it was first wetted with distilled water. After excess water was blotted off, the plate was lowered through the oil phase to the interface where it stayed.

A number of the interfaces studied gave force measurements too low to detect. This corresponds to an IFT value of zero. However, the interfacial forces in such cases are not believed to be zero, but simply too low to measure by the Wilhelmy plate method. Because this method is not sensitive enough to reliably measure IFT values below approximately  $0.2\text{mJ/m}^2$ , all IFT values too low to measure by the Wilhelmy plate method are designated as "0" values.

## RESULTS

Figures 1-4 illustrate the IFT behavior of four citrus oils against water as a function of time at different temperatures. All but one of the lemon oil 2 and orange oil 2 runs were made with triple distilled water. All lemon oil 1 and orange oil 1 runs were made with mono distilled water. Surface tension of the two water samples differed by  $0.2$  dynes/cm (mean of 6 runs). This difference is not believed to make a major contribution to the IFT aging behavior observed.

Initial IFT values are low, and range from  $6.6$  to  $8.2\text{mJ/m}^2$ . Interfacial aging is common. The rate and extent of aging depends upon the citrus oil and temperature. In the case of orange oil 2 (Figure 1), IFT aged to  $2.1\text{mJ/m}^2$  after 10 hrs. at  $30^\circ\text{C}$ . The same interface at  $50^\circ\text{C}$  aged to a IFT value too low to measure in approximately 10 hrs. Figure 2 shows that IFT of the orange oil 1/water interface ages faster at  $50^\circ\text{C}$  than the orange oil 2/water interface at the same temperature. At  $1.2^\circ\text{C}$ , aging of the orange oil 1/water interface is reduced significantly.

Figures 3 and 4 compare the interfacial aging behavior of lemon oil 2 and 1 respectively. As in the case of orange oil, aging behavior is a function of temperature and lemon oil used. At  $45$  and  $50^\circ\text{C}$ , the lemon oil 1/water interface aged to an IFT value too low to measure in 3 to 4 hrs. The lemon oil 2/water interface retained a finite value after 10 hrs. at  $50^\circ\text{C}$ . The rate of aging for both lemon oils decreases significantly as the temperature decreases.

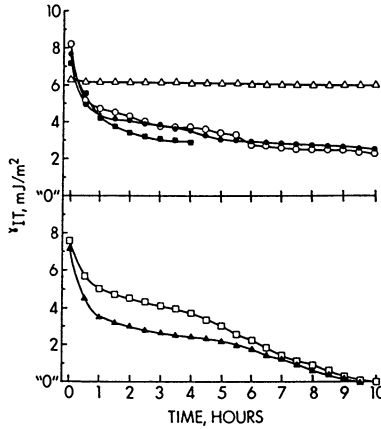


Figure 1.  $\gamma_{IT}$  aging behavior of the orange oil 2/triple distilled water interface:  $\Delta$ , 1.2°C;  $\circ$ ,  $\bullet$ ,  $\blacksquare$ , 30°C;  $\blacktriangle$ ,  $\square$  50°C.

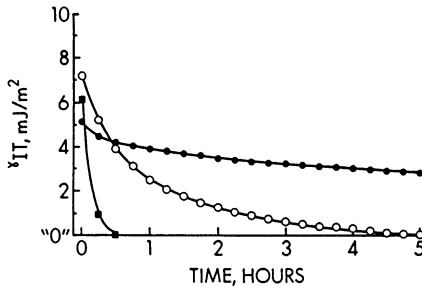


Figure 2.  $\gamma_{IT}$  aging behavior of the orange oil 1/monodistilled water interface:  $\bullet$  1.2°C;  $\circ$ , 25°C;  $\blacksquare$ , 50°C.

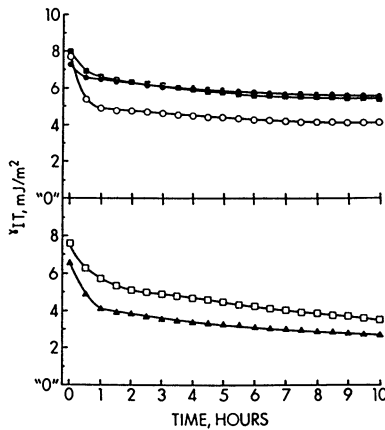


Figure 3.  $\gamma_{IT}$  aging behavior of the lemon oil 2/triple distilled water interface:  $\circ$ ,  $\bullet$ ,  $\blacksquare$ , 30°C;  $\square$ ,  $\blacktriangle$ , 50°C.

The duplicate or triplicate IFT aging curves included in Figures 1-4 show that replicate IFT values for a given system may differ by up to  $1.8 \text{ mJ/m}^2$ . Shape of the aging curves may vary slightly also. Nevertheless, the replicate IFT data clearly show that aging occurs consistently and is due to the nature of the citrus oil/water interface.

In an effort to gain more insight into IFT aging of the orange oil 2/water interface, two storage experiments were made. The first experiment consisted of layering orange oil 2 on water and letting the system equilibrate for 47 hrs. at  $30^\circ\text{C}$ . The system was then heated to  $50^\circ\text{C}$  and IFT was measured as a function of time. In the second experiment, orange oil 2 was layered on water and the system was equilibrated for 47 hrs. at  $30^\circ\text{C}$ . The portion of orange oil away from the oil/water interface was removed and layered on a fresh water sample. The IFT of this new interface was measured at  $50^\circ\text{C}$  as a function of time. Figure 5 contains IFT aging data for both experiments. When orange oil 2 was left in continuous contact with water at  $30^\circ\text{C}$  for 47 hrs., and the system was then heated to  $50^\circ\text{C}$ , IFT decreased in 1.25 hrs. to a value too low to measure by the Wilhelmy plate process. When the aged orange oil 2 was layered on fresh water, IFT declined from 3.5 to 0.5 dynes/cm. over a 13 hr. period at  $50^\circ\text{C}$ .

Figures 6-11 contain IFT aging curves for several supernatant phases against citrus oils. Figure 6 shows the interfacial aging of a G/A supernatant phase against orange oil 2. At 45 and  $50^\circ\text{C}$ , IFT of the G/A supernatant phase/orange oil 2 interface decayed to a value too low to measure by the Wilhelmy plate method in 2 to 3.75 hrs. At 30 to  $40^\circ\text{C}$ , a finite IFT value exists for more than 5 hrs. Comparison of these IFT data with that in Figure 1 reveals the  $30^\circ\text{C}$  G/A supernatant phase/orange oil 2 interface ages more slowly than the  $30^\circ\text{C}$  orange oil 2/water interface. After approximately 2 hrs. aging, the G/A supernatant phase has a higher IFT value against orange oil 2 than water at  $30^\circ\text{C}$ . At  $50^\circ\text{C}$ , IFT of the G/A supernatant phase ages faster than water at  $50^\circ\text{C}$ .

Figure 7 shows how temperature affects IFT of the G/A supernatant phase against lemon oil 2. All of the IFT curves shown decrease with time. The rate of aging increases as the temperature increases from 30 to  $45^\circ\text{C}$ , but a further temperature increase to  $50^\circ\text{C}$  had no added effect. The rate of IFT aging increases dramatically between 40 and  $45^\circ\text{C}$ . At 45 and  $50^\circ\text{C}$ , aging is so pronounced that IFT becomes too low to measure by the Wilhelmy plate method within 4 hrs. At 30 to  $40^\circ\text{C}$ , the rate of aging is reduced to such an extent that a finite IFT exists after 21 hrs. of aging. At 30 to  $40^\circ\text{C}$ , the IFT aging curve becomes nearly linear as the time of aging increases. At 30 and  $50^\circ\text{C}$ , IFT of the G/A supernatant phase/lemon oil 2 interface is consistently below that of the water/lemon oil 2 interface.

Figure 8 contains duplicate IFT aging curves for a G/A supernatant phase against orange oil 1 at  $50^\circ\text{C}$  as well as an IFT aging curve for this interface at  $1.2^\circ\text{C}$ . The duplicate  $50^\circ\text{C}$  aging curves approach linearity as the aging time increases. Both curves decay to a value too low to measure by the Wilhelmy plate method in 4.7-6.2 hrs. They differ by up to  $1.5 \text{ mJ/m}^2$ . Comparison of the IFT data in Figures 8 and 2 reveals that IFT of the  $50^\circ\text{C}$  G/A supernatant

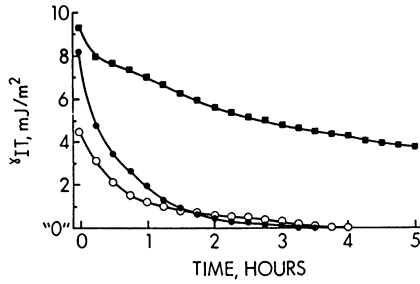


Figure 4.  $\gamma_{IT}$  aging behavior of the lemon oil 1/monodistilled water interface: ■, 35°C; ○, 45°C; ●, 50°C.

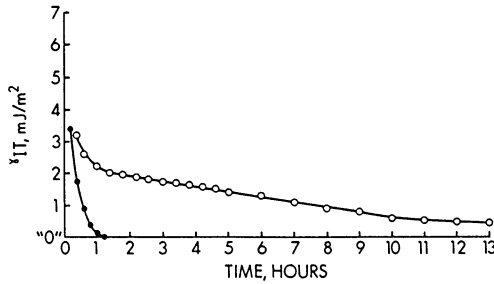


Figure 5. Effect of 30°C storage experiments on the  $\gamma_{IT}$  aging behavior of the orange oil 2/monodistilled water interface at 50°C: ●, orange oil 2/monodistilled water interface stored at 30°C for 47 hrs. before temperature was raised to 50°C; ○, orange oil 2/monodistilled water interface stored at 30°C for 47 hrs. Orange oil 2 then transferred to fresh water and temperature raises to 50°C.

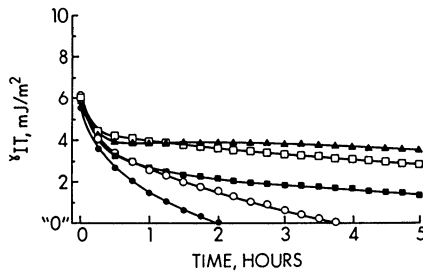


Figure 6.  $\gamma_{IT}$  aging behavior of the G/A supernatant phase/orange oil 2 interface: ▲, 30°C; □, 35°C; ■, 40°C; ○, 45°C; ●, 50°C.



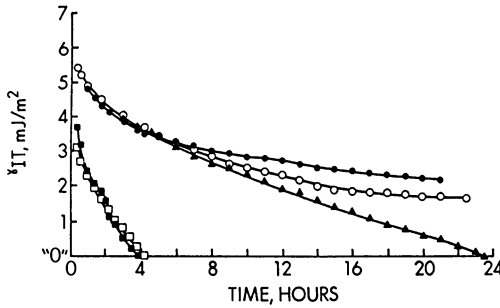


Figure 7.  $\gamma_{IT}$  aging behavior of the G/A supernatant phase/lemon oil 2 interface: ●, 30°C; ○, 35°C; ▲, 40°C; ■, 45°C; □, 50°C.

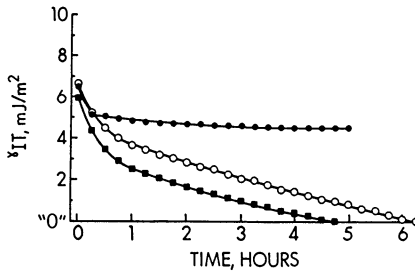


Figure 8.  $\gamma_{IT}$  aging behavior of the G/A supernatant phase/orange oil 1 interface: ●, 1.2°C, ○, ■, 50°C.

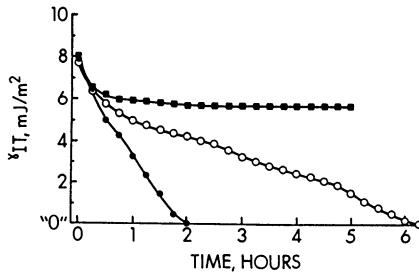


Figure 9.  $\gamma_{IT}$  aging behavior of the G/A supernatant phase/lemon oil 1 interface: ■, 1.2°C; ○, 35°C; ●, 50°C.

phase/orange oil 1 interface ages slower than IFT of the orange oil 1/water interface at 50°C. The rate of aging drops significantly at 1.2°C, so IFT changes by only 0.5 mJ/m<sup>2</sup> between an interfacial age of 0.5 and 5.0 hrs.

Figure 9 contains IFT aging curves for a G/A supernatant phase/lemon oil 1 interface at 1.2, 35, and 50°C. The three aging curves shown graphically illustrate how reduced temperatures lower the rate of IFT aging. At 1.2°C, IFT appears to have reached a stable value of 5.6 dynes/cm after 5 hrs. of aging. In contrast, at 35 and 50°C, IFT decays to a value too low to measure in 6.3 and 2.0 hrs. respectively. At both temperatures, IFT of the G/A supernatant phase/lemon oil 1 interface decreases faster than the IFT of the lemon oil 1/water interface.

Figure 10 contains IFT aging curves at 30 to 50°C for a G/P supernatant phase against lemon oil 1. Duplicate runs made at 50°C differ very little. Decreasing the temperature from 50 to 30°C causes a uniform reduction in rate of aging. At each temperature examined, IFT of the G/P/lemon oil 1 interface ages faster than the interface formed by G/A or G/GA with lemon oil 1. All of the aging curves are nearly linear for much of the aging process and rapidly reach a IFT too low to measure by the Wilhelmy plate method. The aging curves of Figure 10 decay faster than aging curves for the lemon oil 1/water interface at the same temperature (Figure 4).

Figure 11 compares IFT aging curves for a G/GA supernatant phase against lemon oil 1 at 40 and 45°C. In both cases, IFT decreases in a nonlinear manner to a value too low to measure by the Wilhelmy plate method. The 45°C aging curve decays to a value too low to measure in 2.1 hours, somewhat faster than the time needed for IFT of the lemon oil 1/water interface to decay to this value. At 40°C, values of IFT for the lemon oil 1 supernatant phase interface become too low to measure after 3.5 to 5 hrs. of aging. The duplicate 40°C aging curves shown are similar in shape and differ by no more than 1 dyne/cm throughout the aging period studied. The 40 and 45°C aging curves for the GGA supernatant phase/lemon oil 1 interface decrease to a IFT value too low to measure faster than the lemon oil 1/water interface.

Figures 12-14 contain IFT aging curves for several complex coacervate phases against citrus oils. Because these data were obtained by the modified procedure outlined in the Experimental Section, they have been plotted separately from IFT data obtained with the supernatant phases.

Figure 12 contains IFT aging curves for G/A complex coacervate phase against orange oil 2 and orange oil 1. For the orange oil 2 interface, the rate of aging decreases markedly as the temperature is reduced from 50 to 35°C. At 35°C, the coacervate phase is extremely viscous, but has not gelled. It gelled at 30°C. Duplicate IFT aging curves for the interface formed with orange oil 1 at 50°C differ slightly, but decay rapidly to a value too low to measure in essentially one hour.

Figure 13 contains several IFT versus time plots for the interface formed by a G/A complex coacervate phase and lemon oil 2. Two 50°C runs gave aging curves that were similar in shape and decayed to a IFT value too low to measure in 1.4 hrs. A third 50°C run gave a IFT value too low to measure immediately after the interface

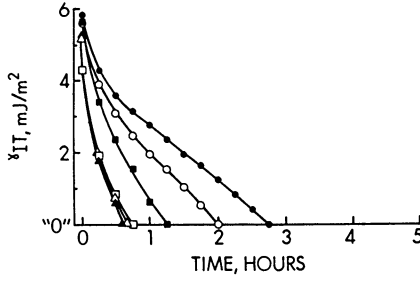


Figure 10. YIT aging behavior of the G/P supernatant phase/lemon oil 1 interface: ●, 30°C; ○, 35°C; ■, 40°C; □, 45°C; △,▲, 50°C.

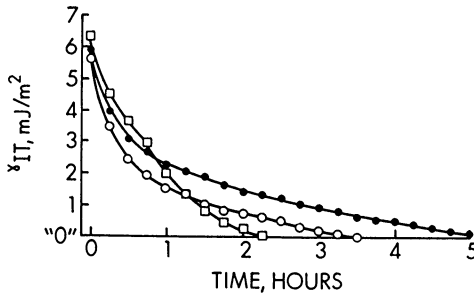


Figure 11. YIT aging behavior of the G/GA supernatant phase/lemon oil 1 interface: ○, ●, 40°C; □, 45°C.

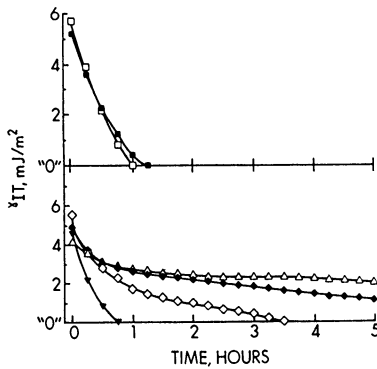


Figure 12. YIT aging behavior of interfaces formed by the G/A complex coacervate phase with orange oils. Orange oil 1 at 50°C; ■, □; Orange oil 2: △, 35°C; ◆, 40°C; ◇, 45°C; ▼, 50°C.

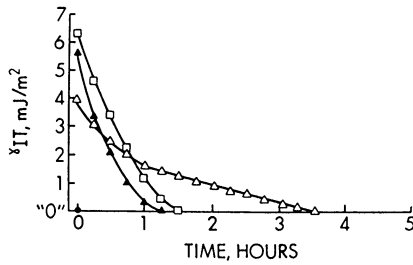


Figure 13.  $\gamma_{IT}$  aging behavior of interfaces formed by the G/A complex coacervate phase with lemon oil 2: ●,▲,□, 50°C; △, 40°C.

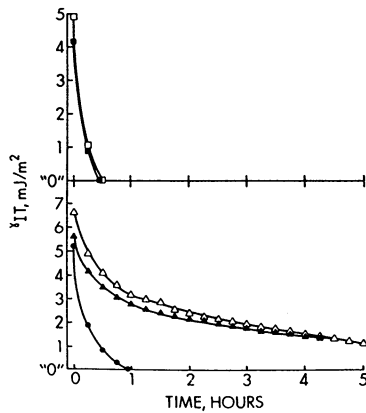


Figure 14.  $\gamma_{IT}$  aging behavior of interfaces formed by lemon oil 1 with complex coacervate phases. G/P complex coacervate phase: □, ●, 50°C; G/GA complex coacervate phase: △,▲, 40°C; ●, 45°C.

was formed. The same result was obtained at 45°C. At 40°C, this interface gave an aging curve that decayed to an IFT value too low to measure in 3.6 hours (Figure 13). Values of IFT were not measured at 35°C because the G/A complex coacervate phase appeared to be too viscous. It gelled at 30°C.

Figure 14 contains IFT aging curves for several additional interfaces formed with lemon oil 1. Duplicate IFT runs for the 50°C G/P complex coacervate phase/lemon oil 1 interface behaved similarly and decayed to a value too low to measure in 0.5 hour. At 45°C, IFT of the G/P complex coacervate phase/lemon oil 1 interface was too low to measure immediately after it was formed. No IFT measurements were made at 30–40°C because the G/P complex coacervate gelled at these temperatures.

Figure 14 also contains IFT aging curves for a G/GA complex coacervate phase/lemon oil 1 interface at 40°C and 45°C. The duplicate 40°C aging curves decay in a nonlinear manner to a value of 1.3 mJ/m<sup>2</sup> in 5 hours. At 45°C, IFT decays to a value too low to measure in 0.9 hrs.

Table 1 summarizes solids content data for a series of complex coacervate and supernatant phases prepared under identical conditions. These data show that the solids content of both phases vary, even though the samples are made in exactly the same way.

## DISCUSSION

Citrus oils contain a number of components and are complex liquids. The same is true for the aqueous phases formed by complex coacervation of gelatin. Accordingly, the IFT behavior of citrus oils against water and the aqueous phases produced by complex coacervation reflects the interfacial behavior of complex systems. Changes in IFT can be caused by a number of possible chemical and/or physical changes. For example, several chemical reactions could occur. Citrus oils readily form oxygenated products that are likely to congregate at oil/water interfaces and thereby cause a detectable change in IFT. The aldehydic components of citrus oil could react with the amine groups of the gelatin molecules present in the aqueous phases formed by complex coacervation and thereby affect IFT. In addition to chemical reactions, physical changes can occur at an interface and alter IFT. A visible interfacial film can form simply due to interfacial interactions that alter the interfacial solubility of one or more components. No chemical reactions need occur. An example is the formation of a visible interfacial film when 5 wt. per cent aqueous gum arabic solutions are placed in contact with benzene (3). Interfacial films or precipitates can also form when chemical reactions occur and yield products that congregate at interfaces.

The many events that can occur at interfaces between citrus oils and aqueous phases make it virtually impossible to give an unambiguous interpretation of the IFT data in Figures 1–14. Nevertheless, these data provide valuable insight into how IFT is affected by a range of conditions, many analogous to those encountered during a complex coacervation encapsulation process. A general observation is that the four citrus oils studied give relatively low IFT values against all of the aqueous phases examined. Freshly formed citrus

Table I. Total Solids Content of Complex Coacervate and Supernatant Phases

Coacervation	Temperature, °C	Solids Content, wt %		No. Runs
		Coacervate	Supernatant	
G/A (pH 4.2; 1.8 wt percent initial solids)	50	19.2 ± 1.0*	0.40 ± 0.11*	12
	45	18.3 ± 2.6	0.44 ± 0.10	2
	40	17.6 ± 2.3	0.41 ± 0.11	2
	35	17.0 ± 2.8	0.31 ± 0.09	3
	30	14.6 ± 4.10	0.35 ± 0.08	2
	2	12.4 ± 0.1	0.38 ± 0.02	2
G/P (pH 4.4; 4.45 wt percent initial solids)	50	16.5 ± 1.2	1.59 ± 0.16	3
	45	17.4	1.16	1
	40	16.1	1.54	1
	35	15.8	1.60	1
	30	12.8	1.50	1
G/GA (pH 4.0; 3.3 wt percent initial solids)	50	15.1 ± 0.8	0.61 ± 0.21	4
	45	17.3	0.60	1
	40	15.5 ± 2.1	0.46 ± 0.01	4
	35	15.8	0.47	1
	30	17.5	0.50	1

\* ±: standard deviation

oil/aqueous phase interfaces consistently had IFT values of  $8\text{ mJ/m}^2$  or less. The interfaces between complex coacervate phases and citrus oils periodically had a IFT value too low to measure immediately after formation. Interfaces that had measurable initial IFT values usually aged or decreased with time. Most aging curves show a rapid initial decrease in IFT followed by a slower decrease that is often nearly linear. At  $50^\circ\text{C}$ , many interfaces aged within 5-6 hours to a IFT value too low to measure by the Wilhelmy plate method. At  $30^\circ\text{C}$ , most interfaces retained a finite IFT after 5-6 hours. At  $1.2^\circ\text{C}$ , the IFT of mono distilled water/orange oil 1, mono distilled water/lemon oil 1, G/A supernatant phase/orange oil 2, and G/A supernatant phase/orange oil interfaces decreased by only  $0.25$  to  $2\text{ mJ/m}^2$  over a 5 hour period. Several of these interfaces appear to be stable at  $1.2^\circ\text{C}$  for a prolonged period. Even if IFT aging is not completely stopped by cooling to  $1.2^\circ\text{C}$ , it is markedly reduced. Complex coacervate phases are gelled below  $30$ - $35^\circ\text{C}$ , so their IFT aging behavior against citrus oils could not be examined at lower temperatures. Nevertheless, it is reasonable to suggest that the interface between a complex coacervate gel and citrus oil is greatly stabilized by cooling to low temperatures.

The pronounced reduction in IFT aging observed at low temperatures is attributed to a marked reduction in the rate at which interfacially active species congregate at citrus oil/aqueous phase interfaces when such mixtures are stored cooled. This is believed to reflect primarily a reduction in rate at which these species are produced in systems that are kept at low temperatures. If cooling simply reduced the solubility of interfacially active species that existed initially in these systems, IFT should decrease, since reduced solubility favors adsorption at an interface.

It is interesting that the IFT of the G/A supernatant/orange oil 2 interface at  $30$  and  $50^\circ\text{C}$  was more stable than the IFT of the orange oil 2/water interface at these temperatures. The G/A supernatant phase stabilizes the interface. All of the other coacervate and supernatant phases formed interfaces with citrus oils that were less stable than the corresponding citrus oil/water interfaces.

The data of Figure 5 were obtained in order to examine how accumulation of interface active species at the orange oil 2/water interface affect IFT aging. In the first experiment, the interface active species that accumulated at the orange oil 2/water interface during 47 hour equilibration at  $30^\circ\text{C}$  were left in the system when the temperature was raised to  $50^\circ\text{C}$  and IFT was measured. In the second experiment, the bulk orange oil 2 phase was transferred to a fresh water sample after 47 hours of  $30^\circ\text{C}$  equilibration and IFT of the fresh interface was measured at  $50^\circ\text{C}$ . The transfer step was designed to remove from orange oil 2 the interface active species that accumulated at the orange oil 2/water interface during prolonged  $30^\circ\text{C}$  storage. It was reasoned that the removal of these species should have a significant effect on the IFT behavior of the aged orange oil 2/fresh water interface at  $50^\circ\text{C}$ .

The two IFT aging curves in Figure 5 show that this is the case. When the interface active species that accumulate at the orange oil 2/water interface at  $30^\circ\text{C}$  are left in the system, IFT ages rapidly to a value too low to measure. When they are removed, IFT ages much more slowly. However, IFT aging still occurs. The inter-

facially active species responsible for aging of IFT slowly appear at the orange oil 2/fresh water interface. It would be of value to repeat the cycle of storing orange oil 2 over fresh water several times. An orange oil 2/water interface that does not age with time should occur at the point where all molecular species responsible for interfacial aging have been removed from the system. Analysis of the orange oil at this point would identify which components were involved. The interface active species responsible for aging of IFT could be generated continuously because of chemical reactions that occur at the 50°C orange oil 2/fresh water interface. If so, repeated changes of the water phase will not eliminate IFT aging until all components that are responsible for such reactions have been consumed. If D-limonene is one of these components, the orange oil 2/water interface will exhibit IFT aging after an indefinite number of cycles, since orange oil is over 90 percent D-limonene. Such behavior would be evidence that D-limonene or a compound derived from D-limonene is involved in the aging process.

When a citrus oil and aqueous phase are equilibrated together under static conditions for prolonged periods at 30-50°C (e.g., 12 hours), a film or precipitate is often seen at the interface. If an interfacial film forms, it is transparent and clearly visible only when the Wilhelmy plate is pulled away from the citrus oil/aqueous phase interface. Such films appear to be continuous and are located on the oil side of the interface. They are very thin and cannot be seen on the plate or hanging from the plate once the plate is removed from the citrus oil. The film acts as though it dissolves as the plate is slowly pulled away from the interface and through the citrus oil phase.

A discontinuous precipitate often was observed at citrus oil/aqueous phase interfaces kept at 50°C for prolonged periods. The precipitate particles congregate on the water side of the citrus oil/aqueous phase interface and disperse into the aqueous phase upon agitation. If the aqueous phase is distilled water, or a supernatant phase, the precipitate particles cause the aqueous phase to become noticeably cloudy. Precipitate particles or interfacial films were not detected at citrus oil/complex coacervate phase interfaces. However, such interfaces normally were not kept for prolonged periods, because their IFT values rapidly decayed to a value too low to measure.

Duplicate and triplicate IFT aging curves were obtained at one or two temperatures for most of the interfaces characterized in this study. The replicate IFT data reported in Figures 1,3,4,7,8 and 10-14 show that many IFT aging curves for citrus oil/aqueous phase interfaces differ by a maximum of  $1.7 \text{ mJ/m}^2$ . Replicate curves often differ by less than  $1 \text{ mJ/m}^2$ . Because each IFT aging experiment involved formation and separation of a new complex coacervate and supernatant phase, replicate IFT aging curves measure the combined effect that several factors have on reproducibility. These factors include variability of the complex coacervation procedure, protocol followed for separation of the coacervate and supernatant phases, and the IFT measurement process itself. The variability in solids content of replicate coacervate and supernatant phases shown in Table 1 could contribute to the observed IFT variability.



Marked variations in IFT aging behavior of replicate complex coacervate phase/citrus oil interfaces were observed occasionally. Figure 13 illustrates an example of this. Two IFT aging curves for the G/A complex coacervate phase/lemon oil 2 interface differ by 0.3 to 1.3 mJ/m<sup>2</sup> throughout the 1.3-1.5 hour of aging needed for the IFT to reach a value too low to measure. A third run gave a value too low to measure immediately after the interface was formed. This type of behavior was encountered periodically, especially with complex coacervate phase/citrus oil interfaces at 40-45°C. Experimental technique probably caused most of these observations since it is difficult to place the Wilhelmy plate at complex coacervate phase/citrus oil interfaces. However, the possibility that an IFT too low to measure immediately after formation of an interface is a characteristic feature of some complex coacervate phase/citrus oil interfaces at 40° and 34°C cannot be completely ruled out.

Complex coacervation procedures used to prepare microcapsules loaded with citrus oil involve three mutually immiscible phases: the complex coacervate phase, the supernatant phase, and the citrus oil. The IFT requirements necessary for successful capsule formation in three-phase systems like this have been developed by Torza and Mason (4). Their analysis revealed that encapsulation will occur spontaneously when the IFT of the complex coacervate phase/citrus oil interface is lower than the IFT of the supernatant phase/citrus oil interface, provided the IFT of the complex coacervate phase/supernatant phase interface is negligible. Since DeRuiter and Bungenberg de Jong (4) found a G/GA complex coacervate phase/supernatant phase interface had an IFT of 0.0023 mJ/m<sup>2</sup>, this is a valid assumption. Accordingly, it is of interest to compare IFT data for interfaces formed by specific citrus oils with complex coacervate and supernatant phases isolated from the same complex coacervate system. The purpose is to determine if these data shed some insight into wetting phenomena that occur in encapsulation processes based upon complex coacervation. It is recognized that the IFT data reported in this study were determined under static conditions rather than the dynamic conditions that exist in actual encapsulation systems. It is also recognized that the modified protocol used to obtain IFT data for interfaces formed by complex coacervates could have affected the results obtained. Nevertheless, it is still appropriate to make the comparison.

Figures 6 and 12 contain IFT aging curves at 35 and 50°C that show the IFT of the G/A complex coacervate phase/orange oil 2 interface is clearly lower than that of the supernatant/orange oil 2 interface at all interfacial ages examined. At 45°C, IFT values of the interface formed with the complex coacervate phase are slightly lower than that of the supernatant phase at 45°C. At 40°C, both phases have about the same IFT aging curve. These data indicate that wetting (and encapsulation) of orange oil 2 by a G/A complex coacervate phase will occur readily at 35 or 50°C, but there could be a problem at intermediate temperature.

Comparison of the G/A complex coacervate and supernatant aging curves against lemon oil 2 in Figures 7 and 13 reveals that the G/A complex coacervate phase consistently has an IFT below that of the G/A supernatant phase between 40 and 50°C. This is evidence that the complex coacervate phase will preferentially wet and encapsulate lemon oil 2 at these temperatures.

The data in Figures 10 and 14 show that the G/P complex coacervate phase gives a lower IFT against lemon oil 1 at 50°C than the supernatant phase. Thus, at 50°C the G/P complex coacervate phase should preferentially wet and encapsulate the lemon oil 1 phase. The low IFT value found immediately after formation of the G/P complex coacervate phase/lemon oil 1 interfaces at 45°C also favors preferential wetting of lemon oil 1 by the G/P complex coacervate phase. The G/P complex coacervate phase is too viscous for an IFT measurement at 40°C, and it has gelled at 35°C, so wetting of lemon oil 1 by a G/P complex coacervate phase should not be a problem during a G/P complex coacervation encapsulation process.

In contrast, comparison of the IFT data in Figures 11 and 14 reveals that a G/GA complex coacervate phase has a higher IFT against lemon oil 1 at 40°C than does the G/GA supernatant phase. The reverse is true at 45°C. The 40°C IFT data indicate that a G/GA complex coacervate phase will not preferentially wet or encapsulate lemon oil 1 at 40°C while encapsulation will occur at 45°C. This is consistent with the experimental observation that changes in wetting behavior of a G/GA complex coacervate phase occur during G/GA encapsulation processes. Additional IFT data at 35°C are needed to complete the picture. Such data should yield IFT values for the G/GA complex coacervate phase/lemon oil 1 interface below those of the G/GA supernatant phase, since the G/GA encapsulation process has been used to encapsulate lemon oil.

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## Chapter 16

# Stabilization of Flavors by Cyclodextrins

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Among enzyme modified starch derivatives, cyclodextrins behave as empty molecular capsules with the ability to entrap guest molecules of appropriate geometry and polarity. The included molecules are protected from surroundings: light, heat, oxidation, etc. The flavor cyclodextrin complexes show the above advantageous properties while they are in the dry, solid state. On contact with water, cyclodextrin complexes release their flavor content. In Hungary, the spice flavor beta-cyclodextrin complexes have been on the market since 1982.

The industrial flavor producers offer a very broad selection of natural and synthetic flavors, mainly in the form of liquid concentrates. The majority of flavor constituents in such concentrates exhibit considerable sensitivity to air, light irradiation and elevated temperature. These flavor concentrates are moreover oily, greasy rather lipophilic materials, which are difficult to work with. The natural plant extracts also have microbiological contaminations that need to be removed.

Among the most recent and sophisticated flavor encapsulation processes, cyclodextrin complexation represents a special way of encapsulation: entrapment of flavors on the lowest possible scale, which is called molecular encapsulation. In this process, every flavor constituent is surrounded by a cyclodextrin ring which offers an almost perfect protection against damaging effects of the environment. The most significant advantages of the application of molecular encapsulation in the food industry and cosmetics are as follows/1/:

Protection of flavors and fragrances against:

- oxidation
- light induced transformations
- heat decomposition
- loss by volatility or sublimation, upon storage

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Elimination or reduction of:

- undesired tastes, odors
- microbiological contaminations
- fibres and other non-flavor undesired components
- hygroscopicity

Technological advantages:

- stable, standardized compositions
- simple dosing and handling of free-flowing powders
- reduced packing and storage costs
- more economical processes, manpower savings

The present paper is intended to provide a survey on the stabilizing effects of cyclodextrin complexation. Beyond this, other practical consequences of the molecular entrapment of flavors will also be mentioned.

### Major consequences of cyclodextrin complexation

#### 1. Liquid-crystalline transformation

One of the most obvious changes of oily, liquid flavors after cyclodextrin complexation is their solid, crystalline appearance. X-ray powder diffractometry has shown that liquid flavors become free flowing solid materials of rather high crystallinity. Further, X-ray diffractometry can be used as proof of the inclusion complexation by comparing the reflection peaks of the diffractograms taken on the "empty" cyclodextrin hydrate crystals and the corresponding flavor cyclodextrin complexes. /2/ Figure 1 shows the X-ray diffractogram of beta-cyclodextrin and the cinnamon oil-cyclodextrin complex. The significant changes in the reflection peaks indicate the formation of a new type of crystal lattice in the case of the liquid guest molecules.

#### 2. Improved heat stability of flavors

The majority of food flavors are known to be volatile even at ambient temperatures. The molecular entrapment of flavors reduces their equilibrium vapor pressure via fixation in a molecular cavity. The apolar-apolar interaction between the internal wall of the cyclodextrin and the guest molecule results in remarkable heat resistance of volatiles. Signs of this inclusion phenomenon can be seen in heat stability tests.

These studies fall into two groups, "dynamic" and "static" heat treatments. In the dynamic heat treatment, samples are heated using a broad temperature range/20 to 300°C/ for a short time. Such tests include the Thermal Evolution Analysis/TEA/ and pyrolysis thin-layer chromatography /TAS/ /3,4/.

The static heat treatments are carried out under isothermic conditions/40°, 60°C/ for longer periods of time /several weeks/. This can be considered an accelerated long term storage test. The thermal analyses of flavor cyclodextrin complexes and the corresponding adsorbates /cyclodextrin-flavor mixture with identical flavor content/ indicate that the release of volatiles starts

from the flavor-cyclodextrin complexes only at 130-150°C. Flavors in adsorbates, however, show far less heat resistance. Their thermal release starts at room temperature and after continuous evaporation ends at around 120°C. The thermoanalytical description of the heat stability of some flavor complexes and adsorbates is shown in Table I.

Table I. Quantitative description of the volatility of flavors in complexed and adsorbed form /TEA-analyses/

Samples	Loss of volatiles expressed as percentage of the total flavor content of samples			
	85-90°C	130-145°C	150-160°C	175-250°C
garlic-A <sup>x</sup>	94	2	-	-
" C <sup>x</sup>	2-3	5	12	43-45
caraway A	88	6	-	-
" C	3	5	15	52-55
onion A	90	4	-	-
" C	5	7	13	64-66
dill A	96	-	-	-
" C	2-4	9	17	53-56
bergamotte A	94	2	-	-
" C	3-6	8	11	64

<sup>x</sup>A:adsorbate, C:complex

As Table I. shows, TEA-analysis provides accurate quantitative data on the thermal escape of adsorbed and entrapped flavors, but does not give information about the composition of the evaporated fraction of flavors. TAS-chromatography/pyrolysis TLC/can provide the missing qualitative data thereby offering the possibility to identify the major constituents of the thermally released flavor fraction. Figures 2 and 3 illustrate the improved heat stability of natural thyme and caraway oils in adsorbed and complexed form by combining data from the TEA-and TAS-assays. To obtain quick information regarding the storability of flavor-cyclodextrin complexes, accelerated storage tests were performed. Complexed and adsorbed flavor samples were placed in test tubes at 40 and 60°C and the loss of flavor content as a function of time was followed. The results of the storage stability studies are shown in Table II.

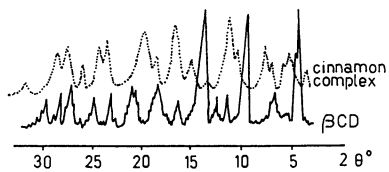


Figure 1. X-ray powder diagrams of crystalline beta-cyclodextrin-hydrate and the cinnamon oil beta-cyclodextrin complex.

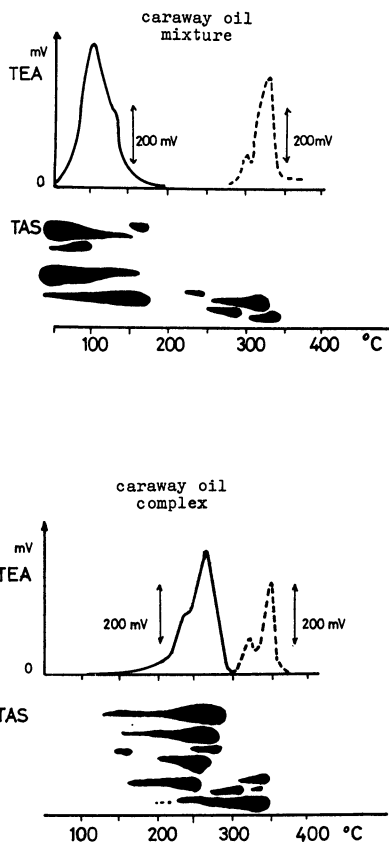


Figure 2. Illustration of the thermal stability of complexed and adsorbed caraway oil by TEA and TAS-assay.

Table II. Accelerated storage stability of complexed and adsorbed flavors

Samples		Flavor content of solid formulations/%/					
		40°C			60°C		
		0 day	7 day	14 day	Oday	7day	14day
lemon oil	A <sup>x</sup>	10	2,2	0,6	10	0.9	0
	C <sup>x</sup>	9.8	9.4	9.6	9.8	9.0	8.8
jasmin oil	A	9.5	6.4	3.0	9.6	3.1	0.2
	C	9.2	9.4	9.5	9.2	8.9	9.0
peppermint	A	10	7.0	4.1	10	2.3	0
	C	9.8	10	9.7	9.8	9.0	9.0
grape fruit	A	8.5	4.0	2.2	8.5	1.5	0
	C	8.2	8.8	8.5	8.2	8.0	7.7

Experiments were also carried out at 80 and 100°C. According to our observations at these high temperatures, solid-phase chemical transformations may take place between certain flavor constituents and cyclodextrin hydroxyls/monoterpene alcohols and phenolic compounds appear as a result of a solid-phase transacetylation of terpeneacetates and phenyl-acetates with the simultaneous formation of cyclodextrin-acetates/. Long term heat treatments of cyclodextrin-flavor complexes should not be run above 60°C in order to avoid such phenomena.

### 3. Improved stability of flavors to oxygen

Two remarkable and unique properties of molecular encapsulation are protection against atmospheric oxidation and disproportionations between components of flavors. In addition, intermolecular transformations are almost entirely eliminated due to the surrounding cyclodextrin ring.

The stabilizing power of cyclodextrin complexation against oxygen was characterized by using the classical Warburg method. Flavor-cyclodextrin complexes and the corresponding adsorbates were exposed to pure oxygen in Warburg apparatus at 37°C for several days, and the oxygen consumption was followed manometrically. This method describes the kinetics of the oxidation of the flavors in the formulations. As Figure 4 illustrates, the oxygen uptake of non-complexed benzaldehyde significantly surpasses that of the molecularly encapsulated one. Similar Warburg oxygen consumption curves were obtained with other flavor formulations, but the kinetics of oxygen uptake were different./2,5/

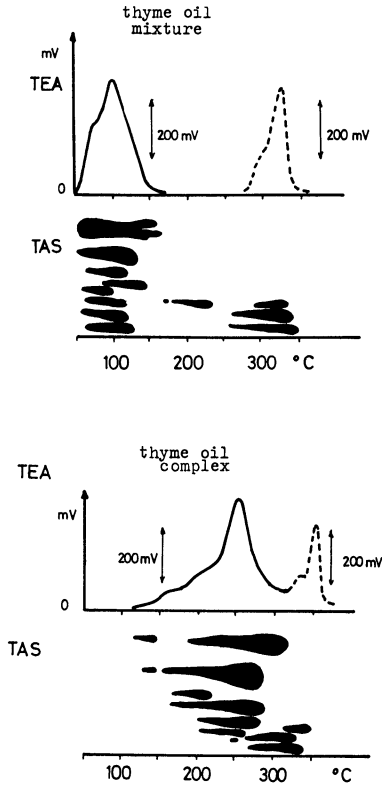


Figure 3. Illustration of the thermal stability of complexed and adsorbed thyme oil by TEA and TAS-assay.

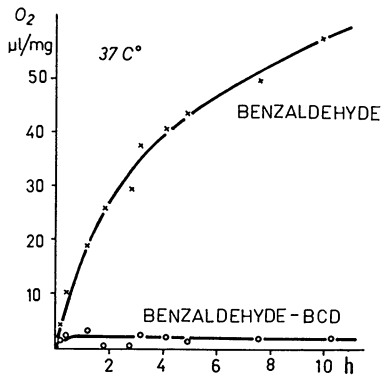


Figure 4. Oxygen consumption of cyclodextrin complexed and adsorbed benzaldehyde by Warburg method.



After oxygen exposure, flavors were re-extracted from the formulations and investigated by TLC and GLC to see how the treatment altered the chemical composition of the flavors. The chromatographic investigations gave further support to the Warburg manometrical results, indicating that cyclodextrin complexation enables the storage of flavors in pure oxygen atmosphere without considerable changes in their compositions./6/

#### 4. Improved stability of flavors to light

The molecular encapsulation of flavors with cyclodextrins was found to improve the resistance of light sensitive flavor constituents against daylight and ultraviolet irradiation. The photodecomposition of adsorbed and complexed flavors was tested both in the solid state and in aqueous solutions. The results of the light stability tests are demonstrated in the example of complexed and adsorbed citral, beta-ionone and cinnamaldehyde formulations /Table III./.

Table III. Stability of complexed and adsorbed flavors to UV/365nm/ irradiation in the solid state at room temperature

Samples	Residual flavor content of samples/%/ Exposure time, hours					
	0	4	8	12	24	48
citral A <sup>x</sup>	9.7	6.1	4.0	2.4	0.7	0
" C <sup>x</sup>	9.4	9.0	9.1	8.8	9.0	8.5
cinnamaldehyde A	9.0	4.4	4.0	3.7	2.0	2.2
" C	9.0	9.1	9.0	8.7	9.0	7.0
beta-ionone A	13.5	10.0	8.8	4.7	3.3	2.7
" C	13.3	13.0	11.0	11.2	10.1	10.5

A<sup>x</sup>: adsorbate, C: complex

The above flavor formulations were exposed to UV-irradiation in aqueous solutions as well. It has been observed that the protective effect of molecular encapsulation against light induced alterations was 15-25% that of the solid state experimental data. This phenomenon might be due to the partial release of the entrapped flavor constituents upon the dissociation of the inclusion complexes in aqueous systems.

### 5. Improved storage stability of flavors

Long term storage stability tests of flavor beta-cyclodextrin complexes under "non-stress" conditions at room temperature showed that molecular encapsulation in most cases provided an almost perfect preservation of flavors upon ten years storage. The degree of preserving power of cyclodextrin complexation is expressed using a comparison of total flavor content of complexed flavor samples determined in 1977 and 1987, respectively./Table IV./

Table IV. Changes of the flavor content of cyclodextrin spice complexes after ten years storage under normal conditions

Samples	Flavor content/%/ of the samples	
	in 1977	in 1987
garlic oil complex	10.2-10.4	10.0-10.3
onion " "	10.4-10.6	10.2-10.4
caraway " "	10.5	9.9-10.2
thyme " "	9.4-9.8	9.0-9.2
lemon " "	8.9-9.1	8.6-8.8
carrot " "	8.8-9.0	7.9-8.3
anise " "	9.0-9.2	9.0-9.3
peppermint "	9.4-9.7	9.0-9.2
marjoram "	8.8-9.0	8.0-8.2
orange "	9.0-9.5	6.0-7.0
tarragon "	10.0-10.3	8.8-9.0
mustard "	10.8-11.0	11.0-11.2

### 6. Hygroscopicity of cyclodextrin flavor complexes

A remarkable advantage of cyclodextrin complexed flavor formulations over spray-dried and micro-encapsulated ones is their negligible hygroscopicity under high humidity conditions. To characterize the clumping tendency of flavor beta-cyclodextrin complexes, samples were stored at room temperature under normal/50-60%/ and extreme/96%/ humidities. The clumping tendency was determined using a screening test. After storing complexed and adsorbed flavor samples for two days under the above conditions samples were passed through a screen of 400µm aperture, and the weight percentages of the passed and retained fractions were measured. As Figure 5 shows, cyclodextrin complexed flavors exhibit low hygroscopicity even after two days storage under 96% rel. humidity. The corresponding lactose adsorbates, however, had an unfavorable clumping tendency.

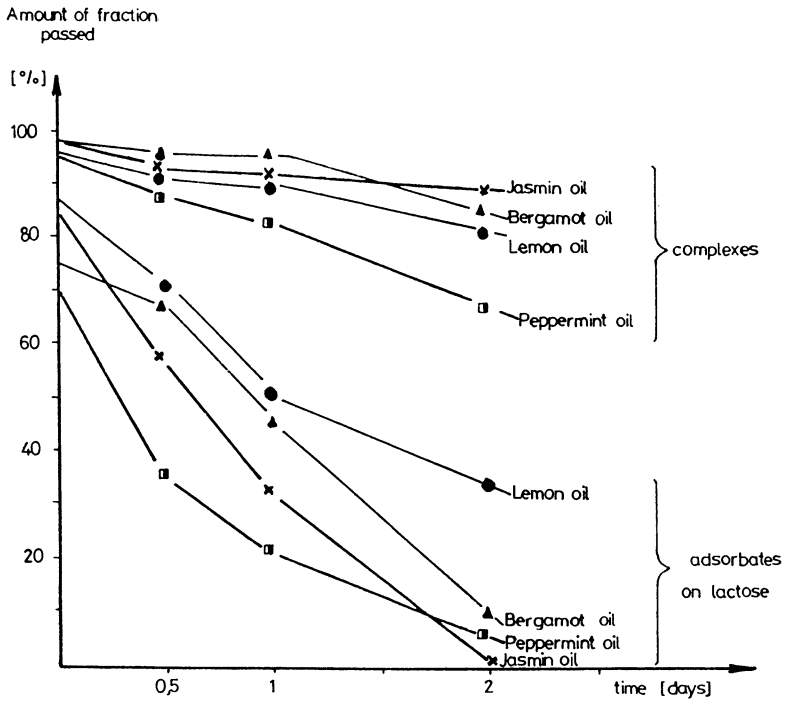


Figure 5. Comparison of the hygroscopicity of complexed and adsorbed jasmin, bergamott, lemon and peppermint oils upon storage under 96% relative humidity.

### 7. Limits of the use of molecular encapsulation in Flavor formulation

The limits of the application of cyclodextrin complexation in the formulation of flavors can be listed as follows:

- limited flavor content in the formulations /average contents are between 9 and 14% by weight, in contrast to 80% flavor content of some microcapsules/
- the size and polarity of flavors to be complexed limit the usefulness of the process/e.g. small flavor components, like short chain esters, aldehydes are not suitable for complexation with beta-cyclodextrin/
- the host molecule, cyclodextrin can act as artificial enzyme, enhancing the rates of hydrolysis of some ester type flavor components which results in undesired alteration of flavors /e.g. fruit flavors/
- the water solubility of beta-cyclodextrin flavor complexes is generally much lower than that of spray-dried and microencapsulated samples. Cyclodextrin complexed flavors have limited use in instant soft drinks. /7/

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## Chapter 17

# Controlling Particle Size and Release Properties

## Secondary Processing Techniques

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Secondary processing techniques are often required to optimize the functional properties of a material or to create a new product. Examples include but may not be limited to drying, dedusting, particle size enlargement to enhance dispersability, or coating to provide protection or some type of functional release. Batch type fluidized bed processing readily lends itself to these forms. Developed more than 30 years ago to improve drying efficiency, primarily in the pharmaceutical industry, the system has evolved into a highly effective and controllable technology for many applications. Its chief limitation is volume capability. Because it handles material on a batch basis, throughput is far less than in continuous fluidized beds. This is not a problem in the pharmaceutical industry, which is the largest user, because handling products in batches is desired from perspectives of quality control and cost (many active drugs cost in excess of \$100/kg). In the food and chemical industries, high volume products generally prohibit the use of this technology. However, specialty type products involving expensive components and very precise processing are ideal candidates for the batch fluid bed process.

### Equipment and Process Description

**Fluidized Bed Dryers** In order to illuminate the possibilities, it is helpful to have an understanding of the characteristics of this technology. As mentioned previously, fluidized bed processing started simply as drying (illustrated in figure 1). Many granulation processes involved wet massing in a high or low shear mixer and subsequent tray drying. Depending on the type of product, the tray drying process could take as long as 24 hours. The benefits of fluid bed drying were obvious because the particles were fluidized by the drying media which reduced drying time often to less than one hour. The damp granulation is transferred to the product container which is cylindrical or slightly conical and has a screen, and gas or air distributor plate at its base. The product

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container is then placed in the machine and heated air drawn through to fluidize the material and carry away the evaporated moisture. The cylindrical space above the product container acts as a deceleration zone or expansion chamber. In the space above this chamber, a filter is used to separate the product from the air stream. During fluidization and drying, fines collect in the filter reducing air volume and possibly drying efficiency (decreasing water removal rate). Periodically, fluidization must be interrupted by stopping air flow to shake fines out of the filter and back into the batch.

Fluidized Bed Granulation The next evolution was to position a nozzle in the expansion chamber, to spray a water or binding medium downward into the dry fluidizing powders (figure 2). By incorporating a variety of process controls, granulation or agglomeration was feasible.

Fluidized Bed Top Spray Coater Film coating is very similar to granulation using a film forming binder. Slightly different processing conditions and some equipment modifications yield the ability to apply films or molten materials to a wide range of particle sizes. The diagram in figure 3 shows the modifications to a conventional granulator which would facilitate top spray coating. A primary difference is that a higher fluidization velocity is desired resulting in the need for an expanded deceleration zone, hence the extended conical expansion chamber. Additionally, continuous fluidization is desirable from both economical and functional points of view. For this reason, the filter housing is enlarged and designed to shake fines back into the batch without stopping fluidization or spraying.

Fluidized Bed Wurster Coater Almost simultaneously with the development of conventional fluid bed granulation, work was being conducted on the coating of materials ranging from powders to tablets. The Wurster system, illustrated in figure 4, was invented more than 20 years ago by Dr. Dale Wurster (1), then a professor at the University of Wisconsin. The coating chamber which is generally cylindrical, has a separate cylinder (usually half the diameter of the first) in the center known as a partition. The second critical component is the orifice plate at the base of the coating chamber. A nozzle is positioned in the center of the plate to spray upwardly through the partition. The orifice plate is configured such that air flow is directed at a high volume and velocity through the partition, pneumatically transporting the product past the nozzle which sprays concurrently into the fluidizing material. The number of smaller perforations in the plate outside the area of the partition depend on the density and size of the particles to be coated. Their primary function is to enhance fluidization, keeping the particles in the down bed in near weightless suspension. Finally, a ring of larger holes at the outer perimeter of the plate prevents the occurrence of a "dead space" which would result in a portion of the product remaining uncoated. This "cylinder in a cylinder" concept is seen in lab and pilot scale machines up to about 24" in coating chamber diameter. For production machines, multiples or clusters of partitions which are 9" in diameter are

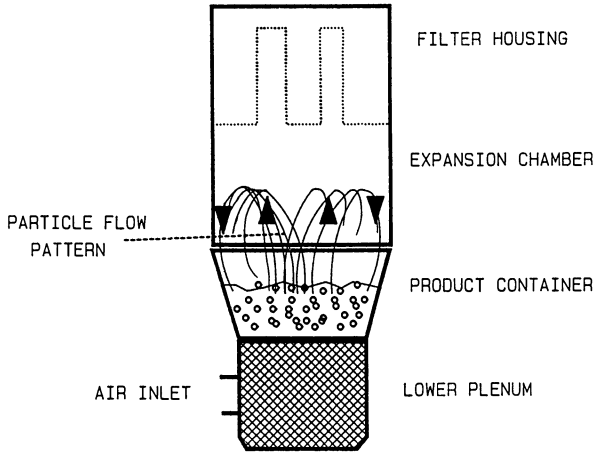


Fig. 1. Diagram of a Fluid Bed Dryer. (Courtesy Glatt Air Techniques, Inc.)

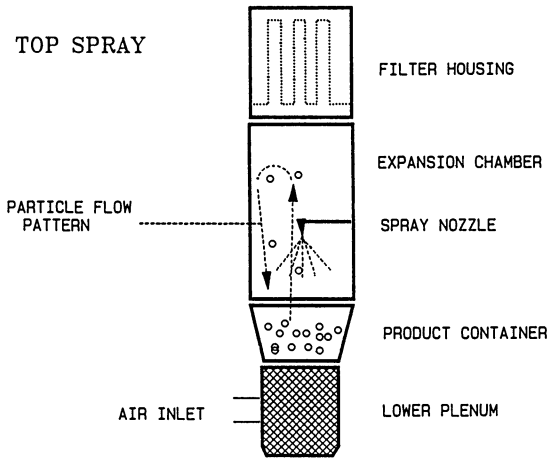


Fig. 2. Diagram of a Fluid Bed Granulator. (Courtesy Glatt Air Techniques, Inc.)

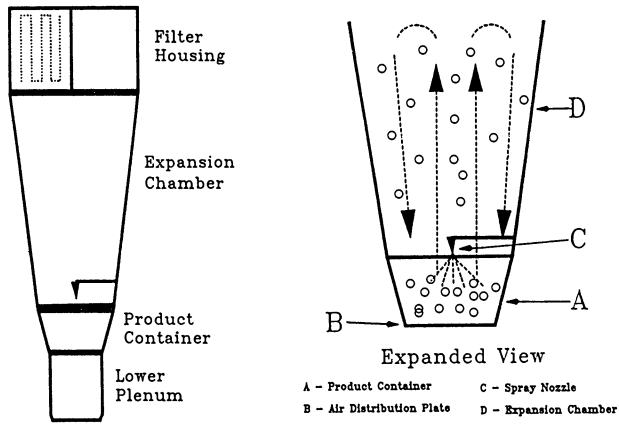


Fig. 3. Diagram of a Top Spray Coater. (Courtesy Glatt Air Techniques, Inc.)

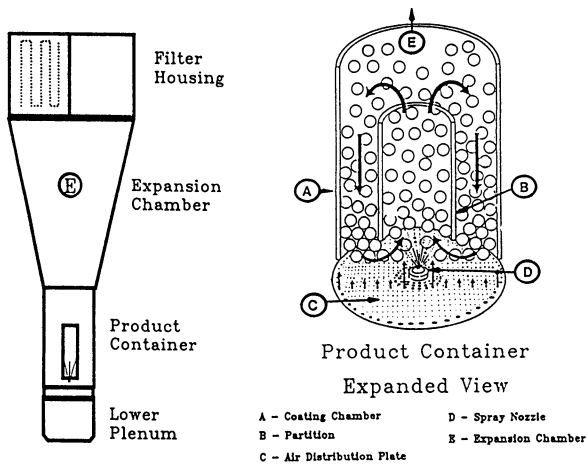


Fig. 4. Diagram of a Bottom Spray (Wurster) Coater. (Courtesy Glatt Air Techniques, Inc.)



used. For instance a 32" Wurster consists of three partitions and nozzles inside a 32" diameter chamber, and a 46" Wurster chamber uses seven partitions and nozzles. This is primarily due to nozzle limitations and the tacky nature of most coating substances.

Fluidized Bed Rotary Processor A relatively new type of fluid bed process involves the use of a rotating disc in a cylindrical product container (figure 5). Originally conceived to produce higher density granulations than the conventional fluidized bed without sacrificing the positive attributes such as particle size control and granule structure, the machine has evolved into an excellent pelletizer. The three forces at work are centrifugal, from the rotation of the disc which is generally speed adjustable; vertical fluidization as the high velocity air stream rushes through the narrow slit at the periphery of the disc; and gravity which causes the product to cascade downward toward the disc surface. The pattern can best be described as a spiralling helix. A nozzle is positioned to spray liquids concurrently and tangentially into the fluidizing particles.

#### Process Techniques - Agglomeration

There are primarily 3 methods by which powders can be increased in size in the fluidized bed -- agglomeration by recrystallization, film forming binders, and layering.

Agglomeration by Recrystallization Generally, very hydrophilic fine powders, when placed into water wet rapidly on the surface, but tend to form a mucous around the bulk of the powder. To fully dissolve, the clump must erode which may take quite a while. Agglomeration by recrystallization is a solution for materials that are soluble in water. The raw materials are placed in the product container of the conventional top spray granulator, fluidized, and sprayed at a controlled rate and droplet size with water. The droplets of water contact the surfaces of the powders, partially dissolving them. These wetted powders in turn contact other outer surfaces resulting in the formation of agglomerates that are characterized by a very high amount of interstitial void space. Dispersibility is dramatically improved using this technique because, although overall surface area is reduced, the structure of the granule (figure 6) is such that water contacting the surface is wicked inside and dissolves the agglomerate from within. A disadvantage is that agglomerate strength is related to porosity, hence these granules tend to be more friable than materials produced using film forming binders.

Agglomeration by Film Forming Binders When using materials that are insoluble in water, and also where granule strength is an issue, agglomerating using a film forming or hardening binder is recommended. Granule size and strength are a function of the type and concentration of the binder and, in general, the agglomerates have a much lower internal porosity (figure 7) than those produced by recrystallization. (2-6, 7)

ROTOR

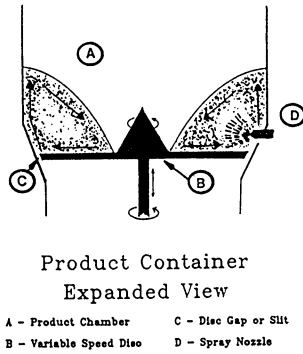
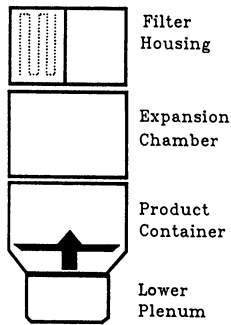


Fig. 5. Diagram of a Tangential Spray Coater. (Courtesy Glatt Air Techniques, Inc.)

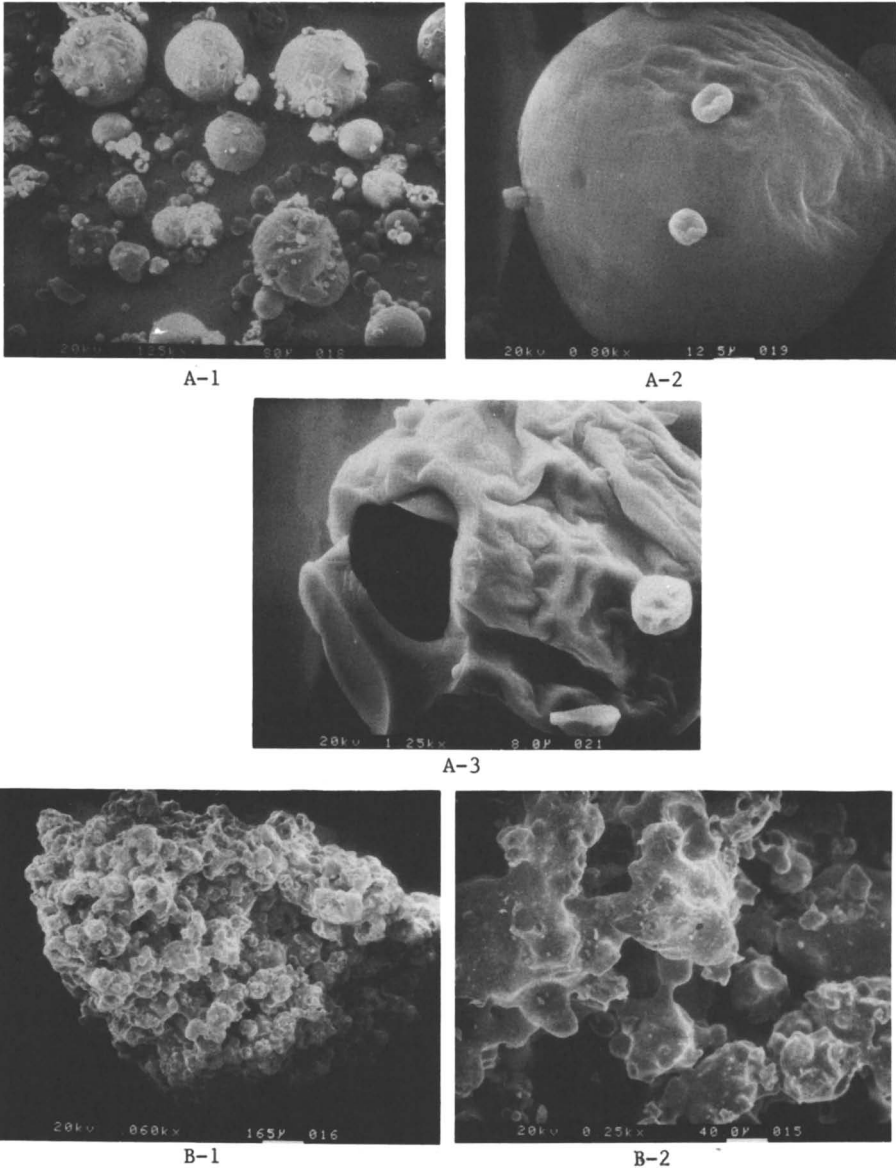


Fig. 6. Scanning electron photomicrographs of spray dried flavor before and after agglomeration by recrystallization.

A. Before processing.

- A-1. magnification = 125x;
- A-2. magnification = 800x;
- A-3. magnification = 1250x.

B. Agglomerate after processing.

- B-1. magnification = 60x,
- B-2. magnification = 250x.

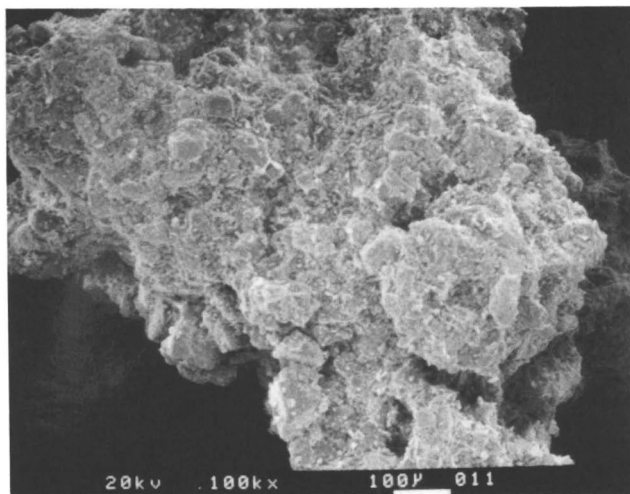


Fig. 7. Scanning electron photomicrograph of a granule created by film forming binder method. Magnification = 100 x.

**Agglomeration by Layering** In the layering technique, as small agglomerates are formed, primary particles become attached to the nuclei and several small agglomerates coalesce into larger ones. The difference between these granules and those produced by other techniques is that there is very little internal porosity. As a result they tend to dissolve more slowly, but have good strength and will likely withstand further processing such as coating or a vigorous blending operation. The ability to produce agglomerates in this manner is very much dependent on the nature of materials being processed. Generally these types of products are produced in the rotor (tangential spray) system because of its high amount of shear and circular tumbling action.

#### Process Techniques - Instantizing

A category of processing referred to as instantizing can use a combination of recrystallization or a hardening binder as described previously, but may also make use of the fluidized bed's mixing abilities. A surfactant can be uniformly distributed in a bed of powders and improve the dispersibility without altering particle size. A possible disadvantage of this technique is that surfactants may impart some taste to the product.

#### Process Techniques - Coating

With some changes in processing conditions and machine styles, coatings can be applied to materials ranging in size from approximately 100 microns to several millimeters in diameter. Coating materials are available which can provide for sustained release of the substrate, acid resistance, other pH controlled release, moisture resistance, temperature controlled release, taste and odor masking, as well as aesthetics. The desired finished product characteristics may require a close look at all three fluidized bed methods, which are by no means functionally equivalent. Before doing so, however, a general review of factors affecting particle coating is in order. Of primary concern is the size of particle to be coated. Table I is a chart profiling the

**Table I. Comparison of the Amount of Coating Required to Apply a Coating of 0.01 mm onto Particles of Various Sizes**

UNCOATED PARTICLES				COATED PARTICLES		
PARTICLE SIZE (US MESH)	DIAMETER (mm)	PARTICLES PER GRAM	SURFACE AREA/GRAM (mm <sup>2</sup> )	COATED DIAMETER (mm)	COATING ADDED (%)	COATING IN PRODUCT (%)
5	4.00	23	1,157	4.02	1.2	1.18
10	2.00	183	2,312	2.02	2.4	2.34
18	1.00	1,468	4,610	1.02	4.7	4.49
35	0.500	11,764	9,235	0.520	9.6	8.75
60	0.250	94,350	18,490	0.270	20.0	16.7
120	0.125	751,880	36,917	0.145	43.3	30.2
200	0.074	3,663,000	63,004	0.094	82.3	45.1
325	0.044	17,543,860	107,018	0.064	163.5	62.0

amount of coating required to apply a layer 10 microns thick to particles of various sizes. As can be seen, very small particles (150 microns and smaller) require significant quantities of coating to perform as desired. As an example, a 325 mesh, or 44 micron, particle would require 163.5 kg of coating material (solids) to be applied for each 100 kg of core material. Additionally, the coating must be applied in some sort of medium and at some concentration in liquid. If we assume a 10% solution concentration, 1,625 kg of solution will need to be sprayed and the resulting product will be only 38.0% substrate; the remainder, coating material. In most circumstances, this is not very economical. Also, it is extremely difficult to coat particles that small because of equipment and formulation limitations.

Another concern is the volatility of the application medium. Table II shows the heats of vaporization of commonly used solvents.

Table II. Heats of Vaporization of Commonly Used Solvents

SOLVENT	BOILING POINT (°C)	DENSITY (g/cc)	HEAT OF VAPORIZATION (Kcal/ML)
Methylene Chloride	40.0	1.327	0.118
Acetone	56.2	0.7899	0.172
Methanol	65.0	0.7914	0.232
Ethanol	78.5	0.7893	0.266
Isopropanol	82.4	0.7855	0.213
Water	100.0	1.000	0.542

The difference in film coating quality between the three fluid bed techniques is dramatic when using volatile organic solvents as opposed to water based systems. The evaporative efficiency of the fluidized bed makes it possible to coat water sensitive products with aqueous coating materials. Coatings can be applied from water and organic solvent based solutions, latex or pseudo-latex materials, and materials which are sprayed molten. Films applied from solution tend to behave very much as hardening binders and it is difficult to avoid agglomeration especially in small particle coating. This tendency is less prevalent when using the other types of coating materials.

### General Process Variables

Regardless of whether the fluid bed process is being used for agglomeration or coating, several process variables are common and are listed in Table III. The applicable variables for fluid bed granulation have been well defined (2-6). The two most significant categories are evaporation rate and droplet size. In general, the higher the evaporation rate, the more porous and weaker the agglomerates will be. However, since most processes do not address the problem of a perpetually changing specific humidity, it is advantageous to operate using a high fluidizing air temperature (and hence a high evaporation rate) to minimize variations in drying

capacity due to seasonal changes in the weather. Granule size is directly proportional to droplet size. This process almost

Table III. Fluid Bed Processing Variables

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Evaporation Rate
1. Fluidizing air temperature
2. Fluidizing air volume
3. Fluidizing air specific humidity
Droplet Size
1. Spray Rate
2. Atomizing air pressure/volume
3. Solution concentration (viscosity effects)
Nozzle Port Size
Position of Spray Nozzle
Batch Size (Mass effects)

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exclusively uses binary nozzles; liquid is supplied at low pressure and atomized to droplets by air. The higher this atomizing air pressure and volume, the smaller the droplets will be at a given liquid delivery rate. Another factor affecting droplet size is viscosity of the spray solution. As a result it is important that viscosity remain constant during processing (keeping a heated binder solution covered and agitated, for example).

Nozzle port size is selected to accommodate spray liquid viscosity and delivery rate and may influence droplet size because it affects the velocity of liquid at a given spray rate. At low atomizing air pressures and volumes, a low liquid velocity allows more complete atomization of liquid. Using a smaller nozzle port at the same spray rate generally results in a larger mean droplet size due to the higher liquid delivery velocity. At high atomization air pressures and volumes, this effect is minimized.

The position of the nozzle has an effect on the distribution of liquid, a term known as wetted bed surface area. To achieve the most uniform granulation, the nozzle would be placed high above the static bed to yield the largest wetted bed surface area (see Figure 2). If a wide range of particle sizes is desired, the nozzle can be positioned low resulting in local overwetting producing a quantity of coarse granules.

In scale-up from laboratory quantities (up to 10 kg) to production batches (300 kg and up), bed depth increases significantly. The most notable consequence is an increase in finished product bulk density, typically in the range of 15% to 20%. In some instances, this is a disadvantage (if product is packed by volume and a low density is desired). However, granule strength is usually greater as a result of the decreased interstitial void space.

When coating, the same group of processing variables applies. A high fluidization air temperature may adversely affect film properties and may present some real challenges with thermoplastic materials. Fluidization air volume is generally held constant because it significantly impacts the flow pattern of the substrate which is critical in coating operations. Specific humidity affects the coating process in two ways. If a low dry bulb temperature is chosen to accommodate a volatile solvent, the heat content of the air will vary as specific humidity varies. In an aqueous coating process, specific humidity has an effect on drying capacity similar to the fluid bed granulation process.

Droplet size is again affected by spray rate, atomizing air pressure and volume, and liquid viscosity. In coating, droplets should be small relative to the particles being coated to avoid agglomeration. By comparison to fluid bed granulation, spray rates are usually slower, atomizing air pressure is higher, and liquid viscosity is lower.

Nozzle port size is also selected to accommodate desired spray rate and viscosity. The position of the nozzle is very significant. In top spray coating operations, the nozzle is positioned to spray liquid counter currently to the flow of product (see Figure 3). In the Wurster system, the nozzle sprays concurrently with the well organized flow of substrate (see Figure 4), and in the rotor technique, the nozzle sprays concurrently in the spiralling bed of product (see Figure 5).

The influence of batch size in scale-up is similar to granulating in that it is a mass effect. However, the core material is generally much more resilient and the problem, if any, is erosion from the surface of a friable substrate.

#### Top Spray Coating Applications/Characteristics

The top spray system has been used to coat materials as small as 100 microns. Smaller substrates have been coated, but agglomeration is almost unavoidable due to nozzle limitations and the tackiness of most coating substances. Batch sizes range from a few hundred grams to approximately 1,500 kg. Typically, a single nozzle wand with up to six liquid delivery ports is used, but multiple nozzle systems have been applied.

Fluidization is affected by batch size. Thus, it is recommended that the bowl volume be completely occupied by the product upon completion of the coating process. Batch size can be determined by the following equation:

$$B = V \times D \quad \text{where:}$$

B = Batch size of the coated product in kg.

V = total product container volume in liters.

D = Bulk density of the coated product in g/cc.

A minimum of 50% of the product container volume should be occupied by the uncoated material to allow an adequate fluidization pattern. Under these conditions, approximately 100% coating (based on starting weight) can be applied. Because of the random fluidization pattern using this process, coating for very precise



release properties using water or organic solvents is discouraged. However, top spraying is the system of choice for coating without any solvent (hot melt).

The most significant characteristic of the top spray method is that the nozzle sprays countercurrently or down, into the fluidizing particles. The fluidization pattern is very random and unrestricted. As a result, it is impossible to control the distance that the droplets travel before contacting the substrate. Applied films may contain imperfections such as pinholes and craters (8). The problem seems to be most severe with films applied from solutions, especially from organic solvents.

The product container of the top spray system is designed such that there are no restrictions to particle flow, an important consideration when attempting to apply a hot melt coating. Materials with a melting point of less than 100°C can be applied to the fluidized particles by carefully controlling the liquid and atomizing air temperatures, and the product bed temperature. The degree of protection offered by the coating is related to the rate at which it is applied and congeals. However, keeping the product temperature close to the coating's congealing temperature results in a significant increase in the viscous drag in the bed. It is for this reason that, for hot melt coating, the unobstructed product container of the top spray system is superior to other fluidized bed techniques. Figure 8 shows examples of a product before and after coating using a molten material.

The advantages of the top spray system include the fact that it is the least complicated of the 3 machines, has the largest batch capacity, and downtime between batches can be only minutes. Its biggest disadvantage is that its applications are somewhat limited.

#### Bottom Spray (Wurster) Coating Applications/Characteristics

The Wurster bottom spray system has also been used successfully to coat particles as small as 100 microns. Attempting to coat smaller particles may result in the same difficulties as discussed in the previous segment. Batch capacities range from a few hundred grams to approximately 600 kg. Because fluidization quality is affected by batch size, at least 50% of the volume outside of the partition should be occupied by the uncoated product. Finished product batch size (for fine and intermediate particles) can be determined by the following equation:

$$B = \frac{[\pi r_1^2 L - 1/2 n \pi r_2^2 L] D}{1,000}$$

Where:

- B = finished product batch size in kg.
- r<sub>1</sub> = radius of Wurster chamber in cm.
- r<sub>2</sub> = radius of partition in cm.
- n = number of partitions
- L = partition length in cm.
- D = finished product bulk density g./cc.

Minimum batch size before coating of small particles can be determined by multiplying "B" by 0.4 (or approximately 40% of finished product capacity). The batch capacity for coating of

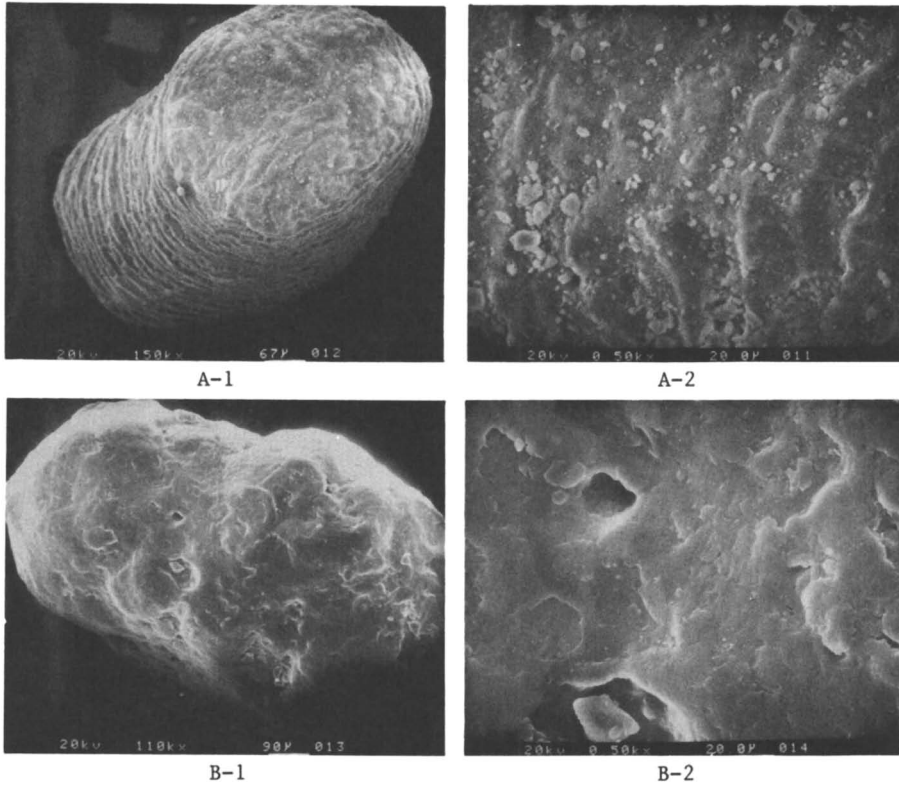


Fig. 8. Photomicrographs showing a molten coating applied by top spray method.

A. Before processing.

A-1. magnification = 150x;

A-2. magnification = 500x.

B. After processing.

B-1. magnification = 110x;

B-2. magnification = 500x.

tablets is approximately 90% of  $(\pi r_1^2 L / 1,000)D$  for coatings of up to 10% w/w.

If the coating and core bulk densities are similar, coatings of 100-150% (based on starting weight) may be applied. Fluidization is also affected by the air distribution plate configuration and the partition height. The finer the particles to be coated are, the less will be the open area in the downbed section of the orifice plate and the smaller the gap between the partition and orifice plate.

The Wurster system has the widest application range using both water and organic solvents; only coating with hot melts is discouraged. Organized particle flow and the immersed nozzle, concurrent spray system appear to offer superior film forming capabilities. An example of a Wurster film coating is shown in the scanning electron photomicrograph in Figure 9. The primary disadvantages of this system are that it is somewhat complex, is the tallest of the three types, and the nozzles are inaccessible during the processing.

#### Tangential Spray Coating Applications/Characteristics

The rotary, or tangential spray system, also an immersed nozzle, concurrent spray technique, appears to offer similar film characteristics as the Wurster system. The scanning electron photomicrographs in Figure 10 compare the surface views of both types of film coating. The rotary system has been used successfully to coat particles as small as 250 microns using organic solvents and water based coatings. The process is more susceptible to adhesion of particles to the upper wall of the product container (see Figure 5) due to static electricity, hence coating of smaller and lighter particles is difficult especially when using organic solvents. Batch capacities range from approximately 1 kg. to 500 kg. Laboratory equipment (up to 500 mm disc diameter) typically uses a single nozzle, and pilot to production scale rotors (up to 2,000 mm disc diameter) use from 2 to 6 nozzles. Fluidization is not affected by batch size as significantly as in the other process techniques. Working capacity is approximately 50% of total bowl volume, and the minimum batch size is that which is necessary to cause the nozzle to be fully immersed such that the coating liquid is not sprayed through the bed. This volume is typically about 15-20% of the working capacity. If the bulk densities of the core and coating material are similar, coatings of 600-800% (based on starting weight) may be applied.

The rotary process excels in producing high potency pellets using three techniques of layering onto a seed material: (a) spraying a water or solvent solution of substrate and binder, (b) spraying a water or solvent suspension of substrate (with a dissolved binder), or (c) spraying a water or solvent binder solution and dosing the substrate powder onto the damp seed material. The choice of technique depends on several factors including solubility and stability of the substrate. Additionally, for suspension layering and powder dosing, it is almost mandatory that the layered powder be micronized (less than 10 microns) to maximize yield and provide a smooth surface for subsequent

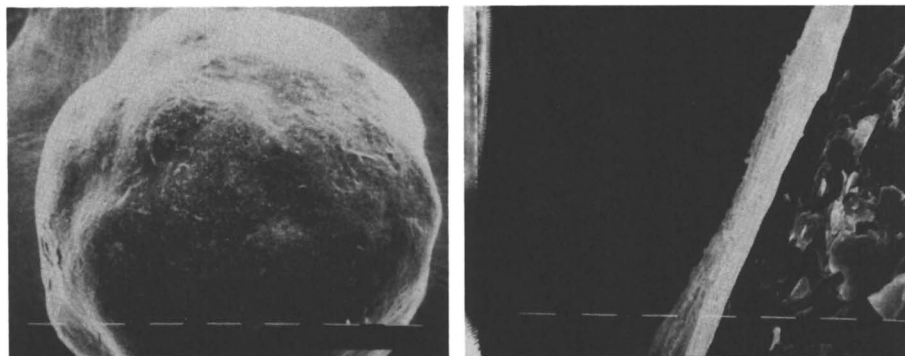


Fig. 9. A bottom spray (Wurster) film coating, surface and cross-sectional views. (Reprinted with permission of Pharmaceutical Technology, copyright 1985.)

- A. Surface view, magnification = 100x.
- B. Cross section, magnification = 1000x.

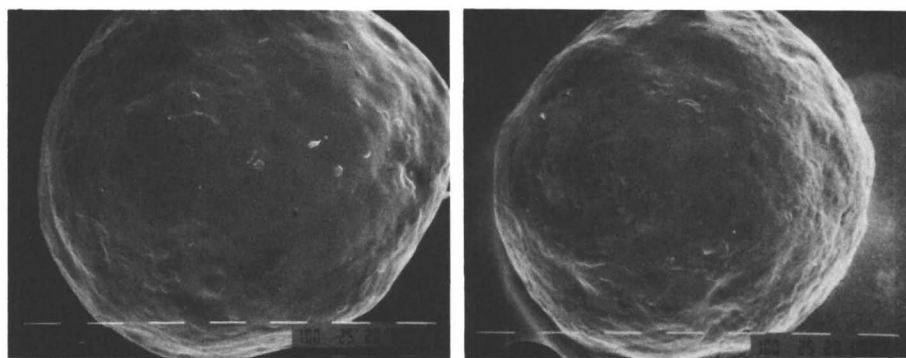


Fig. 10. Pellets coated with ethyl cellulose in an organic solution. (Reprinted with permission of Pharmaceutical Technology, copyright 1985.)

- A. Wurster coating, surface view, magnification = 100 x.
- B. Rotor coating, surface view, magnification = 100 x.

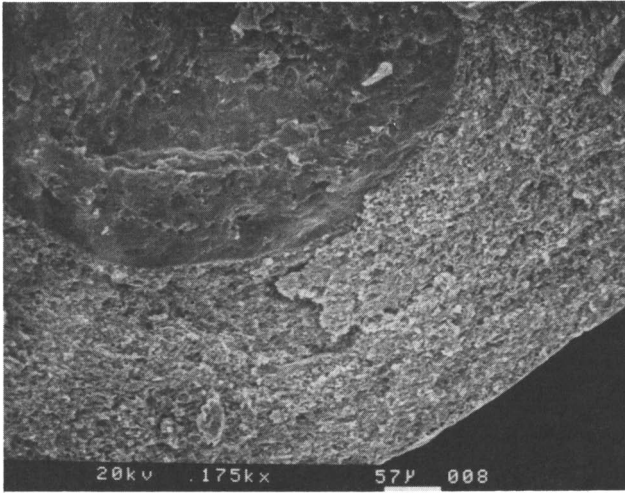


Fig. 11. Scanning electron photomicrograph showing product layered by tangential spray method. Magnification = 175 x.

overcoating. The resulting pellets will be very uniform in particle size distribution because of the narrow size distribution of the starting seed material, typically a non-pareil sugar seed, or regular shaped crystal. Figure 11 shows a cross section of a drug layered pellet.

The process variables which are unique to the rotor system primarily involve the disc slit width, the disc configuration and rotational speed. The rotary system was conceived as a higher intensity granulator than the conventional fluidized bed. The disc surface, which may be configured with a variety of surfaces from simple anti-slide baffles to a multi-pyramid type waffle plate, and high rotational speed impart an increased mechanical force on the substrate. The velocity of the fluidization air through the peripheral slit controls the rate at which the bed tumbles or spirals. For layering or coating, the disc should be smooth and a rotational speed selected (less than one-half of the speed used when granulating) such that particle motion is rapid, but uniform. There is a large velocity gradient from the disc surface through the particle bed and any type of baffle may cause fracture of the pellets, especially as the layer becomes thicker.

The rotary tangential spraying system has a relatively wide application range, is the shortest machine in height of the three, and allows nozzle access during processing. It has the ability to produce high potency pellets as well as to allow subsequent overcoating (for all types of release). Its primary disadvantage is that it exerts the greatest mechanical stress of the three methods and, thus, is discouraged for use with friable substrates.

### Summary

Although there are limitations in capacity, the batch fluidized bed system has enjoyed popularity in the pharmaceutical industry and with specialty products for the food and chemical industries. Its abilities in mixing and heat and mass transfer make it very effective for processing a variety of products. The three fluidized bed techniques have some common features and process variables, but each has unique advantages and limitations. Criteria such as economics, product and process variables, and desired product performance affect the selection of the process from the laboratory scale to commercialization.

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## Chapter 18

# Controlled Release of Food Additives

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A number of situations in food processing, and in processing of related biological systems require control of diffusion of specific components of the system. This is particularly true in the use of functional food additives. A substance in formulated food may be released upon consumption, but prevented from diffusion during the series of operations in food processing: (e.g. flavors, nutrients). Similarly an additive may be released in a specific processing step, but protected in preceding steps, (e.g. acids, leavening agents, crosslinking agents). In other cases preservatives which are needed in given portion of the food (e.g. surface) are to be prevented from diffusion to other portion (to avoid dilution). A variety of food additives may be utilized in food processing and their typical functions are shown in Table 1. The types of approaches taken in food technology to control diffusion through encapsulation of ingredients are shown in Table 2, and typical approaches to release, either in a single burst or in a more controlled manner, of encapsulated food additives are shown in Table 3.

For the most important applications in food technology, namely the encapsulation of flavor compounds, and for protection of oxidation-sensitive compounds including vitamins, the formation of hydrophilic amorphous matrices is often used. These matrices are formed of sugars, sugar-polymer mixtures and from other edible mixtures capable of forming glasses impermeable to organic compounds and to "fixed" gases including oxygen and carbon dioxide. Starch hydrolysis products (maltodextrins) are particularly useful. Many industrial products including freeze-dried coffee depend in their success on the properties of these impermeable glasses (Flink, 1975). The retention of flavors within the matrix, and the protection against atmospheric oxygen remains excellent, provided the temperature remains below the transition temperature for the matrix. Since these transition temperatures are strongly dependent on plasticizer content, and in the case of sugars, and many food polymers the plasticizer is water, -protection against water must be provided either by external packaging, or by double encapsulation, that is, a hydrophilic



TABLE 1TYPES OF FUNCTIONAL ADDITIVES USED IN FOOD, FOR WHICH  
DIFFUSION CONTROL MAY BE USEFUL

1. Preservatives
2. Antioxidants
3. Redox agents (bleaching, maturing)
4. Acids, alkalies, buffers
5. Colors
6. Flavors
7. Sweeteners
8. Nutrients
9. Enzymes
10. Crosslinking Agents

**TABLE 2**

**PRINCIPLES OF ENCAPSULATION OF COMPOUNDS USED  
IN FOOD FORMULATION**

1. Entrapment in amorphous (glassy) matrices achieved by rapid cooling or by drying.
2. Encapsulation in fat-based matrices.
3. Encapsulation in crosslinked or coacervated polymers.
4. Entrapment within sugar crystals.
5. Strong physical adsorption.
6. Chemisorbed compounds.

**TABLE 3**

**METHODS OF RELEASE USED IN FOODS**

Commonly used:

For hydrophilic encapsulants:

Temperature and moisture control.

For fat capsules:

Thermal release

Other release methods:

pH Control

Addition of surfactants

Enzymatic release

(e.g. proteolysis)

Ultrasonics

Grinding

Photo-release

matrix encapsulating a lipophilic flavor mixture is in turn encapsulated in a lipophilic matrix, usually a fat with a known melting point. The technology of these encapsulations is well known industrially, and is based on preparation of a suspension, or solution of the flavor and of the encapsulating material and subsequent dehydration through spray drying, freeze drying (Karel, 1985b); or solvent dehydration (Zilberboim et al. 1986).

The effectiveness of encapsulation depends strongly on the concentration of the encapsulating material in the solution from which it is dried. Very extensive studies on the dependence of efficiency of encapsulation on the concentration of solute, and on conditions of dehydration, cooling, or desolventizing have been reviewed by Karel and Flink, (1983); King et al. (1984) and Toei, (1986). It is known that in general the success of encapsulation depends on formation of a metastable amorphous structure, a glass, with a very low permeability to organic compounds, which are encapsulated within it. The mechanisms of encapsulation which are operative in drying processes depend on the fact that in food materials containing sugars and/or polymers reduction of water content lowers the glass transition temperature and the resulting amorphous matrix is impermeable to organic compounds, as well as to oxygen. Permeability to water, however, remains finite. This phenomenon of "selective diffusion" theory of (Thijssen and Rulken, 1968) is the basis for encapsulation using spray drying and freeze drying. In spray drying, upon droplet formation, rapid evaporation from the surface, produces a surface layer in which the selective diffusion mechanism comes into play. In order to be most effective the spray drying process should have the following features:

1. Short residence time prior to droplet formation
2. Rapid evaporation once droplets are formed
3. High degree of selectivity of the relatively "dry" surface layers
4. Absence of liquid circulation within the droplets
5. Avoidance of surface "cracks"

In freeze drying, upon water crystallization, the non-frozen solution is viscous and the diffusion of flavors is retarded. Upon beginning of freeze drying, the surface of this solution becomes an amorphous solid in which selective diffusion comes into play.

The success of freeze drying as an encapsulation method depends on the following critical factors:

1. Formation of thick layers between pores which are created by ice crystals
2. Selectivity of the amorphous solid
3. Absence of structure "collapse" which implies mobility (possibly transient) allowing flavor diffusion
4. Absence of "cracks"

The physicochemical principles governing the "softening", or glass transition of the encapsulating matrices have been studied by Karel and his co-workers (1983) and most recently by Levine and Slade (1986). These studies have shown that the release occurs when the glassy, impermeable structure undergoes a transition to a more mobile rubbery state. (Figure 1)

The relation of transition temperature to composition of encapsulating formulations has been studied by To and Flink (1978), and by Levine and Slade (1986) for the case of starch-derived encapsulating agents. It must be noted however, that even after the critical moisture content or the critical temperature is exceeded, the rate of release is also a function of water content, of temperature and of time (Karel, 1985). This fact allows the generation of controlled-release systems. The maltodextrins and similar materials with controlled collapse temperatures are important not only as encapsulating agents but are also extremely useful in protecting enzymes and other sensitive biological materials during dehydration and storage. The principles are similar in that the sensitive materials are placed in a medium in which their mobility is restricted. In addition to starch-derived maltodextrins there are important food encapsulation advantages to materials based on marine biopolymers. These colloids including alginates, carrageenan, and chitosan offer a wide range of useful properties for a number of important applications. They have been widely used in food technology for improving the rheological properties of foods, for coating and for prevention of crystallization of lactose in ice cream. Recently they have begun to play important roles in immobilization of enzymes and or other proteins and of whole cells, (Kupchik et. al. 1983). An important application of marine colloids lies in creation of internal environments in local regions which is more desirable than the normal environment of the food. Thus it may be desired to have the pH lower in some portion of the food than in bulk either during storage (e.g. to protect sensitive surfaces from microbial growth), or during a given process (e.g. keeping pH in an optimal range during heating may result in reduced losses of some sensitive components). We have achieved such stabilization in the case of cheese analogs having an intermediate moisture content preventing microbial growth except potentially on a moist surface. We have stabilized these foods by concentrating the preservative sorbic acid in the surface (Figure 2), and to keep the preservative effective have lowered the surface pH with the anionic polyelectrolyte carrageenan (Figure 3). This approach is quite effective in increasing shelf life from hours to weeks (Torres and Karel, 1985). In other applications of the marine colloids use may be made of chitosan, a polyelectrolyte obtained from chitin by deacetylation to provide a positively charged polymer with a controllable charge density.

A different approach to controlled release of flavor lies in controlled release of enzymes which catalyze reactions of the flavor precursors to form the desired flavors. One of the approaches to this emerging technology has been the use of lipid vesicles, or liposomes. Lipid vesicles have been studied widely

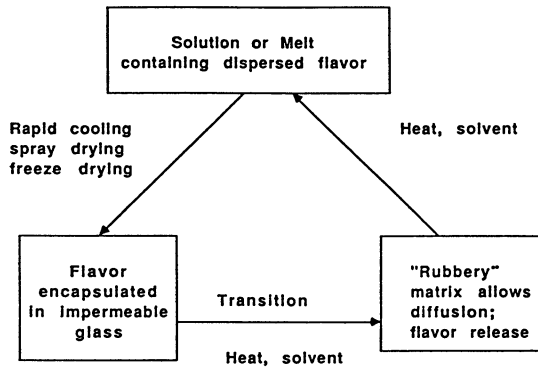


Figure 1. Transitions in dried materials and their effect on flavor release.

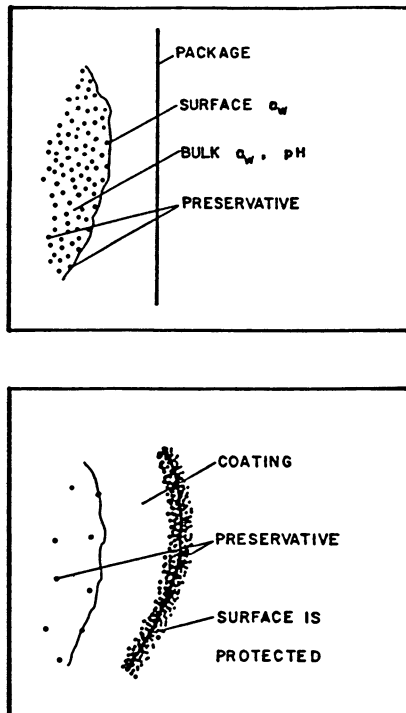


Figure 2. Schematic representation of preservative concentration in bulk and in surface of foods. The top figure represents encapsulation of the preservative in the surface layer which is the portion of food most susceptible to microbial growth.

by researchers in the medical and pharmaceutical area because of their potential use as targetable carriers of drugs including bioactive macromolecules. Recently, applications of lipid vesicles in the food industry have also been suggested especially for encapsulation or immobilization of enzymes. Enzyme-loaded lipid vesicles systems may assist in such complicated processes as improved flavor development through controlled modification of enzymic reaction. Law and King (1985) and Piard et al. (1986), were the first to suggest the applicability of such systems in the field of accelerated cheese ripening. In their experiments, extraneous proteinase was encapsulated in lipid vesicles and, simply added to the milk. The enzyme remained encapsulated in the vesicles during curd formation process, preventing casein matrix from being degraded prematurely. As the curd began to undergo ripening, the enzyme was released but the mechanism of the release was not explored.

In order to utilize enzyme-loaded lipid vesicles as a tool for modifying enzyme reaction in any food processing, the following requirements should be fulfilled:

1. To prevent enzyme denaturation the vesicle preparation must be mild and simple.
2. Vesicles should accomodate large amounts of enzyme.
3. All ingredients must be safe and edible, (i.e. acceptable under the regulations relevant to the country in which the products are to be consumed)
4. Lipid vesicles have to be stable in either liquid suspension or in dried form with minimal unintentional release of enzyme under usual storage conditions. In addition, enzymes have to be released in a controlled manner. Innovative designs are needed to control release.

A method meeting these criteria is the dehydrating-rehydrating method which can use lecithin (phosphatidylcholine), without using cholesterol. Commercial grade lecithin products containing practically no triglycerides are available and have been proved suitable for vesicle preparation. (Kirby and Gregoriadis, 1984b; Strahm *et al.* 1981).

Exploration of this method for controlled release of enzymes to produce flavors of importance in cheese ripening has been pioneered by Kirby and Law (1986), and was recently the subject of basic studies in our laboratory (Koide and Karel, 1987).

The principle of the cheese ripening improvement is the controlled release of proteinases. It has been shown that incorporation of non-encapsulated enzyme in milk is not very effective because enzymes are lost during the "cheddaring" step (Kirby and Law, 1986). The liposomes, however, survive the "cheddaring" step intact but are disrupted during ripening to give slow proteinase release. The different modes of addition of the enzymes have a dramatic impact on the quality of cheese. Addition of enzymes to milk, prior to cheesemaking results in poor textural quality, high level of whey contamination, and reduced cheese yield. By adding unencapsulated enzyme to the

curd, the yield is returned to normal, but the distribution of the enzyme is poor, and the texture is crumbly. Encapsulated, slowly released enzyme results in the best cheese (assuming that accelerated ripening is desired). (Kirby and Law, 1986). Our work has concentrated on developing methods for stimulation of release from liposomes in a controllable manner. For preparing the vesicle the method proposed by Kirby and Gregoriadis (1984a, b) was employed. One hundred mg of phosphatidylcholine in chloroform were dried to a film in a 100 ml round-bottom flask by a rotary evaporator. To the film, 4 ml of distilled water was added and vortexed with glass beads and then sonicated in a bath-type sonicator for 10 minutes under nitrogen gas to homogenize the lipid suspension. The suspension was opaque and white in color, implying that multilamellar vesicles were formed. After 4 ml of the solution of the enzyme to be encapsulated (original enzyme solution) was mixed with the suspension and kept at room temperature for 15 minutes, the whole mixture was flash-frozen by liquid nitrogen and lyophilized. Rehydration of the dried protein-empty vesicles complex was performed in three steps:

1. The dry mixture was exposed to humidified nitrogen gas for 30 minutes in a round-bottom flask.
2. Distilled water was added while the flask was moved in a swirling manner, to have the lipid-protein mixture evenly rehydrated.
3. Rehydrated mixture was kept under the nitrogen gas, then diluted.

The vesicles were separated by centrifugation at 30,000 x g from the enzyme solution. Precipitated PC vesicles underwent a washing process once and were resuspended with the phosphate buffer solution (PBS) and adjusted to 25 ml. Stimuli which have the potential to induce the controlled release of enzyme from PC vesicles in suspension were examined in terms of the releasing pattern. Original vesicles suspensions were stimulated by mixing with an equal volume of a stimulus solution in glass vials with screw caps and were stored at 10°C (+2°C) or 37°C (+1°C).

The stimuli tested are listed in Table 4. In a series of experiments, it was proved that such stimuli as sonication, acid pH, or Triton X-100 have strong stimulating ability while Ca<sup>++</sup> ion and Tween 80 have relatively less effect. Among these stimuli, acidic pH, Ca<sup>++</sup> ion and Tween 80, with or without the enhancing effect of high temperature, are of special interest, since they can be used as additives in food processing. The patterns of release attainable by the different stimuli are shown in Figure 4. Recently the applicability of the above techniques to cheese ripening has received confirmation by the work of Kirby et al 1987, who showed the superior quality of rapidly ripened cheese using enzymes in liposomes.

Although not yet tested in foods, approaches have been developed that combine the desirable properties of encapsulants and liposomes. In particular, a microencapsulated liposome system has been developed that can provide either delayed or pulsed release (Wheatley and Langer in press).

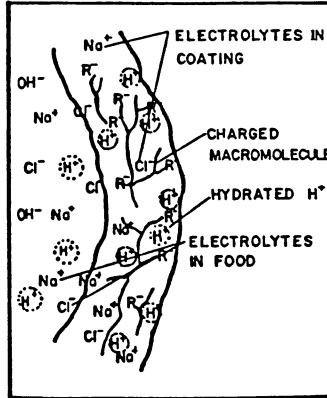


Figure 3. Maintenance of a differential surface pH by coating with an acidic polysaccharide. The incorporation of carrageenan in the surface layer allows the lowering of pH in the surface.

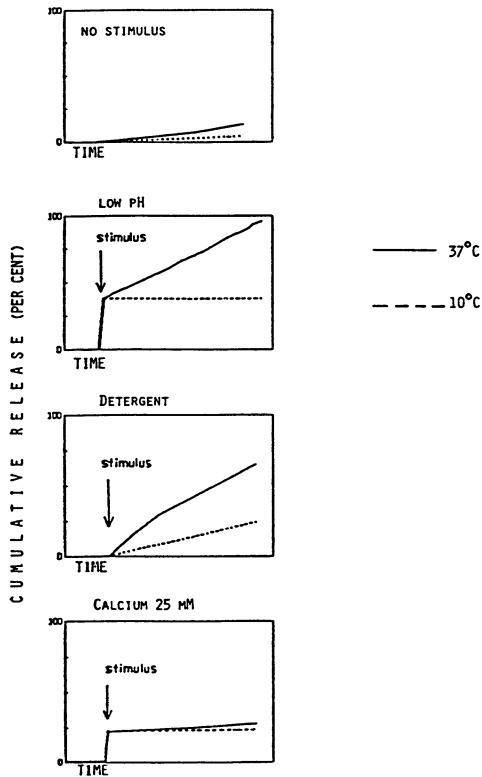


Figure 4. Patterns of enzyme release from liposomes using different release stimuli.



TABLE 4STIMULI WHICH INDUCE ENZYME RELEASE FROM VESICLES

<u>MECHANISM</u>	<u>STIMULI</u>
1. <u>CHANGE OF THE STATE OF BILAYER</u>	
Effect on head group of phosphatidyl choline	pH change Ca <sup>++</sup> , Mg <sup>++</sup>
Effect on tail group of phosphatidyl choline	Temperature change
Gel-fluid transition	
Oxidation	O <sub>2</sub> , catalyst
2. <u>CHANGE OF VESICLES STRUCTURE</u>	
	Sonication Surfactants
3. <u>BREAKDOWN OF PC</u>	
4. <u>SOLUBILIZATION</u>	

In this case, unilamellar vesicles with a large capture volume were prepared by the reverse phase evaporation technique and alginate was used to microencapsulate the liposomes. The alginate spheres were double coated, first with poly-L-lysine and then with polyvinyl amine (Wheatley and Langer in press).

The liposomes did not interfere with alginate capsule formation and were retained within the finished capsules. When myoglobin (used as a model protein) was not entrapped within liposomes but was simply enclosed as "free" protein within the coated alginate beads, 60% of it diffused out of the capsule over the first two days. In contrast, delayed release was achieved with microencapsulated liposomes containing myoglobin. Very little myoglobin appeared outside the capsules until 10 days after the start of the release experiment. It required a further 12 days to reach a level of 60% and not until 50 days after the start of the experiment was 100% release achieved. (Figure 5)

A five minute treatment with Triton X-100 at the onset of the experiment resulted in pulsed release (Figure 6). It is likely that Triton X-100 increases the permeability of the capsules to myoglobin, since 15% of the myoglobin appeared rapidly in the extracapsular solution immediately after Triton X-100 was added to the capsules, compared to the gradual release of myoglobin from untreated capsules that contained the "free" protein, (-x-, Figure 6). Myoglobin continued to be released from the Triton-treated encapsulated liposomes for 6 days but then very little additional myoglobin was released until a second pulse of release began 20 days after the start of the experiment.

A non-chemical treatment leading to pulsed release was achieved by a five minute sonication of capsules containing liposome-entrapped myoglobin. Microscopic examination of the capsules revealed no visible damage to the capsule after sonication. In the initial pulse of release following sonication (-●-, Figure 7), 30% of the total myoglobin diffused out of the capsules over the first 6 day period and, after a 14 day lag period, a second pulse of release started 20 days after the beginning of the experiment. The release in the second pulse was more sustained than in the first, with 84% of the total myoglobin being released by 33 days after the start of the experiment and 100% being released by 50 days.

When the microencapsulated liposomes are left untreated the lipid bilayer provides a barrier to diffusion through which the entrapped protein does not pass until the liposomes gradually become leaky, primarily due to oxidation of the phospholipid side chains. This mechanism results in a delayed release. Triton or sonic treatment of the microencapsulated liposomes provide pulsed release. Since both detergent and sonication disrupt lipid bilayers, the mechanism by which pulsed release is achieved may be that these stimuli initially disrupt the liposomes and then the lipid reforms around some of the protein solution inside the capsule, possibly in an altered lamellar form; alternatively, the treatment could disrupt only the more susceptible liposomes, leading to two phases of release, first from the freed protein and later from protein that remained liposome-entrapped.

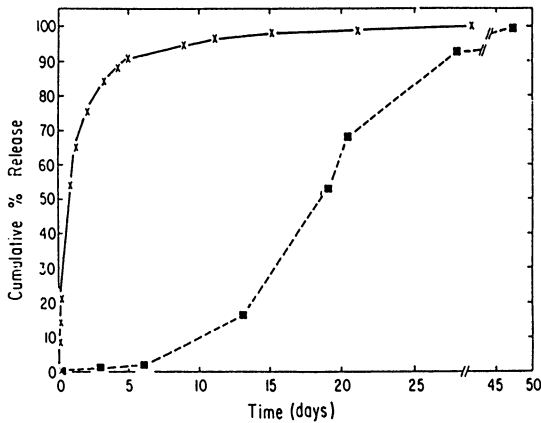


Figure 5. Release from alginate-encapsulated liposomes. In vitro experiments were performed as follows: Encapsulated liposomes were suspended in 10 ml of physiological saline in a screw-capped vial. In cylindrical polypropylene mesh cages (mesh size 105 $\mu$ ; the mesh was obtained from Fisher Scientific, cut into 2x2.5 inch rectangles, sewn up the side with nylon thread, and sealed at the bottom with a wax plug). Release was at 37°C on a rotary shaker. The encapsulated liposomes were frequently transferred to vials containing fresh buffer in order to mimic the infinite sink conditions of the body. The concentration of myoglobin appearing in the release buffer was measured spectrophotometrically by absorbance at 410 nm. Release of myoglobin from encapsulated liposomes (-■-) is compared with myoglobin released from capsules containing free myoglobin (-x-).

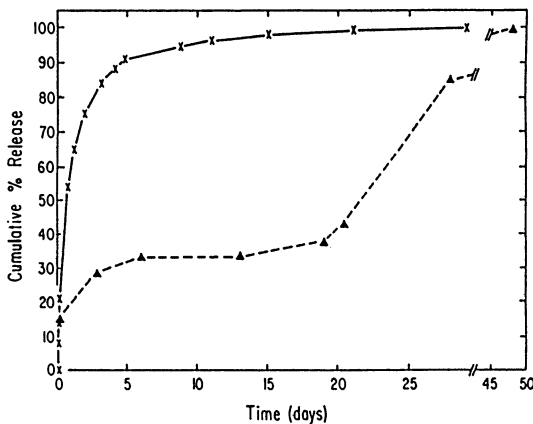


Figure 6. Release profile from Triton-treated capsules. Samples that were to be treated with detergents were placed in the polypropylene cages and immersed in 10 ml of 0.1% Triton X-100 in physiological saline for 5 minutes. The capsules were then transferred to normal saline and the release of myoglobin followed spectrophotometrically (-▲-). This release was compared with release from capsules containing free myoglobin (-x-).

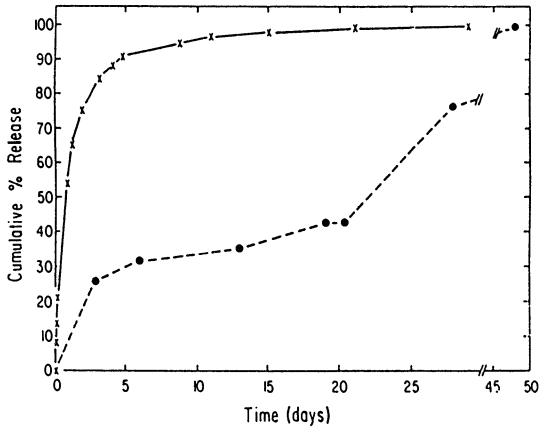


Figure 7. Release profile from sonicated capsules. Samples that were to be treated with sonic energy were placed in the polypropylene cages and immersed in 10 ml of physiological saline in scintillation vials. The vials were subjected to 3 minutes of sonication at 4°C in a sonic bath. The capsules were then transferred to fresh buffer and the release of myoglobin was followed (—●—) and compared with release from capsules containing free myoglobin (—x—).

In the dual liposome-microcapsule system, two factors control the release of the active substance: escape from liposomes into the microcapsule interior, and diffusion across a rate limiting capsule wall into the external environment. This system can take advantage of the inherent instability of some liposomes while over-coming many of the problems associated with their use by protecting them from the environment by the capsule. At the same time, a new measure of control over the time at which a microcapsule will commence delivery of the enclosed agent is introduced by careful choice of the liposome composition. By changing the nature of the liposomes or of the encapsulant (e.g. alginate) different release times and patterns can be obtained.

In summary the above examples and applications suggest a number of approaches that can be used for controlled release of foods. While this field is in its infancy, it offers the promise of extensive application in the future.

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