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Encapsulation and Controlled Release of Food Ingredients

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Foreword

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Preface

ENCAPSULATION INITIALLY WAS USED IN THE FOOD INDUSTRY to produce flavoring materials in a dry form and to provide protection to those flavoring materials. The application of encapsulation techniques to other food ingredients has recently received increased attention as a means of protecting ingredients from the surrounding environment and from other ingredients in foods. In addition to protecting specific compounds, encapsulation methods are being developed to allow the controlled release of compounds. Ingredients are now designed to be protected during certain stages of food processing and released at the desired time.

Providing an update on encapsulation techniques, applications for those techniques, and information on new areas of interest was the focus of the symposium upon which this book is based. The first ACS flavor encapsulation symposium, held in 1987, detailed specific methods of flavor encapsulation, with an emphasis on spray drying. The 1993 symposium followed up on earlier encapsulation issues in addition to providing broader flavor and food ingredient information as it relates to encapsulation and controlled release.

Traditional encapsulation techniques and materials are presented in this book. Emerging application techniques such as use of liposomes, coacervation of flavors, fluidized bed coating, and centrifugal suspension–separation are also covered. Other chapters include overviews of current applications, patent activities, and theories of encapsulation. Food scientists and flavor chemists will gain insight into better ways of producing improved flavors in food products and improving the functionality of other ingredients.

We thank the chapter authors for their time and efforts. In particular, we acknowledge Colleen Whorton, who spent considerable time gathering information and helping in other ways with details of the book. We thank Rhonda Bitterli of ACS for providing unending support and encouragement.

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Chapter 1

Encapsulation: Overview of Uses and Techniques

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A variety of encapsulation techniques are used in the food and pharmaceutical industry. These techniques include spray drying, spray chilling and cooling, coacervation, fluidized bed coating, liposome entrapment, rotational suspension separation, extrusion and inclusion complexation. This chapter will provide an overview of these techniques. Encapsulation is used to protect ingredients, to convert liquid components into solid particles and to provide a means for controlled release. Research is continuing to improve the methods used and to find new applications.

Encapsulation is a process by which one material or mixture of materials is coated with or entrapped within another material or sytem. The material that is coated or entrapped is most often a liquid but could be a solid particle or gas and is referred to by various names such as core material, payload, actives, fill or internal phase. The material that forms the coating is referred to as the wall material, carrier, membrane, shell or coating. Encapsulation is used in a number of different industries with a wide variety of techniques or processes available. This overview will highlight techniques commonly used in the food industry. A number of the techniques will be covered in detail in later chapters in this book. Consideration will be given to some techniques which are not currently used on a widespread basis in the food industry but which may have practical applications.

A number of reviews on encapsulation have been published in the past few years. Dziezak (*1*) reviewed the encapsulation of ingredients focusing on methods most often used in the food industry. The review discusses the reasons for

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encapsulation and provides a good description of techniques used as well as specific applications. The techniques described in (*1*) include spray drying, air suspension, extrusion coating, spray cooling/chilling, centrifugal extrusion, rotational suspension separation, coacervation and inclusion complexing. Sparks (*2*) discussed microencapsulation techniques for food and industrial applications, including criteria for selecting one process over another for various types of core materials. Microencapsulation techniques and applications ranging from graphic arts to pharmaceuticals were reviewed by Thies (*3*) in Encyclopedia of Polymer Science and Engineering. Another more recent review was published by Jackson and Lee (*4*) focusing on microencapsulated food ingredients. The review covers properties of microcapsules, potential uses as well as techniques for encapsulation. The reader can refer to these reviews for more details concerning particular techniques as well as the chapters later in this book.

Encapsulation provides protection for a flavor or ingredient. With some encapsulation techniques, the product can be designed to either release slowly over time or to release at a certain point. This concept of controlled release is discussed in the chapter by Reineccius entitled "Controlled Release in the Food Industry". The protection provided by encapsulation can be to prevent degradation due to exposure to light or oxygen or to retard evaporation. It can be used to separate components of a flavor that would react with each other, such as acetaldehyde and methyl anthranilate. Encapsulation can be used to separate components within a food system such as oil from egg whites so that the egg whites will yield a larger foam volume when whipped. Virtually any material that needs to be protected, isolated or slowly released can be encapsulated. In food systems, this includes acids, lipids, enzymes, microorganisms, flavors, artificial sweeteners, vitamins, minerals, water, leavening agents, colorants and salts.

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Spray Drying

Traditionally, the most common method of encapsulating food ingredients has been spray drying. Spray drying is still the most economical and widely used method of encapsulation, finding broad use in the flavor industry. Equipment is readily available and production costs are lower than for most other methods of encapsulation. In addition to being an encapsulation process, spray drying is also a dehydration process and is used in the preparation of dried materials such as powdered milk. A complete review of spray drying was written by Reineccius (*5*)and can be referred to for more detailed information.

To prepare materials for spray drying, the carrier or wall material (such as maltodextrin, modified starch, gum or combination of these) is hydrated. The flavor or ingredient to be encapsulated is added to the carrier and homogenized or thoroughly mixed into the system using a similar technique. A typical ratio of carrier to core material is 4:1, however, in some applications higher flavor loads can be used.

The mixture is homogenized to create small droplets of flavor or ingredient within the carrier solution. The creation of a finer emulsion increases the retention of flavor during the drying process (*6*). Numerous studies have been conducted to evaluate the properties of wall materials, including a comparison of encapsulating agents for artificial flavors by Leahy et al (*7*) and comparisons of retention of volatiles in systems including combinations of carbohydrate, protein and lipids (*8*).

The core/wall material mixture is fed into a spray dryer where it is atomized through a nozzle or spinning wheel. Hot air flowing in either a co-current or counter-current direction contacts the atomized particles and evaporates the water, producing a dried particle that is a starch or carrier matrix containing small droplets of flavor or core. The dried particles fall to the bottom of the dryer and are collected. A thorough understanding of the core material and intended application is important to select the appropriate wall material and to optomize drying conditions. The chapter later in this book by Kenyon discusses a variety of materials used as carriers for encpasulation techniques, but in particular with applications for spray drying.

As mentioned, the advantages of spray drying include low processing costs and readily available equipment. It generally provides good protection to the core material and there is a wide variety of wall materials available. One main disadvantage is that it produces a very fine powder which needs further processing such as agglomeration to instantize the dried material or make it more readily soluble if it is for a liquid application. Due to the heat required for evaporation of water from the system, spray drying is not good for heat sensitive materials.

Development of improved carrier materials has been an active area of recent research. Companies such as Colloides Naturels and TIC Gums have both investigated processing of gum arabic and as well as using it in combination with various starches to yield higher volatile retention and better shelf life. Chapters in this book by Reineccius, Ward, Whorton and Andon and by Thevent discuss the results of these studies. An earlier study by Risch and Reineccius (*9*) showed that one particular brand of gum arabic yielded good retention of orange oil and provided good protection against oxidative deterioration.

An application of a new type of spray dryer has been proposed (*10*). The dryer is a Leaflash spray dryer in which the drying air is at a very high temperature (300 - 400 C) and flows at a very high velocity. It was found that citral and linalyl acetate could be spray dried with little impact on the compounds themselves.

An alternative to spray drying was investigated by Zilberboim et al (*11*) for compounds with low boiling points or that are heat labile. In this method, the emulsion of core material in hydrated carrier, such as gum arabic, is atomized into ethanol which acts as a dehydrating liquid. The microcapsules can be separated from the solution by filtration and dried in a vacuum oven at low temperature. Additional work by Zilberboim et al (*12*) studied the microcapsules produced by this technique in an attempt to determine the effects of different process parameters on retention and shelf life. This method does provide an alternative to the high temperatures

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encountered in spray drying, however, the lack of readily available equipment to accomplish it in a continuous flow instead of as a batch operation makes it much more costly than spray drying. There are no significant commercial applications of this procedure, however, it does provide an alternative for expesive, heat labile materials where the additional cost might be justified.

Spray Chilling and Spray Cooling

Spray chilling and spray cooling are similar to spray drying in that core material is dispersed in a liquified coating or wall material and atomized. However, unlike spray drying, there is generally no water to be evaporated. The core and wall mixture are atomized into either cool of chilled air which causes the wall to solidify around the core. In spray chilling, the coating is typically a fractionated or hydrogenated vegetable oil with a melting point in the range of 32 - 42 C. In spray cooling, the wall is typically a vegetable oil, although other materials can be used. The normal melting point is 45 - 122 C. These two methods, which differ only in the melting point of the wall material used, are most often used to encapsulate solid materials such as vitamins, minerals or acidulants. With the ability to select the melting point of the wall, these methods of encapsulation can be used for controlled release.

Extrusion

Encapsulation by extrusion involves dispersion of the core material in a molten carbohydrate mass. This mixture is forced through a die into a dehydrating liquid which hardens the coating to trap the core material. The most common liquid used for the dehydration and hardening process is isopropyl alcohol. The strands or filaments of hardened material are broken into small pieces, separated and dried. This method was firtst patented in 1957 (*13*) with another patent issued 1962 (*14*). The work which led to this development was accomplished by Schultz et al (*15*) of the United States Department of Agriculture. They mixed orange oil into a molten carbohydrate mass and allowed it to cool on a stainless steel sheet. When solidified, the material was pulverized. Swisher further developed this idea by extruding the material instead of just pouring it onto a sheet, as revealed in his patents (*13*, *14*).

Extrusion provides true encapsulation in that the core material is completely surrounded by the wall material. When the material contacts the dehydrating liquid and the wall is hardened, all residual oil or core material is removed from the surface. The absence of residual surface oil and the complete encapsulation gives products manufactured in this manner an excellent shelf life. This method does produce larger particles which can be used when when visible flavor pieces are desirable. More details on this method of encapsulation can be found in (*16*).

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Other Techniques

A number of other techniques are also finding applications in the food industry. Fluidized bed coating, also referred to as air suspension coating or the Wurster process is typically used to coat solid particles. In simpllified terms, the particles to be coated are circulated through a chamber with high velocity air. As they circulate, the coating material is atomized into the particle stream and deposited on the surface. The amount of coating applied can be controlled by controlling the length of time that the particles are in the chamber. The chapter by Zimmermann discusses the method in detail while the chapter by deZarn presents applications for this technique.

Liposome entrapment, which found initial applications in the pharmaceutical industry and is now being investigated for the food industry, is discussed in a chapter by Reineccius. Liposomes consist of an aqeous phase that is completely surrounded by a phospholipid-based membrane. When phospholipids are dispersed in an aqueous media, the liposomes will form spontaneously. It is possible to have either aqueous or lipid soluble material enclosed in the liposome. The only application that is not possible is for any materials that are soluble in both aqueous and lipid phases which limits the use of liposomes for most flavor compounds.

Coacervation was patented by National Cash Register Company in the 1950's for carbonless paper. This technique is often regarded as the original and true method of encapsulation. A liquid phase of the coating material is separated from a polymeric solution and surrounds the suspended core material. The coating is then solidified. Until recently, this method was not used for food ingredients due to the fact that the materials available for hardening the wall materials were not food grade. This technique will be discussed in detail in the chapter entitled "Coacervation of Food Ingredients" by Risch.

Inclusion complexation is the only method of encapsulation that takes place on a molecular level. It is accomplished using cyclodextrins, typically B-cyclodextrin which consists of 7 glucose units linked 1 - 4. It has a hollow, hydrophobic center with a hydrophilic outer surface. When in solution, molecules that are less polar will replace the water molecule that is held in the center of the cyclodextrin. This complex becomes less soluble and will precipitate out of solution. The development and applications of cyclodextrins are discussed in detail by Hedges later in this book.

Rotational suspension separation is discussed in chapters by Sparks and Schlameus. It involves the suspension of the core material in the selected wall material. This mixture is introduced onto a rotating disk. The encapsulated particles are spun off the disk and then dried or chilled.

Other chapter include research on factors influencing retention during spray drying and a specific application for spray dried flavors. There are ongoing research efforts to determine new and better ways to protect food ingredients. Much of this work is confidential and protected by trade secrets. Some of the work is patented and one chapter later in the book will review some of the significant patents that have

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been issued in the past few years. We will continue to see more technology developed for specialized applications of encapsulated and controlled release products.

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Chapter 2

Controlled Release Techniques in the Food Industry

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The encapsulation and subsequent controlled release of food ingredients has been practiced in the food industry for over sixty years. Despite this time period, the technology that has developed remains relatively unsophisticated compared to may other fields of application (most notably the health field). This is largely due to the limitations imposed on the food industry for the use of edible low-cost ingredients and low-cost processing. The mechanisms of controlled release broadly applied across the scientific and industrial fields are discussed in this review. Techniques which are currently in use in the food field are elaborated on in greater detail. The potential to apply some of the unused technologies in the food field is also discussed.

Microencapsulation has found broad application in the pharmaceutical, heath, food, paper and cosmetic industries as well as minor application in a host of other industries (e.g. lubricants for oil-drilling applications). While most of these applications are relatively recent developments, encapsulation has been used in the food industry for more than 60 years. One of the earliest applications was the encapsulation of flavorings by spray drying (1930's). Encapsulation in the food industry is a large volume low cost operation compared to encapsulation applications in the areas of cosmetics or health. While anyone familiar with the food industry is well aware of the variety of food ingredients which are encapsulated today, a list provided by Karel and Langer (1) is given in Table I.

Food ingredients are encapsulated for a variety of reasons including separation from their environment (water, acid, oxygen, other food ingredients, etc.) which may be detrimental to the encapsulated material (or the food itself), stabilization of the ingredient during processing, to impart a controlled release (perhaps later during

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processing or storage, or during final preparation prior to consumption), or simply to change the state of the food ingredient from a liquid to a solid to permit its use in a dry application. Overviews of the numerous applications of encapsulation in the food industry have been presented by several authors including Risch (refer to chapter in this text) and Dziezak (2). The processes themselves have been the subject of numerous short courses, workshops and symposia (3, 4, 5, 6, 7) as well as books (this text; 8, 18) and journal articles too numerous to cite. Due to the host of available literature in these areas, this review will focus more on the aspect of controlled release in the food industry than on the processes used for encapsulation.

Table I. Types of Food Additives Which may Benefit from Encapsulation and Controlled Release (1)

Preservatives	Antioxidants
Redox agents (bleaching, maturing)	Acids, alkalies, buffers
Colors	Flavors
Sweeteners	Nutrients
Enzymes	Crosslinking agents

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Applications of Controlled Release

As is noted in the literature much remains to be done in the encapsulation area. New technologies are needed for encapsulation and new functionally different carriers are desired. While many techniques exist for the encapsulation of food ingredients, many needs are still unaddressed. Examples in the flavor area include the following: include the following:

(1) accomplishing a slow controlled release of volatiles from dry beverage powders to provide a pleasant aroma to the consumer when the product is opened;

(2) maintaining the aroma in fruit fillings, leathers or confectionery products during storage;

(3) protecting the flavor of a food during baking, extrusion or retorting so as to be delivered to the consumer upon eating;

(4) slow sustained release of volatile flavors, acids and high intensity sweeteners in chewing gums.

Karel and Langer (1) have provided further discussion of the needs and applications of the controlled release of enzymes in foods, especially with respect to the protection of viable enzymes during food processing.

To address the issue of controlled release, one needs to look at the basic principles of controlling the release of encapsulated materials and then consider which technologies can be applied in the food industry. Brannon-Peppas (10), Beimesch (11), Peppas (12) and Lee (13) have provided recent overviews of mechanisms involved with controlling the release of encapsulated materials. A categorization of mechanisms of release is provided by Brannon-Peppas (10) and presented in Table II. A categorization of methods proposed by Karel and Langer (1) for use in foods is presented in Table III.

Table II. Mechanisms of Release from Controlled Release Delivery Systems in Consumer Products (10)

Diffusion controlled release	Membrane controlled release
Pressure activated release	Tearing or peeling release
Solvent activated release	Osmotically controlled release
pH sensitive release	Temperature sensitive release
Melting activated release	Hybrid release

Table III. Methods of Release Used in Foods (1)

Commonly used:
For hydrophilic encapsulants: Temperature and moisture release
For fat capsules: Thermal release

Other release methods:
pH control
Addition of surfactants
Enzymatic release (e.g. hydrolysis)
Ultrasonics
Grinding
Photo-release

Mechanisms of Controlled Release

Diffusion control. This mechanism acts to limit the release of active materials by controlling diffusion of the active substance from its location in the capsule to the surface of the particle. The bulk of the capsule material itself may control release (matrix controlled release) or a membrane may be added to the capsule for controlling release (membrane controlled release). The similarities of these two techniques permit them to be discussed together.

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Diffusion controlled processes have found such general application that considerable information is available for direct application to food products. For example, this technique of controlling release is similar in principle to the pervaporation technique. In pervaporation, a liquid (e.g. a waste stream from a strawberry processing operation) is in contact with one side of a membrane and the other side is open to the air. The membrane acts to control the diffusion of substances (e.g. strawberry aroma constituents) across the membrane to effect a separation. The strawberry aroma may be collected on the vapor side of the membrane while the bulk of the water remains on the liquid side of the membrane. Considerable information is also available from the fragrance, deodorant (personal hygiene or room applications), pheromone and insect repellant areas of application. The most directly applicable information comes from the fragrance field where a uniform release of fragrance components is desired without any fractionation which could change the aroma (13).

Diffusion is controlled by the solubility of a component in the matrix (this establishes a concentration in the matrix for driving diffusion) and the permeability of the component through the matrix. It should be obvious that if the food component is not soluble in the matrix it will not enter the matrix to diffuse through irrespective of the pore size of the matrix. This generalization must be tempered with the recognition that the true driving force for diffusion is the activity or chemical potential as related to be the vapor pressure of the volatile substance on each side of the membrane. Solubility in the matrix will play a lesser role in determining release in this case.

The problem of uniformly releasing the aroma of an encapsulated flavor into the headspace of a food package as a balanced characteristic food aroma has been discussed by Lee (13). Table IV demonstrates this problem by demonstrating how vastly different the relative volatilities may be for various compoounds. While any given flavor is not likely to contain these particular aroma constituents, it is likely that such a range in volatility of the aroma constituents exist in many flavors. One can readily appreciate how vastly different the driving forces (vapor pressures) and resistances to diffusion (including solubility, molecular size and shape) are for the various components of an encapsulated aroma and thus, how aromas could become imbalanced as the constituents diffuse through the capsule.

Table IV. Relative Volatilites of Selected Flavor and Fragrance Materials

Compound	bp °C	Activity Coefficient	Vapor Prssure (mm Hg)	Relative Volatility
Octanol	194.5	11,000	0.18	85
Hept-2-one	151.5	1,600	4.80	330
Hexanal	131.0	1,000	12.00	500
Nonanal	191.0	71,000	0.84	2700
Methyl Acetate	57.5	24	170.00	240

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Although the physical and chemical properties of volatile compounds are governed by their structures and can not be changed, one can work with the matrix (or membrane) as well as the formulation of the flavor itself if the flavor is a compounded flavor. By choosing a capsule matrix (or membrane) with limited selectivity (may in fact be selective to discriminate against vapor pressure differences) and the desired flux rate (to release slowly or quickly but uniformly), flavor imbalances may be minimized. Additionally, if the flavor is a formulated flavor there may be some opportunity to chose flavor compounds which will have similar release rates. For example, one may choose to use a benzyl ester instead of an ethyl ester to create a given flavor note. While the two compounds have a quite similar flavor character, the benzyl ester would be of similar molecular size, volatility, etc. as the majority of other flavor compounds used in the flavor formulation. Thus, the benzyl ester would likely be released from the flavor system at a similar rate as other flavor compounds. The ethyl ester is a small molecule and would be very rapidly released resulting in an imbalanced aroma.

In terms of the ability of a membrane to control the release properties of an aroma, an example from the patent literature demonstrates this effectively (14). The top plot of Figure 1 shows the release of three fractions of an essential oil (fractionated by boiling point group) when the oil is simply open to the air. As one would anticipate, the most volatile components are lost most quickly and the oil would change in sensory properties as a function of time. If the proper membrane is put over the oil as a barrier to diffusion, the profile changes and all three fractions can be released uniformly. The membrane used in this example is composed of a water insoluble polyvinyl alcohol.

Membrane permeability is influenced by the permeating molecules (discussed earlier) and the chemical nature of the membrane, its morphology and its glass transition temperature (these parameters will be discussed later in the specific context of food systems). In many non-food applications there is considerable variety in membranes available and there are also data bases available to knowledgeably chose one of these membranes (e.g. 15). Unfortunately in food applications, there is a very limited selection of encapsulating materials available for use since we are limited to materials approved for food applications at the required usage level. Secondly, There are few data bases available to guide the food scientist in the selection of an encapsulating material.

The area of polymer science with regard to diffusion and rheology has only recently been applied to food systems (16, 17). This does not mean that relevant work was not conducted prior to the work by Slade and Levine, for much of the work done in the 60's and 70's on flavor retention during drying and subsequent storage is relevant to this topic (e.g. 1, 18, 19, 20, 21, 22). The limitation comes in having the required information on all of the flavor compounds of interest (and often even knowing what flavor compounds are of interest - for example in natural products such as coffee or chocolate) in the food systems of relevance. Most of the work in the literature was not directed towards gathering this type of information but was aimed at studying certain basic phenomena with selected molecular probes (e.g. normal, iso- and tertiary butanol for studying diffusion). There has been no general effort to collect diffusion data on a host of molecules associated with food flavor and, thus, there are no complete data bases available for food systems.

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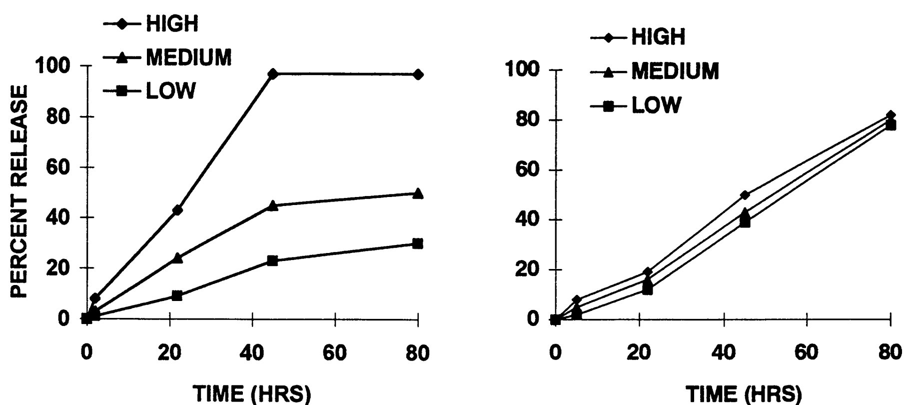

Figure 1. The loss of fractions of essential oil when allowed to freely evaporate from a cup (right) vs losses when a selective membrane covers the cup (left) (13).

Despite this limitation, we have a great deal of information on the basic properties of flavor compounds relevant to diffusion (vapor pressures, size and shape) and we are collecting data on the food (or encapsulation) matrices (refer to chapter in this text by Whorton and Reineccius; 17, 20, 23, 24, 25, 26). The physical state of the food polymer has a considerable role in influencing diffusion and thus release as is discussed by Whorton in another chapter of this text and by the authors cited above. Matrices in the amorphous glass structure are considered quite impermeable to diffusion while matrices in the rubbery state are more amenable to diffusion of solutes. Thus the glass/rubber transition of a matrix material is a relevant consideration in evaluating release properties. The proportion of crystalline material in a matrix is also relevant. It is generally stated that crystalline areas in polymers represent barriers to diffusion while the amorphous regions may support diffusion (12, 13). In foods, crystallization of the matrix may be a progressive phenomenon initially creating barriers to diffusion but later becoming so extensive that crystallization forces the encapsulated material from the matrix and rapid release results. Thus, one needs to know a great deal about the glass transition and crystallization properties of a matrix to anticipate its performance in a controlled release application.

Other factors which will influence the diffusion of a food ingredient through an encapsulating material are degree of swelling and cross-linking. Plasticization with water increases both the intramolecular free volume and the extramolecular pore space. Swelling may be caused by water adsorption (water activity of the matrix) or the presence of other matrix solvents (e.g. propylene glycol or glycerin). The importance of swelling and crystallization on diffusion is discussed in greater detail by Whorton in another chapter of this text, by Karel and Buera (27) and Karmas and Karel (28). The effect is as one would anticipate in that greater swelling of the matrix provides larger pores and greater free volume to facilitate diffusion. Thus increasing the water activity or including plasticizing agents in the matrix of an encapsulant would increase the release rate of core material. This is largely true until the moisture level reaches a point at which a matrix might crystallize (if the matrix will crystallize).

Crosslinking of a matrix has little meaning in most food applications. This is because very few situations exist where the matrix can be crosslinked considering the limitations imposed by having food approved materials. There are many crosslinking reagents available in the chemistry laboratory (e.g. formaldehyde or divinylbenzene) which may function to crosslink proteins or starches but these materials are not approved for food use. However, the last Maillard Symposium provided some interesting information in this respect (29) and it would be of interest to determine if sufficient crosslinking of proteins occurs due to Maillard reactions to influence the diffusion of solutes in heated protein-based encapsulation matrices.

In addition to the crosslinking which may be accomplished due to the Maillard reaction, one of the few applications where we can accomplish crosslinking of food ingredients is in encapsulation via coacervation. The FDA has approved glutaraldehyde as a food processing material for the crosslinking of gelatin in the making of coacervates of flavors. As Thies (3) has noted in his discussion of coacervation, glutaraldehyde can be used to harden (crosslink) the walls of coacervates. Thus crosslinking of capsules is possible and controllable in coacervation processes (3). It is reasonable that the greater the degree of crosslinking the lesser the rate of diffusion through the matrix (hence, a readily controllable process of making

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a controlled release capsule). When one thinks of the possible applications of coacervation as a means of encapsulating food ingredients, its advantage of controlled crosslinking (release) comes to mind. Coacervation appears well suited to situations where an insoluble particle is acceptable and controlled release is a major consideration. Applications might include controlled release of aroma into the headspace of bulk containers of dry beverage mixes or perhaps chewing gums. Unfortunately, there is little or no information in the food literature on the use of coacervation for these purposes. The use of coacervates for these applications should be evaluated.

Pressure-activated release. A number of controlled release systems prepared primarily by coacervation technology depend on pressure for release of the active core (30). The largest volume of product prepared using this method is carbonless paper. An ink system is encapsulated in a dense but fragile wall material which is crushed when compressed by a writing object (e.g. pencil or pen). The ink system may be comprised of two different components which are encapsulated separately, mixed and uniformly coated onto the paper. The individual parts of the ink system are clear so that the paper itself is not black but remains white. When the capsules are crushed and the ink components are mixed, a color reaction will develop which gives a dark impression.

A second application of this technology is the "scratch and sniff" products used for the advertising of perfumes or the delivery of samples of aromas for other purposes (e.g. flavor samples). The needs in this application are different from those associated with diffusion controlled release discussed earlier in this chapter. While in both situations we are concerned with the controlled release of volatile materials, we do not want a slow release over time (e.g. an air fresher in a car or an aroma in a dry product), but we desire a completely impermeable capsule which releases only on rupture. Slow diffusion from the capsule is, in fact, a detriment rather than an attribute. The wide spread inclusion of scratch and sniff perfume samples in magazines is found to be offensive to many people because the capsules leak aroma and are often found objectionable.

There are only a limited number of applications for this technology in the food industry which come to mind. The requirements that the capsules survive the rigors of food processing and yet must be released on mastication are at odds. One might think of chewing gum as an application. Yet the process of making chewing gum puts considerable physical stress on all ingredients. It is unlikely that the capsule would hold up to this processing and yet be released upon chewing. The same might be said for the flavoring of hard candies.

There may be more uses for the inclusion of rupturable encapsulated aromas in food packaging applications than in direct food contact. Very often one wishes to deliver an aroma with the food but the aroma does not have to actually be a part of the food. For example, coating the sealing surface of a jar lid with rupturable aroma may be a way to deliver an aroma each time the consumer opens a jar of product.

This technique is the focus of a patent by Parliment et al. (31) who have developed a means of forming flavor in an encapsulated system which is applied to the surface of a package used for microwave applications. When the food and its package are put into a microwave oven, the coating on the package heats and liberates

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the appropriate cooking aroma to the oven. The consumer receives the aromas of cooking typically absent during the microwave cooking process.

Delivering the aroma separately from the food may also circumvent issues of food additives, because the encapsulated aroma would not be in contact with the food, or issues related to standards of identity for products where the composition of the food is fixed by law and can not be changed (e.g. instant coffee). However, there are potential legal problems with this approach since the FDA may view the process deceptive under FFDCA Section 402 (b)(4). If the food is presented as having an aroma (or quality) not actually present, the food may be considered "adulterated."

A potential additional application of this technology in the food area may be to delay the delivery of an ingredient in a process. This would require that the capsule withstand the rigors of processing until some step where the capsule would then break down and free its contents. Perhaps this could be useful in the cereal area where an initial cooking step may be sufficiently gentle to not disrupt the capsule but the extrusion step would liberate the encapsulated material.

Tearing or peeling-activated release. The application of this approach for controlled release has been most extensive in the area of delivering fragrance or print media advertising (10). In this application, the encapsulated material (e.g. fragrance) is sandwiched between two layers of paper or polymer. When the layers are separated, they literally pull the capsules apart and liberate the contents.

This author is unaware of any applications of this technology in the food area at the present. Potential applications would likely be limited to food packaging materials. They might be used in applications where the package is ripped open and some aroma is released. This might create the sensation of freshness or quality to the consumer. However, the FDA may again take exception to this approach for the same reasons as noted earlier.

Solvent-activated release. This method of release might completely dissolve the capsule quickly liberating its contents or simply swell the capsule to either begin or enhance the release of active substances. The later situation is used, for example, in moisture activated deodorants (antiperspirants). The active core is not released until there is a need. It is often difficult to separate this release mechanism from diffusion controlled mechanisms (as was noted earlier), since the solvent (often water) may act to erode or swell the encapsulant barrier to permit release (increase diffusion). The distinction between the two mechanisms is not clear-cut particularly in the case of some of the chewing gum technology which is to be discussed hereunder.

Solvent activated or controlled release is by far the most common controlled release mechanism used in the food industry. The largest volume of encapsulating matrices used in the industry are water soluble and dissolve when in the presence of water. One can think of a host of dry food products on the market which contain added flavorings. Flavorings are generally based on volatile liquid chemicals which must be converted to some dry form to permit their use in dry foods. Flavor release occurs as a burst when the product is rehydrated for home preparation. For the most part, a burst of flavor is either required (e.g. dry beverage) or acceptable (e.g. dry cake mix) and there is no problem with this release pattern. However, in some applications (most notably chewing gums), it is desirable to release the flavoring

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gradually over an extended time period (23). This task is complicated by the requirement to release the sweetening system (e.g. aspartame or acesulfame k), acidulants (e.g. citric aid) and the volatile flavoring uniformly at the desired rates. Maintaining a slow release of any two without the other does not result in an acceptable flavor profile.

The unique need of the chewing gum industry has spawned more patent activity than any other area of encapsulation in the food industry (and perhaps as much as all other applications combined). Since this application of encapsulation is reviewed by Risch in another chapter of this text, the discussion here will be minimal. There are numerous encapsulation approaches used in the chewing gum industry to accomplish the desired flavor/acidulant/sweetening system (Table V). As noted in Table V, each of these techniques gives unique properties to the encapsulated matrix. Some of these techniques (e.g. hydrophobic elastomer or resin coating) are relatively simple and involve dispersing the active ingredient (e.g. sweetener) in a molten mass of elastomer (e.g. polyvinyl acetate), allowing it to cool and grinding it to the desired size (32). Handling a hydrophobic matrix in this manner eliminates the need to use nonaqueous solvents in processing environments. Hydrophobic coatings can also be applied by spray congealing or fluidized bed techniques (23).

While many techniques have appeared in the literature for the controlled release of flavorings (aroma or taste substances) in gum systems (23, 33, 34, 35, 36), a common approach is to apply a secondary coating to a spray dried flavoring. Spray drying is used as an initial encapsulation technique for many flavors and ingredients since it will efficiently provide a barrier to oxygen (provide shelf-life) and provide a structure for the application of a controlled release material. One has to appreciate the fact that to lessen the release of flavoring in chewing gum, a water insoluble material must be applied to the flavoring (a polymer or a meltable material). Water insoluble encapsulating materials which require a solvent are difficult to handle in bulk For example, one does not want to use large quantities of alcohol in processing due to tax considerations and flammability. Water is a good solvent (cheap, non-toxic and non-flammable) to use in processing and thus is preferred for handling large quantities of material. Thus, one can use spray drying to make an initial capsule and then apply a thin coating of a water insoluble material (waxes, gums, or edible shellacs) to control water solubility.

The desired release properties may be accomplished using secondary coating of spray dried materials, but there are limitations to this technique. One problem is that the flavoring is no longer full strength but is diluted to 20-30% of the capsule weight by the spray drying encapsulation matrix. The flavor is further diluted by the secondary coating which may be up to an additional 50% of the capsule weight. Therefore, one is now using a flavoring that is as little as 10% active material and a lot of carrier matrix. Due to the high flavoring requirements of chewing gums (up to 1%), one has to use up to 10% encapsulated flavoring. This high level of flavoring creates a problem with gum rheology both because of water binding by the encapsulated flavor and the flavoring, which normally functions as a plasticizer of the gum, is no longer able to serve this function. Rheological problems are addressed by adding additional plasticizers to the gum to replace the flavor, however, the texture may still be somewhat different from a gum made without encapsulated flavor.

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Table 5. Encapsulation technologies applied in the chewing gum industry (23)

ATTRIBUTE			PROCESS			
Sweetener	**Spray Congealing**	**Elastomer Extrusion**	**Spray Drying**	**Fluidized Bed**	**Coacervation**	**Resin Emulsion**
Up Front		X	X			
Delayed	X	X		X		
Sustained Release		X		X		
Process Temp.		X	X	X		
Flavor						
Up Font	X		X		X	
Delayed	X			X		X
Longest Lasting					X	X
High Load					X	X
Acid						
Long Lasting	X	X		X		
Minimum Color Reaction	X	X	X	X		
Minimum Sugar Inversion	X	X	X	X		

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The sweetener system (e.g. aspartame or acesulfame k) will also have to be encapsulated for chewing gum applications. The need here may be two fold. First, aspartame is unstable in the presence of moisture and it is often encapsulated in order to prolong its shelf-life (32, 33, 34). Second, the sweetener is also encapsulated to provide controlled release. The encapsulation may be done by several techniques but they typically involve coating the dry crystals with a fatty or wax-based matrix (to limit moisture contact). The coating may be done using a fluidized bed coating process or a simple melt/congealing /particle size reduction process (23). Encapsulation needs for the acidulants are somewhat different from the flavors and sweeteners. In addition to the controlled release of the acidulants, they may need to be separated from gum constituents to minimize color reactions and the inversion of sucrose (when used). While some of the acidulants are liquids, most are solids which permits their encapsulation by processes similar to the sweeteners. Additional concerns are that the encapsulation matrix may not be stable in the acid. Due to the acidulants being solids, the processes used for their encapsulation are generally quite similar to those used for the sweeteners.

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Osmotically controlled release. In this method of release, the core of the particle will take up a solvent (most commonly water) over time and swell until the capsule bursts (10). If the encapsulated active material has a high affinity for water, internal pressures can be quite large. An example of a commercial product using this type of release is laundry bleaches. It is desirable that the bleach be released later in the washing cycle which can be accomplished by the slow buildup of osmotic pressure.

This release method likely functions to a limited extent in any food ingredient which is first encapsulated in hydrophilic carrier and then secondarily coated with a lipophilic matrix. The primary carrier is very water soluble and when placed in an aqueous environment, would slowly take up water even if coated with a lipophilic matrix. The particle would swell and either expand the surface coating or rupture it. Either action would increase the permeability of the surface coating and increase the rate of release.

pH Sensitive release. There has been a great deal of activity in the cosmetics area related to this mechanism of release (10). The patent literature has made claims of encapsulating systems which respond to pH changes of the skin (37, 38). When the pH changes, the capsule collapses expelling the core material.

One could theoretically envision some type of analogous system in the foods area where proteins serve this pH sensitive function. Protein solubility is quite strongly influenced by pH. The major problem with this approach in practice is that we do not have any proteins which will form a dense impermeable membrane in water at one pH and then suddenly become permeable at a different pH. The permeability of a protein-based microcapsule will certainly change as a function of system pH but not to the extent necessary to serve this function. Karel and Langer (1) studied enzymes encapsulated in liposomes using pH as a stimulant to initiate release (Figure 2). Karel and Langer postulated that pH changes destabilized the phospholipid-based lipsomal structure thereby releasing the enzymes from the liposome core. The use of liposomes for the controlled delivery of food ingredients is discussed separately in another chapter of this volume by Reineccius.

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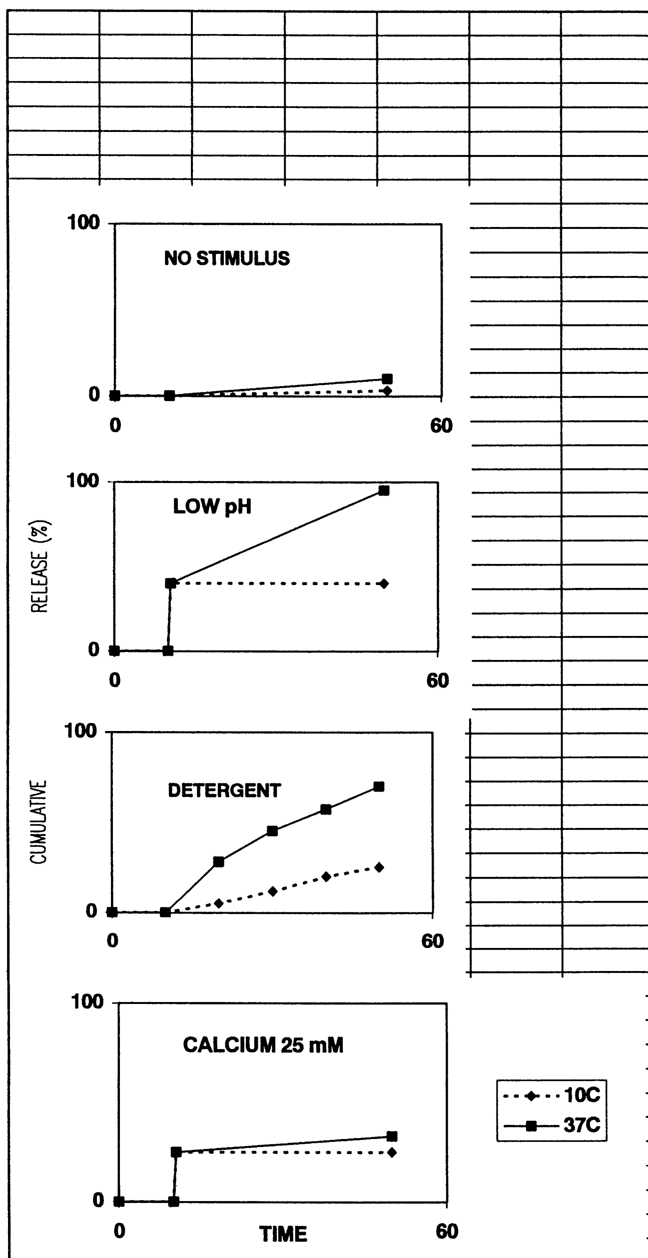

Figure 2. Patterns of enzyme release from liposomes using different stimuli (1).

Temperature sensitive release. While the following method for controlled release (ie. melting) could also be considered in this category, this technique is going to be limited to the unique ability of some materials to either collapse or expand at some critical temperature. Miles (38), Brannon-Peppas (10) and Peppas (12) have presented a discussion of polymers which have this ability at temperatures close to room temperature.

While the author is not aware of any food applications strictly based on this mechanism of release as narrowly defined above, one can appreciate that temperature often plays a role in the release of food ingredients through its effect on glass/rubber transitions, and degradation or solubilization of polymer coatings. As we better understand the factors that cause a complex food matrix (or encapsulation matrix) to change state (referring to glass/rubber transitions), we will likely be able to tailor-make an encapsulation matrix which will change state at the desired temperature and start to release the active material at the desired temperature.

Melting-activated release. This mechanism of release involves the melting of the capsule wall (or a coating placed on the capsule wall) to release the active material. This type of release is readily accomplished in the food industry through the use of prilling (spray chilling), two fluid nozzle extrusion (Southwest Research Center, San Antonio, Tx; 39) or secondary coating techniques. Spray chilling techniques of capsule formation simply involve dispersing the active material in a molten wall material and then spraying this mass into a cold spray drying tower or coating it on a chilled drum dryer (40). The wall material hardens as it falls through the spray drying chamber or cools on the drum surface. Two fluid processes involve a two fluid nozzle where the active material is passed through the inner part of the nozzle while the wall material is passed through the outer part of the nozzle (the driving force for extrusion may be pressure or centrifugal forces). The stream of materials break into droplets with the wall material enclosing the core. The outer wall material solidifies before it falls to a collection system. Secondary coating techniques for making melt release capsules involve coating an already encapsulated material with a meltable wall material. This may be done using any number of fluidized bed systems or a centrifugal coating system (refer to chapter by Sparks in this text). All of these systems are based on applying a meltable coating to an active core. One can readily appreciate that each of these techniques will provide very different capsules and thus properties.

This method of release is readily accomplished in the food industry since there are numerous meltable materials which are approved for food use (lipids, modified lipids or waxes). One can appreciate the numerous applications of this release mechanism since many foods are heating prior to consumption and thus, an ingredient can be protected until its final use. It is of interest that meltable coatings (lipophilic materials) are often used in the controlled release of gum flavorings not to use the lipophilic material to accomplish a meltable release mechanism but to limit or control release in an aqueous environment (36). Food applications in general include the release of encapsulated salt, nutrients, leavening and flavorings (refer to chapter in this text by Risch).

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The problems related to this methodology are varied. The two fluid extrusion coating techniques have limitations in that the wall and coating must be immiscible. This limits the technique for many flavor applications. Flavors tend to be lipophilic and will readily migrate right through the wall material. Therefore, this technology is most useful for encapsulating a few water soluble flavorings. The spray chilling processes have similar limitations for flavor applications. However, these two processes have application for coating crystalline solids (e.g. high intensity sweeteners, nutrients and salt).

It is of interest that some food ingredients are encapsulated simply to improve handling properties. This is true of the antioxidant BHT which has been coated with methyl cellulose (41). BHT has low melting point and it will readily form a sticky mass during storage making its use difficult. The methyl cellulose will dissolve in fatty materials releasing the BHT which then assumes its role as antioxidant.

The coating of already encapsulated materials (e.g. flavorings produced by spray drying) can be accomplished using the centrifugal coating technique of Sparks (refer to chapter by Sparks in this text) or any fluidized bed method (as mentioned above). The major problem in this approach is the dilution of the flavoring by additional wall material and the additional cost. One must recognize that the food industry is typically a large volume, low cost and low profit industry. A few cents additional cost per pound of product may add up to large dollar amounts at the end of the year. The industry tends to avoid these additional costs whenever possible.

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Hybrid systems. Brannon-Peppas (10) has included this last category to note that combinations of release mechanisms may be used to provide unique release properties. We also find this possible in the food industry although this may be less common due to cost constraints imposed by the food industry. An example, however, is the secondary coating of flavorings to provide melt release properties (40). Once the capsule outer coating has melted, the capsule itself must also be degraded (e.g. by dissolution in saliva or water) to release the active core materials.

Miscellaneous systems. Karel and Langer (1) have included some additional specific means of controlled release (Table III). The release mechanisms included are applicable to the release of liposome encapsulated materials in general but applied specifically to enzyme release in Figure 2. In particular, pH has been noted to have a significant effect on liposome structural stability. For example, the influence of salts (e.g. Ca^{++} or Mg^{++}) on release was less than observed for a pH change. This effect was related to the disruption of the charge on the liposome structure. Increasing temperature increased the release rate of enzymes. Increasing temperature would potentially change the phase of the liposome membrane from a rigid gel to a liquid membrane which is more porous. Detergent (Triton X-100) had a large effect on the release of enzymes as detergents can effectively disperse the liposome membranes.

Conclusions

One can not help but be a little envious of some of the other fields using microencapsulation for the controlled release of active materials. Numerous

technologies and different capsule wall materials are available to them for capsule manufacture which can yield a host of tailor-made products to meet the needs of a given application. Unfortunately, the food industry has a large number of potential applications for controlled release technology which currently are not being met. A lack of safe and edible materials and associated technologies as well as cost considerations severely limit the availability of controlled release in the food industry. New technologies are needed. Perhaps coacervation techniques will be developed to fill some of these needs. The control of the capsule properties attained by coacervation methods are quite attractive for some food applications.

The understanding of food polymer glass/rubber transitions as well as other theoretical studies may also contribute to a better usage of traditional technologies. Blends of materials (e.g. selected starches and sugars) may be knowledgeably chosen to provide certain release properties. The work reported by Karel and Langer (1) is rather provocative. The level of sophistication is well beyond what is normally employed in the food industry. It will be of interest to observe how well this basic research can be transferred from the laboratory to the food industry. Some discussion of this potential is included in the chapter of this book by Reineccius dealing with liposomes.

The whole area of developing encapsulation matrices which have limited water solubility and technology for their application to food ingredients is of great need. The food industry has many needs in the area of controlled release still awaiting solution.

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Chapter 3

Encapsulation of Food Ingredients

A Review of Available Technology, Focusing on Hydrocolloids

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The encapsulation of food ingredients is usually accomplished with either lipids or hydrophilic polymers. A plethora of techniques have been used, including spraying, extrusion, entrapment, phase separation, crystallization, and polymerization. Each of these techniques may be used to encapsulate food ingredients, i.e., a thin coating surrounds particles of the food ingredient, or to entrap the food particles in a matrix. Application examples illustrating these methods are presented, both for direct encapsulation of food ingredients and 'indirect' encapsulation of precursors. Hydrocolloids as encapsulating agents are emphasized.

At the outset, a discussion of 'encapsulation' calls for a definition of terms. In the title of this paper, the term is used in its broadest sense so that no commonly used or potentially useful technology need be excluded. In subsequent discussions, however, a distinction will be made between encapsulation and entrapment.

Definitions. Encapsulation may be defined as the process of forming a continuous, thin coating around encapsulants (solid particles, droplets of liquids, or gas cells), which are wholly contained within the capsule wall as a core of encapsulated material. On the other hand, entrapment refers to the trapping of encapsulants within or throughout a matrix (e.g., a gel, crystal, etc.). A small percentage of entrapped ingredients will normally be exposed at the particle surface, while this would not be true of encapsulated ingredients.

The size of particles formed by either encapsulation or entrapment may be classified as: Macro -(> 5000μ), Micro - (0.2 - 5000μ), and Nano - (< 0.2μ or 2000 Å) (*1,2*).

Nomenclature. The problem of naming microcapsules was tackled by Arshady (*3*), who proposed a nomenclature system to provide short descriptive names which reference either microcapsule 'core', 'wall', or 'both core and wall', as desired. He proposed three rules.

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1. Naming microcapsule after its core for general usage: Name of core + microcapsule. Example: carboquone microcapsule.
2. Naming microcapsule after its polymer wall when a knowledge of the polymer wall is more appropriate than the core substance. *Abbreviated* name of polymer + microcapsule. Example: GEL microcapsule (GEL = gelatin).
3. Naming microcapsule after both its core and wall, when a knowledge of both core and wall is desirable. Name of core - *abbreviated* name of polymer + microcapsule. Example: carboquone-GEL microcapsule.

Obviously this system requires standardized abbreviations, so Arshady provided a table of commonly used polymers with appropriate abbreviations.

Reviews of Food Encapsulation

Several good reviews of food encapsulation techniques have been published. In 1971, Balassa and Fanger (*4*) reviewed spray drying, freezing, dehydration, chilling, and coating in fluidized beds; spraying on a hydrophobic powder, spraying on a moving oil surface, aqueous phase separation (coacervation), and organic phase separation. Several illustrations of each technique as well as general schematics on capsule configuration were presented, with advantages and disadvantages for each technique and examples of foods encapsulated. 48 patents and 17 articles were cited.

Bakan (*5*) published a 1973 technical review of coacervation, complete with phase diagrams and instructions on how to use the process to encapsulate food ingredients.

In 1988 Dziezak (*6*) reviewed early developments in the technology and commercial techniques being used or evaluated (including spray drying, air suspension coating, extrusion, spray cooling and chilling, centrifugal extrusion, rotational suspension separation, coacervation and inclusion complexing). Important criteria to consider, lists of commercially available encapsulated ingredient types and how to use them, and lists of suppliers of encapsulated ingredients and custom encapsulation services were provided with 28 references.

A comprehensive review of commercially significant flavor encapsulation processes was published by Reineccius in 1989 (*7*). He stated that the two major processes are spray drying and extrusion. The review is heavy on spray drying, complete with graphs of encapsulation efficiency and effects of various parameters. "Extrusion" was defined as "a flavor emulsion forced through a die, with pressures of typically < 100 psi and temperatures seldom > 115°C." Reineccius also briefly reviewed cyclodextrins (molecular inclusion), coacervation, and fat encapsulation, providing 74 references.

In 1991 Jackson and Lee (*8*) published a review article covering the properties of microcapsules in general. They considered specific uses by ingredient/system or food type for acids, lipids, enzymes, micro-organisms, flavors, artificial sweeteners, gases, vitamins and minerals. Microencapsulation techniques were covered under the headings of, spray drying, spray chilling and spray cooling, extrusion, air suspension coating, multi-orifice centrifugal extrusion, coacervation/phase separations, liposome entrapment, inclusion complexation, co-crystallization, and interfacial polymerization. They emphasized liposomes, especially for cheese applications, giving 74 references.

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Kirby (*9*) also emphasized liposomes in a 1991 review. He proposed the use of encapsulation to increase the effectiveness and range of applications of many types of functional ingredients, especially the more 'natural' ingredients, as opposed to 'chemical' ones.

Kim et al. (*10*) produced another review of liposomes technology. They listed typical applications for microencapsulation in food technology and typical classes of materials microencapsulated. Spray drying, molecular inclusion, and extrusion were also briefly covered.

Classification of Encapsulation Technology

Although, as the above mentioned reviews suggest, there are various ways to classify encapsulation technology, this paper will do so by reference to the encapsulating or entrapping materials used. In other words, the 'core' materials to be treated are 'modified' with one or more of the following: fats and/or emulsifiers, low molecular weight sugars (co-crystallization), or polymers (including polysaccharides (gums), proteins and synthetic polymers). The type of process used, whether spraying techniques, extrusion, crystallization, etc., depends largely on the properties of the encapsulating or entrapping material, as well as requirements or limitations of the food ingredient being treated.

Fats and/or Emulsifiers. Since the use of hydrocolloids is our main emphasis, their capabilities will be our primary focus. Under the category of fats and/or emulsifiers, however, there is an interesting process that may become useful in the future. Phospholipids, such as various types of lecithins, spontaneously form spherical vesicles called liposomes. These are structures composed of a lipid bilayer that encloses an aqueous volume (i.e., encapsulation). Liposomes, investigated quite extensively for encapsulating drugs for medical research and treatment, are now also being explored for food systems (*8,10*).

In efforts to enhance the stability and control permeability of these structures, phospholipids recently were polymerized. Hollow, tubule-shaped microstructures were fabricated by self-organization of polymerizable diacetylenic phospholipid molecules. The polymerization produced tubules between 0.3 - 1μ in diameter, and ranging in length from a few to hundreds of micrometers (*11*). The tubules looked like miniature paper straws under scanning electron micrography (SEM), and acted as capillaries, taking up liquids in which they were placed. Since the tubule ends remain open, unless covered by some other means, this must be classified as an inclusion or entrapment method, similar to that of cyclodextrins. Although in relatively early stages of development and lacking food approval, this new technology should be considered for future novel applications.

Low Molecular Weight Sugars. Two additional entrapment methods are inclusion complexation with β-cyclodextrins, covered in other symposium papers, and co-crystallization with sucrose. The co-crystallization process involves concentration of a sucrose syrup to the point of supersaturation, addition of the material to be encapsulated, and mixing to induce nucleation and agglomeration. A drying step is usually needed to adjust the final moisture content (*12*).

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Polymers. The list of hydrocolloids used for encapsulation is quite extensive. Hydrocolloids may be grossly categorized into 'synthetic' and 'natural' polymers (*13*).

Synthetic polymers. Lactide/glycolide, poly(alkyl α-cyanoacrylate) and polyacrylamide polymers, have been used extensively to prepare microspheres for medical applications. Theis and Bissery (*13*) reviewed these polymers and their uses for biodegradable microspheres for parenteral administration. Polymers of this classification are beyond the scope of this paper, since they are not food approved.

Natural Polymers. The list of natural polymers used, or potentially useful for encapsulation, includes; starch derivatives, maltodextrins, cellulosics, gum arabic, agar, carrageenans, alginates, chitosan, low methoxyl(LM) pectin, gellan gum, and gelatin.

Although not addressing encapsulation per se, Roller and Dea (*14*) covered most of these hydrocolloids in their review. They reviewed the various polysaccharides used in foods (citing 95 references), including market size information and summaries of the functions each one provides to food formulations. They especially noted how polysaccharides are currently modified through biotechnology, and speculated about future modifications leading toward the eventuality of "designer polysaccharides".

All the above listed hydrocolloids are charged polymers, with the exception of starch derivatives, maltodextrins, and the cellulosics (excepting carboxymethyl cellulose (CMC), which is the only anionic cellulosic).

Charged polymers are good candidates for coacervation reactions. Most of them will form gels under specific conditions, which also qualifies them as encapsulation or entrapment materials.

Natural Polymer Properties. A brief review of the properties that make these polymers useful for encapsulation-entrapment applications follows.

1. Starch derivatives and maltodextrins are mainly used for their low viscosity, film forming, and emulsifying characteristics (*7*), which permit their use at high concentrations in the emulsions to be sprayed, facilitate atomization, and produce uniform coating of the dried particles.
2. Gum arabic is also used extensively for spray drying applications (*7*) like starch derivatives, and possesses excellent emulsification properties. Additionally, gum arabic is anionic and can react with other polymers to form coacervates.
3. Cellulosics, except for CMC, are all uncharged, ether derivatives of cellulose with surface active properties. All of these derivatives possess good film forming characteristics, and therefore function well to spray coat particles (via fluidized bed or pan coating, for example). They are non-gelling polysaccharides, with the exception of methylcellulose, which forms gels when solutions are heated above 45°C (they melt when cooled back to room temperature)(*15*).
4. Agar is one of the strongest gelling polysaccharides known, being able to form perceptible gels at concentrations as low as 0.04%, without the aid of salts. Gels set at about 35°C by cooling hot agar solutions, and don't remelt until reheated to > 90°C (*16*).

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5. Chitosan is deacetylated chitin, the very insoluble polymer found in crustacea shells. Chitin is a polymer of N-acetyl glucosamine, or N-acetyl-2-aminocellulose, so chitosan is essentially 2-aminocellulose (*17*). Although not yet approved for human consumption, it is approved for animal feeds and is the only positively charged (under acidic conditions) polysaccharide available, making it a useful candidate for coacervation reactions.
6. Gelatin, though a protein, is also useful as a thermally reversible gelling agent for encapsulations of various types, including macro-encapsulations. Because of its amphoteric nature, it also is an excellent candidate for coacervation.
7. Carrageenans, alginates, LM pectin, and gellan gum, are anionic hydrocolloids which form ion-mediated gels. Consequently, these polymer solutions may be added to salt solutions and form gels upon contact (diffusion setting), gel on cooling after addition of the respective salts to their hot solutions, or, under proper conditions, may gradually gel after the addition of slowly soluble salts to their respective polymer solutions (internal setting).

   κ-Carrageenan, the most common form, reacts with potassium ions to form thermally reversible gels; ι-carrageenan forms gels most readily with calcium ions; and λ-carrageenan does not form gels.

   Alginate salts, especially sodium and potassium alginates, react with calcium ions to produce thermally stable gels.

   LM Pectins also react with calcium ions, much like alginates, so many of the things true of alginates will also be applicable to LM pectins.

   Gellan gum, the newest of the food approved hydrocolloids, will gel with all of the aforementioned ions, both monovalent and divalent, although divalent ions are more efficient (*18*). Since gellan gum is so new, not much has been done with it for encapsulation applications. As with LM pectin, however, much of what is said for alginates could also apply to this hydrocolloid.

Capsule Formation Methods with Natural Polymers

Two major classes of capsule formation methods will now be considered: formation by drying techniques and by liquid techniques.

Drying Techniques. The major encapsulating agents used for spray drying applications are gum arabic, modified starches, and hydrolyzed starches (maltodextrins). They all have the requisite low viscosity at high concentrations, but maltodextrins do not possess emulsifying properties so are normally combined with the other two materials, which are excellent emulsifiers (*7*).

Imagi et al. (*19*) developed a laboratory method to measure the efficiency of encapsulation by drying. One droplet of an emulsified sample was dried and then analyzed for the amount of lipid exposed at the surface. Using this method, Imagi et al. (*20*) evaluated several encapsulating agents, singly and in combinations. Either gum arabic or gelatin effected complete encapsulation of the lipid, while maltodextrin was ineffective, even with added emulsifiers. Efficient viscosifiers, like xanthan gum, were very effective encapsulating agents when used in combination with emulsifiers. These results suggested that effective entrapping agents of liquid lipids

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were ones which emulsified well, stabilized the emulsion (i.e., they caused the continuous phase to be very viscous), and created a dehydrated matrix of fine, dense network layers. In actual practice, high viscosity hydrocolloids do not usually work well for spray drying applications, unless they are used at low levels to maintain emulsion stability, but not as a primary coating material.

Kirn and Connaughton (*21*), successfully used gum arabic and gum arabic/modified starch to encapsulate oleoresin capsicum (ORC) via spray drying. This process protected against oil bath contamination by the ORC and permitted its application (as a spice) on chicken before frying.

Schobel used the good film forming characteristics of ethylcellulose, a plasticizer, and an "enteric" composition (an acrylic polymer, soluble at pH $\geq$ 5.5) to spray coat (fluidized bed drying) flavors or fragrances. This treatment was effective in controlling the release of flavor for such products as chewing gum (*22*).

Liquid Techniques There are three main ways to form microcapsules in liquids: phase separation (coacervation), emulsion encapsulation, and extrusion into a setting bath.

Phase Separation (Coacervation). As a batch-type process, coacervation generally involves three steps, which are carried out under continuous agitation: **formation** of three immiscible phases (a coating material phase, a core material phase, and a liquid manufacturing vehicle phase); **deposition** of a liquid polymer coating around the core material; and **solidification** of the coating (*5*). This process forms truly encapsulated material, and may be illustrated with the following example. The amphoteric hydrocolloid gelatin works well to form complex coacervates with anionic polysaccharides like gellan gum. These hydrocolloids are miscible at pH > 6, since they both carry net negative charges and repel one another. However, when the pH is adjusted below gelatin's isoelectric point (ca. 5), the net charge on the gelatin becomes positive, causing an interaction with the negatively charged gellan gum. An oil may be encapsulated with this system by making an emulsion with about 40% oil and a hot solution of high bloom strength gelatin (ca. 10% gelatin). The hot gelatin/oil emulsion is then added to two parts of a hot 1% gellan gum solution and mixed slowly, while diluting the mixture with about 1/2 part of hot, deionized water. The pH of the system must be > 5. As the pH is gradually lowered to 4.5, microcapsules form from coacervate material (positively charged gelatin and negatively charged gellan gum) depositing around the oil droplets. Wall material continues to build up as the system is slowly agitated and cooled. After sufficient wall formation, cross-linking with an aldehyde (glutaraldehyde, for example) is normally required to produce greater wall integrity (*23*).

Other systems used the positively charged chitosan to react with the anionic hydrocolloids, algin or carrageenan. Both alginates and carrageenans maintain negative charges under acidic conditions. Knorr et al. (*24*) used both chitosan/algin and chitosan/carrageenan coacervates to grow plant tissue cultures, which offer the potential of producing "naturally derived food ingredients", such as flavors and colors. "The concept of cellular totipotency suggests that living cells are independent individuals and (would be) capable of developing when separated from the organism if provided with the external conditions under which they exist in the organism."

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These conditions were approached by their coacervation experiments. Knorr, et al.'s results showed that chitosan/algin and chitosan/carrageenan coacervates produced higher cell viability, compared to encapsulates using algin, carrageenan, or chitosan individually. Chitosan/κ-carrageenan coacervate capsules were also demonstrated to be more permeable than those from chitosan/alginate coacervates.

Emulsion encapsulation/entrapment. Although this procedure has been used extensively to form microcapsules for pharmaceutical uses, it is relatively new to the food industry. Thies & Bissery (*13*) described the basic manufacturing process. The key step is to form a water-in-oil (w/o) emulsion. The 'active' material to be encapsulated or entrapped is added to a hydrocolloid solution. A small volume (1 part) of this aqueous phase is then added to a large volume (several parts) of oil and the mixture is homogenized to form the emulsion. Once the w/o emulsion is formed, the water-soluble polymer must be insolubilized (cross-linked) to form tiny gels within the oil phase. The smaller the internal phase particle size of the emulsion, the smaller the final microparticles will be. The insolubilization method of choice will depend on the hydrocolloid being used. Many applications of this technique use alginates and are contained in the patent literature.

Lencki (*25*) disclosed a method for producing alginate microspheres by diffusion setting. Insoluble calcium citrate was added to the algin solution, along with a core material to be entrapped. The algin suspension was subsequently added to 3 - 5 parts of vegetable oil, under agitation, to form an o/w emulsion. An organic acid (acetic, lactic, or citric), soluble in the oil phase, was then added to the system to gel the algin microspheres via diffusion setting (acid penetrates the oil, releases calcium ions at the oil/alginate interface, which cross-link the algin molecules). Lencki claimed that beads of 50 - 500 μ were obtained.

Wan et al. (*26*) also used an o/w emulsion, but used organic solvents and prepared the emulsion through phase inversion to encapsulate a drug (theophylline) in spheres, mostly smaller than 150μ. They used $CaCl_2$ as the setting agent, and reported an encapsulation efficiency of 65%.

Spiers et al. (*27*) also used the emulsion technique, but cross-linked the algin by internal setting, i.e., using the slowly soluble calcium sulfate dihydrate. Consequently, no oil miscible acid was needed. They also claimed that LM pectin could be used in place of alginates and that microparticulate alginate or pectate beads so formed were useful as fat substitutes. Microbeads were incorporated in several food formulations (salad dressing, milk drinks, skimmed milk, ice cream, etc.), to illustrate their fat-like properties.

Extrusion into a Setting Bath. This is the oldest and most common liquid formation approach to making capsules with hydrocolloids. The method simply involves preparing a hydrocolloid solution, adding the 'active' ingredient (core material) to the solution, and extruding (forming droplets, 'strings' or fibers) into a setting (cross-linking) bath. This method usually produces entrapped, rather than encapsulated core material, although encapsulation can be achieved through co-extrusion devices or dropping into a bath of coating material which reacts at the droplet surface. There is a plethora of specially designed equipment to form droplets for this type of procedure, but few capable of large scale production. Dziezak (*6*) cites several examples of such equipment in her review.

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As mentioned earlier, the anionic hydrocolloids, carrageenan, algin, LM pectin, and gellan gum, may be added to salt solutions to form gels upon contact (diffusion setting). In practice, however, alginates are most often chosen for this technique.

Handjani et al. (*28*) patented a process for manufacturing capsules fragile enough to break under pressure or abrasion. The capsules were designed for use in cosmetics, but the system should easily extend to food ingredients as well. They controlled the gel strength by carefully choosing the alginate, concentration of $CaCl_2$ cross-linking bath and residence time in the bath.

Ueda (*29*) patented an interesting process for preparing edible products in the form of capsules. This process used alginate to form truly encapsulated products. A xanthan gum solution containing $CaCl_2$ was dropped into an alginate solution to form the capsules. The calcium caused gelation at droplet/alginate solution interface, and the 'beads' were removed and washed with water after a short residence time in the algin solution (ca. 2 minutes). The 'beads' were then soaked in water for 1 - 2 hrs, replacing $CaCl_2$ and any sugar with water. Subsequently, the beads were soaked in an edible liquid for about 2 hours to exchange with the water, thus filling the capsules with the desired liquid (e.g. orange, grape, apple, or vegetable juices, wine, sugar solutions, artificial sweetener, and even coffee). The 'beads' were then added to various beverages.

A similar process was disclosed by Hoashi (*30*) to encapsulate meat soup or juice. In this case calcium lactate was included in meat soup or concentrated juice, which subsequently was added drop wise to a 1% solution of sodium alginate to encapsulate the droplets. The patent claims that food products such as wonton, hamburger, sausage, and meat-filled buns benefit from these heat stable capsules of concentrated flavor which rupture during mastication, producing much greater flavor impact than unencapsulated controls. Since calcium lactate contributes little flavor, its presence in the capsules was easily tolerated.

A co-extrusion process was used by Veliky and Kalab (*31*) to encapsulate viscous, high-fat foods in calcium alginate gel tubes at ambient temperatures. Such foods as cream, egg yolk, and mayonnaise were extruded through the center tube, while a 3% alginate solution was extruded through the outer tube into a 50 mM $CaCl_2$ bath. A dual syringe (two 5 ml syringes) apparatus was designed and used to prepare samples for freeze fracturing and subsequent evaluation by SEM (scanning electron microscopy) or TEM (transmission electron microscopy). The method was developed for heat-sensitive food samples, to replace agar.

Capsule Properties

Properties such as permeability, temperature stability, mechanical stability, and stability to various ingredients (e.g., pH and salts) are critical to successful encapsulation/entrapment applications. Each hydrocolloid will offer different spectra of properties, but even within an individual polymer type, significant variations in these properties may exist. Consequently, control of critical capsule properties is very important. Because of their popularity as capsule wall materials, considerable study has focused on alginates.

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In 1977 Kierstan and Bucke (*32*) studied the immobilization of microbial cells, subcellular organelles and enzymes in calcium alginate gels. They were interested in the immobilization of various enzymes and the entrapment of yeast for ethanol production. Their enzyme encapsulation results indicated that the algin gel was easily permeable to molecular weights (M.W.s) of 3,000 - 5000. Their work with columns of alginate beads also helped to quantify the mechanical stability of the capsules.

Martinsen et al. (*33*) were able to correlate the chemical and physical properties of alginate gel beads. They investigated such physical properties as the mechanical strength, porosity, shrinkage, and stability toward monovalent cations of alginate beads formed from various types of algin (i.e., with various guluronic contents). At molecular weights (M.W.s) > 250,000, they found gel strength was independent of M.W. (intrinsic viscosity determination). Pore size of the gel network was found to range from 50 - 5000 Å. Therefore they concluded that, globular proteins with radii of gyration of ca. 30 Å and with net negative charges should be able to diffuse through the gel at rates dependent upon their sizes. High guluronic content algins produced gels with the greatest porosity.

A review of "alginate as (an) immobilization matrix for cells" was published by Smidsrød and Skjåk-Bræk (*34*) in 1990. Alginate immobilization of living or dead cells was evaluated for applications in bioreactors, plant protoplasts for micropropagation, hybridoma cells for production of monoclonal antibodies, and entrapment of animal cells for implantation of artificial organs, based on existing knowledge of structural and functional relationships in alginate gels. The review discussed various sources of algin, the porosity of gels and methods to measure it, and general algin chemistry.

In a study of three different M.W. alginates from a single kelp source, Peters et.al. (*35*) found that low viscosity (hence low M.W.) sodium alginates react with calcium ions faster than high viscosity (high M.W.) polymers, and were able to quantify the diffusion rate .

Capsule Applications with Natural Polymers

'Biologicals'. Encapsulation/entrapment of biologically active materials has been extensively investigated. Skjåk-Bræk et al. (*36*) provided tables listing nine examples of cells immobilized with agar/agarose gels, eight with carrageenan gels, and twelve with algin gels. Many of the cell encapsulates produced food ingredients such as, acids (L-aspartic, L-malic, vinegar, citric, and lactic), hydrocarbons, isomaltulose, and glutamate, while others produced biologically active materials such as insulin or antibiotics. Algin and carrageenan are the two hydrocolloids most often used for immobilizing cells (*37-40*). Various researchers differ in their opinions about the two gums, some stating that carrageenan offers optimal conditions (*41,42*), while others prefer the properties and stability of alginates (*43,44*).

Yeast. The most heavily researched area for this application is the encapsulation/entrapment of yeast, mainly for wine production. Most researchers immobilizing whole cells to reduce the acid content in wines, used *Leuconostoc oenos* with alginate (*45*) or carrageenan (*46,47*). Bonilla and Rand (*48*) used *Schizosaccharomyces Pombe* for this purpose and also compared the effectiveness of alginate and

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carrageenan as immobilizing agents. Their results showed that alginate beads performed significantly better, producing higher activity (i.e., alcohol production) and possessing 10 times better stability than carrageenan beads. Zerajic et al. (*49*) reported the immobilization of yeast cells in calcium alginate gel beads. The beads were produced with a special nozzle, designed to apply a second, cell-free alginate layer around the algin beads.

Yeast encapsulation/entrapment for wine production has actually been commercialized. In 1986 Diviès (*50*) received a patent covering "Yeast encapsulation with sodium alginate, for industrial production of sparkling wines" and later wrote a chapter on algin encapsulation for industrial production of Champagne (*51*). In late 1992 Russell et al. (*52*) mentioned that a major French champagne producer was using alginate immobilized yeast in a large-scale trial (1 million bottles).

Nagashima et al. (*53*) report that yeast encapsulated in alginate gels have been used for semi-commercial production of ethanol in Japan since 1982. An algin/yeast mixture was added to 1 - 10 kl reactors filled with 2% $CaCl_2$ to form beads in the vessels (no separate tank needed). Beads were viable for up to six months without the need for medium-sterilization and seed-fermentation steps, and the productivity of alcohol was more than 20 times higher than with conventional batch wise fermentation. Computer control of the system was also easily introduced, which all translated to significant savings of energy and labor costs. Other encapsulants were also evaluated (e.g., LM pectin, carrageenan, agar, and several synthetic polymers), but alginate was judged the best from the standpoint of alcohol production efficiency and ease of use.

Bacterial Cells. Other cells have also been beneficially 'modified' by encapsulation and/or entrapment. Sheu and Marshall (*54*) used the oil-in-water (o/w) emulsion method to microentrap *Lactobacilli* cells in calcium alginate gels, breaking the emulsion by the addition of 0.056% $CaCl_2$ to form beads of 25 - 35μ median particle size. This procedure protected the bacteria from destruction by freezing in food products like ice cream and frozen yogurt. They also studied the effects of various ingredients and processing parameters on final bead size.

Prevost and Diviès (*55*) immobilized a mixed culture of *Lactococci* in calcium alginate gel beads and used them to produce cultured dairy products. Both 'simple beads', i.e., an alginate/bacteria suspension extruded into $CaCl_2$, and two-layer beads, 'simple beads' coated with a second cell-free alginate layer, were used to inoculate cream. The immobilization process reduced the fermentation time (from 18 hrs to only 5 hrs) and the residual free-cell count in cream, which greatly improved shelf life, since souring and wheying-off were considerably delayed. The two-layer method was more efficient and significantly reduced the number of free-cells in the fermented cream, permitting greater control of the final acidity.

Enzymes. 'Natural' polymers have also been used to immobilize enzymes. De Jong et al. (*56*) utilized the emulsion encapsulation method with combinations of gelatin, starch, microcrystalline cellulose, and algin to achieve "long term antimicrobial activity obtained by sustained release of hydrogen peroxide". They used one system of gelatin and micro-crystalline cellulose, cross-linked with glutaraldehyde, to encapsulate/entrap enzymes suitable for production of hydrogen peroxide

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(up to 48 days). A second suspension of corn starch, gelatin, suitable enzymes and alginate was cross-linked with a mixture of $CaCl_2$ in ethanol and glutaraldehyde.

Fat Encapsulation/Entrapment and Fat Substitutes. Spiers et al.(*27*) disclosed "A method for preparing microparticulate alginate or pectate beads useful as fat substitutes or simply as food encapsulates". In the patent they cited US Pat# 4,911,946 as another algin fat substitute, prepared by atomizing an algin solution into $CaCl_2$ to give particles which ranged from 0.1 - 2 μ. They also cited Pat # WO91/04674, which teaches the use of "thermolabile sequestrants" to heat set algin gels, and used this technique, combined with the w/o emulsion and internal setting methods, to form microparticulates. The microbeads were subsequently incorporated in several food formulations to replace fat (for example, salad dressing, milk drinks, skimmed milk, and ice cream).

In a 1991 review entitled, "New fat replacers sourced from GRAS ingredients", Duxbury (*57*) reported that PRIMO-O-LEAN, an alginate-based product for meat, was a matrix of water, partially hydrogenated canola oil, hydrolyzed beef plasma or whey protein concentrate, tapioca flour, sodium alginate, salt, and caramel color that "looks and tastes like chopped animal fat."

Cox et al. (*58*), in a 1992 patent entitled "Saccharide/Protein Gel", claimed a simple and inexpensive method to produce artificial adipose which is lower in cholesterol and may be lower in saturated fats than the tissue it replaces. An emulsion was prepared with an albumin-containing protein (preferably blood plasma from the particular meat of interest), sodium alginate, and various types of fat. The emulsion was then gelled by extrusion into a $CaCl_2$ bath, which entrapped the fat and other ingredients. Upon subsequent heating of the product, protein coagulation further strengthened the matrix, and flavors were developed which were exactly like those associated with the meat from which the plasma was derived.

Another Cox (*59*) patent also involves entrapping lipid material. An emulsion was prepared by adding a lipid material to an alginate solution, followed by extruding the emulsion into $CaCl_2$ to produce gelled beads, or some other shape. The gels then were dried and used as animal feed additives (to enhance milk production in cattle, for example). Commercial products have been produced using technology from both of these Cox patents.

Macro-Encapsulation/entrapment. A "Whole Egg Analogue Composition and Method" was disclosed by Cox and Cox (*60*). The patent describes how to make an entire 'whole egg' analogue which can be treated like natural chicken eggs. The 'yolk' portion, containing egg whites, algin, and other optional gums, is extruded into a calcium ion bath to gel an algin membrane around the 'yolk', or, frozen yolk analogue may be dropped into an alginate solution to form an algin membrane around it.

Conclusion

As the forgoing examples illustrate, hydrocolloids, especially those of the 'natural' class, have already served as important wall materials for a variety of food encapsulation applications. It is reasonable to assume that their use will continue to grow and that in the future additional new applications will be developed.

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Chapter 4

Modified Starch, Maltodextrin, and Corn Syrup Solids as Wall Materials for Food Encapsulation

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Modified starch, maltodextrins, and corn syrup solids are used extensively for encapsulation of food ingredients. Their aqueous solubility, low viscosity, and ease of drying characteristics lend themselves to spray dried, spray coated and extruded encapsulations. Understanding the various characteristics of these products can help in selection of the optimum system for ingredient encapsulation.

Gum arabic has historically been used as the most common "natural" matrix material for food encapsulations. Its solubility, low viscosity, and emulsification characteristics make it very versatile for most encapsulation methods. but historically it has also been plagued with problems of drought causing short supplies and also high costs.

Starch is one of the most common natural polymers on earth. It has been commercially extracted from numerous sources including corn, tapioca, potato, wheat, rice and waxy maize. Its availability is normally unquestioned, and due to the adequate supply, it is relatively inexpensive.

Chemically, starches are polymers of anhydrous units linked together primarily by alpha 1-4 bonds and secondarily by alpha 1-6 bonds. There are two polymer types found in starch, amylose which is the straight chain polymer, and amylopectin which is a branched chain polymer. Amylose, with its long, straight chains, is known for forming strong, flexible films. Amylopectin, due to its branching, does not form as strong a film, but is noted for clarity and stability when forming gels and may show a slightly greater tendency towards absorption or binding of flavors. The amount of amylose and amylopectin varies by the starch source. Typically, dent corn starch may

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be up to 28 percent amylose, tapioca starch is approximately 17 percent amylose and waxy maize is typically <1 percent (1).

Starch, in its natural state, is cold water insoluble. When mixed with water and heated sufficiently to swell the granule, starch forms pastes which can produce strong films, but has viscosity too high for most encapsulation processes used in the food industry.

Dextrins

One method used to modify starch viscosity and cold water solubility is pyroconversion or "dextrinization". In pyroconversion, the starch is heated in a dry granular form, usually in the presence of acid or akali. Partial hydrolysis of the starch polymers takes place as well as repolymerization to form more highly branched polymers. The resulting product is called pyrodextrin or dextrin. The Code of Federal Regulations (CFR), Title 21, Chapter 1, Part 184.1278 covers allowable produciton and use of dextrin in food systems (2). O.B. Wurzberg, in the book Modified Starches: Properties and Uses presents an intersting history of the commercial development of this method (3). The amount of hydrolysis and repolymerization can be varied to give products with different solubility and viscosity characteristics, but, the greater the heat used for hydrolysis and repolymerization, the darker the product becomes, and stronger reaction flavors are noted.

Dextrins have increased cold water solubility and lower solution viscosity than gelatinized native starch and have been used to replace gum arabic in certain applications. However, strong color and flavor characteristics in low viscosity products and the lack of lipophilic emulsifying qualities make them less than ideal for encapsulation especially of oil-based ingredients.

Lipophilic Starches

Other modifications of starches can be made to change their functional characteristics. Probably the most important for encapsulation products is the reaction of starch with 1-octenylsuccinic anhydride to form a substituted starch with hydrophobic and hydrophilic groups. CFR, Title 21, Chapter 1, Part 172, lists specific treatments allowable to modify starches used in food (2). This regulation limits anhydride treatment to 3 percent of the starch for food use. This level will give a degree of substitution in the range of 0.02. By varying the type of base starch used, such as waxy maize, tapioca or corn, and the types of other treatments given the starch, such as acid thinning, dextrinization, pregelatinization, etc., specific modified starches have been developed for individual encapsulation applications.

The placement of the lipophilic groups along the long starch polymer allows the formation of emulsions with tight alignment of the polymer around an oil droplet. This greatly stabilizes the emulsion, an important factor for encapsulation of lipid

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products. The emulsification abilities of lipophilic starches are reported to be equal to, or even greater than gum arabic, and oil retention in the spray-dried powders is equal to or greater than gum arabic, especially in products with higher oil loads (4). However, it has been noted the shelf life of spray-dried encapsulated citrus oils using this type of modified starch is not as long as that of gum arabic (5). The cause of this problem has not been well documented. Generally, the cost of lipophilic starches is approximately half that of gum arabic. There is also a flavor noted in these products that is characteristic of the modifications.

Maltodextrins and Corn Syrup Solids

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Other starch-based encapsulation ingredients are maltodextrins and corn syrup solids. The Food and Drug Administration (FDA) defines maltodextrin $(C_6H_{12}O_5)_nH_2O$ (CAS Reg. No. 9050-36-6) as "non-sweet, nutritive saccharide polymers that consist of D-glucose units linked primarily by alpha-1-4 bonds and that have a 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" (21 CFR 184.4444).

Corn syrup solids $(C_6H_{12}O_5)_nH_2O$ (CAS Reg. No. 68131-37-3) are defined by the FDA as "dried glucose syrups in which the reducing sugar content (DE) is 20.0 or higher" (21 CFR 168.121).

Dextose equivalence, the major characteristic used to define maltodextrins and corn syrup solids, is a measure of the degree of starch polymer hydrolysis. It is a measure of the reducing power of a sample compared to an equal weight of dextrose and is expressed as percent. Maltodextrin is a general category of separate products that are again characterized by their DE. Common designations are 5 DE, 10 DE, 15 DE and 18 DE. Corn syrup solids products are also divided into product categories, usually as 20 DE, 25 DE, 36 DE and 42 DE. Products with a DE greater than 42 cannot be easily dried so are sold only as syrups.

Figure 1 shows a typical production flow chart for the production of maltodextrins and corn syrup solids. The difference from a "dextrin" process can be noted. The starch in this process is completely cooked prior to hydrolysis as opposed to dry hydrolysis of the intact granule for dextrin production. Acid or enzyme, or a combination of acid and enzyme, is used to hydrolyze the starch polymers to the desired DE. Then hydrolysis is inactivated and the resulting product is generally filtered, concentrated and spray dried. The resulting products, if prepared appropriately, are cold water soluble and have very little flavor.

Since there is only partial hydrolysis of the starch with the acid or enzymes when producing maltodextrins and corn syrup solids, the resulting products are heterogeneous mixtures of various chain length glucose polymers. High-performance liquid chromatography (HPLC) methods can be used to characterize the various products and the amounts of short chain polymers [degree of polymerization

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(DP)<10] each contains. Table I shows a comparison of the percent by weight of several maltodextrin and corn syrup solids products. In spray-dried encapsulation of citrus oils, Anandaraman found that the higher the DE of the corn syrup solids used, the longer the stability of the encapsulated oil (8). This may be due to the reducing groups acting as "antioxidants" or possibly due to a difference in the porosity of the matrix, although this has not been measured (9). Bangs and Reineccius, however, found intermediate or lower DE products to be more efficient for spray-dried encapsulations of volatile artificial flavor compounds (10). This is possibly due to a balance of polymer lengths helping capture the volatiles as the surface of the droplet dries.

It is possible, by varying the type of hydrolyzing agent used, to have products with the same DE value that have very different carbohydrate profiles. For example, Table II shows carbohydrate profiles for two 36 DE corn syrup solids products, one of which has a high maltose content. Selection of enzymes may be used to optomize the amount and type of polymer hydrolysis to optomize the carbohydrate profiles. Several references cite possible advantages to mixtures of very short polymers such as maltose with much longer polymers to give increased oxidative stability to encapsulation systems (11, 12).

The average molecular weights for maltodextrins and corn syrup solids (approximately 1800 for a 10 DE) show the hydrolysates are composed of much smaller polymers than the original starch (approximately 2,000,000). Viscosity and solubility characteristics of maltodextrins and corn syrup solids vary with the average molecular size. The higher the DE, the higher the concentration of product that can be put into solution. Figure 2 shows typical viscosity levels at various concentrations of maltodextrins and corn syrup solids. Maltodextrins and corn syrup solids have much lower viscosities relative to traditional gum arabic and lipophilic starches and may normally be used at higher dryer feed solids. In spray-dried encapsulations, increased soluble solids at a low viscosity is a major factor in the efficiency of production. Menting and Hoogstad showed increased retention of volatiles with increased concentrations of maltodextrin in spray dryer feed solids (6). They related the increase to faster formation of a shell or membrane on the droplet surface which let water diffuse through but captured the volatiles. Reineccius and Bangs showed that individual encapsulating ingredients have different optimum in-feed concentrations for retention of artificial flavors (7). Again they relate to maximizing solids but within the stability limits of the matrix ingredient. An encapsulation using maltodextrin dried at 35 percent solids would not perform as well as one dried at 50 percent solids due to the time it takes for the droplet surface membrane to form in a more dilute system. In evaluating encapsulating ingredients, comparisons based on dryer feeds of equal viscosity (with consideration of solubility) rather than equal solids may present a truer picture of encapsulating ability.

As described above, maltodextrins and corn syrup solids are varied chain length glucose polymers. They have no lipophilic characteristics. In spray-dried

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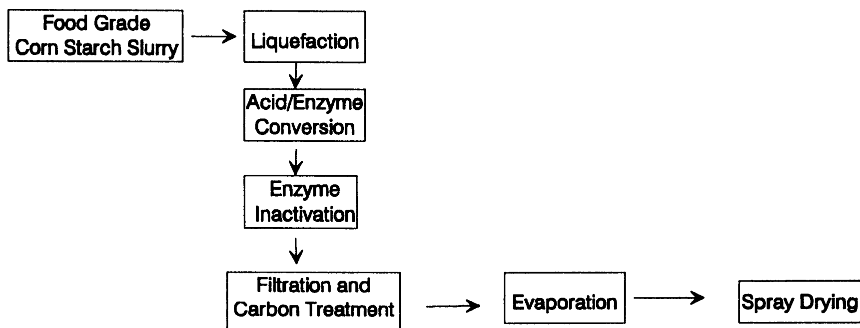

Figure 1. Production flow chart for maltodextrins and corn syrup solids (19)

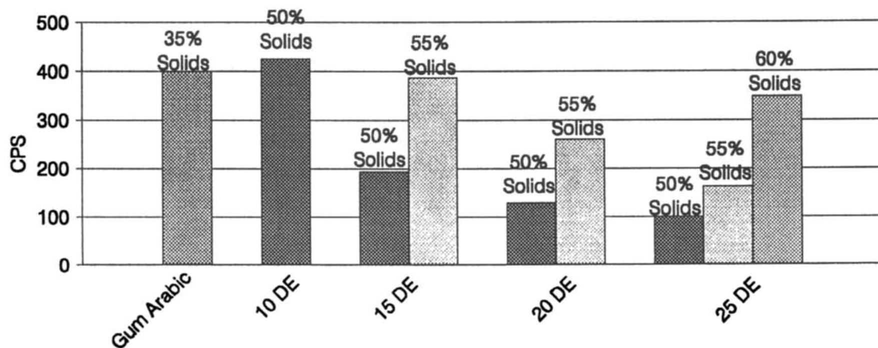

Figure 2. Viscosity of maltodextrins and corn syrup solids compared to a standard gum arabic

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Table I. Saccharide Composition of Maltodextrins and Corn syrup solids Average % of Carbohydrate (dry basis) (19)

	5 DE	10 DE	15 DE	20 DE	25 DE
DP1	0.3	0.8	1.3	2.3	7.6
DP2	0.9	2.8	4.8	7.4	6.9
DP3	1.4	4.4	6.7	9.1	7.0
DP4	1.4	3.8	5.5	6.8	6.8
DP5	1.3	3.4	4.7	6.3	6.3
DP6	1.8	5.7	8.4	11.9	5.6
DP7	2.4	6.8	9.1	10.0	5.1
DP8	2.0	4.5	4.8	3.7	4.6
DP9	1.8	3.1	2.9	2.1	4.1
DP10	1.7	2.5	2.1	1.7	3.4
Above DP10	85.0	62.1	49.7	38.7	42.6

Table II. Use of Enzymes can change the carbohydrate profile of corn syrup solids products Saccharide Composition Average % of Carbohydrate (dry basis)

	Standard 36 DE	High Maltose 36 DE
DP1	10.5	6.7
DP2	10.3	26.2
DP3	10.4	17.8
DP4	8.2	9.8
DP5	8.6	5.4
DP6	8.4	2.5
DP7	5.7	2.6
DP8	4.2	2.1
Above DP8	33.7	26.9

encapsulations of lipid products they exhibit poor emulsion stability and low oil retention, but the oil that is encapsulated has good oxidative stability (shelf life) (5). They have little flavor and can be used at high solids levels. The cost of maltodextrins is generally less than half that of lipophilic modified starches.

Product Blends

Each of the starch-based encapsulation ingredients has its own strengths and weaknesses. A blend of several of these ingredients can give performance superior to using any one ingredient alone. It is possible to blend maltodextrin with either modified starch or gum arabic and significantly reduce costs without reducing, and sometimes improving, encapsulating ability. Alexander (13) found it was possible to use maltodextrin in a blend with lipophilic starch and still achieve comparable oil retentions to the starch alone. Thevenet (14) found that a blend of maltodextrin and acacia gum could be dried at higher solids (50 percent) and produce product equal to that produced using pure acacia gum dried at 35 percent solids. Another study (15) showed that a blend of maltodextin and acacia gum had better oxidative stability (shelf life) than arabic alone. Levine and Slade (16) found that a complex blend of modified starch, maltodextrin, corn syrup solids and mono- or disaccharide gave them an optimum system for extruded encapsulations. They relate the glass transition of their system to its improved performance. In spray-dried encapsulation of fats or shortening, caseinates are most commonly used as emulsifying ingredients with the addition of corn syrup solids to improve stability, ease of drying and cost economics. All of these starch-based ingredients have been established as effective encapsulation ingredients for at least several decades.

In November, 1992, there was an amendment to 21 CFR Part 172 relating to food starch-modified that allows the use of enzymes (specifically alpha amylase) to be used for starch modification (17). This amendment allows the production of very low viscosity modified food starch including products with lipophilic properties with a DE less than 20. An experimental sample of such an enzyme-modified lipophilic starch was evaluated in a spray-dreid encapsulation of orange peel oil. In this preliminary test, the experimental product produced powder with oil retention comparable to the control lipophilic starch (Figure 3) and with much longer shelf life as determined by limonene oxide formation (Figure 4) (18). Further evaluation is needed to determine if this type of product can perform equal to or better than standard lipophilic starches or starch/maltodextrin blends on a commercial scale.

Modified starches, maltodextrins and corn syrup solids are used extensively in spray-dried encapsulations and extruded encapsulations of food ingredients. They can also be used for spray coating or other encapsulation methods when a water soluble coating is desired. Blends of these ingredients may be more effective than the individual ingredients alone. New regulations on starch modification may allow production of new, single ingredients that are as effective as current ingredient blends.

In Encapsulation and Controlled Release of Food Ingredients; Risch, S., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1995.

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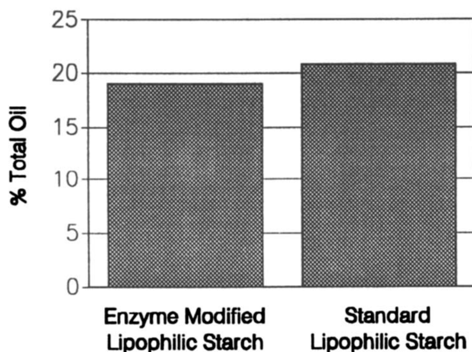

Figure 3. Total oil found in encapsulated powders (formulation to the dryer 25%) (18)

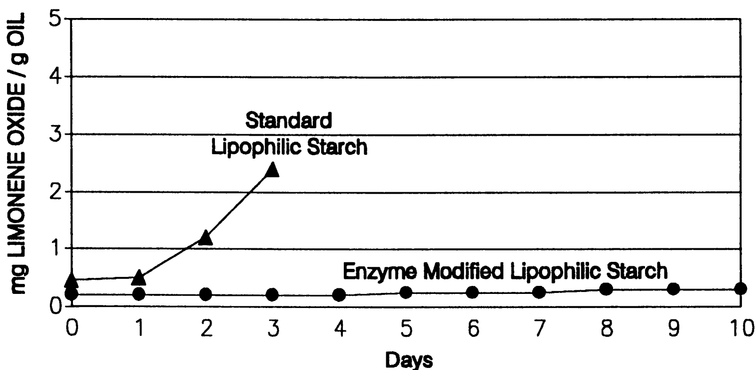

Figure 4. Shelf-life as measured by limonene oxide concentration (18)

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Chapter 5

Acacia Gums

Natural Encapsulation Agent for Food Ingredients

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Gum acacia, also called gum arabic, is a natural hydrocolloid produced by natural exudation of Acacia trees. This hydrosoluble gum has the unique property of being soluble at very high concentration in water, up to 50%. Recent studies have confirmed the presence of three fractions in the gum structure, each with its own properties. Studies have been conducted to investigate acacia gum as a protective film in citrus oil encapsulation. The stability and volatile compound retention after accelerated oxidation are shown. Also discussed are the analytical results on a citral and linalylacetate emulsion that was dried on acacia gum using two different drying techniques.

Acacia gums, also known as gum Arabic, are defined as "the gummy exudate flowing naturally or obtained by incision of the trunk and branches of Acacia Senegal and other species:. There are many acacia species (over 700) of which few are able to provide the amount of gum required for industrial production (25,000 to 30,000 tons/year). Acacia gums which are used as food additives belong to two botanical complexes following the Bentham and Vassal classification. These are the Series Gummiferae (Acacia Seyal Complex) and Series Vulgares (Acacia Senegal Complex).

Structure of Acacia Gum

The chemical structure of these two families shows a comparable quantitative analysis. After hydrolysis in acidic medium, the high pressure liquid chromatography

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reveals the presence of the same simple sugars, galactose, arabinose, rhamnose and glucuronic acids. The percentages are slightly different from Gummiferae and Vulgares. Low rhamnose content and a ratio of arabinose: rhamnose higher that one are characteristic from Seyal complex. Although the protein content of Seyal complex is lower than the Senegal complex, the amino acid composition is the same. The amino acids present in the largest percentages are serine and hydroxyproline. The viscosity of the Seyal complex is normally lower than that of the Senegal complex.

The highly ramified structure of acacia gums makes the gum Arabic soluble in water at up to 50% concentration. This is very rare for this type of hydrocolloid. Comparative viscosities between various colloids (1% concentration) using a Brookfield RVT at 20 RPM are shown in Table I (*1*).

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

Colloid	Viscosity
Guar	3,500 cps
Locust bean	3,000 cps
Xanthan	3,000 cps
Gum arabic	5 cps

The latest structural studies indicate the multimolecular structure of acacia gum. It is an association of various fractions with different molecular weights. The arabinogalactan (AG) fraction is the low molecular weight fraction (3.0×10^5) and has a low protein content (0.5%). AG represents about 90% of the gum molecule. The arabinogalactan protein fraction (AGP) has a high molecular weight (1.5×10^6) and a high protein content (10%). It makes up less than 10% of the molecule. The glycoprotein (GP) fraction has a very high protein content (50%) and a low molecular weight (2.5×10^5). It makes up about 1% of the molecule. The proposed structure of gum acacia Senegal is shown in Figure 1. The representation of the acacia gum molecule following the Wattle Blossom model (*2*) is supported by the gel permeation chromatography (GPC) profiles published by Osman et al (*3*). The Wattle Blossom model depicts a long chain protein support that serves as the linkage between arabinogalactan units.

Structure and Properties Relationship

For the emulsifying properties, the most interesting parts of the molecule are the AGP and GP fractions containing a high percentage of proteins. These proteins act as an interface between oil and water. It should be noted that the amino acid composition (serine and hydroxyproline) of the proteins is hydrophobic.

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Fig. 1-Modern hypothesis of the structure of gum Acacia Senegal.

The glucuronic acids which are partially salified and partially nephylated, develop negative charges that surround an oil particle in an emulsion. The ideal diameter of the oil droplet is one micron. There is a charge repulsion which helps stabilization. The AGP fraction has a high viscosity which slows down the motion of oil particles and will help prevent agglomeration of the oil droplets.

The film forming properties of acacia gum comes from the arabinogalactan fraction. The low viscosity and consequently high solubility of this portion is likely responsible for the barrier film that is formed after the evaporation of water.

Applications of Gum Acacia

Acacia gum is widely used in the food and pharmaceutical industries. It is the know how of the gum industry to develop special varieties of acacia exudates that will have an internal structure that will be best for the final use of the gums. A wide variety of acacia gums in purified form are now availble, each having its own application.

Texturizing, film forming, emulsifying and binding properties are the main characteristics specific to acacia gums. They are also used as a carrier when it is desired to have a product that is non-cariogenic, low in caloric value and/or is a good source of soluble fiber.

In confectionery, the acacia gums are used as texturizing agents in products such as gum drops, gum pastilles and wine gums. They can also be used in association with modified starches or gelatin to modify the final texture. All types of texture can be obtained with the acacia gums giving a product that will not stick to peoples' teeth in addition to having a long lasting good flavor release. As a film forming colloid, acacia gum is used to isolate the centers in dragees. Peanut or chocolate centers in candy can be coated with a gum syrup to avoid oxidation of the fat or migration of the fat through the sugar coating. Either hard or soft coatings can be made.

In the flavor industry, acacia gums are used for two primary applications. These are as a stabilizer for the concentrate used for soft drink manufacture (oil in water emulsion) and as a protective carrier for spray drying liposoluble and sensitive products. The process summary for soft drink applications is shown in Figure 2. The association of the tensoactive properties of the gum in combination with the mechanical fractionation of the oil phase are keys for a good stability of the concentrate and the final dilute beverage.

Recent Research

Different types of products including citrus flavors, vegetable fat, oleoresins, coloring agents and vitamins can be encapsulated. Analytical work on orange oil encapsulated with various acacia gums has been published by Risch and Reineccius (*4*). This work has been continued by Colloides Naturels International and Reineccius

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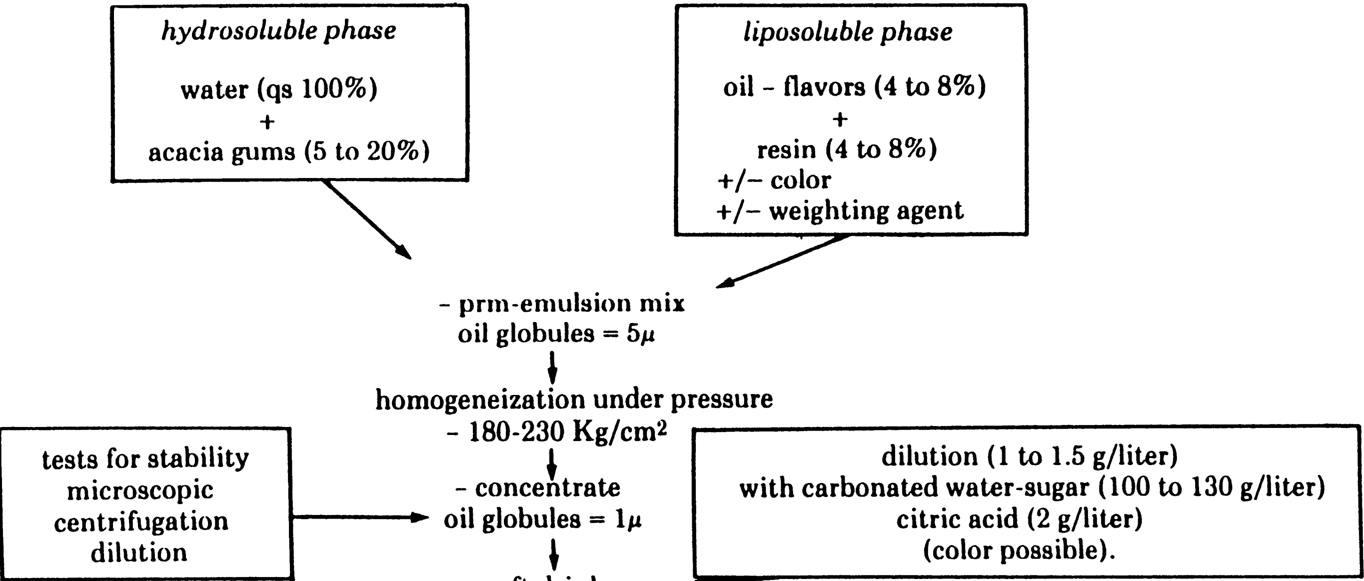

Fig. 2-Emulsion for soft drinks.

(University of Minnesota, 1990, personal communication) using a more complex oil system encapsulated with conventional spray drying on a blend of acacia gum and maltodextrins. The tests conducted included emulsion stability, spray dry flavor retention and oxidative stability of the orange oil. A modified starch was used for comparisons.

Four different ratios of acacia gum to maltodextrin were used. These were 1:0, 1:1, 1:3 and 1:5. The blends were hydrated overnight to make 40% solutions. A flavor blend comprised of 2% each of ethyl propionate, ethyl butyrate, ethyl caproate, benzaldehyde and cinnamic acid in orange oil was prepared just before making the emulsion. Prior to spray drying, emuslions were prepared by mixing 20% flavor blend into the hydrated gum/maltodextrin blends with a high shear mixer. Spray drying was done using a Niro spray drier with an inlet air temperature of 200 ± 5 C and an exit air temperature of 100 ± 5 C.

Emulsion Stability. The stability of the emulsions was determined by centrifugation. Spray dried powder we diluted in water (3 g per liter) and centrifuged. After centrifugation, the absorbance at 400 nm was determined. The results are shown in Figure 3. The addition of maltodextrins to the acacia gum tends to result in a small decrease in the initial absorbance and this trend held generally throughout centrifugation. It is known that the acacia gums suitable for stabilization of a liquid emulsion are not the best for encapsulation and vice versa. Acacia gum behavior in liquid form (oil in water emulsion) and in powder form (coating in dry film) is not the equivalent for the same gum.

Flavor Retention During Spray Drying. The flavor retention was determined by a gas chromatographic method. The more volatile compounds (ethyl propionate and ethyl butyrate) were lost to a greater extent than the less volatile compounds as shown in Figure 4. The blend of one part spray dried gum acacia and one part maltodextrins showed excellent retention of volatiles. There was a general trend that retention of volatiles decreased as the proportion of maltodextrins increased. The modified starch gave flavor retention that was inferior to the 1:1 blend of acacia gum and maltodextrins.

Oxidative Stability. The oxidative stability of orange oil was monitored using gas chromatography to measure the formation of limonene oxide with time. Samples were stored in an incubator at 37 C. The results are shown in Figure 5. The modified starch shows significant oxidative changes in the orange oil during storage. The orange oil was stable to oxidation in the pure gum acacia as well as in the gum acacia/maltodextrin blends. This agrees with the previous work which has been done to compare the protective effect of various species of acacia gums. It appears that a 1:1 ratio of acacia gum to maltodextrin will yield a flavor in the powder form that has almost the same stability as pure acacia gum as the carrier.

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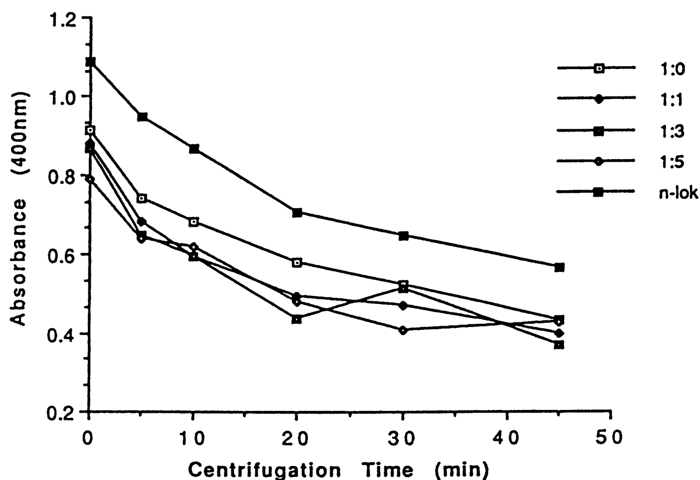

Fig. 3-Stability of emulsions prepared from different matrices.

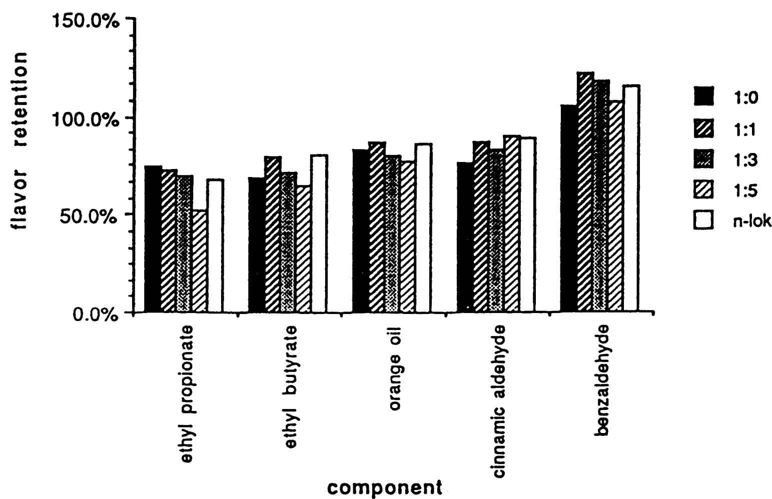

Fig. 4-Flavor retention of spray drying.

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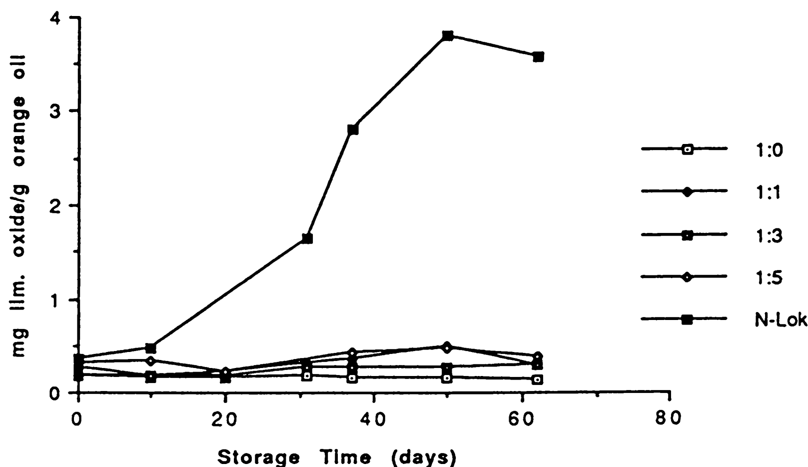

Fig. 5-Oxidative stability of orange oil prepared from different matrices.

Alternative Drying Technique

The use of maltodextrins decreases the cost of the carrier and allows spray drying at higher infeed solids because of the lower viscosity of the emulsion. In view of spray drying at a higher solids concentration, Bhandri et al (*5*) have recently studied a spray drying system able to dry liquids at very high viscosity. This is referred to as the Leaflash technique. In Leaflash spray drying, hot air flows at a very high velocity in the dryer. This hot air converges at the dryer head and simultaneously atomizes and dries the resultant atomized droplets. This system uses very hot air (300 to 400 C) and is able to dry very viscous liquids at high dry solids contents. In the work, they used various emulsions that were prepared using blends of acacia gum and maltodextrins into which a mixture of citral and linalyl acetate (80/20) was emulsified using homoginization under pressure. The emulsion was prepared at 50% dry solids. The air temperature of the Leaflash was 350 C and the outlet temperature was 105 C. The viscosity of the emulsions is shown in Table II.

Table II. Viscosity of Gum Acacia and Maltodextrin Blends

% Gum Acacia	% Maltodextrins	Viscosity
100	0	10,000 cps
60	40	3,000 cps
40	60	1,700 cps
20	80	255 cps
0	100	105 cps

SOURCE: Adapted from ref. 5.

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They reported that the retention of volatiles, as determined by hydrodistillation, was higher in the samples with a higher gum content. (*5*)

Acacia gums have been used in the food industry for many years for their unique texturizing, film forming and stabilizing properties. A better knowledge of the botanical species in conjunction with a sophisticated purification process allows a selection of the harvested grades to provide a continuity of quality of the gum. The research in the past few years into the complex structure of the acacia gum molecule has led the way to development of gums for specific needs.

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Chapter 6

Use of Cyclodextrins for Encapsulation in the Use and Treatment of Food Products

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Cyclodextrins are chemically and physically stable molecules formed by the enzymatic modification of starch. They have the ability to form complexes with a wide variety of organic compounds. As a result of complexation of compounds by cyclodextrins, the apparent solubility of the molecule can be altered, the stability of the compound in the presence of light, heat and oxidizing conditions is increased and volatility of compounds is decreased. Cyclodextrins can also be used as processing aids to isolate compounds from natural sources and to remove unwanted compounds, such as cholesterol, from food products.

Cyclodextrins are enzymatically modified starch molecules. They are made by the action of cyclodextrin glucosyltransferase upon starch. After cleaveage of starch by the enzyme, the ends are joined to form a closed circular molecule with alpha 1-4 linkage.

Three cyclodextrins are typically formed, alpha, beta, and gamma cyclodextrin, having six, seven, or eight glucose units forming the ring, respectively. Depending upon the enzyme used and the conditions under which the reaction is performed, the ratio of the cyclodextrins can vary from various mixtures to a single cyclodextrin being formed. Beta cyclodextrin is the predominant cyclodextrin produced by most enzymes. Purification of the reaction mixture is performed to isolate the individual cyclodextrin.

Physical and chemical properties of cyclodextrins Structure.

Structure. The molecule is shaped like a hollow truncated cone. The hydrogen atoms and the glycosidic oxygen atoms of the glucose monomers are located in the cavity of the cyclodextrin ring. These groups give the cavity hydrophobic character and interact with various organic molecules or moieties forming complexes. The hydroxyl groups of the glucose monomers are located on the rims of the molecule and are directed away from the cavity. These groups interact with water giving the cyclodextrins their aqueous solubility properties and will interact with polar groups of some molecules to form hydrogen bonds.

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Cavity size. Table I shows the dimensions of the alpha, beta and gamma cyclodextrins.

Table I. Dimensions, in Angstroms, of the cyclodextrins.

CD Type	Inner Diameter	Outer Diameter	Height
Alpha CD	5.7	13.7	7.8
Beta CD	7.8	15.3	7.8
Gamma CD	9.5	16.9	7.8

The size of the cavity of the cyclodextrin allows some selectivities for the complexation of guest molecules. The more interaction that occurs between the walls of the cyclodextrin and the guest molecule, the stronger is the binding. If the molecule is small compared to the cavity, only some of the surface of the guest molecule is in contact with the walls of the cavity and the full potential of the guest molecule to interact with the cyclodextrin is not realized. For molecules with five or fewer carbon atoms, the small cavity of alpha cyclodextrin allows more interaction of the molecule with the walls of the cavity and better binding than beta or gamma cyclodextrin where a portion of the surface of the guest molecule would not be in contact with the wall of the cyclodextrin cavity because of the larger volume of the cavities.

Some large molecules are too large to fit into the cavity of one or more of the cyclodextrins. The molecule can be totally excluded or only a portion of the molecule fit into the cavity. The more of the molecule that can fit into the cavity, the stronger the binding. Large bulky molecules, such as anthracene, fit into the cavity of the gamma cyclodextrin better than into alpha or beta cyclodextrin.

Many molecules will complex with more than one cyclodextrin. Most molecules that will complex with alpha or gamma cyclodextrin will also complex with beta cyclodextrin. Beta cyclodextrin is the most readily available cyclodextrin and most initial work is done with beta cyclodextrin. Comparative evaluations are done with alpha and gamma cyclodextrin to determine if the intended function is obtained with these cyclodextrins and to determine which cyclodextrin provides the best cost performance.

Solubility of cyclodextrins. The solubility of alpha, beta and gamma cyclodextin in grams per 100 ml of water at room temperature is 12.8, 1.8, and 25.6 grams respectively (*1,2*). As the temperature increases, the solubility of the cyclodextrins increases. The solubilities are for the free or uncomplexed cyclodextrins.

The solubility of a cyclodextrin is changed when a guest is complexed. Complexation of a cyclodextrin with a guest which is highly soluble in water generally increases the solubility of cyclodextrin. The polar or ionic group of the guest molecule projecting out of the cavity contributes to the solubility of the complex along with the interaction of the hydroxyl groups of the cyclodextrin.

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Complexation of the cyclodextrin with a guest which is not soluble or only slightly soluble in water generally results in a decrease in the solubility of the cyclodextrin. The solubility is usually less than that of the cyclodextrin, but greater than the solubility of the guest molecule.

Because one cyclodextrin is more soluble than another cyclodextrin does not mean that a complex of a guest with the more soluble cyclodextrin will be more soluble than the complex of the guest with a less soluble cyclodextrin. A variety of factors, which are not completely understood, contribute to the solubility of the complex.

Thermal stability. Cyclodextrins are heat stable. Differential scanning calorimetry shows two peaks upon heating alpha, beta or gamma cyclodextrin. The first peak occurs at 100°C as the water in the crystals is evaporated. The second peak occurs at about 300°C where melting of the crystals and thermal decomposition of the cyclodextrin are occurring simultaneously. No endotherms or exotherms occur between these peaks, unlike starch for which energy is absorbed as changes in the secondary and tertiary structure occur.

Hygroscopicity. Cyclodextrins are not hygroscopic. If cyclodextrins are dried and then transfered to an environment where water can be adsorbed from the atmosphere, some water will be adsorbed. An equilibrium is reached in about twenty four hours with the cyclodextrins containing about 10 to 14 % water depending upon humidity and temperature conditions. This is about the same amount of water normally found in starch. The cyclodextrins remain a dry, pourable powder at the equilibrium moisture.

Chemical stability. Strong acids such as hydrochloric or sulfuric acid hydrolyze cyclodextrins. The rate of hydrolysis is dependent upon the concentration of the acid and the temperature with the rate of hydrolysis increasing as the temperature and concentration increase (*3,4*). Weak acids, such as organic acids, do not hydrolyze cyclodextrins. Only citric acid has been found to hydrolyze beta cyclodextrin, but at a temperature greater than 50°C and at a 0.5 molar concentration.

Bases do not hydrolyze cyclodextrins. Many syntheses are done using 0.1 molar and greater concentrations of sodium hydroxide at temperatures of 65°C or above and no evidence of hydrolysis of the cyclodextrins is found.

Enzymatic stability. Cyclodextrins are hydrolyzed by cyclodextrin glucosyltransferase, the enzyme used to produce cyclodextrins (*5,6*). The enzyme which catalyzes the degradation of starch to cyclodextrins also catalyzes the degradation of cyclodextrins to oligosaccharides. The enzyme also performs transglycosylase reactions using oligosaccharides as the acceptor and alpha amylase reactions using water as the acceptor.

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Glucoamylases and beta amylases do not hydrolyze cyclodextrins. These enzymes require a reducing end group to initiate hydrolysis. Since cyclodextrins are closed circular molecules, there is no reducing end group available for initiation of hydrolysis.

Many alpha amylases will hydrolyze cyclodextrins (*7,8,9*). Fungal alpha amylases hydrolyze cyclodextrins more readily than bacterial alpha amylases. Cyclodextrins also vary in their susceptibility to hydrolysis by alpha amylases. Gamma cyclodextrin is hydrolyzed as readily as starch. Beta and alpha cyclodextrin are hydrolyzed less readily than starch with beta cyclodextrin being more susceptible to enzymatic hydrolysis than alpha cyclodextrin.

Complexation and chemical modification of the cyclodextrins reduces or prevents enzymatic hydrolysis of cyclodextrins. With a guest molecule occupying the cavity of the cyclodextrin, the alpha amylase is sterically hindered from attacking the cyclodextrin molecule. Substitution of the cyclodextrin with various groups prevents the binding of cyclodextrin to the active site of the enzyme. As the degree of substitution increases, the probability of hydrolysis by amylases is decreased.

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Toxicology and metabolism.

Alpha and beta cyclodextrin are resistant to salivary and pancreatic amylases (*10*). As a result, they pass through the digestive system to the colon intact (*11*). In the colon, enzymes produced by the colonic flora hydrolyze beta-cyclodextrin to some extent. The extent of hydrolysis has not been well studied. Once the ring is opened, the cyclodextrin is metabolized as other starch hydrolysate in the colon. Alpha cyclodextin is believed to pass through the colon without being hydrolyzed by the colonic enzymes (*12*).

Gamma cyclodextrin is susceptible to hydrolysis by salivary and pancreatic amylases. As a result, it is completely hydrolyzed and adsorbed and metabolized similarly to starch.

No LD_{50} has been established for oral administration of beta cyclodextrin. The largest amount of beta cyclodextrin was incorporated in the diet of rats and mice without removing required nutrients and no treatment related mortality was observed. LD_{50} values were determined for injection of beta cyclodextrin. Upon injection, the beta cyclodextrin has been found to crystallyze in the kidneys causing renal damage (*13*).

Rats were fed on the diets containing from 1.25 % to 10.0 % of beta cyclodextrin for ninety days. No adverse toxicological or pathological effects were found upon autopsy of the animals at the conclusion of the study. The caeca of the rats which were fed at high doses of beta cyclodextrin were found to be enlarged. This was typical for rats when the rats were fed on a diet containing slowly digested carbohydrates. A similar result was found in the control group whose diets contained lactose, which is slowly digested. A small amount of beta cyclodextrin, 0.1 % to 0.3 % of beta cyclodextrin was found in the urine of rats fed diets containing 5 % and 10 % of beta cyclodextrin in the diet, but no abnormal renal pathology was found (*14*).

Various other toxicological tests; dermal irritation, eye irritation, inhalation, Ames test, chromosomal abberation, Drosophila slrl, and teratology showed no adverse effects due to beta cyclodextrin.

Complexation.

Complexes are typically formed with organic compounds. A wide range of organic molecules is capable of forming complexes with cyclodextrins such as aliphatic compounds, phenyl derivatives, conjugated rings and heterocyclic compounds. Several forces, such as van der Waal forces, hydrophobic interaction and dipole-dipole interaction are involved in the binding of guest molecules with the cavity of cyclodextrin. These forces are sufficiently strong to form a stable complex, but are not so strong that the guest molecule can be released from the complex to become available for the intended effect of the guest molecule.

Shape of the molecule is an important determinant in forming the complex. Complexes are formed because of the interaction of the hydrophobic group or groups of the guest molecule with the walls of the cavity of the cyclodextrin. Binding becomes stronger as the contact of hydrophobic groups with the cavity increases. Some side chains on a molecule might limit the degree of penetration of the guest molecule into the cavity of cyclodextrin, but a sufficient amount of the guests frequently penetrates the cavity sufficiently to form a stable complex. Polar or ionic groups do not interact with the hydrophobic walls of the cavity of cyclodextrin. Complexation can be achieved with the hydrophobic portion of the molecule interacting with the walls of the cavity and with the polar or ionic groups projecting out of the cavity. In many cases, the polar or ionic groups will interact with the hydroxyl groups on the rim of the cyclodextrin to form hydrogen bonds resulting in increased binding of the guest to the cyclodextrin. The shape of the molecule is more important than molecular weight in complexation. Larger molecules can complex with more than one molecule of cyclodextrin and more than one small molecule might complex with a molecule of cyclodextrin. In general, one molecule of cyclodextrin forms an inclusion complex with one molecule of guest. As a result, the guest molecule is isolated from other molecules in contrast to other means of encapsulation where several molecules are enclosed in a film formed by the encapsulation material. For many examples, there is an advantage to this isolation. The isolation prevents contact with other molecules which might be reactive with the guest molecule. Direct contact with the walls of cyclodextrin stabilizes some molecules to prevent oxidation by light or heat. Loads of the complexes are around 10% by weight, which is typically lower than that from other encapsulation methods.

Production of Complexes. Production of complexes of cyclodextrin is a rather simple process. The cyclodextrin and guest are mixed in water. In the laboratory, a beaker and a hot plate with stirrer are the only equipment needed. The amount of water can vary depending upon the guest to be complexed. If a dry complex is

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desired, conditions are selected so that the solubility of the complex will be exceeded and the complex can be collected by filtration or centrifugation and dried in an oven. The amount of water can be reduced so that one is working with a paste, which eliminates some drying and water treatment concerns for scale up to commercial operations. Virtually any mixing device can be used and the amount of mixing time will vary with the mixing device and the material to be complexed.

The complexation reaction can be scaled up to produce commercial quantities of complexes. Generally the coprecipitation reaction used in the laboratory is not preferred because of the large amount of water used. A slurry or paste containing 20 % to 40 % water is preferred for scale up. Virtually any mixing device, such as a kneader or extruder, which can handle the high viscosity of the reaction can be used. Testing must be performed to determine the amount of time required to complete the complexation reaction. The required time is less in high shear mixers than in low sheer mixers. The paste or slurry can be used as it is produced or dried for use.

Complexes can be dried using conventional means such as hot air ovens, spray dryers or freeze dryers. In our experience, most complexes can be dried at 100°C or slightly higher temperature to remove water rapidly. Suspensions of complexes can be successfully spray dried as long as the particle size is kept small by agitation to prevent blocking of feed lines and atomizers. Some optimization of drying temperatures and other process conditions should be done for highly volatile guests having boiling temperatures below 100°C.

Drying of complexes can also be done on a commercial scale. A variety of dryers can be used. Ovens passing hot air over the complex or having heated surfaces can be used. It is best to keep the complex constantly turning over in the dryer for uniform drying and to prevent loss of volatile guests during the drying process. Fluidized bed and spray dryers can also be used. Lower temperatures can be used in freeze dryers of vacuum dryers.

Equilibria. In solution, there is an equilibrium between the free and the complexed states of guest and cyclodextrin. The direction of the equilibrium depends upon the guest molecule. For some guests, the complexed state is predominant while for others, especially those guests having high aqueous solubility, the free state is predominant. The complexes exist in water and are stable enough to be isolated from water and dried.

Guests are readily released from complexes. In water or when dissolved in water some guest will be in the free state because of the equilibrium that is established. Other factors will affect the release of the guest. Other molecules can be present that will occupy the cavity of the cyclodextrin preventing the originally complexed guest from reentering the cavity. The rate of release will depend upon the relative affinities of the original guest and other guests for the cavity of the cyclodextrin and the relative concentrations of the guests. The guest as it is released can bind to other materials such as membranes or proteins resulting in an increased rate of release compared to the equilibrium alone. The

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guest might not have to be in the free state in order to function. For example, a molecule used for flavoring might complex in a manner such that the portion of the molecule eliciting the taste response projects from the cavity and can contact the taste receptor without having to be released.

Applications of Cyclodextrins.

Alteration of Solubility. Complexation of compounds with cyclodextrins can alter their solubility, either to increase or decrease the solubility of the compound. Traditionally, encapsulation has been used to stabilize a compound and the encapsulated compounds are added to or remain in the product. Complexation of compounds with cyclodextrins can result in decreased solubility and removal of the compound from a food product or isolation of a compound to be used in a food product.

Cholesterol is present in many foods of animal origin such as dairy products, eggs, lard and tallow. In milk and eggs, the cholesterol is suspended in water by emulsification systems. When beta cyclodextrin is added, the cholesterol is complexed with the beta cyclodextrin forming an insoluble complex which can be recovered by centrifugation.

Table II shows the results obtained when beta cyclodextrin and derivatives were used to remove cholesterol from egg yolk, cream or butter. Egg yolks were treated according to the method described by Vollbrecht (15) using 5 % beta cyclodextrin or derivative. Cream was treated by stirring with 5 % beta cyclodextrin at 25°C for one hour followed by centrifugation to remove the cyclodextrin - cholesterol complex. Butter was treated using the method described by Courregelangue and Maffrand where the amount of ß-cyclodextrin used was 5 % of the weight of the butter (16). Derivatives were used at the same molar concentrations as the beta cyclodextrin.

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Table II. Per cent of the original cholesterol removed from food after treatment with beta cyclodextrin.

Cyclodextrin	% cholesterol removed		
	Egg yolk	Cream	Butter
Beta Cyclodextrin	80	76	24
a	17	25	10
b	98(1)	95(2)	23
c	27	79	24
d	7(3)	96	34
e	23	52	9
h(polymer)	6	9	26

Treated with beta cyclodextrin, only the cholesterol and some lipid material, which was not characterized, were removed. Most of the complexed

material was cholesterol. Some differences were observed with the derivatives. Derivative b removed color from the egg yolk in addition to the cholesterol. Cholesterol was removed more efficiently from the egg yolk and cream than with the unmodified beta cyclodextrin, but the efficiency remained the same with the butter. With cream, the complex had a smaller mass than the complex formed with beta cyclodextrin. While derivative d, did not remove cholesterol from the egg yolk, it did form a gel. Such physical changes were not observed with other derivatives. Derivative d, was most effective for removing cholesterol only in the cream. Derivatization changed the ability of beta cyclodextrin to remove cholesterol from different foods.

Recovery of cyclodextrin. The cholesterol and the beta cyclodextrin in the complex can be further treated and separated for other applications or reused in the process.

Heating can destabilize complexes. A slurry of the cholesterol complex was stirred during heating and upon reaching the decomplexation temperature, stirring was stopped. The amount of cyclodextrin in the slurry was selected so that the decomplexed cyclodextrin was completely soluble at the decomplexation temperature and the cholesterol and complexed lipids floated to the surface when the stirring was stopped. The separation of the aqueous and lipid phases can be accelerated by centrifugation. The cyclodextrin in solution was treated with charcoal and filtered to remove any precipitated material and other impurities.

The partitioning of the cholesterol and lipids from the aqueous phase can be aided by addition of sodium chloride to the aqueous phase. As shown in Table III , the recovery of beta cyclodextrin from treatment of milkfat increases as the amount of salt is increased. Depending upon the process, ion exchange resin can be used to remove the salts and other materials that might have been trapped during processing or added to facilitate phase separation. The cyclodextrin can be reused from the solution ,or the solution can be cooled and the cyclodextrin recovered as crystals for reuse.

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Table III. Effect of Sodium Chloride on the Recovery of Beta Cyclodextrin

	% ß-cyclodextrin Recovered		
Concentration of Salt	10% Slurry	15% Slurry	20% Slurry
2% NaCl	68.57%	68.08%	65.99%
5% NaCl	80.29%	69.99%	71.44%
10% NaCl	83.33%	75.08%	74.91%
15% NaCl	83.71%	84.40%	80.64%

Other compounds can be removed from other food products using beta cyclodextrin or insoluble derivatives. Naringin and limonin can be removed from citrus juices using a crosslinked polymer containing beta cyclodextrin (*17*). Only the naringin and limonin were removed using the polymer to treat the juice by

passing the juice through the polymer. Other components of the juice, vitamins, flavor oils, etc were not removed by the polymer.

Caffeine can also be removed from tea and coffee using the beta cyclodextrin polymer (*18*). Up to 75 % of the caffeine was removed. Caffeine removal did not show the same degree of specificity as other processes. Analysis of the beverages was done using HPLC. Other materials, which were not identified, were also removed by treatment of the beverage with the polymer. The amount of other materials removed varied, depending upon the source of the tea or coffee.

Cyclodextrins can also be used to directly complex and recover materials, such as flavor oils, from natural sources. Onions or garlic were macerated with water in a Waring blender. The macerated material was passed through cheese cloth to remove the larger debris and beta cyclodextrin was added to the filtrate and stirred. The complex that was formed was collected by centrifugation and dried. The flavor of the complex was like that of the fresh onion or garlic and did not have the off flavors found in many traditionally extracted onion and garlic oils.

Cyclodextrins can be used to increase the solubility of compounds. Hesperidin is an insoluble compound found in oranges and imparts cloudiness to the syrup of canned oranges. Cyclodextrin was added to the syrup to complex the hesperidin resulting in a clear syrup (*19*). An additional benefit was to mask the bitter taste imparted to the orange by the hesperidin and other compounds.

Cyclodextrins can be used to stabilize vitamins and essential oils from the effects of light, heat, oxygen and other compounds that might react with them. There is a finite amount of space in the cavity of a cyclodextrin molecule. If that space is filled, other molecules cannot occupy that space thus protecting a complexed guest molecule from other molecules. Interaction with the walls of the cavity of the cyclodextrin can stabilize certain forms or molecular or electron configurations of a molecule resulting in increased activation energy being required in order for the molcule to undergo reaction. This also results in stabilization of complexed guest molecules.

Vitamin A rapidly degrades when exposed to light and air. A complex was made using beta cyclodextrin. After twenty four hours of sitting in an open petri dish in the laboratory, the free vitamin A had oxidized as evidenced by the shift of the absorption spectrum. The peak for the fresh vitamin A occurred at 320 nm while that of the oxidized vitamin A occurred at approximately 240 nm. The absorption spectra of the complexed vitamin A and fresh vitamin A were identical after the same twenty four hours of exposure of the complex.

Vitamin D_3 is heat labile and excess vitamin is used to insure that sufficient activity remains after processing of food products. Complexing vitamin D_3 prior to processing stabilizes the vitamin so that the amount of vitamin used can be reduced and sufficient activity remains after processing of the food product. In one experiment (*20*), complexed and uncomplexed vitamin D_3 were incubated at 80°C. Virtually all of the activity of the uncomplexed vitamin D_3 was lost in one day. The complexed vitamin was much more stable, with 49 % of the original activity remaining after 43 days of exposure to the high temperature.

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Benzaldehyde is easily oxidized to benzoic acid. Complexes of benzaldehyde are stable and not oxidized readily (*21*). The aldehyde group is polar and does not interact with the hydrophobic walls of the cavity of the cyclodextrin, but projects out of the cavity. This demonstrates that the group to be stabilized does not have to be included in the cavity of the cyclodextrin to be protected.

Flavors tend to be volatile and are lost with time giving some products a limited shelf life. The volatility of compounds can be eliminated or reduced by complexation of the compound with cyclodextrin. Because of the interaction of the compounds with the walls of the cavity of the cyclodextrin, additional energy is needed to volatilize the compound. Analysis of compounds by differential scanning calorimetry generally demonstrates an increase in the boiling temperature of complexed compounds of about 10°C.

Menthol and mustard oil provide examples of the effect of complexation of compounds with cyclodextrin. Menthol sublimes and bottles of menthol which have been kept for sufficient time have menthol crystals forming on the lid and walls of the storage container. When the menthol is complexed with cyclodextrin, the menthol remains in place in the cavity of the cyclodextrin, the complex is odorless and no crystals are observed on the walls or lid of the storage container. Menthol complexes, even those not stored in a tightly sealed container, have been stable in our laboratory more than five years. When the complex is tasted, a strong menthol flavor is released.

Mustard oil is very irritating to the eyes and respiratory system. Complexation of the mustard oil with cyclodextrin reduces the volatility of the mustard oil and the irritating effect of the mustard oil allowing one to work with the material much more easily. The dry complex is odorless, but when placed in the mouth, a strong mustard flavor is released.

Off flavors and odors can be masked by complexing materials with cyclodextrin. The bitter taste of hops can be completely masked. The astringency of protein hydrolysates is also masked by addition of beta cyclodextrin to solutions of protein hydrolysates. Off flavors and odor of garlic oils are masked and the volatility of the oil is reduced. The bitterness of naringen and lemonin in citrus juices is masked by addition of beta cyclodextrin to the juice.

Fruit and vegetable juices develop a brown color due to enzymatic conversion of phenolic compounds to a brown color. The phenolic compounds are complexed by cyclodextrins and when complexed, the phenolic compounds are not acted upon by the enzyme and the formation of brown color is prevented (*22*). If the juice is passed through an insoluble epichlorohydrin crosslinked polymer of beta cyclodextrin, the phenolic compounds are complexed by the beta cyclodextrin in the polymer and removed from the juice and the treated juice does not become brown.

Many flavors are produced as oils. Oils can be difficult to mix uniformly with dry solids. Complexation with cyclodextrin converts these oils to powdered solids which can be mixed much more easily with the dry solids. Complexation

of flavor oils with cyclodextrin can also remove the need for diluents needed to make measuring and dosing easier since the cyclodextrin used to make the complex can also serve as the diluent.

Conclusion.

Cyclodextrins have been a laboratory curiosity for many years. During that time, much has been learned about their chemistry and the effects of complexation upon a wide variety of compounds. Cyclodextrins are now available in commercial quantities.

Cyclodextrins are chemically stable and can be used under the various conditions found in foods and food processing. There are many examples for use of cyclodextrins and only a few applications were described to illustrate the basic concepts such as stabilization of compounds against the effects of oxidation, heat and light and reduction of volatility. Complexation of compounds with cyclodextrin gives longer shelf life to products, reduces of loss of volatile or heat labile materials during processing or cooking, and allows the use of materials which could not be previously used due to their instability.

Cyclodextrins can also be used as process aids to remove unwanted components from food products or to isolate compounds from natural sources to be used in food products. The cyclodextrin and complexed material can be separated and the cyclodextrin can be reused.

Cyclodextrins are in use in foods and as processing aids throughout the world. For some uses, the unmodified cyclodextrins have some limitations and as a result, research is in progress to develop new derivatives to remove these limitations. As these new derivatives are approved for use in food, cyclodextrins will be used even more widely in food products throughout the world.

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Chapter 7

Food Ingredient Encapsulation

An Overview

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Fluid Bed encapsulation has proven to be a viable method of coating solid particle food ingredients to allow their successful use in a number of key applications. When designing a custom encapsulated ingredient, one must first determine the desired release mechanism and a method for quality measurement. Then by manipulating a number of factors, including the shape and size of the substrate and key processing parameters, the optimum encapsulated ingredient can be produced.

The science of encapsulation deals with the manufacture, analytical evaluation, and application of encapsulated products. Encapsulated products are those which contain an active core material, or substrate, surrounded by a protective film of coating. Generally, it can be said that encapsulation allows the user to separate an ingredient from its environment until a point in time when its release is desired.

The pharmaceutical industry has long used encapsulation technology to coat vitamins, minerals, prescription drugs, and over-the-counter drugs, for the purposes of time release, flavor masking, and improved stability within a formulation system. Similarly, ingredient encapsulation has a number of uses in the food industry. It can separate the reactive components within a mixture; mask objectionable flavors; protect unstable ingredients from degradation, such as from heat, moisture, air and light; provide controlled or delayed release; reduce hygroscopicity; and change the physical characteristics of the original material, such as improving its flowability and compression properties, reducing its dustiness, and modifying its density.

Food ingredient encapsulation was once thought of as a formulator's choice of last resort, i.e., a rather high priced and custom route to solving unique problems. Today however, higher production volumes and well-developed technologies have made a number of encapsulated products standard items and available at cost effective prices.

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There are a variety of encapsulation methods available today. Air Suspension encapsulation is one particularly versatile method and is traditionally available in two configurations: Top Spray and Bottom Spray (Wurster). Newer technologies, some of which are specifically discussed in other chapters of this book, include Centrifugal Extrusion, Centrifugal-Suspension Separation, Co-Crystallization, Mechanofusion Imbedding, and Molecular Inclusion Complexation. Whatever the type of method, it functions optimally when certain classes of ingredients are used. Additional methods become options when optimal coating integrity is not critical. It can be said with certainty that no one method can encapsulate everything well, or cost effectively. The following discussion on processing will focus on air suspension, or fluid bed, encapsulation, and specifically the top spray configuration.

Fluid Bed Encapsulation Technology

Fluid bed technology is generally used for encapsulating solid materials with hot melt or solvent-based coatings. Fluid bed encapsulation is accomplished by suspending solid particles in an upward-moving stream of air, which is temperature and humidity controlled. Once this moving, "fluid" bed of particles has reached the prescribed temperature and is moving uniformly, it is sprayed from the top with a finely atomized, liquid coating whose droplets are of smaller size than the substrate being coated. In the case of hot melts, the coating is hardened by solidification in cool air. In the case of solvent-based coatings, the coating is hardened by evaporation of the solvent in hot air. The working zone of a top spray fluid bed encapsulation unit is also known as the spray region. During the encapsulation process, each particle is gradually covered with a film of coating by making numerous passes into the spray region. Above the spray region resides the filter housing. There the upward-moving stream of fluidizing air passes through porous filter material which effectively traps very small particles entrained in the air and returns these particles to the process for further application of coating.

Key Processing Variables. As with every method of processing, fluid bed encapsulation has a number of important processing conditions one must be concerned with to achieve optimum results. One key processing variable is the volume of fluidization air used, which controls the height of the substrate particles within the coating region and gives proper bed movement for uniform coating. Another variable which is absolutely critical to the encapsulation process is the fluidization air temperature within the coating region. If the proper temperature is used, it will promote wet-out, or surface spreading, of the coating material onto the substrate. Using the improper temperature or having poor temperature control will result in incomplete coverage by the coating material and subsequently product quality will be poor.

Each of the following parameters fall within the processing category of Spray Conditions. Spray port size and nozzle height determine the size of droplets and the spray pattern that the substrate will be exposed to in the spray region. Droplets

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which are too large, or a spray pattern which is too close to the moving product bed, will tend to promote agglomeration instead of proper coating coverage. Similarly, coating spray rate and temperature, as well as atomizing air temperature and pressure, must be adjusted depending on the particle size of the substrate. This is necessary to ensure that the coating droplets are of the correct size and viscosity to properly spread out and coat the surface of each substrate particle.

Substrate Characteristics. To determine the feasibility of encapsulating a certain raw material using fluid bed technology, its physical characteristics must be investigated. Substrate shape and size are very critical to the quality of the final encapsulated product. In general the more spherical a particle's shape is, the better its encapsulation will be. This is due primarily to the absence of sharp edges which could protrude through the applied coating surface and become vulnerable to release. To a lesser degree it is thought to be due to the reduced amount of surface area requiring coverage, therefore the applied protective coating is thicker. Materials with irregular shapes normally require structure modification to improve their shape prior to encapsulation. Because of it's needle-like crystals, aspartame, for instance, must be agglomerated before it can be effectively encapsulated for baking applications.

In general it has been found that dense particles with a narrow particle size distribution and good flowability are the most suitable for encapsulation by fluid bed. Ideally a particle size distribution between 50 and 500 microns is best, although it is possible to encapsulate particles ranging from 35 to 5000 microns, albeit with limited success. Table I illustrates the particle size distribution of a few ingredients which are commonly encapsulated. It can be said that the maximum particle size allowed is dependent on the fluid bed's turbine capacity, while the minimum particle size allowed is dependent on the porosity of the exit air filter. When attempting to encapsulate fine powders, agglomeration in the beginning of the process is unavoidable. However, later in the process, effective coating of those same agglomerated particles can be achieved. Substrate bulk densities vary considerably and must be taken into consideration. Substrates with bulk densities below 0.3 grams/cc tend to be too friable and break apart during processing and therefore are not recommended.

Larger particle size versions of substrates have less particle surface area than their smaller particle size counterparts. Therefore, on a coating weight basis, encapsulated substrates with large size particles have thicker coatings on each particle than substrates with small size particles. Since an encapsulated product's degree of protection is directly related to the thickness of its applied coating, one can say that better encapsulation can be achieved, on a coating weight basis, using larger particle substrates than with smaller particle substrates.

Coating Material Characteristics. When evaluating a coating material for its feasibility in fluid bed encapsulation, a number of factors must be considered. A coating's viscosity, thermal stability and film-forming ability are critical. For

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Table I. Particle Size Distributions of Common Substrates

US Mesh No.	*Opening (Microns)*	*Coarse Salt*	*Coarse Citric Acid*	*Fine Gran. Citric Acid*	*Granular Salt*	*GDL*
10	2000	1	-	-	-	-
20	840	72	6	-	-	-
30	590	25	62	-	-	-
40	420	1	31	44	15	-
50	297	1	1	42	57	27
60	250	-	-	8	18	10
80	177	-	-	6	10	10
100	149	-	-	-	-	10
120	125	-	-	-	-	22
400	37	-	-	-	-	21

instance, in order for a coating material to be pumpable, and atomizable, it must have an acceptable viscosity. In the case of aqueous-based coatings, the acceptable viscosity will itself limit the solids concentration allowed in the coating solution. Coatings must typically withstand processing temperatures ranging from 15 to 75°C. Finally, since encapsulation is accomplished by the continual formation of a film on each particle, all coating materials must be able to spread over the particle surface.

Materials which are ideally suited for hot melt coating are hydrogenated vegetable oils, or stearines, such as soybean, cottonseed, palm, and canola (low erucic acid rapeseed); fatty acids; various emulsifiers; and waxes, such as beeswax and carnauba wax. Coating levels typically range from 5 to 50%, depending on the substrate's particle size and final degree of protection required. Commonly used water-soluble coatings are maltodextrins, starches, gums, and cellulose derivatives, or their combinations. Typical coating levels for water-soluble coatings also range from 5 to 50%, however processing to levels above 30% is generally cost prohibitive due to the lengthy processing times required to remove the water added during coating.

In gaining an understanding of encapsulation, it is particularly useful to observe the structure of encapsulated products under the microscope. Figure 1 depicts uncoated, large granular citric acid crystals, while Figure 2 shows the same large granular citric acid which has been well encapsulated with a coating of stearine. During processing some attrition naturally occurs. This along with the application of the coating itself has served to smooth the rough edges of each particle. The translucent appearance of the coating also indicates that the product has been manufactured using the correct temperatures and spray conditions.

Designing Custom Encapsulated Ingredients

Up to this point, encapsulation technology and the requirements for substrates and coating materials have been discussed. However, before designing a custom encapsulated ingredient, a significant amount of work must be done upfront to identify the desired release mechanism and a method for analytically estimating it, as well as to identify all conditions which the encapsulated product must survive.

Release Criteria. Hot melt encapsulated ingredients are widely used in the food industry in a number of different applications, the most obvious of which are those where it is desired to protect an ingredient up to the point that a certain temperature is reached. In those cases, the specific coating chosen is determined by its particular melting point range. The use of hot melt encapsulation is not limited only to thermal release situations. It has found wide use in mixing applications, where release is induced by physically stressing the encapsulated product's surface to cause breakage. These types of encapsulated ingredients are also used successfully when the desired release is caused by the gradual intrusion of water.

Ingredients which are encapsulated with water-soluble coatings, are typically useful in dry mix applications, where quick release through contact with water is

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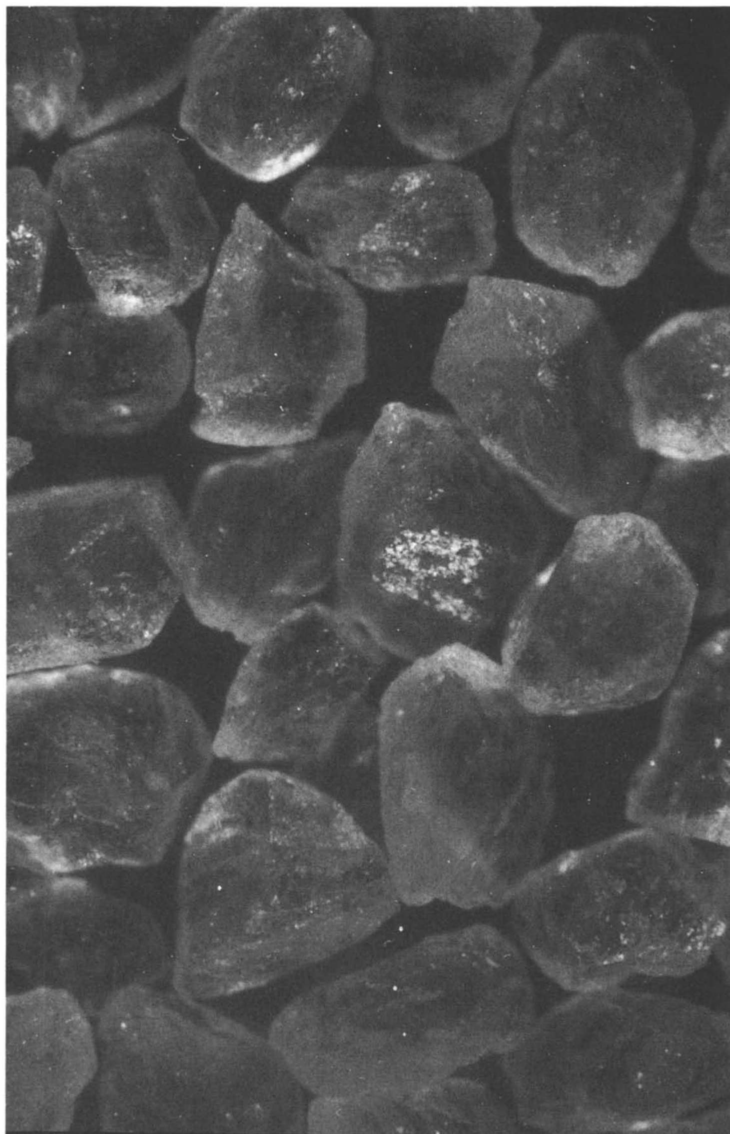

Figure 1. Large granular citric acid crystals, uncoated.

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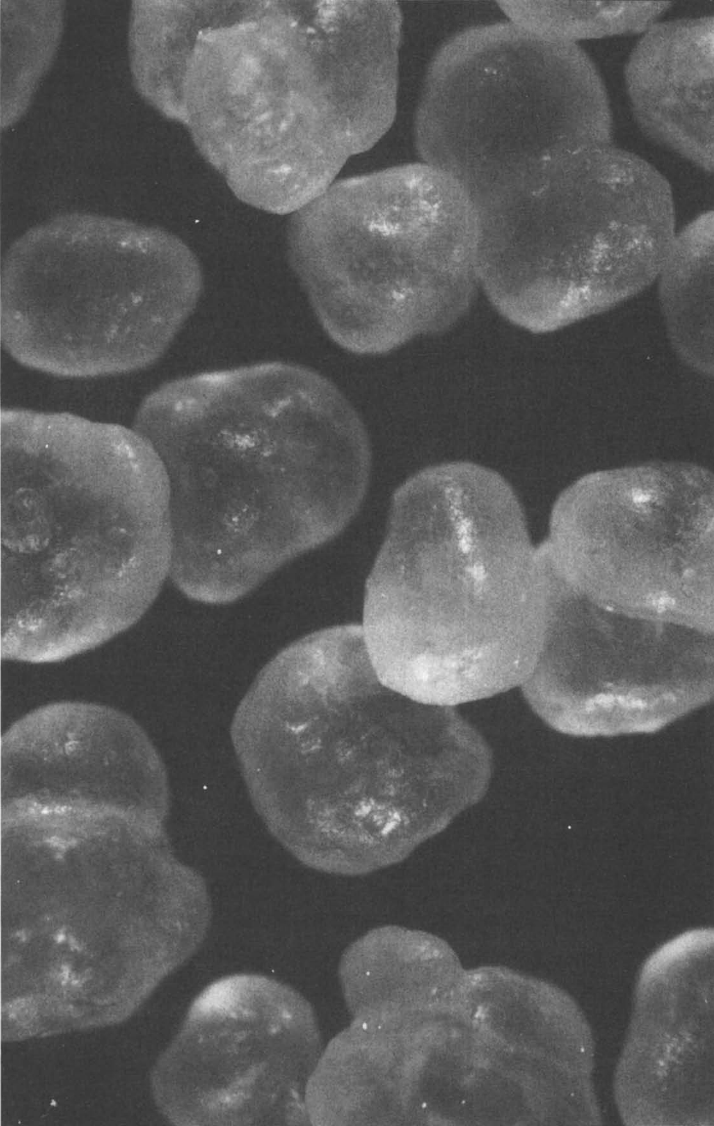

Figure 2. Large granular citric acid crystals, well encapsulated.

desired. Enteric coatings, although not yet widely applied in the food industry because of cost and regulatory constraints, can protect a substrate in water until a certain pH is reached. Currently these are commonly used in pharmaceutical digestive tract applications and can be applied using fluid bed technology.

Quality Control Measurements. The most basic test of encapsulated food ingredient quality is the analysis of substrate concentration or activity. This is normally accomplished through titration, but for substrates which are difficult or impractical to analyze, the concentration of coating material can be measured and reported instead.
Particle size distribution and bulk density are other common analyses used as well to characterize finished encapsulated products.

However, probably the most important determination of encapsulated product quality is an analysis called the leach rate test, which measures the amount of substrate released over a specified time period. This test is generally accomplished by adding a known amount of encapsulated product to a flask containing water and/or propylene glycol. The flask is then agitated on a Burrel Shaker for a set period of time. At the end of the time period, the solution is removed and analyzed for active material content. U.S. Patent #4,511,584 (Percel et al.) gives a specific procedure for determining the leach rate of a fat encapsulated, lactic acid/calcium lactate product.

The final determination of an encapsulated product's quality is its functionality when applied in the end user's food system. An example which illustrates this is glucono-delta-lactone (GDL), the mild food acid. When encapsulated with stearine hot melt, it can be used in some refrigerated bakery applications to control the rate of leavening. In one particular application it performs best only when its leach rate is within a very narrow range. Product manufactured outside the range results in packaging problems or poor finished product quality upon baking. The determination of the proper range of leach rates for this particularly sensitive application was only learned through trial and error, by evaluating a number of different encapsulated GDL products with various leach rates.

Leach Rate Data. In order to make some key observations, it would be helpful at this point to see some plotted leach rate data collected on various encapsulated products. The next few figures show the effect on leach rate brought about by varying the type of substrate and the coating level. Figure 3 compares different substrates, both with 15% coating; the top line is flaked topping salt, while the bottom line is table salt. The graph indicates that by simply changing the raw material's shape from that of a flaked topping salt to a high grade table salt, which has a more sphere-like shape, a formulator can significantly improve the salt's protection in a typical application. Figure 4 compares two coating levels on the same salt substrate, in this case, medium flaked topping salt. By increasing the coating level from 15 to 30%, a significant increase in protection is realized.

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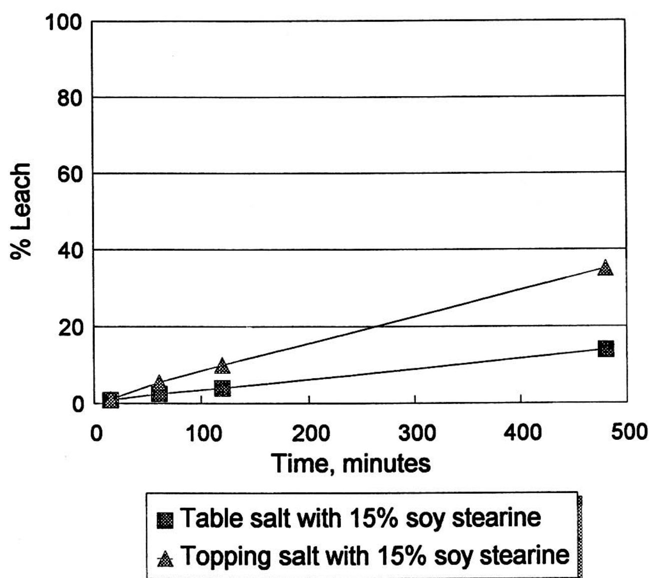

Figure 3. Effect of Shape on Leach Rate.

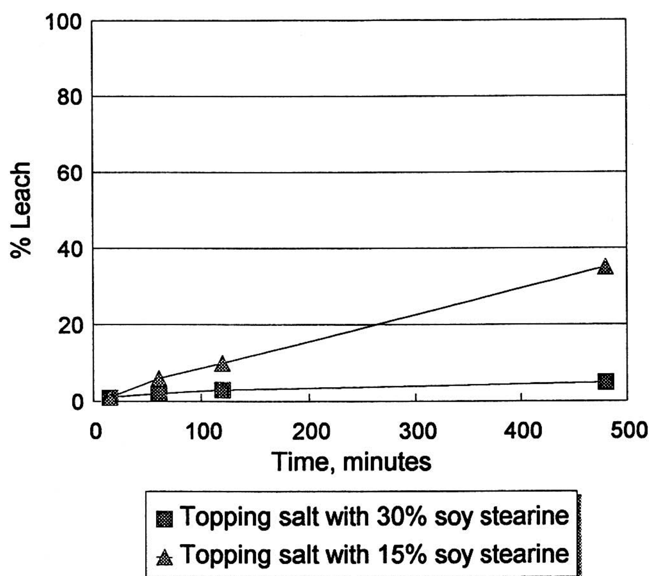

Figure 4. Effect of Coating Level on Leach Rate.

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The effects of varying processing conditions during manufacturing can be clearly seen in Figure 5. Here leach rate data from five different encapsulated GDL products is shown, each product made using one of two sets of slightly different processing conditions. The three products made using set #1 were each coated with a different level of stearine, namely 20, 30, and 40%. The two products made using set #2 were each coated with a different level of stearine as well, in this case 20 and 30%. As the figure shows, better protection, i.e., lower leach value, 60 vs. 82, was achieved when a 20% coating was applied using set #2 compared to a 20% coating applied using set #1. It also should be noted that a full 10% less coating was required to achieve the same level of protection when only slightly different processing conditions were used. Similarly, a product made with a 30% coating using set #2 was as well protected as one made with a 40% coating using set #1, i.e., leach values of 35 vs. 33. This analysis clearly shows the importance of optimizing processing conditions.

Experimental Design. Finally it should be said that a properly planned Design of Experiment (DOX) can yield a tremendous amount of data which can be statistically analyzed to determine the optimum set of processing conditions required. However, a limited amount of information regarding specific fluid bed processing techniques is available in the literature. Because of its direct relevancy to the encapsulation of food, one reference focusing on pharmaceutical coating technology should be consulted (1).

APPLICATIONS

Nutritional Supplement Industry. Encapsulation is commonly used in sustained release drug capsules and tablets. Many active drugs also have objectionable flavors and odors and need encapsulation technology for taste masking. For similar reasons, this technology is used in the nutritional supplement market to supply encapsulated versions of such nutritional substances as vitamin C, vitamin B's, ferrous sulfate, ferrous fumarate, sodium ascorbate, potassium chloride, and a variety of vitamin/mineral premixes.

Specifically, fat coatings prevent reaction between ascorbic acid and iron-containing ingredients in multi-vitamin tablets and powdered infant formula. Encapsulating ferrous fumarate and ferrous sulfate also improves their flowability and compressibility, as well as reducing their dustiness compared to their raw material versions. In applications where small tablet size is a critical element, such as in children's chewable tablets, fluid bed encapsulated ingredients have an advantage over conventional spray chilled versions. Because of the higher concentration, or loading, of active material in fluid bed encapsulated ingredients, formulators can reduce the total amount of material required to deliver the desired benefit to the consumer.

Today's "engineered foods" are nutritional systems in which modern science has influenced their development. Encapsulated ingredients are used in prepared

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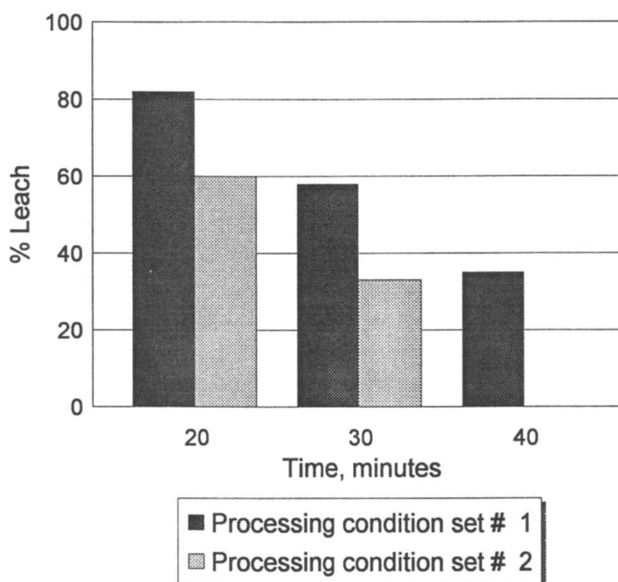

Figure 5. Effect of Processing Changes on Leach Rate.

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foods, fortified foods, nutritional mixes, seasonings, fillings, desserts, dry mix puddings, teas, dry mix beverages, dairy mixes, confectionery tablets, and starch gel candies. Encapsulation can also improve the flow and metering of ingredients used in high speed packaging equipment, as well as decreasing the dustiness often experienced during processing.

By encapsulating typically hygroscopic food acids, such as citric acid, one can prevent clumping during processing, because the encapsulated acid cannot collect moisture from the air. Encapsulated acids have also found use in certain dry pudding and pie filling mixes. The shelf-life of these products can be extended through encapsulation by preventing premature acid hydrolysis of the starch during storage. Once cooked, however, the optimum product firmness is achieved and the acid releases to perform its flavor function.

Baking Industry. The Baking Industry has long been aware of the need for stable acids and baking soda for use in wet and dry mixes to control the release of carbon dioxide during processing and subsequent baking. Products commonly encapsulated for bakery applications include a variety of leavening system ingredients, as well as vitamin C, acetic acid, lactic acid, potassium sorbate, sorbic acid, calcium propionate and salt. Encapsulated vitamin C in particular has found use as an effective potassium bromate replacer, which is becoming an increasingly unpopular substance.

For yeast raised doughs, encapsulated versions of salt, potassium sorbate and sorbic acid are required for the yeast to grow because they do not allow the pH to drop too early in the baking process. However, once baking is complete, the ingredient's mold inhibiting properties are released. In frozen breads, ice crystal migration in the dough is known to cause chemical and physical reactions to occur. If the dough formula specifies the use of salt or acidulants, encapsulated versions can be used in order to prevent the breakdown of yeast cell walls, which would result in low CO_2 production after thawing and during proofing.

Compared to fresh doughs, chemically leavened doughs typically exhibit inferior rise and texture upon baking. By encapsulating the sodium bicarbonate, its reaction with acid-bearing components in the dough is not simply prevented but controlled. This is especially necessary in refrigerated ready-to-bake biscuit doughs. Here some leavening is required initially when the dough is formed, but ideally no more should occur until after the packaging step. In this application it has been shown that encapsulating either the acid or the base is equally effective. Likewise, in frozen pancake batters, encapsulated SAPP and SALP improve product performance by minimizing gassing during batter make-up. Encapsulated calcium propionate can also be used to prevent calcium ion interference with other leavening agents in chemically leavened products. As before, mold inhibiting properties are released once baking is complete.

Encapsulated salt has also been applied to pretzels and other post-baked products to protect the salt from being absorbed into the baked good due to water migration.

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Meat Industry. In the meat industry, encapsulated acids, such as lactic, citric and GDL, are used to develop color and flavor systems in meat emulsions, dry sausage products, uncooked processed meats and meat-containing products, such as pasta meals. Fat encapsulation allows the acid to survive the blending process, yielding a uniform dispersion within the meat. Later, the encapsulated acid controls the drop in pH and prevents the meat from prematurely setting.

Cured meat products, especially summer sausages, pepperoni, and hard salami, have historically been produced using lactic acid-producing bacteria cultures in order to develop the flavor and lower the pH. However, using bacteria cultures requires considerable processing time, and a certain degree of batch-to-batch variation is inherent. It is possible to use lactic and citric acids instead, but their uncoated versions react immediately with the meat and render it too stiff to be workable. By encapsulating the acids so that they will not release until they reach smokehouse temperatures, the formulator can achieve a very reproducible pH and drastically shorten the total processing time compared to the fermentation process.

Encapsulated salt is used in meats to prevent development of rancidity, as well as premature set due to myofibular protein binding. Auburn University developed a low-fat ground beef formula specifying encapsulated salt for this very reason. Because of the reduction of fat in the total formula, extra salt was required to assist in fully developing the flavor system. It was found that the required extra salt had to be added in the form of encapsulated salt, in order to extend shelf life and maintain formability of the meat patties during processing.

Future Potential. In today's value-added world, the benefits that encapsulation technology "brings to the table" in solving unique processing and formulation problems are quite substantial. As new technologies emerge in the field of encapsulation, so too will the markets in which new encapsulated ingredients can be successfully utilized.

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Chapter 8

Centrifugal Suspension–Separation for Coating Food Ingredients

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A new coating method, centrifugal suspension-separation (CSS), has been developed which permits the coating of particles and droplets over a wide range of diameter with a variety of coating materials. The process has now been tested in several food and flavor applications. A number of advantages, limitations and problems have become apparent from this work. The following discussion will focus on general principles important in coating food particles, observations on potential applications of CSS in this field and some comparisons of CSS with other coating processes.

The CSS coating process has been described elsewhere (1,2,3). The essence of the method is the formation of a suspension of core particles in the coating liquid, and the passage of this suspension over a rotating disk under conditions giving a film of the coating liquid at the edge of the disk which is much thinner than the diameter of the core particles.

Under these conditions, two different types and sizes of particles are formed at the edge of the disk: core particles coated with a layer of residual coating, and smaller droplets of pure coating material. The coating apparatus is mounted at the top of a drying or cooling tower. All the particles are solidified as they fall through the tower and the smaller coating particles are removed (using a sieve of a cyclone) for recycle.

The process has several characteristics which recommend it for coating of particles and droplets for food and flavor applications. It requires only seconds, is a continuous process and can coat particles from roughly 30 microns up to several millimeters at high production rates.

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The food-grade coatings can be solutions, suspensions or meltable materials such as fats, diglycerides, PEG, etc., applied directly without solvents.

Mechanisms Of Release

All coating, protection and controlled release systems must be designed with the release mechanism in mind. For foods (and many other applications) there are several mechanisms which can be employed.

Dissolution of the Coating. Coating dissolution can be used as a release mechanism when the coated ingredient is part of a dry formulation which is placed in water before use. The coating might be a sugar, a starch derivative, a gelatin-based coating, poly(vinyl pyrollidone), polyethylene glycol or several other materials. Dissolution of the coating will occur quite rapidly unless the particle is large and the coating is thick. Unfortunately, very few water-soluble materials can be applied directly as melts, so there is an additional cost associated with drying most of these coatings.

Melting of the Coating. In some cases, melting of the coating material can also be used as a release method. In such applications, the coated particles are stored at temperatures well below the melting point of the coating, then heated above this temperature during preparation or cooking. This is particularly effective when the melted coating has a low viscosity. In that case, stirring the product after the coating has melted will release the coated ingredients.

Osmotic Rupture of the Wall. Osmotic phenomena can cause the release of a water-soluble core material when it is coated and then placed in water. Water will enter the particle by diffusion, form a saturated solution of the water soluble core, lowering the chemical potential of the water inside the particle. This maintains a gradient for inward water diffusion. Since water is virtually incompressible, the entrance of a small amount of water will increase the pressure inside the particle. The pressure will increase until the wall ruptures, releasing the active ingredient. This is the major mechanism of release of water-soluble materials. In the example of a highly water-soluble core particle of 100 microns diameter having a coating of fat which is 50% of the particle weight, the half-release time might will be measured in tens of seconds or a few minutes, depending upon the exact core solubility and the properties of the coating.

Wall Rupture by Chewing. Chewing can be used as a release mechanism in products where there is no concern about feeling the particles in the mouth. An example would be 1000-micron capsules of garlic or herb flavor for a frozen pizza. In this case, feeling the particles in the mouth would have no adverse effects.

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Considerations Of Particle Size And Shape

Particle Diameter. For protection of a core material, or to slow its release or loss of volatile components, a coated particle should be as large as possible to minimize area/volume and to permit a thicker coating (for a given fraction of coating on the particle.)

For example, a coated particle which is 30 microns in diameter and consists of 50% coating has a coating thickness of only 3.1 microns. It is difficult to obtain protection with such a thin coating. A 300-micron particle having the same fraction of coating would have a coating thickness of 31 microns. The larger particle would not only have one-tenth the area/volume but also a protective wall ten times thicker. The gain from this increase in particle diameter would be a 100-fold increase in protection.

In practice, the maximum diameter will be set by considerations such as mouth-feel, release mechanism, visual appearance, etc. If there must be no gritty feeling in the mouth for a liquid suspension, the mean diameter must be roughly 80 microns for hard coatings, and can be up to 120 microns for coatings which are slightly pliable. However, in products such as smooth chocolate, the tongue behaves differently. In this application, even 75-micron particles are detected as gritty.

Size Limits For Various Coating Processes. Fluid-bed coating can apply many coatings to particles which are 150 microns and larger, and can apply low-viscosity coatings to somewhat smaller particles without aggregating them, although the coating time increases. For particle diameters of below 100 microns, the limitations are usually severe.

Coacervation processes permit coating of particles down to a few microns in diameter, but the ethyl cellulose coacervation process cannot be generally used for foods, and the gelatin-gum arabic process is relatively expensive and is approved only for certain flavor, mineral and vitamin applications.

Interfacial polymerization and urea-formaldehyde coating processes permit easy coating of small liquid droplets, but the chemicals used in these processes are not acceptable in foods.

CSS permits coating of single particles down to 20-40 microns, depending upon the viscosity of the coating fluid. Particles of 60-120 microns diameter have been coated singly for numerous applications, including foods, chewing gums and taste-masking of drug particles for non-gritty suspension formulation.

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Particle Size Distribution. This variable has received little attention, partly because it cannot often be controlled. However, there are many applications where it is critical. In any problem of retarding the loss of volatile materials, protecting a material from its environment, taste-masking, controlled release or delayed release, there is a strong effect of particle diameter and, therefore, of particle size distribution.

For example, in a food application, if the average-sized coated particles of 100 microns give adequate protection of a core material from moisture, the smaller particles in the size distribution will be degraded much too fast. At the other end of the size distribution, the larger particles may be gritty. In this case, a narrow size distribution would be of great value, since all particles could be made just below the largest acceptable diameter, permitting all particles to be acceptable but have optimal protection.

There is another effect which is not so apparent. If a wide size distribution of core particles is fed to many coating processes, the fines will be agglomerated with themselves and with larger particles during the coating process. A significant amount of coating will then be needed to fill the interstitial space in the aggregates, and yet there will be thin spots over the outer edges of the aggregates, causing premature release or poor protection.

An analogous effect occurs in particles coated by CSS. This is the direct inclusion of the distribution's fine particles in the coating on the coarser particles. The coating over these included fines is thin and this gives areas where premature leakage can occur. As a rough guide, good coating by CSS requires that the size distribution of core particles not be broader than 3/1 from 5% to 95% of cumulative volume. 2/1 is even better.

Shape of the Core Particles. For virtually all coating methods, the higher the sphericity of the core particles the more uniform the coating. For fluid-bed and pan coating, the core shape is less important, since the coating deposited by these methods tends to follow the contour of the particle fairly well. Nevertheless, even for these processes, a given degree of protection can be provided with less coating material if there are no protrusions or sharp corners on the particles.

Shape of the core particle is more important in CSS, since the outer shape of the particle coming off the disk is largely determined by surface tension, causing the shape of the coated particle to be more rounded than the core particle. Hence, there will be thin areas of coating over corners and edges. Spherical core particles are not necessary for good coating by CSS, but the core particles should be somewhat round, with no protrusions or sharp corners.

The smaller the core particles, the more important these effects of shape because the wall is so thin. Any additional thinning of the coasting over protrusions causes very rapid leakage.

Roughness of the surface of the core particle requires that the small indentations be filled before a protective coating can be obtained. This increases the amount of coating which must be applied to obtain a desired degree of protection.

Specific Applications Of CSS

Stabilization of Spray-Dried Flavors. Many spray-dried flavors retain a good flavor profile and are easy to handle, but suffer from loss of the flavor in long-term storage, or may release too rapidly in some applications. It would seem that a protective coating over the spray-dried particles would solve these problems. However, coating the particles is not as simple as it appears.

The small size of the spray-dried core particles is the first difficulty. A typical spray-dried product might have a mean diameter of 15-50 microns, and usually there is a wide size distribution. Very few coating methods acceptable for foods can coat such small particles. With effort, CSS can be used, but the size distribution of the unused coating particles will likely have some overlap with the size distribution of the coated product. Classification of particles in this size range to separate out the excess coating particles can only be accomplished using cyclones, which do not give a sharp cut-off in diameter. The result may be an unacceptable amount of droplets of pure coating material in the final product when CSS is used.

Spray-dried particles are seldom spherical, and the thin coating over protrusions lowers the protection greatly. As described in the previous section, perfect coating of such small particles might not be sufficient because the coating would be so thin. Larger spray-dried particles are needed - up to 100 microns would be ideal in many applications.

Unfortunately, forming spherical core particles of this larger diameter is nearly impossible in a typical spray-drying operation. However, after considerable development work on the typical spray-drying operating variables, such core particles have recently been produced in this laboratory and in the larger-scale equipment of Drytec, Ltd. in England, the company which designs and builds the commercial CSS plants. In one case, spherical particles up to 150 microns in diameter were produced and subsequently coated.

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Protection Against Moisture. There are a number of materials which are of interest in food and animal feed which are unstable to moisture, or which absorb moisture from other ingredients in the product during storage. A coating can be useful in stabilizing these materials.

A hydrophobic wall is needed to prevent the entrance of water vapor into such a particle. For foods, meltable hydrophobic coating formulations may contain such materials as fats, waxes, diglycerides, etc. Such materials having melting points from 12°C to 90°C have been successfully applied by CSS in food and animal-feed studies.

In one application, aspartame was stabilized against degradation in storage by forming spherical particles having a mean diameter of 100 microns which were subsequently overcoated. In another application, granules containing methionine were overcoated to slow release at neutral pH (4). (See Table I.)

Several vitamins for both human food and animal feed applications have been stabilized to degradation by moisture and oxygen.

Stabilization During Steam-Pelleting. Although this is an animal feed application, its successful solution may indicate potential for some uses in human foods. In steam-pelleting, the ingredients are mixed together vigorously as solids, softened by contact with steam (with a final temperature of roughly 80-85°C), then extruded to form pellets. We have tested many coated particles in this process, taking samples at various stages.

Several coating materials tolerate the physical mixing without degradation. Several tough, higher melting coatings can tolerate heating with steam without losing their integrity, even though they soften somewhat. However, in these cases, the softened walls are ruptured in passing through the extruder. Recently, hydrophobic coating formulations having melting points above 90°C have been developed which maintain their integrity throughout the entire process.

Protection and Release in Water. The coating process also makes it possible to protect materials from release in water for a certain period of time during mixing and preparation, but to release them later during cooking. This has already been accomplished for sodium bicarbonate in one food application (Table II).

Since the melting point of the coating can be high, it is possible to protect some materials from moisture in dry mixes, maintaining the texture, but have them released in soups, etc., by melting at high temperature near the end of preparation.

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Table I. Release Of Methionine

Buffer at pH 6
Diameter: 0.5-0.63 Mm
Coating: Wax/Polyethylene Melt

TIME (HR)	PERCENT RELEASED	
	CORE PARTICLE (95.5% ACTIVE)	COATED CORE (65.5% ACTIVE)
0.5	92.7	1.3
2.0	100.0	2.5
3.0	100.0	3.6
24.0	100.0	61.0

Table II. Release Of Sodium Bicarbonate In Water

Mean Diameter: 250 Microns
Coating: Hydrogenated Rapeseed Oil

TIME (HR)	PERCENT RELEASED	
	CORE PARTICLE	COATED CORE
1	90.3	31.8
3		55.8
4	100.0	
5		65.9
10		71.2
15		81.3
20		89.9

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In some food applications the walls must be hydrophobic to protect the core material from water vapor, but the core must release rapidly when the particles are placed in water. This is now possible using food-grade wall formulations which begin to release the core material within 5 seconds after being placed in liquid water.

Aroma Release in Heating and Cooking. Since coatings can be applied which have a controllable melting temperature, it is possible to isolate some flavors and aromas during storage, e.g., in frozen products, but have the aroma and flavor released during cooking at a predetermined temperature by melting the protective wall. This would retard migration of flavors during storage and would add an aroma impact to the product by releasing the flavor just before consumption.

Stabilization and Release of Enzymes. For stabilization in storage, it is useful to form the enzymes into dry particles and coat them. In addition, in some applications, the dry enzyme particles must show a delayed release after being added to water. CSS has been used for some years to coat several families of enzymes. Although enzymes are considered unstable at elevated temperatures, this instability has usually been measured over hours or days. Since the CSS coating process requires only seconds, enzyme granules have been found to be quite stable when being coated with melted materials at, e.g., 100°C.

Retarding Oxygenation. Oxidation of some product particles can be retarded significantly by coating them to slow the entrance of oxygen. If the oxygen sensitivity is not too high, a simple coating of wax or fat can often extend the shelf life of the product. For additional protection, finely divided oxygen scavengers can be suspended in the melted coating before it is placed on the particles. Putting solid particles in the wall is not a problem with CSS because the coating does not pass through an orifice or constriction. Two oxygen-sensitive materials for use in food and animal feed have been successfully protected by coating with CSS.

Coating Natural Food Particles. There are several reasons one might want to coat particles of natural foods in addition to flavors. For example, a coating would retard the oxygenation of nuts and also help in maintaining the proper low moisture content to maintain crispness and avoid the off-taste of aging.

Similarly, raisins might be coated to prevent them from becoming too hard by losing moisture to other materials, as occurs in cereals. Test trials have already been carried out in coating raisins by CSS. Such a technique would also be attractive for coating bits (or concentrates) of raspberry, apricot, blueberries, etc.

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Summary

A variety of food applications of microencapsulation are possible if the coating can be applied as a simple melt or solution, if the process has a very low cost and if the particles for some applications can be small enough to avoid grittiness. Centrifugal suspension-separation is a new method which shows promise for many such applications.

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Chapter 9

Centrifugal Extrusion Encapsulation

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Centrifugal extrusion encapsulation is suitable for specialty applications requiring protection of food ingredients. This technique offers a process for formulating with a variety of shell materials including gelatin, alginates, carrageenan, starches, fats, and waxes. Shell systems may be a blend of two or more polymers to obtain the desired characteristics. Capsule size capability of the process is in the range of 150-2000 µm, with the "comfort range" being in the 500-1000 µm range. Loadings of 20-80% can be obtained.

The centrifugal extrusion process is a liquid coextrusion process utilizing nozzles consisting of concentric orifices located on the outer circumference of a rotating cylinder (head) (Figure 1). A liquid core material is pumped through the inner orifice and a liquid shell material through the outer orifice forming a coextruded rod of core material surrounded by shell material. As the device rotates, the extruded rod breaks into droplets which form capsules.

Background

Simple stationary extrusion using nozzles was first used to make capsules in the 1950's. Several patents were awarded in the 1960's utilizing rotating orifice equipment and a submerged nozzle (1-3). The stationary nozzle system depended on gravity and jet stream break-up to form capsules. The process was somewhat limited in capsule size capability and production rate. The centrifugal extrusion nozzle device was developed to provide higher production rates and better size control of capsules produced.

Process Controls

Controllable parameters that can be used to control capsule size, payload and production rate are nozzle size, rotational speed, and feed rates of the core and

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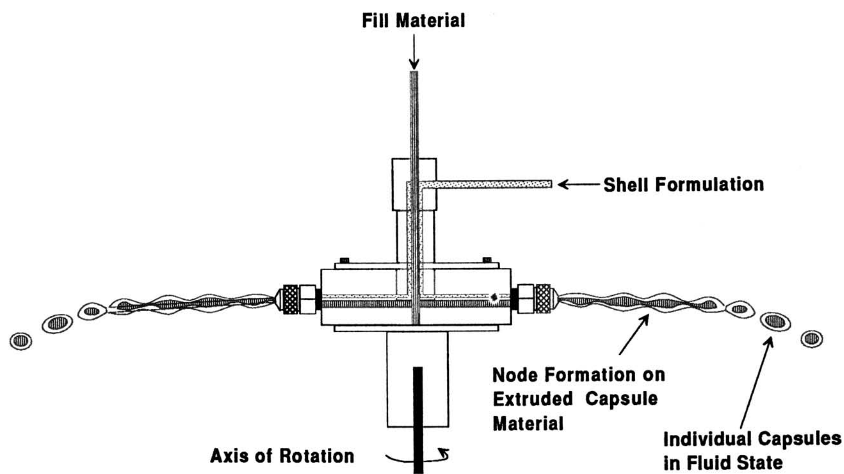

Figure 1. Centrifugal Extrusion Device.
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fill. Nozzle sizes can range from combinations of .010 inch inner/.015 inch outer to .060/.080 are generally used in forming capsules, with choice depending on the target capsule size. Rotational speed also affects capsule size and is usually in the range of several hundred to several thousand RPM. Feed rates are used to adjust the capsule payload and to set production rates. The materials are pumped using positive displacement pumps to accurately control the rates.

Shell Materials

Shell materials (most are GRAS for foods) that can be used with the process include the following.

Aqueous systems

- Gelatin
- Sodium alginate
- Carrageenan
- Starches
- Cellulose derivatives
- Gum arabic

Hot melts

- Fats/fatty acids
- Waxes
- Polyethylene glycol

Shell materials should be good film formers and be capable of being rapidly hardened in order to collect the capsules. Usually a blend of polymers is used as the shell material to provide the hardening mechanism and the desired release properties. The solids content varies for different shell systems and for different molecular weights of each type shell. Controlling factors are viscosity and "stringiness" of the solutions. The viscosity should be low enough to allow for the extruded stream to break into droplets without excessive tailing or stringing between the individual capsules. With some shell systems, heat can be used to influence the viscosity. Generally materials with viscosities up to several thousand centipoise can be utilized.

Core Materials

Core materials for use in the centrifugal extrusion process must be in the liquid form. The following types of liquids can be used.

- Materials that are liquid at room temperature.
- Solids that can be melted at temperatures below about 80° C to form a liquid.
- A dispersion of finely divided solids in a liquid.

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In Encapsulation and Controlled Release of Food Ingredients; Risch, S., et al.;
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The materials must be pumpable and have a viscosity low enough to form droplets when the extruded stream from the nozzle breaks up. Viscosities up to several thousand centipoise can usually be processed. Examples of core materials include

- vegetable oils/hard fats,
- flavor oils,
- vitamins/micronutrients,
- acids,
- dyes,
- seasonings,
- aqueous systems, and
- air.

More information on the types of ingredients suitable for encapsulation are available in previous publications [4,5].

Capsule Size and Loading Capabilities

Capsule size for the centrifugal extrusion device ranges from about 150 micrometers up to several millimeters in diameter. For a specific target size, distribution will be in a normal Bell type curve. Figure 2 shows a computerized image analysis of capsules prepared using a hot melt shell material. The capsules were prepared using a .033 inch inner/.052 inch outer nozzle and at a head speed of 570 RPM. The shell and fill feed rates were 28.5 and 30 grams per minute per nozzle respectively.

The size range for the capsules is 0.798 to 1.933 millimeters with a mean of 1.297 millimeters. The standard deviation is 0.211 with a coefficient of variance of 16.3%.

Capsule size is controlled by orifice size, head speed, and feed rates of the shell and core materials. Methods for preparing uniform size capsules using induced vibration of nozzles is currently being investigated.

Capsule payloads (core content) can be varied from 20-60 wt% for most applications and up to 75-80 wt% for some shell systems. The loading is controlled by setting the pumping rates of the shell and core material to provide the desired dry (after removal of shell solvent) payload.

Capsule Collection Techniques

As the capsules leave the nozzle, they are in the liquid state and must be rapidly hardened before they can be further processed. Depending on the shell material, the capsules can be collected in a liquid reaction bath, by simple cooling, by powder collection, misting, or solvent evaporation.

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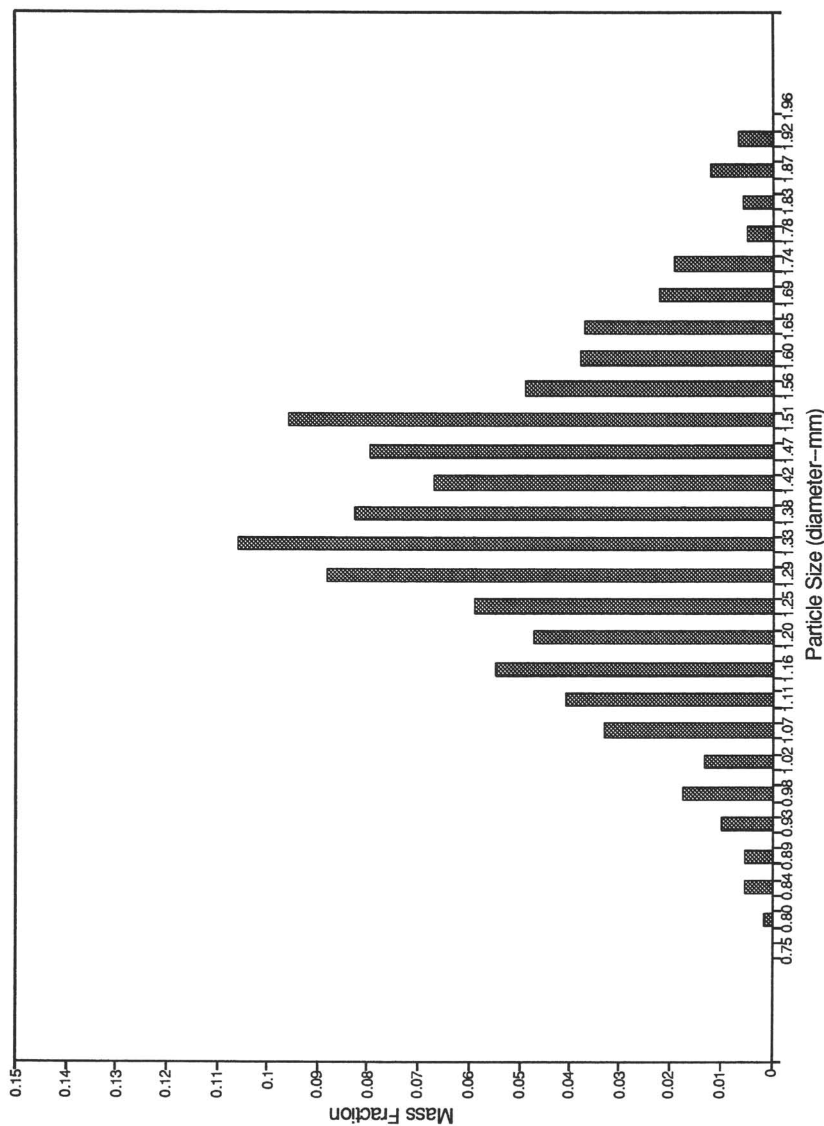

Figure 2. Computerized image analysis of capsule size. Reprinted with permission from Southwest Research Institute

Liquid Bath. When using sodium alginate alone or in combination with other polymers as the shell material, the capsules can be collected in a calcium salt solution. When the capsules come in contact with the bath, the sodium alginate is rapidly converted to the insoluble calcium salt to rapidly harden the capsules. Capsules can then be processed to remove the water in the shell and yield a dry product.

Cooling. Cooling is used when hot melt shell systems are used. Sufficient flight time is allowed for the shell material to solidify before impacting the collection area. No further processing of the capsules is required.

Powder Collection. When using aqueous shell systems such as gelatin or carrageenan (alone or with other polymers) that form a gel on cooling, powder collection is used to prevent the capsules from sticking together during the collection and drying process. A modified hydrophobic starch is well suited for this application as it forms a thin coating on the capsule surface. After collection, the starch is separated from the capsules by screening and the remaining moisture in the shell is removed.

Misting. Capsules having hot melt shell systems can be collected by projecting the capsules into a mist of chilled water to rapidly harden the capsule shell. This allows for the collection of larger capsules in a smaller area than would be possible with simply cooling in flight as described above.

Solvent Evaporation. The process is adaptable to large spray dryers where enough heat can be supplied to dry the capsule wall.

Example and Comparison to Spray Dried Product

Orange oil capsules having a gelatin (300 Bloom)/sorbitol shell (80/20 ratio) were prepared. The capsule size was 400-800 µm and the loading was 40% oil by weight. These were compared (Klaus Bauer, Dragoco, personal communication, 1993) to a proprietary water soluble spray dried formulation of the same oil. Test samples were as follows.

A. Spray dried product containing orange oil without antioxidant (loading 20.8%).

B. Capsules prepared using centrifugal extrusion equipment containing the same orange oil without antioxidant (loading 40.2%).

Samples were stored in a freezer and aged in an oven at 48 °C for 6 weeks.

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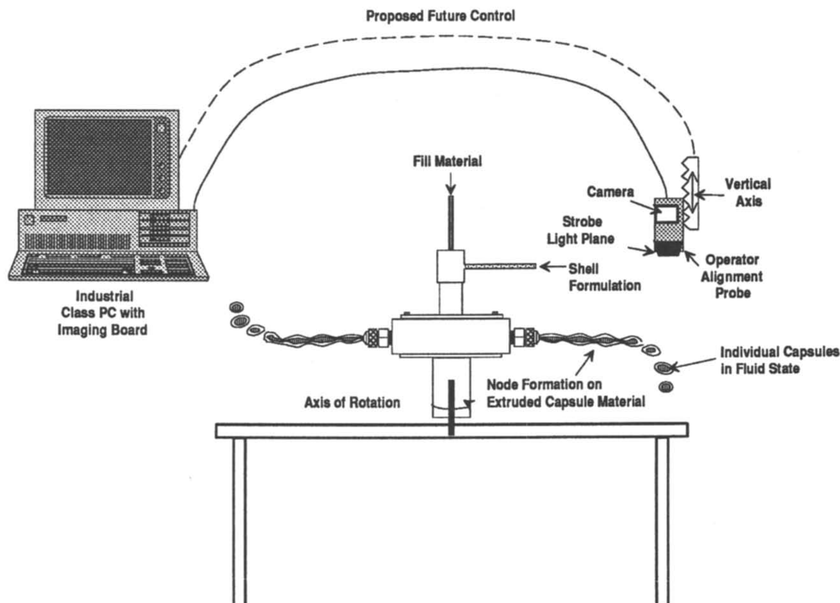

Figure 3. Machine Vision System for Centrifugal Extrusion Encapsulation Unit. Reprinted with permission from Southwest Research Institute

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Test Results. Capsule sample B is insoluble in cold or room temperature water whereas the capsules from A are soluble. This is to be expected because of the gelatin shell used for B. The B sample is initially soluble in hot water but the solubility decreases with aging. This may be due to crosslinking of the gelatin shell by flavor components. This would limit the use of the capsules to applications where release is by rupture of the capsule.

The capsules from sample B show a slight improvement to oxidation over sample A after 4 weeks of oven storage. The loading of sample B is higher than sample A and the capsule size is larger. The larger size is expected because of differences in process capabilities.

The solubility profile of the capsules can be changed by using other shell systems. For example, a shell material consisting of a 30:1 ratio of a water soluble starch:carrageenan (gelling agent) provides a water soluble system.

New Developments

A machine vision system is being developed to provide on-line monitoring of capsule size and sphericity. A camera is being used to capture images of capsules as they are formed. A typical setup is shown in Figure 3. A computer analyses the image for size and shape, providing rapid feed back to the operator.

This allows the operator to make needed adjustments as necessary. Future additions include computerized process controls that would make the needed adjustments to achieve a preset size capsule.

Summary

The centrifugal extrusion process is capable of producing capsules over a broad size range and using a variety of shell materials. Capsules produced are single core in nature, having a distinct shell surrounding a core material. Both aqueous and nonaqueous materials can be encapsulated with the nonaqueous types being the most suitable. Shell material selection can be used to provide good protection against oxidation and light and provide release under specific conditions.

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Chapter 10

Utilization of Coacervated Flavors

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Food Scientists and Application Specialists are continually searching for new methods to protect and deliver flavors. The harsh environments of some food processes like baking, extruding, retorting, and deep frying, to name a few, create unique problems for the survival of flavors in finished food products. Losses in flavor intensity and quality are typically due to evaporation, steam distillation, chemical absorption, chemical reactions, and/or oxidation. Encapsulation enhances flavor delivery by controlling the flavor environment. Coacervation encapsulation creates a barrier of protein between the flavor and the food base. This barrier offers improved flavor performance and shelf-life stability in many food systems. In some cases, encapsulation produces unique flavor performance in food items never before offered to the marketplace.

The incorporation of encapsulated flavors in consumer food product requires expertise in both food science and encapsulation science. Most encapsulation laboratories specialize in the unit operations of microcapsule production. Their inexperience in food processing limits their ability to discover the benefits of encapsulation. Food scientists deal with many food development problems where encapsulation as a formulation tool is useful. The successful formulator must understand the usefulness of microcapsule properties. The lack of good technical articles dealing with the uses of encapsulated products shows that there is a need to teach the important factors in using encapsulated flavors for consumer food products.

The field of encapsulation and controlled release involves a number of different techniques to produce particles. Generally, one material or group of materials (often referred to as the wall) coats or entraps another material (often called the core). One way of classifying the different techniques is to divide them into two categories determined by the medium from which the microcapsules form: liquid suspending or gas suspending (1). The food industry commonly utilizes spray drying, extrusion, and

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fluidized bed coating. Spray drying and fluidized bed coating utilize air or gas as the suspending medium. Extrusion encapsulation involves a liquid suspending medium with the mixture of carrier and flavor extruded into a liquid medium (usually isopropanol) to desolvate the water and solidify the carrier. There are a number of other techniques that involve the use of a liquid medium to form microcapsules including coacervation, polymer-polymer incompatibility and interfacial (or in situ) polymerization.

Coacervation is one of the oldest techniques for encapsulation. Most scientists consider it the true microencapsulation process in that the wall material completely surrounds the core with a continuous coating of wall material. Coacervation is defined as "the partial miscibility of two or more optically isotropic liquids, at least one of which is in the colloidal state" (2). Barrett Green investigated coacervation as early as the 1930s (3). This work, which used specifically aqueous phase separation, led to the development of carbonless paper. National Cash Register Company patented the aqueous phase coacervation process in 1957. (4).

Coacervation Process

Coacervation begins with dissolution of a gelling protein into water. The process then proceeds by emulsifying core material (flavor oil) into the protein solution. Coacervation occurs by one of two methods; simple or complex.

Simple coacervation involves the addition of a non-solvent or another chemical that competes for solubility with gelatin protein (5). The gelatin protein precipitation creates a protein rich coacervate phase.

Complex coacervation involves the use of a second oppositely charged hydrophilic colloid. A polymer to polymer complex forms when the positive charges on a protein polymer are neutralized by the charges of the second anionic gum or other suitable macromolecule. The complex decreases in water solubility creating a protein rich coacervate phase. This is the more commonly employed method of encapsulation.(6)

A protein rich colloidal phase is present in both cases. The colloid will remain liquid if the temperature stays above the gel point of the aqueous gelatin solution. Liquid gelatin colloid will slowly migrate to the surface of the oil, reducing the total interfacial energy. Complete colloidal migration yields a microcapsule consisting of a single drop of flavor oil enveloped within a continuous wall of gelatin material. The process applies a continuous coating to all particles large and small. (7) Lowering the temperature below the gelatin gel point hardens the wall material. The process is reversible with the addition of heat, acids and bases, or dilution. The addition of divalent salts or aldehydes insolublizes the wall material and makes the coacervation process irreversible.

Controllable Attributes

Coacervation capsules can provide reproducible food application results when we understand release mechanisms and properties of flavor payload and capsule size.

Release mechanism is the most important property of any encapsulation technology. The mode of release will determine which technology to use in a food base. Coacervated flavors release by fracturing the protein membrane surrounding the oil

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drop. The protein membrane will not melt or dissolve during the cooking process, thereby reducing the interaction between the flavor oil and the food matrix. The consumer chews the food product to release the flavor. Ideally, isolation of the flavor by the protein wall translates to minimal changes in flavor composition.

Payload refers to the ratio of core material (flavor) to the wall material (carrier). The encapsulator controls fracturing of capsules during food processing by increasing the wall thickness and reducing the payload. Increasing the wall material provides a capsule that is more resistant to fracture. Capsules providing poor flavor impact improve by decreasing wall material. This provides a thinner wall that fractures more easily. The payload is an important attribute to the survival and release character of the microcapsule.

Solid content is important when comparing the performance of the microcapsule against the oil. Coacervated flavors range in flavor oil content from 15% to ~90%, generally dependent on the amount of water present. Physical forms of the microcapsules range from slurries, to pastes, to dry powders. Regardless of water content, each form retains the same controlled release functionality.

Size control is an important attribute of coacervation microcapsules because it determines the flavor dispersion, impact and eventual survival in the cooked food products. Size greatly affects the dispersion of the encapsulated flavor in the food matrix. Table one shows how the number of microcapsules per gram increases as the diameters of the particles decrease.

Table I. Capsule size vs. number of Capsules per gram

Size in microns	# of Capsules per Gram
5	15,279,000,000
100	1,909,000
500	15,277
1000	1,910

The magnitude of change between the number of 5 micron capsules per gram versus the number of 1000 micron capsules per gram is 10^{+7} capsules. The 15 billion capsules per gram at 5 micron size offer excellent dispersion and uniformity in a finished product. While this is seemingly beneficial, each individual capsule is very resilient to fracture and offers very low flavor volume upon fracture. The over all impact of flavor decreases as the size of the microcapsule decreases. Conversely, each 1000 micron microcapsule will have a substantially greater impact upon fracture. Mastication easily achieves fracture of these large particles releasing a large dose of flavor. However, large flavor capsules localize the flavor in the food. The cooked food product may have flavor hot spots and areas devoid of flavor. Each food product has an optimal microcapsule size for proper flavor delivery. The formulator must choose capsule size carefully to balance the factors of the desired impact level and flavor dispersion.

Other considerations for choosing the size of the microcapsule are: mechanical processing to be endured, texture of the food base and typical level of mastication. If the consumer does not chew the food base, then the fracture release technology is not suitable at any capsule size. Foods like soups and ice cream that require very little mastication result in low flavor release. Many foods like crackers, cookies, meats,

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pastas, and breads do require extensive mastication for consumption resulting in optimal flavor release.

The food preparation process must deliver the encapsulate intact or risk negation the controlled release properties. The encapsulate fractured during processing is concomitant to adding flavor oil to the food product. High shear preparations like comminuted meats and machine mixing of stiff gum bases may prematurely release the flavor at any size capsule. It may be necessary to try several capsule sizes to find the best balance between capsule survival during food preparation and finished flavor impact.

Microcapsule Performance

We best demonstrate the effect of encapsulation in the finished food by comparing microcapsules versus flavor oil at equal oil contents. Food scientists must increase the use level of an encapsulated flavor to compensate for water and carrier present. This provides equal flavor oil content in the finished food and allows the scientist to measure the relative efficiency of delivery in the encapsulated form. We view efficient flavor delivery in several ways: survival of cooking process, shelf-life stability, and flavor profile survival to name a few.

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Survival of Flavor in Cooking Process. Baked goods are products where the cooking process exposes flavors to dry heat conditions of 350 to 400 degrees Fahrenheit. Baking times range from a few minutes to over an hour. These high temperatures promote flavor loss due to evaporation and steam distillation. A coacervated protein barrier protects the flavor from these losses and preserves the impact for fracture release.

Our application laboratory experimented with dough containing encapsulated and liquid flavor oil at equal oil contents. The dough was analyzed prior to baking to confirm the profile level of several key components (Table II). Analysis showed similar flavor component levels with slight variances. The partition coefficients of oil in water and oil in air explain these variations. Since the process prepares microcapsules in a water media, we expect oil components that partition into water (like ethyl butyrate) to be of lower concentration in the dough. Components of the unencapsulated oil that have low vapor pressures (like iso-amyl-acetate) evaporate slightly during the dough making process. Flavorists compensate for these types of losses when matching flavor profiles. The baked samples were unaltered in this experiment.

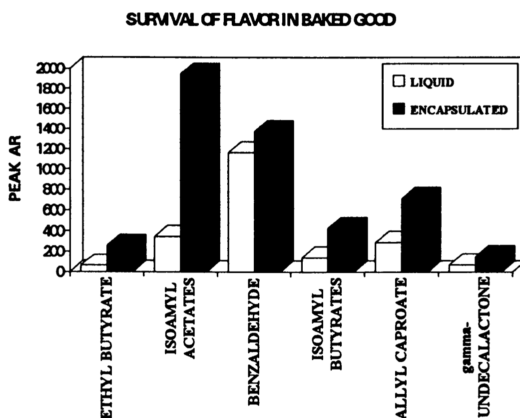
The dough samples were baked in a conventional oven at 350 deg. F for 10 minutes and re-analyzed for flavor content. The encapsulated form consistently retained more of the key components than the unencapsulated control. The protein barrier provided the protection needed to keep the flavor in the finished baked good and minimized partitioning into the air.

Shelf-Life Stability

Mixed Berry Flavor Retention on Product. Maintaining a consistent flavor profile over the shelf-life of the finished product is an important challenge faced by most food scientists. Each flavor compound has a specific rate at which it

Table II. Flavor Comparisons Prior to Baking

Compound Name	Liquid	Protein
Ethyl Butyrate	5.22	4.99
Isoamyl Acetate	9.15	9.32
2-Methylbutyl Acetate	3.81	3.66
Benzaldehyde	19.64	19.76
Isoamyl Butyrates	5.16	3.91
Allyl Caproate	6.61	5.95
Gamma-Undecalactone	4.70	4.87



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evaporates and oxidizes during storage. Compositional changes in flavor during shelf-life create changes in the sensory attributes of the food. Flavors are weaker and no longer balanced as individual components dissipate at varying rates. Food scientists compensate for overall flavor losses by increasing flavor levels to target a mid-point in the shelf-life of the product. However, they cannot compensate for profile changes over the product shelf-life. Food scientists find microencapsulation a powerful tool for improving the flavor of their product initially and through its shelf-life.

A flavor shelf-life study showed the advantages of coacervation with respect to minimized profile changes and retention of flavor components under accelerated storage conditions. This evaluation tested flavorings in sugar coated ready to eat (RTE) cereal. Flavored molten sugar solutions at 212 degrees F coated the cereal samples with equal oil levels of encapsulated mixed berry flavor and mixed berry flavor oil. A convection oven at 175 degree F dried the cereal in 10 minutes. The RTE cereal was analyzed for flavor content and then retested after storage at 40 degrees C for ten weeks (vertically striped and solid colored bars). The initial results (Horizontally striped and dotted bars) showed that three of the four major encapsulated components had higher concentration after processing than their oil counterparts. There were slight organoleptic intensity differences favoring the encapsulated sample. The low level components that give a berry flavor its distinctive character (blackberry versus raspberry) showed mixed results in intensity. Upon accelerated aging, the samples showed dramatic differences between encapsulated and liquid flavor oil. All components in the encapsulated flavor retained higher percentages than the unprotected flavor oil. The two cereal samples, aged and fresh, containing encapsulated flavors (dotted and solid colored bars) retained the same flavor impact when tested in expert panels.

Citrus Flavor Drying Time Study. Encapsulated flavors like lemon, blueberry and peppermint each perform differently in food preparation processes because of their wide range of volatile components. Studies for one encapsulated flavor may not demonstrate the advantages shown for another. Flavors with similar properties like lemon, orange, and grapefruit classify into groups like citrus. Studying flavor blends of a class allows the technologist to develop delivery models that apply to a wider range of flavors.

A cereal process drying time study showed citrus flavor losses due to processing. The study used the same coating techniques as the mixed berry cereals. The initial analysis of the flavor oil blend demonstrated typical losses of citrus flavor. The citrus oil analysis shows how the flavor evaporated in the initial hot sugar solution and continues to evaporate in post processing. The food scientist could either increase the use level of the citrus blend or reduce the drying time to compensate for these losses.

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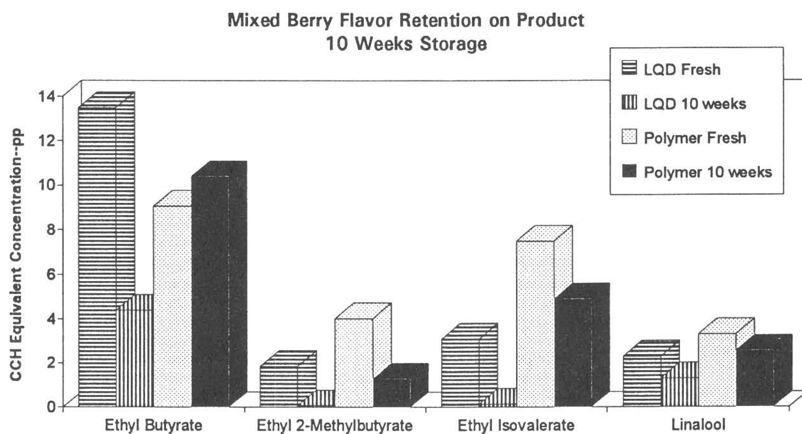

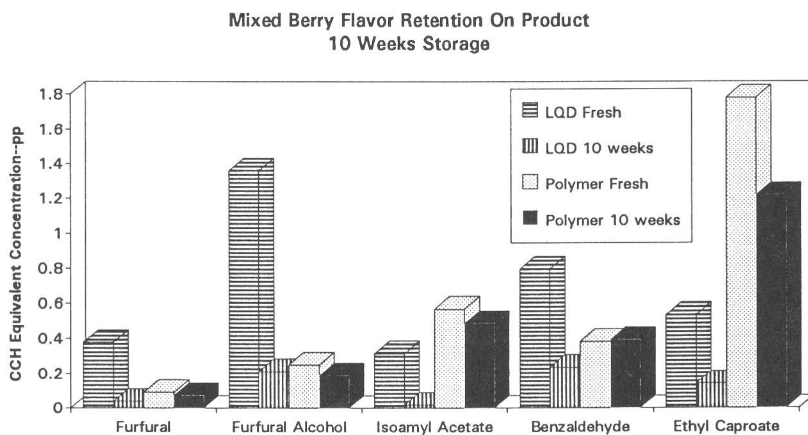

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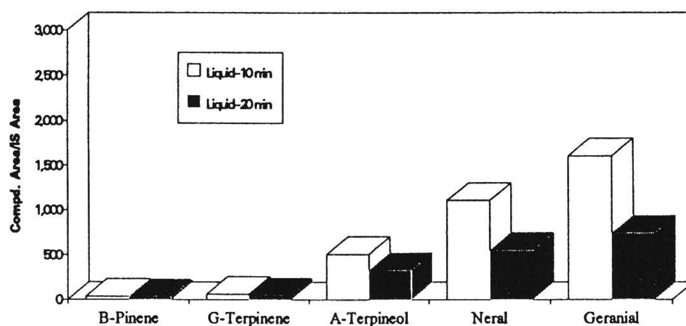
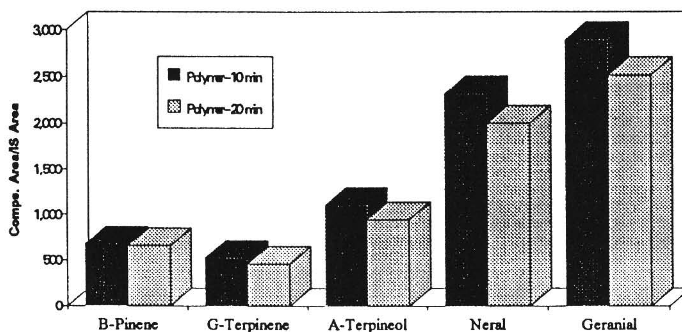
Citrus Flavor Drying Time Study



Citrus Flavored Drying Time Study



Encapsulation becomes a viable option when process changes can not be made. The microcapsules made a two fold improvement in the level of flavor through the process (as compared to the citrus oil blend). Further, the data shows how post processing only slightly effects the encapsulated flavor. The finished cereal benefits from a more consistent batch to batch flavor profile.

Conclusion

Coacervation has long been a powerful formulating tool for the food scientist. Commercial availability to the scientist has been limited slowing the introduction to food products. Because encapsulation is an art as well as a science, it is difficult for the food scientist to become skilled as both an encapsulation scientist and food product developer. Developing an access to the technology is critical to the advancement of coacervation based solutions to food and flavor challenges.

Cost advantages will develop for systems where flavor evaporation is a problem. Coacervation encapsulation applications can reduce the cost of food formulations, by lowering both the initial flavor use levels and retaining flavor components where previously they were lost. The future of coacervation research is proving out these cost savings that demonstrate the effectiveness of encapsulation.

The coacervation fracture release system offers more flavor stability in hot processes like: microwave, retort, hot melt, oven drying, pan or deep frying. Each preparation method yields a more balanced and flavorful food product when employing the thermally stable walls of the coacervation process. The food scientist will benefit by using this tool in developing new creative products with reduced problems of flavor food interaction and thermal process.

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Chapter 11

Liposomes for Controlled Release in the Food Industry

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The use of liposomes for the delivery of food ingredients offers a totally new technology with unique delivery opportunities. There is nothing equivalent currently in use in the food industry. While the application of liposome technology has been very limited to date, work demonstrating the potential of liposomes for the improvement of the flavor of cheese which has been ripened using accelerated methods, the targeted delivery of functional food ingredients, the synergistic delivery of ascorbic acid and tocopherols for enhancing antioxidant activity and the stabilization of vitamins in foods has been demonstrated. Liposomes will continue to find more applications in foods. This article introduces the reader to liposomes, their methods of manufacture and reviews current applications of liposomes in the food area. A related technique, the use of multiple phase emulsions (water in oil) in foods to deliver/contain aqueous systems will also be reviewed in this section even though this does not strictly fit the definition of a liposome. The application of this technique has been for accelerated cheese ripening.

Liposomes are single or multi–layered vesicles which involve the complete enclosure of an aqueous phase within a phospholipid–based membrane. These vesicles form spontaneously when phospholipids are dispersed in an aqueous media. A portion of the aqueous media becomes enclosed in the lipid membrane which then serves as a controlled release particle for the active material dispersed in the lipid or aqueous phase of the particle. Liposomes are, therefore, capable of delivering both lipophilic and aqueous–based active materials. The only materials which cannot be included in the liposome are substances which are insoluble in either lipid or aqueous phases or those which have significant solubility in both phases. While most food ingredients can be encapsulated in liposomes, they would have limited value for flavor delivery since most flavor compounds have some solubility in both phases.

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Liposomes can be made in size ranges that vary from a few nanometers to several microns. They were originally developed to serve the needs of controlled delivery of drugs in the medical field (*1, 2, 3*) and more recently have been applied to the cosmetics field (*4, 5, 6*). Liposomes can be made sufficiently small that they will pass through the smallest blood capillaries and of a composition (may contain attachment ligands) that will target specific sites in the body to deliver drugs to the desired points of need.

The use of liposomes in cosmetics is generally linked to the efficient delivery of moisturizing ingredients (including water) to the skin. A recent presentation at the Controlled Release Society Workshop in Geneva (*7*) suggested that liposomes can be used to deliver oxygen to the skin which will retard skin aging (*8*).

Kirby (*9*) has provided a review of opportunities for the use of liposomes in the food industry. The earliest publications on food applications come from the early 80's. The initial applications were for the controlled release of enzymes in cheese making. The applications for liposomes has increased to include the delivery of both fat soluble and aqueous soluble food ingredients. It is the goal of this chapter to provide the reader with an appreciation of what liposomes are, common means of manufacture, their strengths and weaknesses and an overview of previous research in their application to food systems. A section is added to this chapter which addresses a related technology, the fat encapsulation of aqueous soluble food components, using multiple phase emulsions. While this technique does not form true liposomes, it is sufficiently related to be discussed hereunder.

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Introduction to liposomes

As noted above, liposomes generally depend on phospholipids for their structure. Other structural lipids such as cholesterol may also be included as will be discussed later but are not essential for liposome formation. Phosphatidyl choline (the most abundant phospholipid in lecithin) is most commonly used and may be obtained from either egg yolk or soy beans at low cost. Lecithin is not soluble in water but tends to form planar bilayer sheets to minimize the interaction with water (Figure 1). The polar head groups of the lecithin are oriented into the aqueous phase while the lipophilic tail groups are associated with other tails of phospholipids, other lipids or lipophilic active materials. When the sheets fold into a spherical shape, there is no interaction of the lipophilic groups with water and a very stable particle is formed (Figure 2). The liposome may be composed of a single bilayer or hundreds of concentric bilayers depending on its composition and means of manufacture (*2, 10*).

One should note that lecithin is not a single defined chemical but a mixture of many materials having the general structure shown in Figure 3. The polar group is always the same (phosphatidyl choline) while the fatty acids vary greatly depending upon the source of the lecithin and whether it has been chemically modified (e.g. hydrogenated). The fatty acids incorporated in lecithin from animal sources will be more saturated while lecithin from plant sources will be more unsaturated. The occurrence of unsaturation in the fatty acids is important in determining the phase transition temperature of the liposome membrane as is the carbon chain length of the fatty acids. Phase transition from a tightly ordered gel to a liquid membrane influences its permeability. As one would anticipate, the liquid membrane is much

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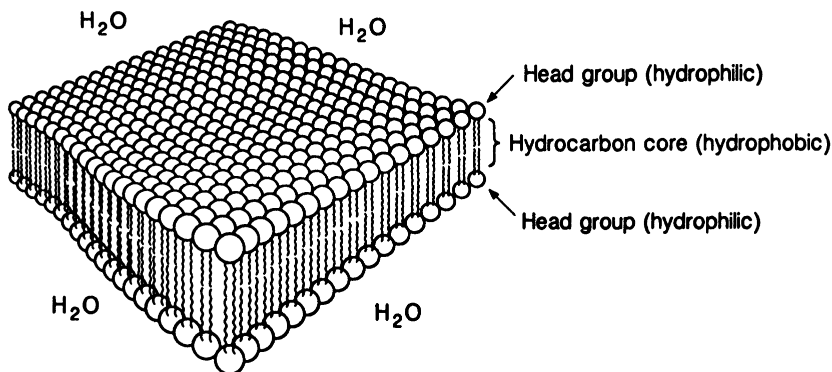

Figure 1. Schematic representation of the lipid bilayer matrix (*10*).

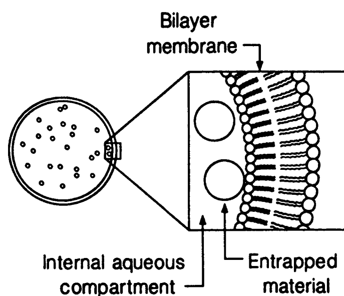

Figure 2. Closed bilayer forming a liposome (*10*).

more permeable to solutes (leaky) than is the gel structure. Thus one has significant control over the release temperature by selection of fatty acid composition. Liposome membranes made from egg yolk lecithin have a transition temperature ranging from −15 to −7C while those made from mammalian sources of lecithin usually range from 0 to 40C (2). As noted earlier, it is important to understand the phase transition properties of liposomes since this will determine liposome permeability, fusion, agglomeration and protein binding.

Liposome permeability

A liposome is a semipermeable membrane which may serve as an effective barrier to sugars and large polar molecules but will permit the passage of lipophilic and some small polar molecules. Despite the fact that lipophilic molecules can pass through the liposome membrane, they may be retained in the liposome simply because the liposome is in an aqueous phase i.e. there is no place for the lipophilic molecule to go. Lipophilic molecules would only be lost from the liposome if they are soluble in the liquid phase or if the liposome collided or was attracted to a lipophilic site (perhaps a fat globule as will be discussed later). Molecules which have significant solubility in both phases will readily pass through the liposome membrane. Small molecules such as water will pass through the liposome while charged molecules (irrespective of size) differ greatly in transport. Hydroxyl ions and protons cross the membrane easily while ions such as K or Na pass only slowly.

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Chemical composition

Cholesterol. Cholesterol and other sterols are found in many natural membranes. While cholesterol itself will not form liposomal membranes, it can be incorporated into liposomes and its inclusion will bring about substantial changes in the liposomal membrane (*10*). Cholesterol can be used in liposomes at molar ratios (lecithin:cholesterol) of up to 1:1 (*11*). The cholesterol has a polar group (hydroxy group) which will orient itself towards the aqueous phase and the aliphatic and cyclic lipophilic portion of the molecule oriented with the acyl chains of the lecithin (Figure 4). The inclusion of cholesterol will tend to stabilize the liposome and make it less leaky. Many of the liposomes used in the pharmaceutical field are based on a composition of egg lecithin:cholesterol:phosphatidyl glycerol of 0.9:1.0:0.1 which form particularly stable vesicles.

The use of cholesterol in making liposomes is not likely in the food industry simply due health concerns about dietary cholesterol and heart disease. Thus the liposomes used in the food industry will likely not include cholesterol but some other lipid fraction (at least in the near future) despite the fact that the amount of cholesterol added to the diet through the use of liposomes as food components would be insignificant.

Other components. As noted earlier, there is no need to use any other component than lecithin and water to form a liposome. However, it is significant that nonstructural lipophilic components can be accommodated in this structure with

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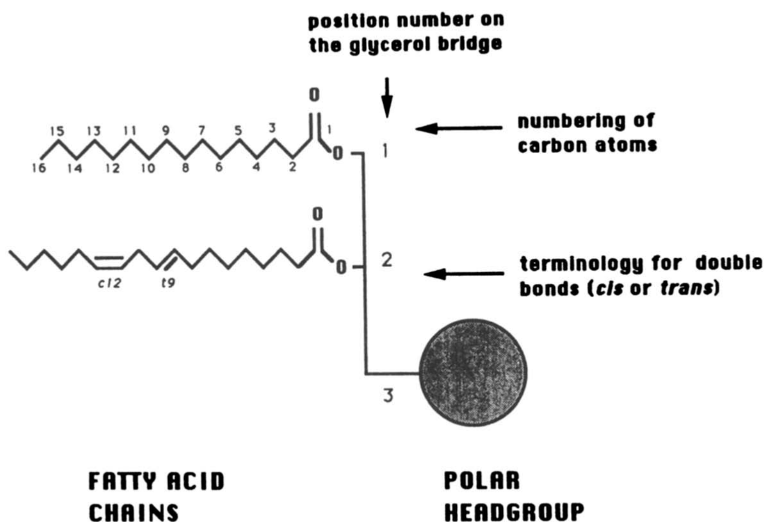

Figure 3. Structure of phospholipids (2).

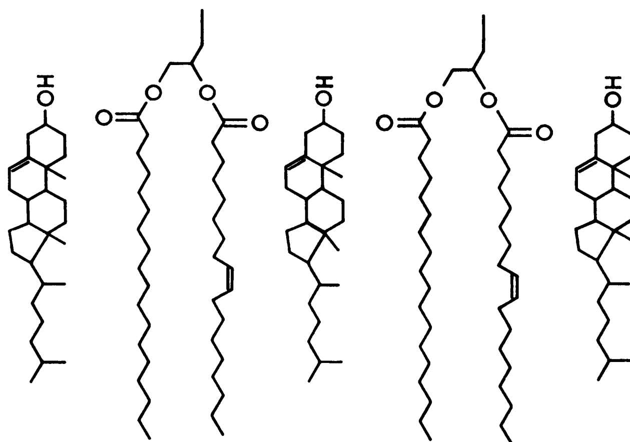

Figure 4. Position occupied by cholesterol in the membrane bilayer (2).

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little effect on membrane integrity up to ca. 10% by weight. This ability permits the inclusion of other lipid components or the carrying of lipophilic active ingredients by the liposome. Certain lipophilic components will interact with the membrane in a favorable manner and higher concentrations can be accommodated (e.g. fatty acids or α–tocopherol) while other materials will readily disrupt the membrane at much lower levels (e.g. some polyene antibiotics)(*2*).

Physical structure of liposomes

As noted earlier, liposomes can be as small as 25 nm up to 1 um or larger, which is visible under a light microscope. The liposome may have a single layer or multiple concentric layers. These particles are often classified according to size as follows: Multilamellar vesicles (MLVs): Consist of five or more concentric lamellae and range in size from 100–1000 nm; Small unilamellar vesicles (SUVs); Single lamellae with sizes approaching the theoretical minimum or 25 nm; Large unilamellar vesicles (LUVs): These are at the high end of size - 1000 nm; and Intermediate–sized unilamellar vesicles (IUVs): vesicles of about 100 nm (*2*).

Other classifications of liposomes are used e.g. those based on the means of liposome preparation. For example, reverse–phase evaporation vesicle (REV), dehydration/rehydration vesicules (DRV) or multivesiclar liposomes (MVL).

Capacity to carry active materials

Large unilamellar vesicles can carry much more aqueous phase than small unilamellar vesicles. This should be obvious from the consideration that surface area increases greatly as particle radius decreases. This means that for small vesicles, a larger proportion of the liposome must be devoted to surface cover (phospholipid) than would be required for large particles. Thus small liposomes must have a high percentage of phospholipid and can accommodate less aqueous phase per unit weight. This can be a problem if one wishes to carry aqueous soluble active materials but is a benefit if one wishes to deliver lipophilic active materials.

The ability of multilamellar liposomes to carry actives is dependent upon the amount of lipid in the vesicle and is independent of size. Liposomes high in lipid (multilayered) will carry much lipophilic active material but little aqueous phase. The multilamellar liposomes are less desirable to carry aqueous active materials since the minimum amount of lipid in liposomes is accomplished with unilamellar vesicles. The choice of liposome form may be influenced not only by the ability of the vesicle to carry active materials but also their durability in potential food applications. While the LUV can carry the most aqueous phase and thus aqueous active material, they are relatively fragile and may not survive a food processing operation.

Release of active materials

As noted earlier, the most stable liposomes are made of lecithin, cholesterol and negatively charged phospholipid. They will resist leakage or deterioration better than

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any other practical composition. The stability of the liposome is also influenced by the purity of solvents and complete removal of solvents since any foreign material in the membrane may weaken the structure. Additionally, the most stable liposomes are made of lecithins which are composed of saturated fatty acids. These fatty acids are more rigid and will be less likely to oxidize thereby resulting in membrane degradation. One must recognize that maximum stability is not always the goal and weak or short lived liposomes may be more desirable. They must be tailored to the task at hand.

Manufacture

An important consideration in the manufacture of liposomes is that they form spontaneously when phospholipids are properly placed in an aqueous environment. Therefore, the problems in the manufacturing of liposomes relate to the formation of the desired size and structure of the vesicles and their efficient loading.

Methods for the manufacture of liposomes generally involve three basic steps (Figure 5). Assuming a defined lipid composition is desired, the lipid formulation must be dried from an organic solvent (if not, this step can be eliminated). The film thus deposited is then dispersed in an aqueous solvent at which time the liposomes are formed. Typically, the liposomes must finally be purified or separated from the bulk liquid. The primary difference between methods of preparation are in the way the lipid fraction is dispersed in the aqueous phase. These steps can be done in many different ways and these techniques for preparation are discussed in detail by New (*12*) and Martin (*10*). The three broad methods to accomplish this task are physical dispersion, two phase dispersion and detergent solubilization. These three approaches will be summarized in the following text but one is encouraged to read the material provided in either of the cited references (*10, 12*) for detail.

It should go without saying that the lipids used in the manufacture of liposomes must be of good quality (not oxidized) and that all solvents be very pure. Purity is essential since some solvent residues will destabilize the liposome membrane. The solvent system most commonly used is a 2:1 mixture of chloroform:methanol. Lipid soluble active materials are generally included in the liposome by adding them to the initial lipid mixture while the aqueous soluble materials are added in different ways depending on the methods used. There are some situations where the active material can be loaded into a finished liposome e.g. when the active has some water and lipid solubility and ionizable group(s). In this case, the active material can be added to the finished liposome solution at a pH such that the active material is uncharged and readily passes through the lipid membrane. After the desired concentration is reached in the vesicle, the pH is changed giving the active material a charge and very polar character. It is then trapped inside the lipid membrane.

Physical dispersion. The making of liposomes can be done with inexpensive laboratory equipment. One technique (mechanical dispersion – hand shaking) simply involves adding a dilute solution of membrane lipid (e.g. 100 mg egg lecithin, 40 mg cholesterol and 10 mg phosphatidyl glycerol) in 5 mL chloroform:methanol (2:1 by volume) to a 250 mL round bottomed flask and then placing this flask on a rotary evaporator. The solvent is removed under vacuum

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(initially from a water aspirator and later under high vacuum) to remove all traces of solvent. This thin film of lipid is then rehydrated by adding 5 mL of aqueous phase containing the active material of interest (e.g. enzyme or sugar), glass beads are added and the flask is shaken by hand or placed again on the rotary evaporator (no vacuum) to agitate. The liposomes will readily form giving a milky white solution. This simple process will yield large MLVs. MLVs prepared from neutral lipids will tend to be tightly packed multilamellar vesicles which will carry little aqueous phase. The inclusion of charged lipids will, as a result of charge repulsion of the membrane layers, substantially increase the volume of aqueous phase in the vesicles.

LUVs can also be formed very simply using a method originally from Reeves and Dowben (*13*). The process differs primarily in the means of swelling the membrane. This procedure involves initially adding 4 mg of lecithin to 0.5 mL of chloroform:methanol and drying this in a 2 L conical flask (formation of a thin film of dry lipid on the bottom of the flask). The dry lipid film is rehydrated slowly by first passing water saturated nitrogen through the flask for 15–20 min (film becomes opaque). Next 10–20 mL of sucrose solution is carefully added to the side of the flask and the flask is slowly stood upright (no agitation). The flask is allowed to stand at 37C for 2 hrs before it is rotated to disperse all liposomes and then it is centrifuged (12,000 g for 10 min). MLVs float to the surface while the LUVs stay suspended in the bulk liquid. The LUVs are harvested by adding iso–osmolar glucose to the liposomes and recentrifuging. The LUVs will precipitate and can be collected.

Both of the processes briefly described above are batch low–volume processes. New (*12*) also described a high volume technique of forming liposomes using a physical process. A Microfluidizer (equipment to do an exceptionally good job of homogenization) is used in this process and it yields "micro–emulsification liposomes (MEL)". The Microfluidizer is well known in the pharmaceutical field for its ability to produce extremely fine emulsions and is becoming known in the food field for its use in preparing cloud/flavor emulsions (*14*).

Small liposomes can be produced by either processing already formed liposomes (size reduction) or an aqueous dispersion of unhydrated lipid. A single pass of unhydrated liposome membrane through the Microfluidizer will yield an MLV of 0.1 to 0.2 um and continued passes will further reduce the particle to even smaller dimensions. The Microfluidizer has the advantage of forming liposomes in a single step and at high production rates but the resultant liposomes are generally low in specific activity due to the use of large amounts of lipid.

Solvent dispersion. Methods of liposome preparation based on this approach generally involve first dissolving the membrane lipids in an organic solvent and then adding this solvent/lipid mixture to an aqueous phase. The organic solvent used to disperse the membrane lipids may be either miscible or immiscible in the aqueous phase. This latter category is further divided into techniques where the immiscible phases are in great excess – either the aqueous phase or the organic phase. New (*12*) presented an example of each which is summarized below.

The example of producing liposomes using a miscible solvent is the injection of ethanol/membrane lipids into an aqueous phase (*15*). The membrane lipid/ethanol mixture is rapidly injected through a fine needle into the aqueous phase (Figure 6).

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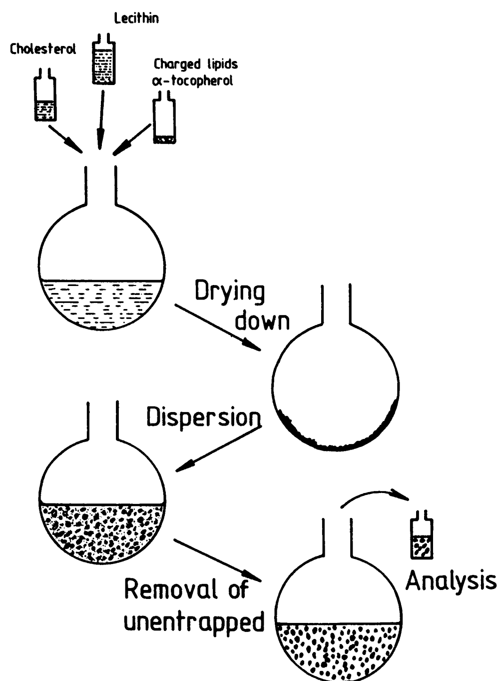

Figure 5. Steps common to all methods of liposome preparation (*12*).

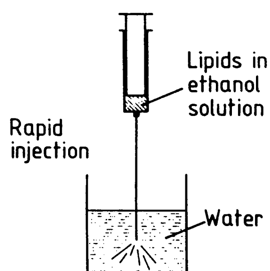

Figure 6. Preparation of SUVs by ethanol injection (*12*).

The force of the injected solvent results in nearly instantaneous solvation of the alcohol to evenly disperse the phospholipid throughout the aqueous phase. This technique results in the formation of SUVs. Disadvantages of this technique are that lecithin has a low solubility in ethanol and thus yields of liposomes are low. Yields are further lowered by the fact that alcohol/membrane mixture can be added only until the solution is 7.5% alcohol which then limits the amount of lipid to be dispersed and the quantity of the aqueous phase (active material) which can be included in the liposome. So despite the fact that the procedure is extremely simple to use, it is not well suited to the incorporation of aqueous soluble active materials and only low yields can be obtained.

An alternative approach is to disperse the liposome membrane lipids in an organic phase such as diethyl ether. In this case, the ether/lipid mixture is slowly injected into the aqueous phase. The temperature of the aqueous phase is such that the ether evaporates as it is added (Figure 7). The method has the advantage that the solvent is removed as it is added and thus there is no limit to the amount of liposomes which can be produced. This also means that high quantities of the aqueous phase can be incorporated into the liposomes and the approach is better suited to the incorporation of aqueous active materials. The main disadvantage cited is the long time needed in production of the capsules and good pumping system needed for the control of the addition of ether. New (*12*) has described several other versions of this methodology which will not be discussed here.

Detergent solubilization. In this method of liposome manufacture, phospholipids are brought into contact with the aqueous phase through the use of detergents. The detergents facilitate the formation of membranes by associating with the lipophilic portion of the phospholipids shielding them from the water. The detergent/phospholipid complex forms micelles as opposed to liposomes as have been discussed. Detergents can form micelles without any phospholipid if the detergent concentration is high enough. The level at which this happens is called the critical micelle concentration. It should be noted that the detergents are "soluble" in both the micelle and the aqueous phase so the detergent exists in an equilibrium with these two phases. The critical micelle concentration of several detergents which are used in the formation of phospholipid membranes are listed in Table I. The micelles which are formed are a combination of detergent and phospholipid. After the desired micelles have been formed, the detergent must be removed from the micelle and then unilamellar vesicles form spontaneously. The detergent can be removed from the micelle by several techniques including dialysis, column chromatography (size separation) or dilution. The advantages of each of these techniques are discussed by New (*12*).

Detergent methods are not well suited to the incorporation of water soluble small molecules since they are likely to be removed from the system with the detergents. The method is well suited, however, to the incorporation of lipid soluble proteins.

One may gain a better appreciation for this method from the following example. To 10 mg of egg lecithin, add 10 mg of sodium cholate (result is a phospholipid/detergent ratio of ca. 0.6). Dissolve this blend in 10 mL of ethanol/chloroform (1:1 by volume) and dry down in a rotary evaporator. The dry material should be redissolved in 10 mL of absolute ethanol and redried in a rotary

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evaporator. Then 2 mL of 10 mM phosphate buffer (pH 7.1) is slowly added to the flask and it is gently swirled to form the micelles. The micelles are then dialyzed to remove the detergent (*12*).

Liposome purification. It is often necessary to purify the liposomes which have been formed by any of the above mentioned methods. The techniques for purification are similar to those used to remove the detergent from the detergent method of making liposomes. One can use dialysis, size separation chromatography or centrifugation techniques for the isolation or purification of the liposomes. For size separations, Sephadex G−50 is commonly used as the stationary phase. The technique is the same as has been used for protein separations for years. Dialysis can be done by any of the classical techniques or the more recent hollow fiber devices can be used.

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Table I. Detergents used in membrane solubilization (*12*).

Name	Critical micelle concentration		
	mM	mg/mL	mol wt.
n−heptyl glucopyranoside	70	19.5	278
n−octyl glucopyranoside	23.2	6.8	292
n−nonyl glucopyranoside	6.5	2.0	306
n−decyl maltoside	2.19	1.1	499
n−dodecyl maltotrioside	0.2	0.16	825
Triton X−100	0.24	0.15	625
(PEG(9,10)p−t−octylphenol)			
Nonidet P−40	0.029	0.02	603
(PEG(9)p−t−octylphenol)			
Tween 20	0.033	0.04	1364
(PEG(20) sorbitol monolaurate)			
Brij 98			
(PEG(29) oleyl alcohol)	0.025	0.04	1527
Sodium deoxycholate	2−6	1.7	415
Sodium taurocholate	10−15	6.7	538
Sodium cholate	14	6.0	431
Sodium dodecyl sulphate	8.3	2.4	289

Centrifugation as a technique for liposome purification depends upon density differences. The density of liposomes depends upon several factors including the type of lipids involved in membrane formation, the total quantity of lipids in the liposomes and the type and amount of material incorporated into the aqueous volume of the liposome. The liposome ultimately ends up being heavier than water and thus will sediment on centrifugation. However, the density differences may not be great and high centrifugal forces may be needed (e.g. 100,000 to 200,000 g for periods up to 20 hr). This is highly dependent on the liposome and centrifugation may be much easier than noted here.

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Stability of liposomes

Despite the fact that liposomes form spontaneously, they will decompose with time. This often occurs due to chemical degradation of the lipid phase (hydrolysis or oxidation). Depending on the application, it may be desirable to have limited stability or one may try for maximum stability. Some of the factors which influence stability will be discussed.

Chemical degradation. A major factor influencing stability is the rate of oxidation of the phospholipids in the liposome membranes. Oxidation is limited by: 1) working with freshly prepared lipids and freshly distilled solvents; 2) minimizing temperatures that the lipids are exposed to; 3) working in the absence of oxygen whenever possible (flush with nitrogen and deoxygenate solvents); 4) storing liposomes in inert atmosphere; 5) including antioxidants in the formulation; and 6) using metal chelators. One may consider the potential for lipid oxidation in the choice of the phospholipid (saturated fatty acids), however, this will influence lipid transition temperature and subsequent release properties as well as the cost of the raw materials.

The stability of liposomes will also be influenced by the rate of hydrolysis. Hydrolysis may be the result of lipolytic enzymes and/or pH extremes. The stability of lipid membranes in acid environments is influenced by solvent purity and amount of residual solvents left in the system.

Physical degradation. Defects in the lattice structure at the time of manufacture will be carried through to influence the leakage or fusion of liposomes. Some defects can be corrected by a process called "annealing" whereby the liposomes are held at a temperature slightly greater than the phase transition temperature. Even with annealed liposomes, some degradation (e.g. fusion or aggregation) will eventually occur. Aggregation and sedimentation will occur with neutral liposomes due to Van der Waals forces between vesicles. The simplest way to minimize this is to incorporate a small amount of charged phospholipid (e.g. 5% phosphatidic acid or phosphatidyl glycerol) in the membrane lipid. The inclusion of charged phospholipids may require the use of metal chelators to avoid the neutralization of charge by the metals.

Small liposomes (<40 nm) will tend to fuse while the larger liposomes will not. This is because there is considerable physical stress in the structure of the small liposomes due to the high curvature of the vesicle. Fusion is most likely to occur at or above the transition temperature and thus liposomes should be stored below their transition temperature.

Food applications

There is little in the literature on the application of liposomes to deliver food ingredients. However, Kirby (*9*) and Karel and Langer (*16*) have published insightful reviews in this area. The review of Kirby (*9*) has the widest breadth and will be drawn upon heavily for the following discussion. The reader is encouraged

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to read Kirby's (*9*) review for more detail and original references to the work discussed.

One rationale for delivering some food ingredients via liposomes is the same as for encapsulation in general, improved stability of the ingredient. It may be desirable to shield an ingredient from the metal ions, pH, free radicals, enzymes or water in a food which might otherwise result in a degradation of the food ingredient. This may be accomplished by creating a stabilizing environment in a liposome which promotes longevity of an ingredient. An example may be to control pH or include chelating agents, cryoprotectants, enzyme cofactors and/or antioxidants to the interior of a liposome (loaded with a labile active material) and not have to add large quantities to the bulk of the food mass. One can even potentially create a concentrated solution of a food ingredient in the liposome if it is more stable in the concentrated form. Thus there are numerous opportunities to create a microenvironment in a liposome which is more hospitable to the longevity of a food ingredient than would be found in the bulk of the food.

Kirby (*9*) suggested how liposomes can be used to target the delivery of a food ingredient. His review gives substantial discussion of how enzymes can be delivered and released at the desired time in cheese making (this will be discussed later in relation to multiple phase emulsions as well). This application of liposomes has been one of the most studied of possible food uses.

Kirby et al., (*17, 18*) have employed the dehydration/rehydration method (DRV) to make liposomes for food applications. This technique offers several advantages for food applications. First, it does not involve the use of organic solvents or detergents, traces of which may remain in the liposomes. These residues would likely result in food contamination and not be acceptable to the FDA. Second, the use of organic solvents or detergents may result in the denaturation of enzymes (if used as the active material) and thus limit applications in this area. Third, this method is well suited for scale up and can deliver high encapsulation efficiencies. In the food industry, costs are critical so these considerations are very important. Finally, high loadings result in high particle densities which permit liposome purification using low centrifugal forces (ca. 12,000 g for 20 min) again related to cost considerations.

DRV formation initially involves dispersing the lipid phase in water to form MLV. The MLV are converted to SUV by either microfluidization or sonication, mixing the active material (e.g. enzymes) with the SUV and then dehydrating the system (freeze drying, Figure 8). Upon rehydration with a controlled amount of water, the SUV will spontaneously fuse around the active material to form MLV containing a large proportion of the active material (*11*).

Accelerated cheese ripening. A substantial part of the cost of producing ripened (aged) cheeses is the cost of this ripening period. While there is little labor cost associated with this period, substantial costs are associated with environmental control and simply space and the commitment of capital. The cheese industry would benefit greatly from reducing this time period. Research has shown that it is possible to produce a good cheese in much less time if enzymes are incorporated into the cheese (endo and exo peptidases)(*19*). It is difficult to deliver proteolytic enzymes to cheese since adding the enzymes to the milk prior to cheese making results in a large

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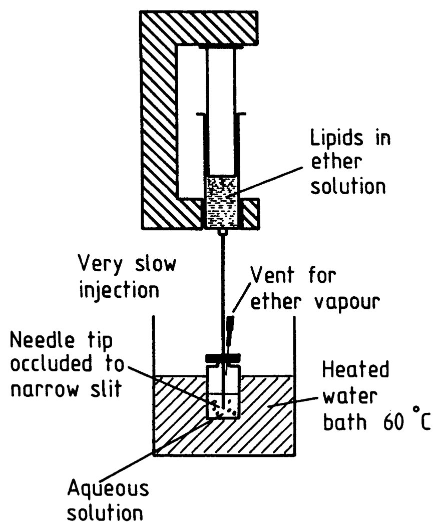

Figure 7. Preparation of LUVs by ether injection (*12*).

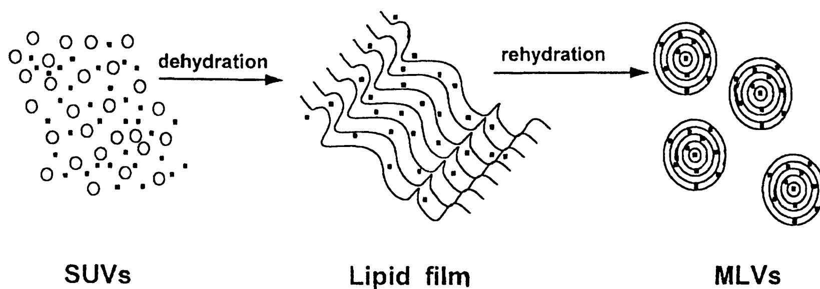

Figure 8. Formation of MLVs from SUVs by the dehydration/rehydration method (*11*).

loss of the enzymes with the whey and the cheese yields are greatly reduced due to enzymatic action. Adding the enzyme after curd formation results in poor distribution of the enzyme and an inferior product. One solution to this problem has been to encapsulate the enzymes in liposomes (*20–22*). The liposomes are effectively trapped in the cheese curd (Figure 9) at the time of clotting and are released during the early stages of ripening of the cheese (one would want very limited shelf life of the liposome for this application).

The stability of the liposomes in milk can be controlled by the addition of cholesterol or α–tocopherol (*23*). As was noted earlier, cholesterol stabilizes the liposome and would delay the release of incorporated enzymes. This was demonstrated by comparing the stability of liposomes prepared from egg lecithin using equimolar cholesterol versus no cholesterol (*23*). When put into milk at the start of cheese making, both types of liposomes were found to be intact 5 hrs after cheese making was finished. However, the cholesterol–free liposomes were found to be degraded after 1 day storage while many of the cholesterol containing liposomes were still intact. The proteinase enzymes maintained their activity until release.

Antimicrobial agents. Kirby (*9*) also observed that liposomes and microorganisms accumulated in the same microcompartments during cheese ripening. This observation suggested that liposomes may be used to deliver antimicrobial agents (e.g. nisin and egg white lysozyme) to microorganisms in foods. Such targeting of the antimicrobial agents to the microorganisms would significantly reduce the overall concentration of antimicrobial agents needed to preserve foods. Reduced usage levels may permit the use of natural antimicrobial agents (more expensive compared to the synthetic counterparts) which is often preferred by the consumer. An added advantage in fermented foods is that the release of antimicrobial agents could be delayed until later in fermentation and thus be added without interfering with the normal fermentation of the cheese.

Vitamin stabilization. Kirby et al., (*24*) have worked with the inclusion of vitamin C (ascorbic acid) into liposomes. Ascorbic acid is very unstable in most food systems due to its reactivity (e.g. Maillard reaction) and susceptibility to oxidation. Since ascorbic acid is more stable in concentrated solution, its inclusion into liposomes at higher concentration should give longer shelf life. Kirby et al., (*24*) found that ascorbic acid incorporation into liposomes (115 mM) exhibited a half life of 100 days compared to a pure solution of ascorbic acid with a half life of only 18 days (4C). The benefit would be much greater in real food situations where there are trace metals, free amino acids or oxidizing enzymes present. In such conditions, the half life of ascorbic acid may be hours rather than days.

Additional benefits of incorporating ascorbic acid into liposomes can occur. Direct addition to foods can result in pigment formation, color bleaching, protein polymerization and flavor changes which may be avoided if the ascorbic acid is in a liposome.

Antioxidants. Ascorbic acid is often used as an antioxidant in foods. The fact that it is water soluble tends to diminish its effectiveness. An alternative is to take

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advantage of the synergistic effect of vitamin E (tocopherol) and ascorbic acid by putting them together in the same system i.e. liposome. Then as tocopherol is delivered to a site of oxidation, the ascorbic acid is there to serve its synergistic function (Figure 10). One such application of this antioxidant system would be emulsion–type foods (e.g. spreads, and margarines).

Multiple phase milk fat–based emulsions

The application of liposomes in the cheese ripening area discussed earlier focused on the delivery of proteolytic enzymes later in the ripening period to speed flavor development. However, adding proteolytic enzymes to the cheese accounts for only part of the total flavor development required in cheese. One needs to enhance cheese flavor development overall to produce cheese with the best flavor. It is, therefore, desirable to use other enzyme systems to provide missing flavor notes. This has been attempted using enzyme systems encapsulated in multiple phase milk fat–based emulsions (*25, 26*). These capsules are made by preparing a water–in–oil emulsion based on an emulsifier/milk fat/aqueous phase. The best emulsifiers found for this purpose were 1:1 or 1:3 ratios of Span 60 and Glycomul TS used at a 3% level in milk fat. The active material is incorporated into the aqueous phase and is contained in the emulsion. This emulsion is sprayed (or delivered under pressure) into a cold solution of dispersion liquid (75–100 mL of emulsion injected into 1700 mL of dispersion liquid). The dispersion liquid consists of 0.01% Tween in water. The milk fat solidifies when in contact with the cold dispersion liquid and forms a hard fat capsule. The particle thus formed is not a liposome but a solidified water–in–oil emulsion. Braun and Olson (*27*), Magee et al., (*28*), Braun et al., (*29*) and Kim and Olson (*30*) have used this fat capsule to deliver enzyme systems in cheese ripening applications.

One problem in working with enzymes is that a single enzyme may not accomplish the desired task. The enzyme may have to work in concert with another enzyme (e.g. one enzyme may hydrolyze a fatty acid from a triglyceride while a second enzyme will oxidize the liberated fatty acid to an aldehyde). Alternatively, an enzyme may need cofactors (e.g. NAD) to function and these cofactors need to be regenerated. The fat capsule has been engineered to contain the cofactors and/or enzyme mixtures needed to accomplish other aspects of flavor development in the aging process. While there is still some distance to go before the entire cheese flavor profile can be engineered in this manner, remarkable achievements have been accomplished using this delivery system.

Conclusions

The application of liposomes to the food field has only recently been investigated and by a few researchers. These individuals have clearly demonstrated that liposomes have a place in the food industry. This may be in protecting certain food ingredients until some desired time of release or in the targeted delivery of a food ingredient. This may result in reduced needs for some food additives or even the ability to produce a product otherwise impossible. There is little question that we will see more research on liposomes in the food industry. The major challenge is to

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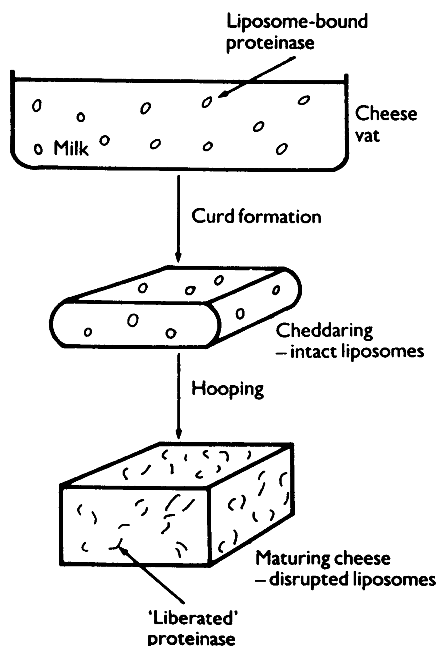

Figure 9. Incorporation of liposome–encapsulated ripening enzymes into cheese (*9*).

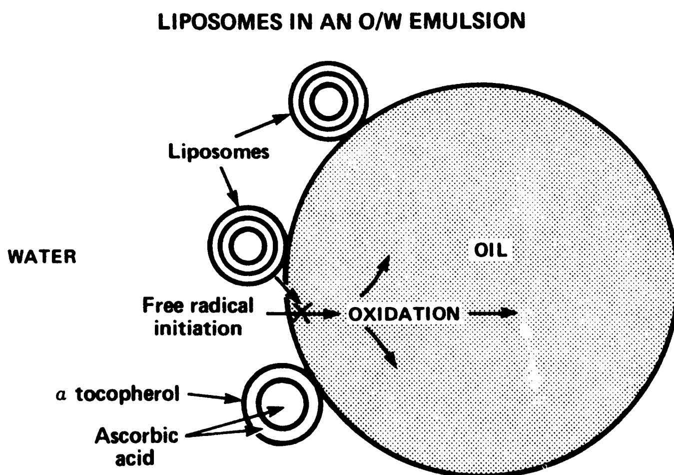

Figure 10. Protection of food emulsion by the liposome–based antioxidant system (*9*).

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make liposomes at a reasonable cost for the industry. The primary applications of liposomes have been in the drug delivery area where costs are of little importance.– the food industry does not enjoy this luxury.

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Chapter 12

Factors Influencing Volatile Release from Encapsulation Matrices

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The encapsulation of flavors within glassy matrices provides a primary means of stabilization and protection of the active from deteriorative reactions. Although most traditional carriers release the active relatively quickly in a burst fashion upon rehydration with water, in certain food applications a controlled or extended flavor release may be required. The purpose of this article is to provide a general review of the various chemical and physical properties of microcapsules associated with release of the encapsulated material or "active." The first part of the paper provides an overview of the basic mechanisms of release and the various polymers used to encapsulate flavors or food ingredients. The second part of the review is a more in-depth evaluation of diffusion and the effects of carrier phase transitions on volatile release.

Flavors are encapsulated for a variety of reasons including protection from volatilization during storage, protection from undesirable interactions with other food components, minimization of flavor/flavor interactions or light-induced deteriorative reactions, and protection against oxidation. Other benefits include ease of handling and mixing, uniform dispersion, and improved product consistency during and after processing (1,2,3,4). However, while such properties are important, they are secondary to a capsule's ability to release the "active" or encapsulated core material at the appropriate time. This review, therefore, focuses on the various chemical and physical properties of microcapsules associated with release of the active. The first part of the review provides an overview of the basic mechanisms of release and the various polymers used to encapsulate flavors or food ingredients. The second part of the review is a more in-depth evaluation of diffusion and the effects of carrier phase transitions on volatile release.

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Mechanisms of Release from Polymer Matrices

In general, release of the active depends upon the type and geometry of the particle and the carrier or wall material used to form the microcapsule. These factors dictate the mechanism of release for the capsule which may be based on solvent effects, diffusion, degradation, or particle fracture (5). Since the majority of flavors and food ingredients are spray-dried or extruded, solvent release and diffusion are the mechanisms of release commonly associated with these products. Solvent release is based upon the solubilization of the particle wall (typically with water) followed by subsequent release of the core material. Release may be a sudden burst or a continued or delayed delivery regulated by controlling the rate of wall solubility, the swelling of the wall material, pH effects or changes in the ionic strength of the surrounding medium. Diffusional release depends upon the kinetic relationship between the core and wall materials and the rate at which the core material is able to pass through the outer wall. Diffusion is strictly governed by the chemical properties of the carrier polymer and by the physical properties of the wall material such as the matrix structure and pore sizes (6).

Degradation and fracture release. Although spray-drying and extrusion are the two major commercial processes for the production of flavors in terms of product volume, minor techniques such as coacervation and fat or wax encapsulation are sometimes used for special applications (2). Degradation and fracture are the release mechanisms typically employed with such particles. Degradation is induced by a physical change in the capsule wall such as melting, hydrolysis, or enzymatic breakdown. Fracture release capsules are designed to release under pressure, shear, changes in vapor pressure, or differences in osmotic pressure between the active and the surrounding medium.

The effectiveness of any encapsulation process or release process is highly dependent upon the carrier used. While we find examples of encapsulation in fats (e.g., spray chilling), proteins (gelatin), and inorganics (fumed silica), carbohydrate carriers such as modified starches, gum acacia, maltodextrins, and corn syrup solids used for spray-drying and pressure extrusion compose the majority of the market (3). These carriers are all typically hydrophilic amorphous matrices capable of forming a metastable structure, or glass, upon the removal of water (7).

Controlled release via chemical modification of the carrier. Although most traditional carriers will rapidly release the active once they are rehydrated, microcapsule matrices may be modified to release the active material at a desired point in time. Release may occur as a burst or in a controlled or delayed manner through changes in processing parameters which regulate the particle size, pore volume, pore diameter or surface area of the capsule matrix. Variations in composition or chemical modifications such as cross-linking or the addition of functional groups may also be used to control release of the active material (8).

Commercial examples of this technology include specialty starches modified to have a greater affinity to certain functional groups on the core material in order to improve emulsion formation prior to encapsulation. Other starch-based controlled

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release approaches include hydrophobic modification, combinations of starches with synthetic polymers, obstructive gelation, and retrogradation of amylose (9).

Combinations of flavors encapsulated in both hydrophilic and hydrophobic carriers have also effectively been used to extend flavor release in commercial chewing gum applications. Studies have shown that hydrophilic encapsulation results in faster upfront release of flavors and sweeteners and improves the stability of aspartame, whereas flavors encapsulated in fat or wax provide a delayed, extended release (10).

Disruption of molecular associations in particle microregions. Understanding of molecular associations through hydrogen bonding within microregions of encapsulated particles between carrier molecules or between the carrier and the active has also opened venues for the research and development of encapsulation processes which protect the active yet release in a delayed or controlled manner. Flink and Karel (11, 12) and Chirife and Karel (13) have reported on such microregions in model systems composed of flavor volatiles freeze-dried in carbohydrate carriers. Within the microregions, associations of the carbohydrate molecules via hydrogen bonding produced complex structures which controlled the particles' permeability to water and to volatiles. Release was observed once the system reached a critical moisture level above the BET monolayer. At these higher moisture levels, the authors hypothesized that the microregion structure was disrupted by the presence of water competing for the hydroxyl groups originally involved in the structure formation of the particle. Once this disruption occurred, volatile loss was governed by the partial pressure of the volatile, the concentration of the volatile and its activity coefficient. Similar results have also been observed by Rifai and Voilley (14) in the evaluation of volatile model systems encapsulated in mono-, oligo- and polysaccharides and lactoserum carriers.

More recently, microregion interaction was involved in an investigation by Bolton and Reineccius (15) of the use of amorphous silica as a flavor carrier. Although flavors plated onto amorphous silicas are not actually encapsulated in an amorphous glassy matrix, the samples evaluated showed significantly extended shelf-life and reduced susceptibility to oxidation compared to traditional flavor carriers. The exact protection mechanism of the silica is uncertain, but it was believed to be a result of hydrogen bonding between the active and the silica, physical protection from oxygen within the active sites, and uptake of singlet oxygen by the silica. In addition, contrary to some irreversible flavor interactions which may occur with long-chain proteins or certain carbohydrates, flavors were observed to completely release from the silica in a burst fashion when water disrupted the hydrogen bonding within the silica microregions.

Effects of Carrier Phase Transitions on Diffusion and Volatile Release

Carrier glass transition. In an attempt to more thoroughly understand low moisture systems, scientists have examined the role of water as a plasticizer and the resulting physical and physicochemical changes which occur in the particle upon exposure to water. As water concentration increases, a transition occurs from the solid "glassy" state to a liquid-like "rubbery" state. The temperature at which this transition occurs is termed the glass transition temperature or Tg, and it varies as a function of

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concentration and time for different ingredients. Once an encapsulated matrix has gone through the glass transition and entered the metastable rubbery state, viscosity decreases while molecular mobility and the free volume of the polymer structure increase. The rates of deteriorative reactions and diffusion of the flavor from the particle matrix also increase (16, 17, 18, 19, 20).

Such phase transitions play an important role in most encapsulation processes where the initial objective is to form a stable amorphous glass which entraps the flavor compounds and inhibits mobility of molecules. Once in the glassy state, amorphous carriers have very low diffusion rates making the matrix structure virtually impermeable to organic compounds. Permeability to oxygen is also reduced thereby protecting the active from deteriorative oxidative reactions (7, 16, 17, 18, 21, 22, 23).

Due to the reduced mobility of carrier molecules, release from encapsulated powders in the glassy state is primarily via Fickian diffusion of the active through the pores in the matrix. Within the matrix, pores of sufficient size may contain a molecule of active which can move into a neighboring hole once it acquires sufficient energy. Diffusion results as pores which become vacant are filled by another molecule of the active (24). The amount of active agent released will, therefore, depend upon the chemical composition of the matrix, pore size, the particle size, the size of the reservoirs entrapped within the particle, and the thickness and area of the walls around these reservoirs (25, 26). As a result, loss of volatile flavors, while the matrix is in the glassy state, depends more upon the rate at which flavors can migrate to the evaporating surface than the relative volatilities of the active.

This rate of transfer is directly proportional to the molecular diffusion coefficient of the flavor component which is strongly dependent upon water concentration in the matrix. In fact, diffusion coefficients in foods between 0.7% and 44% moisture may vary by a factor of 10^3 (27, 28). This occurs in part because of the differences in the transport and solution behavior of the active in rubbery vs. glassy systems. Rubbery polymers typically have very short relaxation times and a greater free volume. As a result, rubbery polymers respond rapidly to stresses which alter their physical condition such as increased temperature or moisture. By comparison, glassy polymers have relatively long relaxation times and are less affected by external forces. Molecular motion below the glass transition is hindered and thus diffusion of the active is slowed (6, 24, 29).

Omatete and King (30) have reported using this diffusion-based analysis to evaluate volatile retention during rehumidification of flavors freeze-dried in a range of carbohydrates. They reported that at low relative humidities, volatile loss data followed the same patterns as diffusion through a slab. They also noted that the diffusion coefficient never became large enough to allow substantial loss of volatiles. At high relative humidities, molecular mobility and the diffusion coefficient increased resulting in a rapid loss of volatiles. Similarly, Voilley and Le Meste (31) observed a decrease of aroma diffusivity as the water content of the system decreased. They also observed decreases in volatile diffusion as the molecular weight of the substrate in concentrated systems increased.

Such changes in the particle structure, initiated by a transition from the amorphous "glassy" to the amorphous "rubbery" state as the system is plasticized, may eventually result in crystallization or collapse of the matrix. Temperature, concentration, molecular weight and time are all factors believed to be involved with

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inducing these phase transitions and the subsequent release of the active flavor or food ingredient which results from disruption of the particle structure (16, 17, 18, 19, 32, 33).

Crystallization. Crystallization typically occurs when viscosity in such systems is low and polymer chains have sufficient mobility to associate and form crystalline junctions (34). The time it takes for crystallization to occur is believed to be determined by the temperature difference between the holding temperature and the glass transition temperature or (T-Tg) (32). Over time, crystallization leads to a cross-linking effect which results in reduced flexibility and mobility of the polymer chains and thus reduced diffusion through the encapsulation matrix. Like collapse, crystallization also leads to a reduction in the areas between polymer chains. Because of this limited free volume, the crystalline state is unable to accommodate impurities within the structure. As a result, volatiles are forced from the crystallized matrix to the surface and left susceptible to degradative reactions. Water may also be released from the crystallized areas into the amorphous regions of the polymer matrix further plasticizing the carrier and decreasing the stability of the system (12, 17, 18, 35).

Several examples of rapid flavor release and decreased stability following crystallization are noted in the literature. In an evaluation of freeze-dried model systems containing sucrose and acetone, lactose and hexanol, or glucose, maltodextrin, and linoleic acid, To and Flink (36) reported more rapid losses of volatiles and increased oxidation of entrapped fat in crystallized matrices than collapsed matrices. In similar studies, Labrousse et al. (37) and Shimada et al. (38) have reported rapid release and oxidation of methyl linoleate from crystallized matrices composed of various carbohydrates and gelatin.

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Collapse. Structural collapse may occur when plasticization of the carrier decreases the viscosity to the extent that the polymer matrix is unable to support itself against gravity. Collapse is typically accompanied by a visible shrinkage of the carrier matrix into a highly viscous, glass-like material (34, 39). Porosity of the system is lost, effectively reducing diffusion through the particle matrix (20, 21, 25, 36, 40).

Research has shown that in some cases of collapse, the dense matrix "reencapsulates" the active. Diffusion slows, and the stability of entrapped volatiles is enhanced. In other situations, however, shrinkage of the collapsing matrix forces all or a portion of the active to the surface of the collapsed mass making these molecules more susceptible to degradative oxidative reactions (1, 11, 12, 14, 25, 27, 36, 37, 40, 41, 42).

The chemical composition of the polymer matrix has been observed to strongly influence both the rate and degree of collapse and the corresponding aroma release. Rifai and Voilley (14) observed that resistance to penetration and aroma retention decreased as a function of maltodextrin dextrose equivalent (DE). They also noted that increased levels of lactose resulted in the increased retention of volatiles within the collapsed matrix. Similarly, Gerschenson et al. (35) found that the addition of pectin aided in the retention of volatiles in freeze-dried tomato juice by enhancing the viscosity of the system and increasing the temperature at which collapse occurred.

In a related study of methyl linoleate encapsulated in matrices containing various levels of sucrose, lactose, maltodextrin, and gelatin, Labrousse et al. (37)

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observed rapid release of the encapsulated oil upon matrix collapse followed by oxidation of the released oil. The authors also noted that in systems with delayed crystallization, the initial flavor release was followed by collapse and reencapsulation. Under these conditions, the entrapped oil remained stable to oxidative deterioration.

In addition to the composition of the polymer matrix, the temperature at which the plasticized system is held also affects the degree of collapse. In an evaluation of collapse of freeze-dried sucrose and maltose mixtures by To and Flink (40), collapse of each series was found to occur to varying degrees depending upon the temperature at which the system was held. These results indicate that collapse is not an "all or nothing" phenomenon and may be stopped at a desired point.

Similar results are reported by Whorton and Reineccius in a later chapter of this book who observed that matrices of partially collapsed maltodextrin/corn syrup solids exhibited high levels of volatile release which could be maintained over time. However, once the system was fully collapsed, volatile release dropped off to levels comparable to those of the glassy state. In a study conducted by Ma et al. (43) of orange oil encapsulated in a maltodextrin matrix, volatile release was also observed to decrease once the system changed from the partially collapsed to the fully collapsed state. In addition, oxidation of the orange oil in the fully collapsed state was significantly inhibited. These studies are significant, because they indicate that collapse could be used either to improve encapsulation efficiency or to impart a desired level of release depending upon the degree to which the collapse is allowed to progress.

Conclusion

Although all of the mechanisms of volatile release from encapsulated powders are not fully understood, the studies presented in this review have provided insight into potential technologies that might be used to tailor new carriers or modify traditional carriers which protect the active yet exhibit specific release properties depending upon the physicochemical state of the encapsulation matrix. To date, many advances have been made in this area, but in order to best utilize this approach, further research is needed on the diffusion of molecular species of varying size from glassy matrices and on the relationship of diffusion coefficients to bulk properties such as the viscosity of the matrix. Further research is also needed to understand the physicochemical changes associated with the phase transitions of carrier matrices which induce flavor release in food systems.

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Chapter 13

Evaluation of the Mechanisms Associated with the Release of Encapsulated Flavor Materials from Maltodextrin Matrices

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In order to evaluate the mechanisms associated with the controlled delivery of encapsulated flavoring materials, maltodextrins and corn syrup solids of Dextrose Equivalent (DE) 10, 15, 20, 25, and 36 were spray-dried with a mixture of odd-numbered carbon aldehydes C-3 to C-11 at a level of 0.1% of the total mixture solids. Samples were equilibrated at 20°C at water activities ranging from 0.00 to 0.75. A gas chromatographic (GC) static headspace method was utilized to evaluate flavor diffusion over time as a function of volatile molecular weight and the rate of flavor exhaustion from the encapsulated powders. The effects of carrier DE, equilibration time and temperature, and sample water activity (a_w) were also evaluated. Results were correlated with the glass transition temperature and collapse of each powder and with morphological changes observed by scanning electron microscopy (SEM).

For many years, conventional methods of encapsulation such as spray-drying and extrusion have been the primary means of converting liquid flavors to a dry form for food applications. However, recent advances in the production technology of products such as microwave entrees, snacks and desserts; intermediate moisture foods such as cereal fruit fillings and fruit leathers; chewing gums, candy and confectionery; and dried beverage mixes have created a need for the development of flavors for these products which have controlled or sustained release properties. Although the pharmaceutical industry has successfully utilized such techniques in the manufacture of their products for a number of years, cost constraints have severely limited widespread application of these technologies in the food and flavor industry. A substantial need, therefore, exists for inexpensive encapsulation technologies which protect the encapsulated material or "active", yet release very slowly with prolonged

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exposure to heat or water, or which retain the flavor in dry or intermediate moisture food systems. The purpose of this study, therefore, was to evaluate the physicochemical factors associated with the retention and release of flavoring materials from traditional spray-dried carriers in an attempt to better understand how and why diffusion and release of the active occurs. Factors evaluated included maltodextrin or spray-dried corn syrup solids DE, the effects of the glass transition temperature (Tg) and collapse, the ability to allow release of the active over time, the rate at which powders were exhausted of flavor, and changes in the morphology of the spray-dried powders.

Materials and Methods

Powder Preparation. A homologous series of odd-numbered carbon aldehydes ranging from C3 to C11 (Aldrich Co., Milwaukee, WI) was dispersed in fresh vegetable oil and encapsulated in a series of maltodextrin and corn syrup solids including M100, M150, M200, M250 and M365 (Grain Processing Corp., Muscatine, IA). Depending upon the hydration properties of the carbohydrate, approximately 35 to 45% distilled spring water (Glenwood, St. Paul, MN) was added to 1900g of each carrier, and the carriers were allowed to hydrate for 24 hrs while stored at 4.5°C. Four hours prior to spray-drying, the mixtures were allowed to equilibrate to room temperature and then adjusted to a constant viscosity measured as a stirring number of 45 $\pm$ 2 at 20°C using a Rapid Visco Analyser (Foss Food Technology, Eden Prairie, MN). Immediately prior to spray-drying, a bench-top high shear mixer was used to form an emulsion between the hydrated carrier and 110g of the vegetable oil to which 2% of each aldehyde had been added. For each sample, a constant flavor/oil:solids ratio of 1:17 (equivalent to 0.1% of each aldehyde on a dry-weight basis) was maintained.

The emulsions were spray-dried using a Niro Utility Dryer (inside chamber dimensions: 150 cm ht and 120 cm diam.) equipped with a 12 cm diam. radial vane centrifugal atomizer operating at 24,000 rpm. Drying conditions were standardized at an inlet air temperature of 180 $\pm$ 5°C and an outlet air temperature of 100 $\pm$ 5°C using concurrent flow. Under these conditions, the dryer was evaporating approximately 12 kg of water per hr. All infeed was introduced into the dryer at room temperature. The resulting powders were allowed to cool and were then stored in sealed glass jars at -20°C until sample analysis.

Sample Preparation and Equilibration. To determine the effect of water activity (a_w) on volatile retention/release and sample collapse, samples were prepared as follows: 4.5g samples of each of the spray-dried powders were weighed into 20 ml standard headspace vials and placed in desiccators containing saturated salt solutions. The desiccators were then sealed under vacuum, placed in a 20°C incubator, and allowed to equilibrate for 15 days. Immediately after equilibration, the vials were sealed with crimp caps and Teflon septa and stored at -20°C until headspace analysis. The salt solutions and the range of water activities evaluated are given in Table I on the following page.

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Table I. Water Activities of Saturated Salt Solutions

a_w	salt
0.00	Drierite
0.11	Lithium Chloride
0.33	Magnesium Chloride
0.44	Potassium Carbonate
0.53	Magnesium Nitrate
0.64	Sodium Nitrite
0.75	Sodium Chloride

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Gas Chromatographic Headspace Analysis. Headspace samples were analyzed using a Hewlett-Packard static headspace unit (model 19395A, Hewlett-Packard, Avondale, PA) in conjunction with a Hewlett-Packard 5890 gas chromatograph equipped with a hydrogen flame ionization detector. All samples were equilibrated at 50°C in the headspace unit prior to pressurization and injection. A bonded phase DB-5 fused silica capillary column (30 m x 0.32 mm, 1 μm film thickness) was used in all analyses (J & W Scientific, Rancho Cordoba, CA). Operating parameters were as follows: Carrier gas: helium; Head Pressure: 15 psig; Split: 20:1; Headspace Sample Loop: 2 ml; Initial Temperature: 60°C; Initial Time: 1 min; Rate 1: 15°C/min to 220°C; Rate 2: 20°C/min; Final Temperature: 250°C. Using these basic parameters, two main static headspace analyses of the equilibrated powders were conducted hereon referred to as the equilibration study and the exhaustion study.

The objective of the equilibration study was to determine the increase in volatile headspace concentration as a function of equilibration time. Samples of M100, M200, and M365 at each water activity were equilibrated at 50°C for time intervals ranging from 40 min (initial sample) up to 30hrs. Each vial was sampled only once. The amount of each aldehyde (C-3, C-5, C-7, C-9, and C-11) was quantitated by an external standard (ESTD) method based upon a standard mix containing 200 to 300 ppm of each of the five aldehydes in the model system. Results were tallied and plotted to evaluate and compare the ability of the different powders to release volatiles into the headspace over time as a function of DE and a_w. Most points represent the average of duplicate or triplicate values.

The objective of the exhaustion study was to determine the rate at which the concentration of volatiles in the headspace was exhausted with repeated sampling of a given vial over time. Samples of the M100, M150, M200, M250, and M365 at each water activity were equilibrated for 40 min at 50°C prior to each sampling. Once the injection was made, the sample was removed from the headspace unit, vented, and immediately recapped with a new septum prior to the next sampling. As above, each aldehyde was quantitated by ESTD. The process was repeated once per hour for 15hrs or until the sample headspace volatiles were depleted (if depletion occurred before hr 15). Results were tallied and plotted to evaluate and compare the rate at which volatiles were lost from the powders as a function of DE and a_w.

Preparation of Washed Powder Samples. In order to determine if residual oil or aldehyde standards remaining on the surface of the spray-dried powders had an effect

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on experimental results, the exhaustion study was repeated with a control group of washed powders. A 100g sample was taken from each of the M100, M200, and M365 spray-dried flavor powders. Each 100g sample was then washed in a 500 ml Erlenmeyer flask with 150 ml of pentane. The pentane was filtered off and the samples were rinsed again with another 150 ml volume of pentane. The entire process was repeated three times, after which the powders were allowed to dry (approximately 1hr) at room temperature under a fume hood. The samples were then weighed (4.5g each) into 20 ml headspace vials and equilibrated to a range of water activities as described above.

Absolute Quantitation of Volatiles by Direct Injection. A direct injection method was used to quantitate the volatiles in the powder before and after water activity equilibration and after exhaustion. For each sample, 0.15g of powder was weighed into a 3 dram vial and solubilized with 0.85g of distilled spring water. The carbohydrate carrier was precipitated with 4 ml of acetone containing 0.26 g/L of 2-octanone as an internal standard. Approximately 2 ml of the acetone layer was then drawn off the top and transferred to a 0.5 dram auto-sampler vial. Aldehydes in the powders were quantitated by the internal standard (ISTD) method using a Hewlett-Packard 5890 gas chromatograph equipped with a hydrogen flame ionization detector and a Hewlett-Packard auto sampler (model 7673A). A bonded phase DB-Wax fused silica capillary column (60 m x 0.53 mm inner diameter, 1 μm film thickness; J & W Scientific, Rancho Cordoba, CA) was used in all analyses. Operating parameters were as follows: Carrier Gas: helium; Head Pressure: 15 psig; Split 40:1; Injection Volume: 1 uL; Initial Temperature: 45°C; Initial Time: 5 min; Rate: 15°C/min; Final Temperature: 180°C; Final Time: 5 min.

Scanning Electron Microscopy (SEM). A Philips 500 SEM (Philips Electronic Instruments, Mahwah, NJ) with a 100 μm objective lens aperture was used to view characteristics of particle structures and to make comparisons of the variations in morphology observed between the different powders equilibrated to various water activities. The powders (or thinly sliced chips from collapsed sample masses) were mounted on stubs using double stick carbon tape. A thin layer (approximately 20 angstroms) of gold/palladium was then applied to the surface in a vacuum evaporator to make the sample conductive. All samples were examined in the secondary electron imaging mode at an acceleration voltage of 12 kV. Photographs were taken at magnifications of 640X and 1250X.

Results and Discussion

Results of the equilibration study for M100, M200, and M365 are shown in Figure 1 depicting the sum total concentration of aldehydes (C-3, C-5, C-7, C-9, and C-11) released from the samples. From the graphs, it was observed that volatile aldehyde release over the 30hr equilibration time varied significantly with water activity. In all cases, release was lowest ($\leq$ 1 ηg/ml headspace) from powders at a_w=0.11; however, the water activity of highest release differed for each sample. M100 was observed to have the greatest release at a_w=0.64, M200 at a_w=0.53, and M365 at a_w=0.44. The corresponding high headspace concentrations at these water activities were 22 to 27

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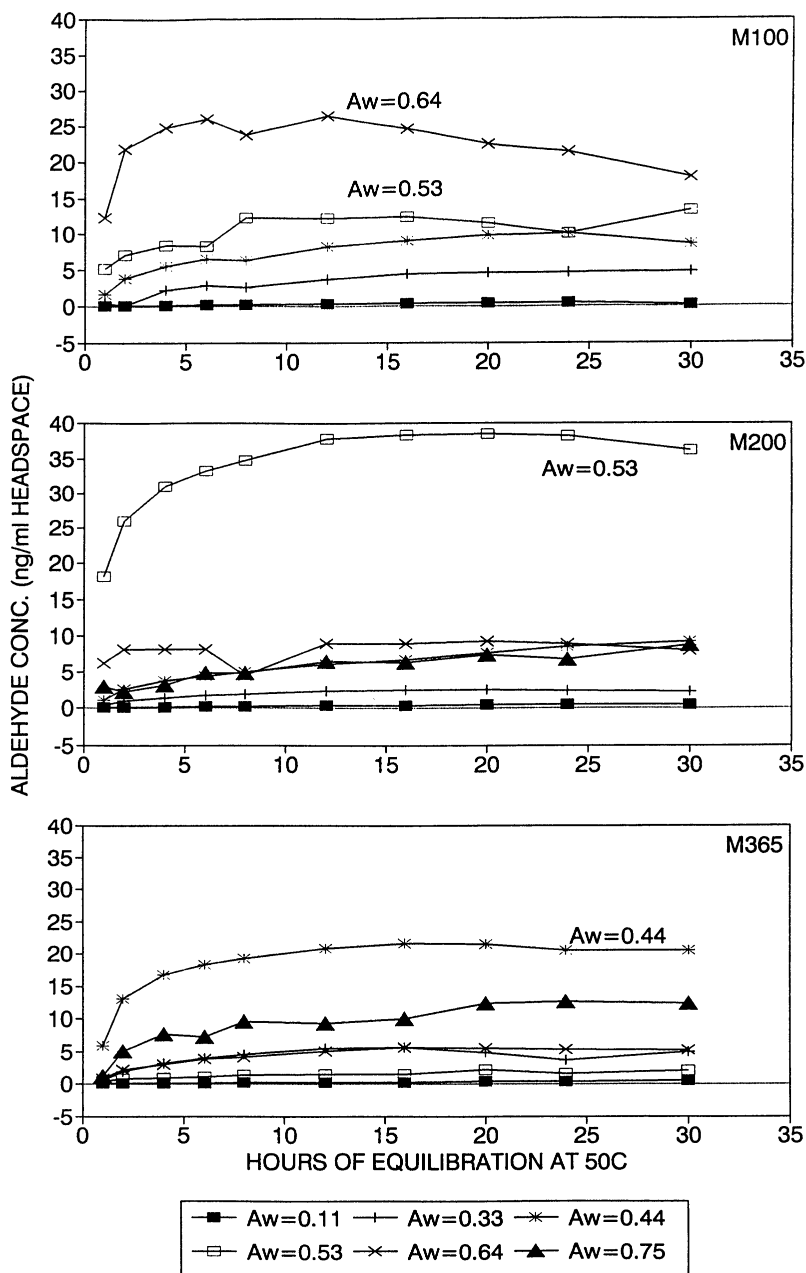

Figure 1. Total volatile release during powder equilibration at 50°C.

ηg/ml headspace for M100, 35 to 39 ηg/ml headspace for M200, and 19 to 22 ηg/ml headspace for M365. As expected, the more volatile aldehydes (C-3, C-5, and C-7) constituted the majority of these total concentration sums for each sample.

Due to the large differences observed between these samples of different water activities, the question arose as to whether the powders at the low a_w values had previously lost a significant portion of their volatiles in relation to the higher a_w powders during the 15d equilibration period in the desiccators. In order to determine if the lower a_w samples did indeed have lower volatile contents at the start of the 30hr equilibration study, absolute volatile concentrations of powders before and after the 15d a_w equilibration were determined. The results for C-3 and C-5 indicated that, in fact, the opposite was observed as shown in the data depicted in Figure 2. From these graphs, it was determined that more of the C-3 (50 to 80%) and C-5 (15 to 30%) was actually lost during the 15d a_w equilibration at the higher water activities, while only 1 to 5% of either aldehyde was lost at a_w=0.11.

Since the concentration of volatiles in the powders was not directly correlated with volatile release during the equilibration study, it was hypothesized that the physical state of the powders after a_w equilibration was likely the most important factor influencing headspace volatile concentration. Caking, collapse, and powder melt had all been observed in powders equilibrated to the higher a_w values. Thus, the effects of physicochemical phenomena such as collapse (Tc) and glass transition temperature (Tg) were further investigated and correlated with the retention data.

Figure 3 shows the Tg values for M100, M200, and M365 and the Tc values for M320 over a range of a_w values as determined by Roos and Karel (1). The center area marked by a dashed line shows the area pertinent to this study at the static headspace equilibration temperature of 50°C. From the Tg data shown in Figure 3, it was observed that each curve shifted downward as carrier DE increased. The graphs also indicated that in the 50°C range, the a_w where Tg occurred was approximately 0.2 a_w value below the a_w of high release for each powder observed during the 30hr equilibration study shown in Figure 1. Conversely, the a_w where Tc occurred was above the high release a_w, indicating that release from the powders was greatest and maintained at a higher level over time as water activity increased to a range between Tg and Tc. These findings are believed to be a result of the decreased viscosity and increased molecular mobility associated with hydration of the maltodextrin/corn syrup solids carriers above their glass transition point (2, 3, 4).

Similar or related results have been reported by other researchers (5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17). It is believed that at low water activities, the carriers are in the glassy state. Release of the entrapped flavoring materials is primarily by traditional Fickian diffusion and thus occurs very slowly. Conversely, when encapsulated powders are hydrated above their respective glass transition points, the particles begin to clump and adhere together. As shown in Figure 4, the water begins to penetrate these particle masses. The surface walls of the encapsulate are stressed, and cracks may appear which allow complete release of flavoring materials at or near the surface of the collapsing mass. In this stage, a large flavor loss would be observed. However, as hydration proceeds, pores in the particle wall close and the powders enter a fully collapsed state, effectively "reencapsulating" remaining flavor volatiles trapped inside the mass. Although the carrier is in the rubbery state at this

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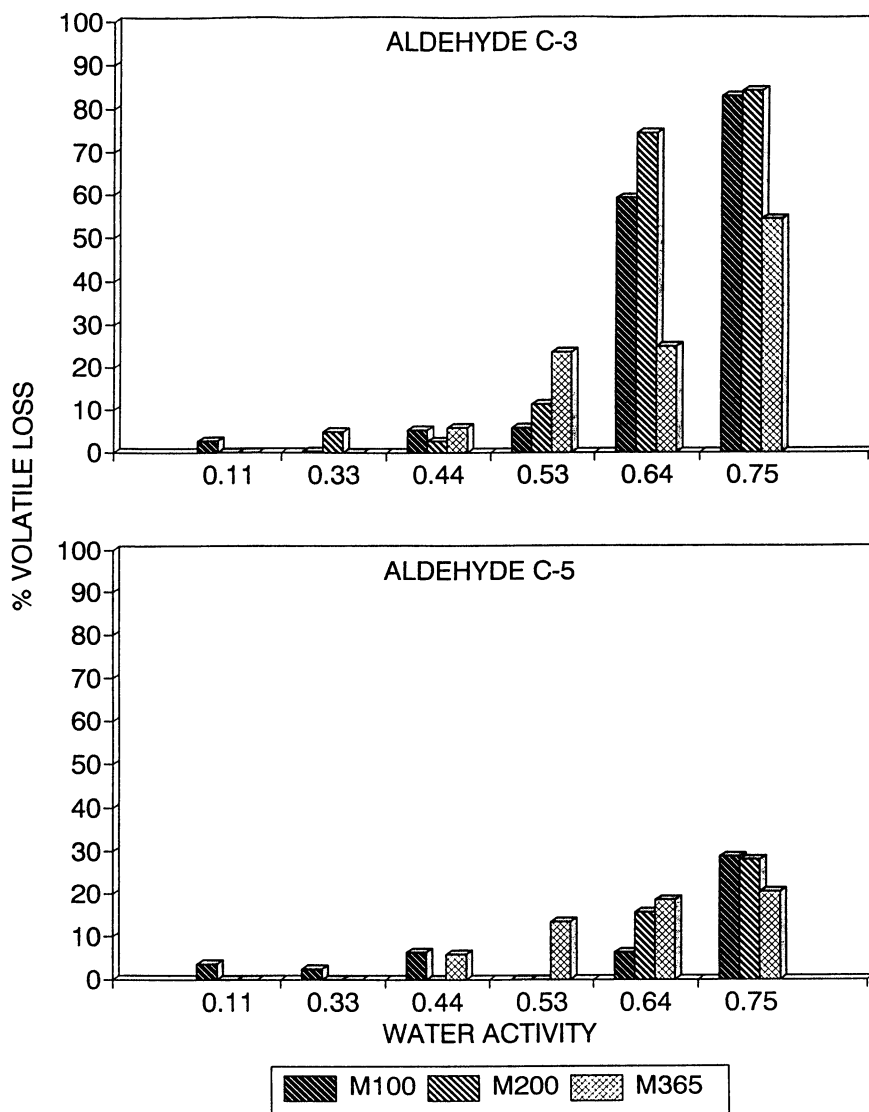

Figure 2. Comparison of C-3 and C-5 volatile loss during the 15d water activity equilibration at 20°C.

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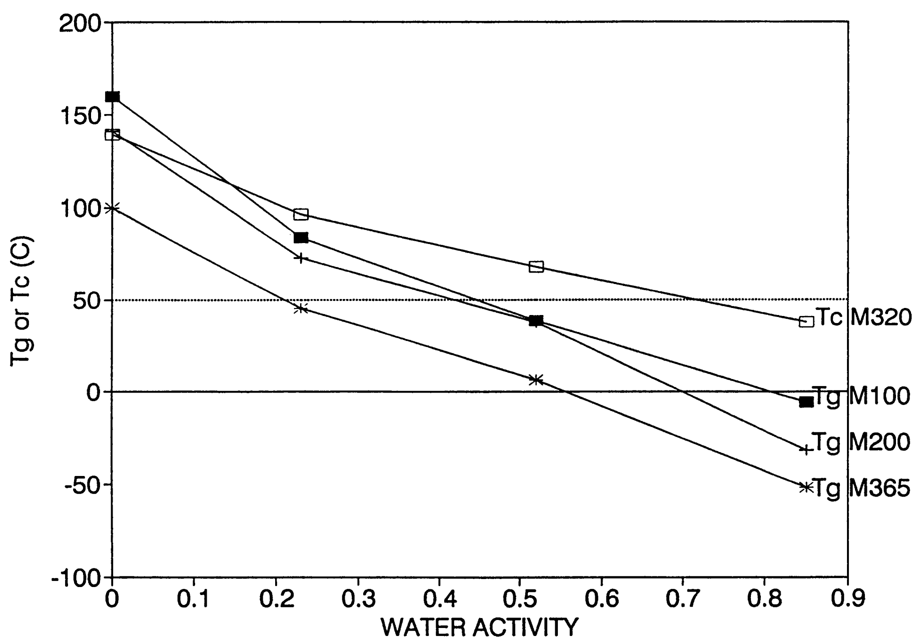

Figure 3. Tg and Tc values for maltodextrin and corn syrup solids over a range of water activity values (adapted from data by Roos and Karel, 1991a).

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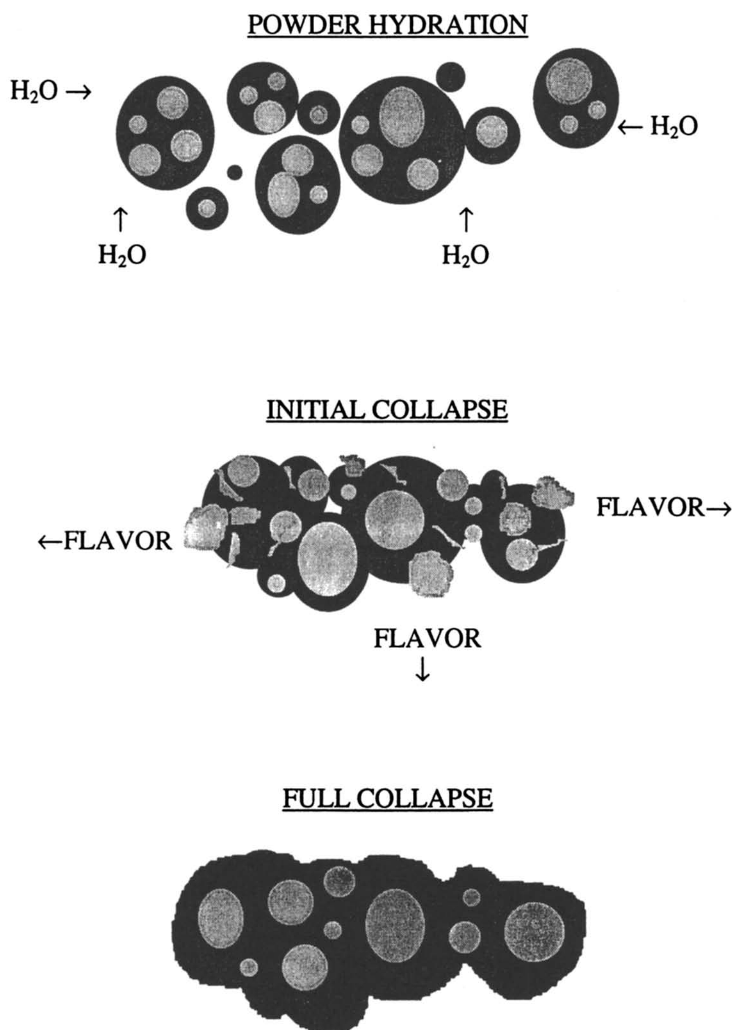

Figure 4. Powder hydration followed by the onset of collapse with subsequent flavor release and eventual flavor entrapment after full collapse.

point, release levels would be low and again resemble the Fickian diffusion characteristic of samples in the glassy state.

Results of the exhaustion study and the absolute quantitation of volatiles before and after exhaustion support this theory and are shown in Figures 5 and 6. For the sake of discussion, only data for M100, M200, and M365 unwashed samples are represented. However, it should be noted that: 1) there were no significant differences in the data observed between the washed and unwashed powders evaluated, and that 2) the M150 and M250 data (not shown in Figure 5 or 6) all fell between the M100/M200 and M200/M365 data sets, respectively.

As was observed in the 30hr equilibration study, Figure 5 shows that each powder sample had one particular a_w value between the glass transition and collapse temperatures at which release was initially high and was maintained at a higher level over the course of the exhaustion study. The high release level was again observed at $a_w=0.64$ for M100, at $a_w=0.53$ for M200, and at $a_w=0.44$ for M365. The glass transitions for M100, M200, and M365 at 50°C were at $a_w=0.48$, 0.32, and 0.21, respectively. These findings correlate with previously reported results showing that the diffusion coefficient of maltodextrins increased as temperatures increased above the glass transition (2).

Collapse of the M100, M200, and M365 samples was observed at $a_w>0.75$, $a_w=0.75$, and $a_w=0.64$, respectively. For each maltodextrin/corn syrup solids carrier, release from powders equilibrated below their glass transition point was consistently $\leq$ 1 ηg/ml of headspace. Release from samples equilibrated at a_w values above the high release level was initially higher than the release from glassy samples. However, as these powders underwent collapse, they quickly lost their ability to replenish volatiles in the headspace and eventually approached release levels near the glassy sample concentrations of $\leq$ 1 ηg/ml. These results again support the idea of high volatile release from the surface of collapsing powders prior to reencapsulation afterwhich, release slows.

Figure 6 illustrates a comparison of the percent volatile loss of C-3, C-5, and C-7 over the duration of the exhaustion study for M100, M200, and M365. These results again demonstrate the high release observed in the range between Tg and collapse and the extremely low release below Tg. In addition, these results also graphically illustrate the differences in each carrier's ability to retain encapsulated flavor volatiles. The highest losses (up to 62% of C-3) were observed with the M100 samples. A lower percentage of volatiles were lost from the M200 samples, but M365 showed less than a 10% total loss of C-3, C-5, and C-7 from all samples.

These results correlate with the findings of other researchers who have reported increased flavor retention with increased carrier DE during spray-drying and the superior oxidative stability of flavors encapsulated in M365 (9, 18, 19); however, the reason for these observations is still not well understood. Although further research in this area is needed, results of this study indicate that, approximately 3X fewer volatiles were lost from M365 in its "high release state" than either the M100 or M200. Thus, the chemical composition of M365 and the fact that collapse occurs early may allow this carrier to pick up enough moisture at lower a_w values to make the walls somewhat "elastic" and therefore more resilient to surface cracks and stresses than the other maltodextrin/corn syrup solids carriers. At a_w values above 0.44, collapse occurs (M100 does not collapse until a_w > 0.75). In either situation, it

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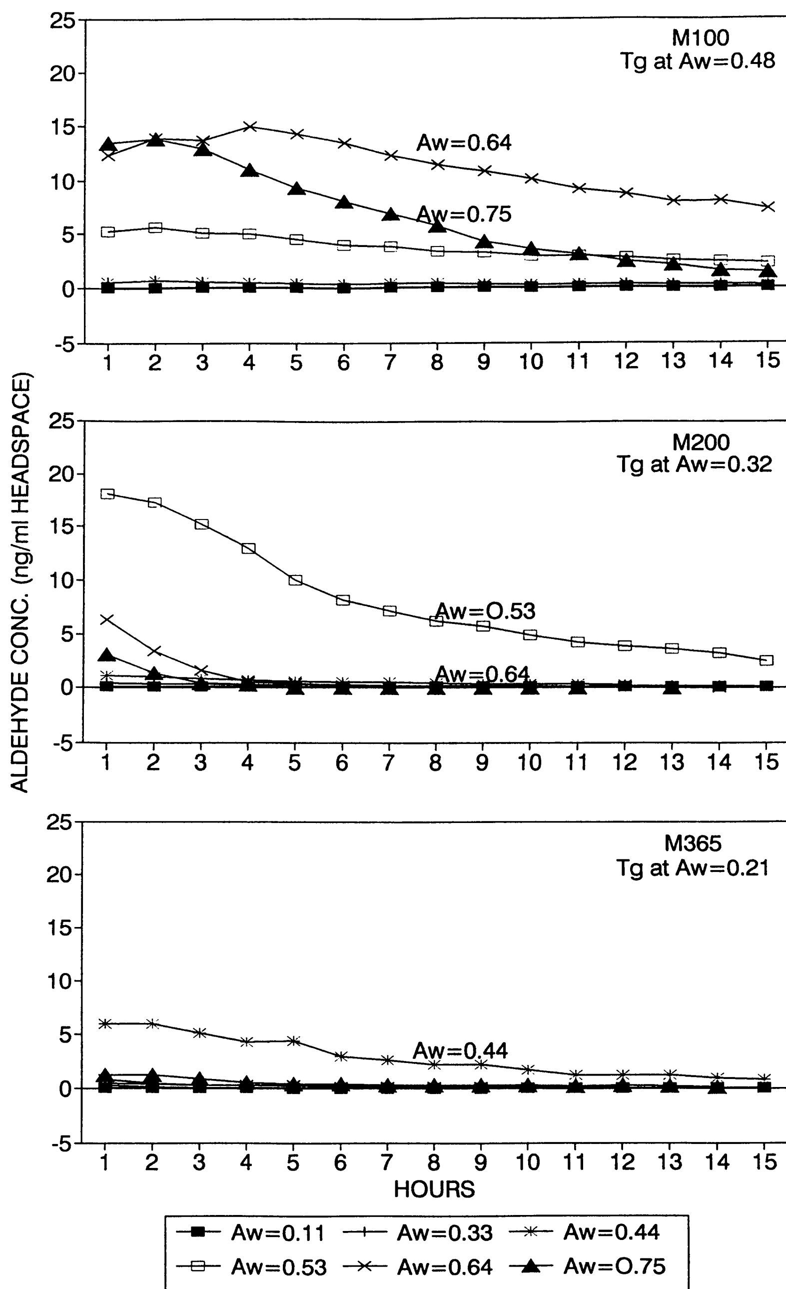

Figure 5. Rate of total volatile exhaustion with repeated headspace sampling.

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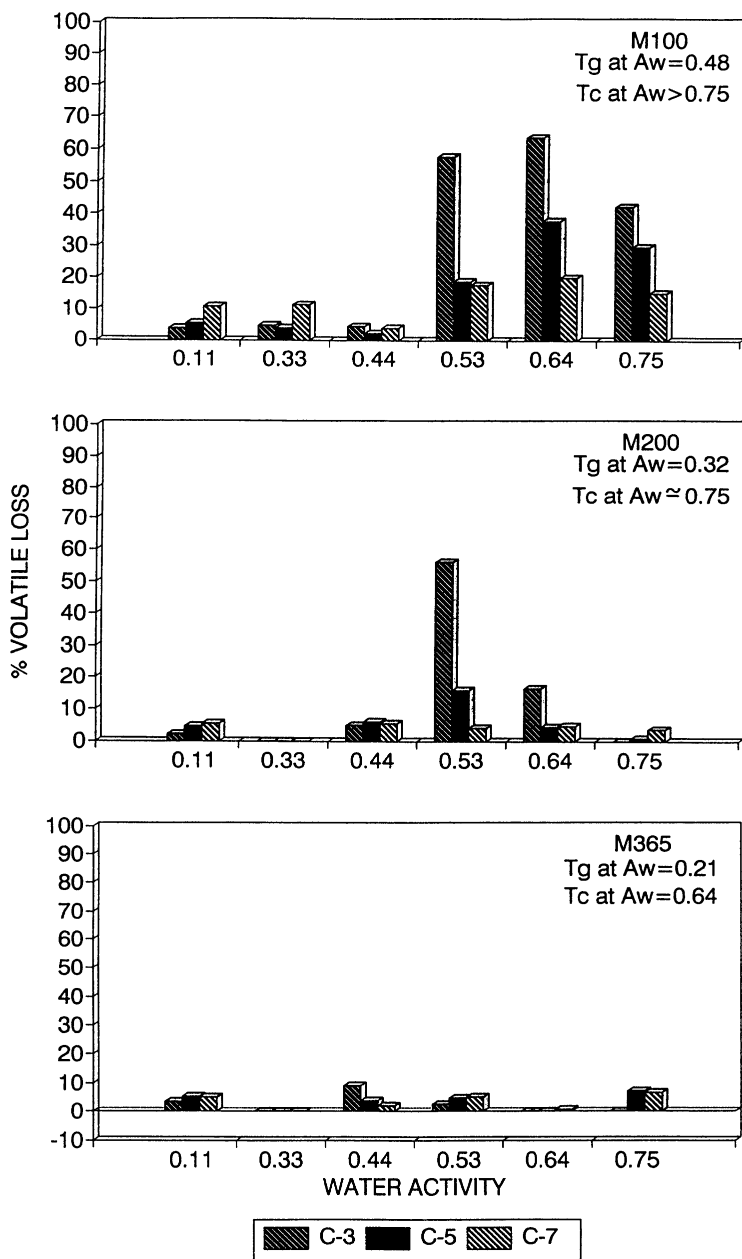

Figure 6. Comparison of percent volatile loss below Tg, between Tg and Tc, and above Tc.

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would be more difficult for volatiles to escape or for oxygen to penetrate the capsule walls.

In an attempt to visibly assess variation in sample morphology and to correlate any observed differences with the results previously obtained in both the equilibration and the exhaustion studies, SEM photos were taken of different powder samples at varying a_w values after 2 and 12hrs of equilibration at 50°C. Results of M100, M200, and M365 are shown in Figures 7, 8, and 9, respectively. Each figure displays the powder morphology while the sample is in a) the glassy state, b) the high-release range between Tg and Tc, and c) in an amorphous state at or beyond full collapse.

The differences in morphology are evident in Figures 7 to 9, and lend validity to the idea that hydration leads to surface stresses which allow for high volatile release in the range between the onset of a glass transition and complete collapse. All powders were observed to have an average particle diameter of approximately 50 to 60 microns interspersed with smaller particles of 5 to 30 microns. However, in the M100 series shown in Figure 7, particles appeared to maintain their spherical shape longer than in either the M200 or the M365 series. Results indicated that hydration occurred slowly and at much higher a_w levels than the other powders, most likely a result of the chemical composition of the M100. As shown in Figure 7 depicting the M100 series, samples in the glassy state were originally spherical (Figure 7a), but began to agglomerate with prolonged heating at 50°C and with additional moisture (Figures 7b, 7c). In the 2hr sample at a_w=0.75, the smaller particles (5 to 30 micron diameter) were the first to collapse on the surface of the agglomerated mass. The high release of volatiles into the sample headspace is believed to have occurred at this point, since these photos (Figure 7c) correspond well with the initial release observed in Figures 5 and 6. After 12hrs at 50°C and a_w=0.75, the particles had formed a partially collapsed agglomerated mass further correlating with the decrease in volatile release also observed in Figure 5.

Similar results are shown in Figures 8 and 9. In both cases, the particles were initially spherical (Figures 8a, 9a). With prolonged equilibration at 50°C or exposure to moisture past Tg, the particles began to agglomerate. Structure was lost, stresses appeared in the particle surfaces (Figures 8b, 9b), and finally, complete collapse was observed (Figures 8c, 9c). Again the photos of these physical changes were well correlated with the data presented in Figures 5 and 6 showing high release during the agglomeration stages (observed in Figure 8b at a_w=0.53 for M200 and in Figure 9b at a_w=0.44 for M365) followed by subsequent declines in volatile release at the higher water activities where particle collapse occurred.

As a final point, the smooth surface characteristics (even at a_w=0.11) of the M365 particles shown in Figure 9 should be noted in comparison to the other carriers. In fact, after 12hrs at 50°C, the a_w=0.11 sample had already started to partially agglomerate. The smooth surface and the tendency to clump are perhaps indicative of the "sticky" or "elastic" nature of the particle walls (even with very little hydration). These characteristics may serve to seal off cracks or holes thus lending further insight towards the explanation of the observed oxidative and retentive stability of flavoring materials encapsulated in this carrier.

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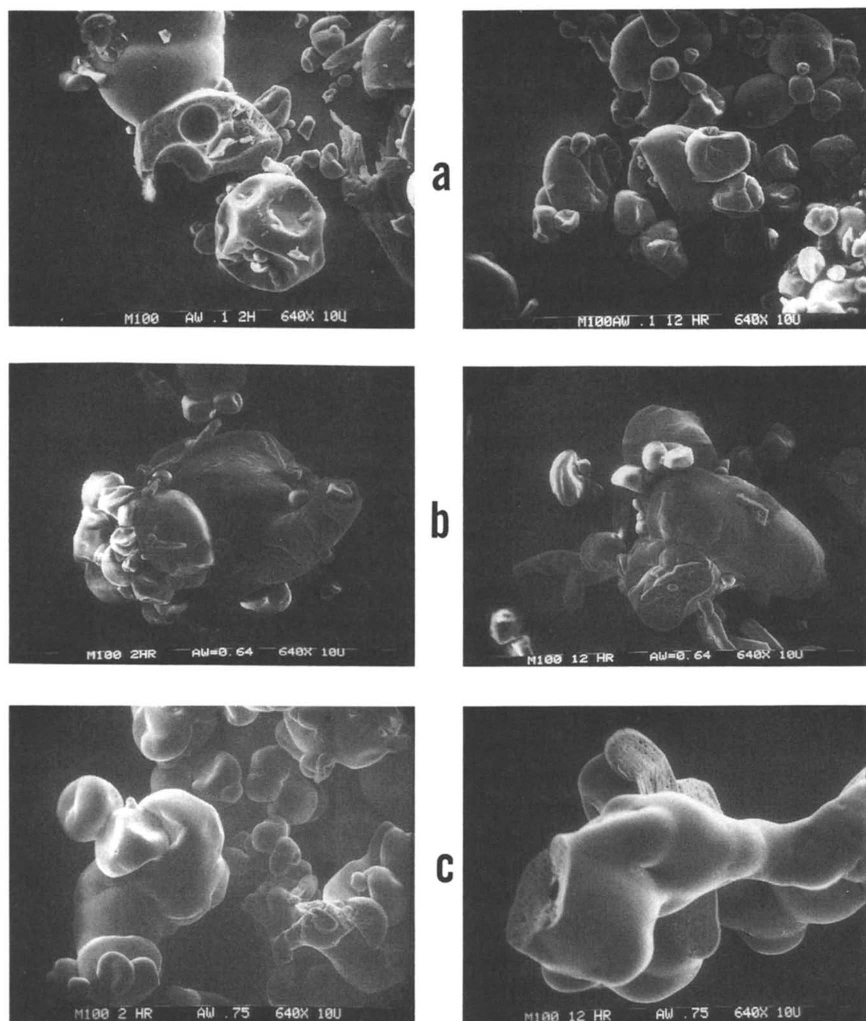

Figure 7. M100 in the a) glassy, b) high release, and c) partially collapsed states after 2h and 12h of equilibration at 50°C.

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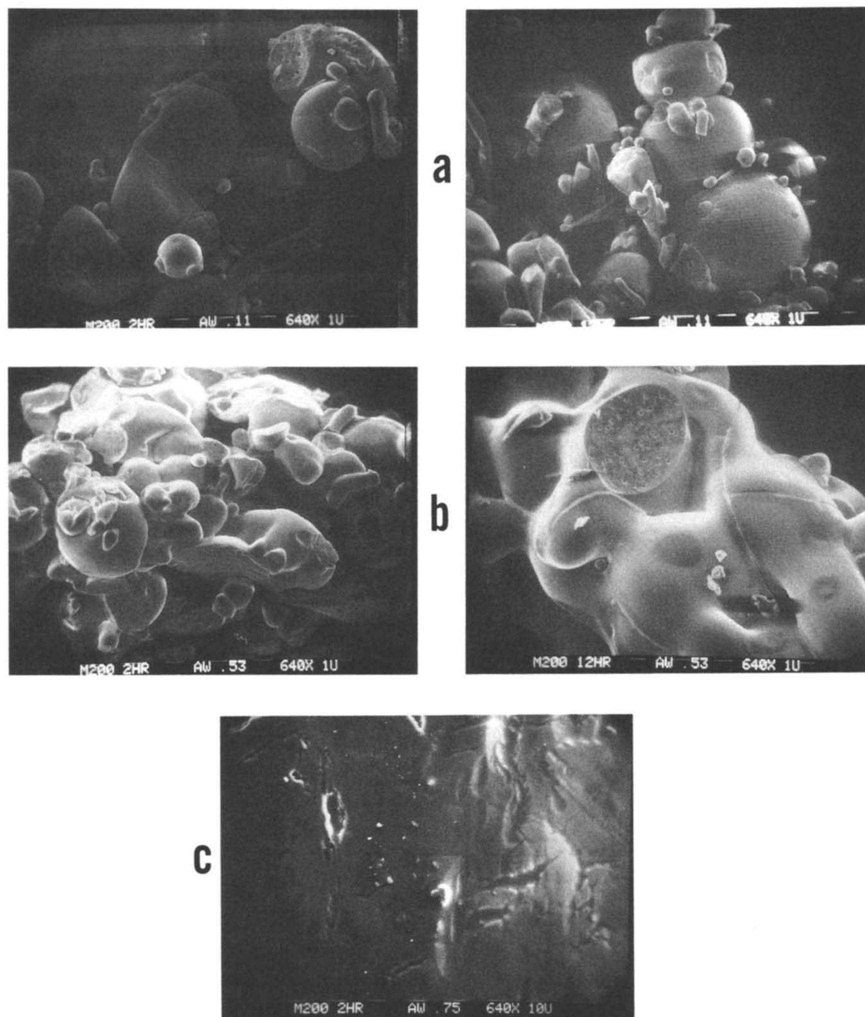

Figure 8. M200 in the a) glassy, b) high release, and c) fully collapsed states after 2h and 12h of equilibration at 50°C.

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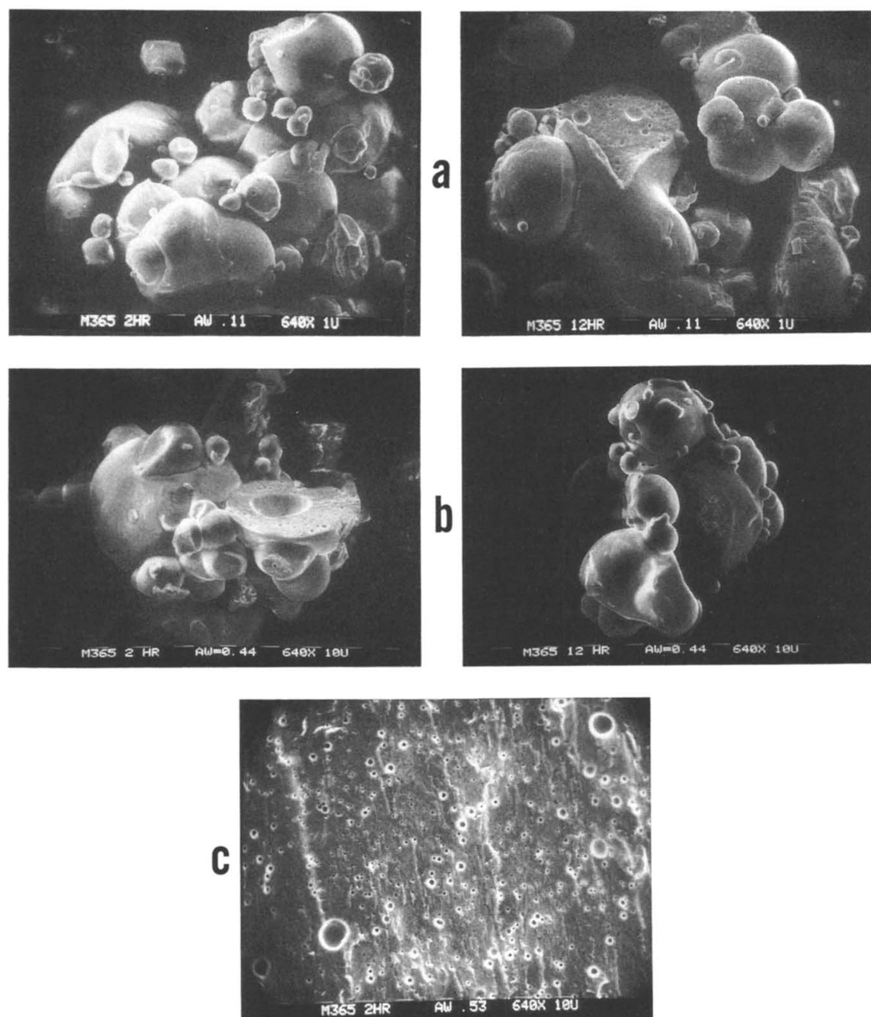

Figure 9. M365 in the a) glassy, b) high release, and c) fully collapsed states after 2h and 12h of equilibration at 50°C.

Conclusions

In summary, five main conclusions have been drawn from this study. First, increased volatile retention was directly correlated with carrier DE. M365 was observed to be the most efficient, followed by M200. M100 retained the lowest percentage of volatiles. Second, volatile release increased with increasing water activity up to the point where collapse occurred and then decreased. However, release from none of the powders was complete. Third, each carrier was observed to have a distinct water activity at which release was greatest and sustained at a greater level of release over time relative to other samples encapsulated in the same carrier but equilibrated to different water activity levels. Fourth, this optimal range of high release typically occurred at a point between the glass transition and complete collapse. Thus, neither the points of glass transition or total collapse of any sample alone could be used to predict when the highest level of release would occur. Finally, all of these morphological changes could be visually monitored by SEM.

Although we currently are a long way from understanding all of the phenomena associated with controlled or sustained release of flavoring materials, this type of work provides a direction for future research and eventual application in the food industry. For example, it was observed that M200 provided prolonged levels of high release at $a_w=0.53$. Since this water activity is already in the range of many intermediate moisture foods currently on the market, further work needs to be done with other homologous series of flavoring materials and with finished flavors to determine if encapsulated flavors adjusted to this water activity prior to manufacture would indeed provide a controlled flavor release in products like fruit leathers or cereal fruit fillings. Perhaps secondary coatings or combinations of carriers would allow us to use this technology to "tailor-make" flavorings for other products as well.

Acknowledgments

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Chapter 14

Developments in Gum Acacias for the Encapsulation of Flavors

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Two species of gum acacia were found to provide substantially better protection against oxidation of encapsulated orange oil during storage than competing modified starches. While emulsification properties were similar, the orange oil encapsulated in both gums had higher surface oil and moisture contents and slightly lower retention than the orange oil encapsulated in the modified starches.

Gum arabic (or gum acacia) is an unusual polysaccharide due to its excellent emulsifying properties and low viscosity, despite its high molecular mass (about 400,000 daltons) (*1*). The gum exudate from Acacia species consists of a beta-1,3-linked galactopyranose backbone chain with several branches linked through 1,6-galactopyranose residues containing arabinofuranose, arabinopyranose, rhamnopyranose, glucuronic acid and 4-O-methyl glucuronic acid. The three principal fractions of gum acacia include an arabinogalactan, a glycoprotein, and an arabino-galactan protein complex (AGP). The hydrophilic carbohydrate blocks are linked to the hydrocarbon chain resulting in strong absorption at the oil-water interface, promoting emulsion stability.

A chemometric study of nine physical and chemical parameters for the gums of Acacia sub-genus (Vulgares and Gummiferae) has been reported (*2, 3*). Results indicate that *Acacia seyal* and *Acacia senegal* can be regarded as closely related gums in regulatory terms. Different formulations using various gum acacia species as protective colloids have been investigated (*4*).

The objectives of the study were to develop and evaluate gum acacias for the encapsulation of flavors and to develop encapsulation matrices which provide protection against oxidation. The emulsifying system would be "natural", unlike modified starches.

Materials and Methods

Materials. The following materials were used as encapsulating agents: Acacia A (Arabic FT), Acacia B (Arabic FT-1), Acacia C (Arabic FT-2), Acacia D (Arabic Super FT), Acacia E (Arabic S.D. Sudanese) blended with Maltrin-100 (a 10 D.E. maltodextrin from Grain Processing Corp., Muscatine, IA), Acacia F (Arabic S.D.

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Nigerian) blended with Maltrin 100, and N-Lok (a modified starch from National Starch Corp., Bridgewater, NJ). All acacia gums were obtained from TIC Gums (Belcamp, MD).

For gums A to D, emulsions were prepared for spraydrying as follows: 65% water, 28% carrier, and 7% oil. For gum Acacia blends E and F, the formulation was 38.6% water, 31.5% Maltrin-100, 17.5% gum, and 12.4% oil. N-Lok was used at 45% level, 12.4% oil and 42.6% water.

Spray Drying. The carrier materials were hydrated the night before they were spray dried and orange oil was added to the rehydrated gum (or gum blend) just prior to spray drying. Emulsions were made using a Greer Co. laboratory homogenizer. The emulsions were then spray dried using a Niro Atomizer (Ramsey, NJ) Utility model spray drier. The inlet temperature was 200°C and the exit air temperature was 100°C.

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Total Oil Determination. The total oil was determined using a Clevenger apparatus. Twenty g of powder were dissolved in 150 ml water in a 500 ml flask. Boiling chips and approximately 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 distilled for 3 h. The volume of oil, read directly from the oil collection arm, was converted to g. of oil by multiplying by the density of the oil (0.83 g/ml).

Surface Oil Determination. The amount of extractable surface oil on the dried powder was determined by Soxhlet extraction of a 20 g powder sample, covered with glass wool, with 150 ml n-pentane for 4 h. 2-Octanone (2.5 mg/ml) was added to the extract as an internal standard. Each extract was then evaporated under nitrogen to approximately 1 ml and the amount of oil in the sample determined by gas chromatography. The analysis was run under the conditions described (*5*) previously.

Moisture Analysis. Moisture was determined by the toluene distillation method. A 40 g sample was added to 250 ml toluene in a 500 ml flask fitted with a Bidwell-Sterling trap. The sample was distilled for 2½ h. The distillate was allowed to cool to room temperature before the water volume was read directly from the trap.

Emulsion Stability Determination. The stability of the emulsions was determined by measuring the optical density of dilute solutions of each material 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 acacia) was used as a blank. This is based on a carrier to flavor ratio of 4:1. The optical density of each solution was read initially and after centrifugation in an IEC International centrifuge at 500 G for 5, 10, 15, 30, 45, and 60 min.

Shelf Life Study. 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°C (duplicate experiments encompassing all materials except the N-Lok). Product from the last run (N-Lok only) was held at 37°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 4°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.

The method for determining limonene epooxide and carvone formation involved taking a sample of powder (0.15 g) and dissolving it in 0.85 g water. Then 4 ml of an acetone solution containing 0.25 mg/ml 2-octanone were added slowly with agitation. The sample was allowed to settle and a 1 µL aliquot of the liquid phase was injected in the GC (Hewlett Packard Model 5880, Little Falls, DE). The analysis was run under the conditions described (*4, 5*).

Results and Discussion

Results of the moisture analyses show that percent moisture in the spray dried powders remained between approximately 2 and 5%. Spray dried gum D (Arabic Super FT) had the lowest percent moisture while gum F (Acacia with Maltrin-100) had the highest percent moisture (Fig. 1). Prior to spray drying, emulsions E and F had approximately 45% moisture.

The average percent total oil in the five different spray dried gums varied between approximately 14 and 20% (Fig. 2). The difference in oil retention appears to be affected by the film-forming properties of the type of gum acacia used. (Gum A 17.54%, Gum B 18.01%, Gum C 17.9%, Gum D 16.83%, Gum E 14.3%, Gum F 14.46%, and N-Lok 19.55%). Acacia E (Acacia with M-100) showed the lowest total oil content and the standard control, N-Lok showed the highest. Maltodextrins have poor emulsifying properties and yield coarse emulsions, hence emulsions prepared with Acacia E have the lowest oil retention.

The surface oil of Acacia A, B, and C ranged from 53 to 70 mg/100 g; 236 to 269 mg/100 g for Acacia D and for samples E and F, from 1010 to 1436 mg/100 g. N-Lok had the lowest surface oil at 6.44 mg/100 g (Fig. 3). The industry has generally used surface oil as an indicator of shelf life. As has been shown before, there was no relationship between these two factors in this study.

Samples E and F (Acacias with M-100) were oxidized (defined as having reached 2 mg limonene epoxide/g limonene) after four days, and samples A (Arabic FT), B (FT-1), and C (FT-2) reached the end of shelf life after 12 days. Acacia D (Arabic Super FT) was superior to all other carriers in terms of retarding or inhibiting oxidation (the levels of limonene epoxide remained constant during the duration of the study). Gum C is second best followed by Gum B. The gum blends A to D were superior to N-Lok in protecting oil against oxidation (Fig. 4 and 5).

The addition of maltodextrin to the traditional acacia (Gums E and F) shortens the shelf life of the spray dried flavor and thus, is less stable than N-Lok (Fig. 4 and 5). Acacia D (Super FT) would likely give more than one year shelf life at room temperature without added antioxidant. This will be significant to a manufacturer who desires a clean label.

Emulsion stability tests show that Gum D was slightly poorer in emulsification properties than the other gums or gum/maltodextrin combinations (Fig. 6 and 7). This effect may be less significant if the orange oil has other weighting agents, such as ester gum and/or brominated vegetable oils.

Conclusions

The results of the study show that there are substantial differences between different types of gum acacia. The acacia gums tested performed better than N-Lok in protecting the orange oil against oxidation, however, they generally resulted in lower retention of flavors during the drying operation. Emulsification properties are similar and considered very good.

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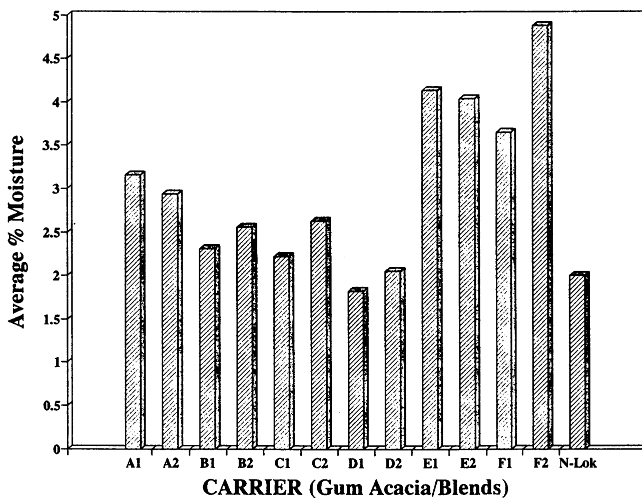

Figure 1. The influence of carrier on moisture content in spray dried flavorings.

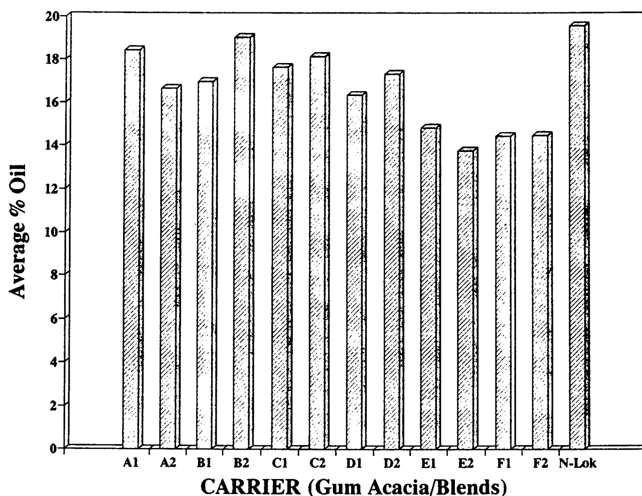

Figure 2. The influence of carrier on the retention of orange oil during spray drying.

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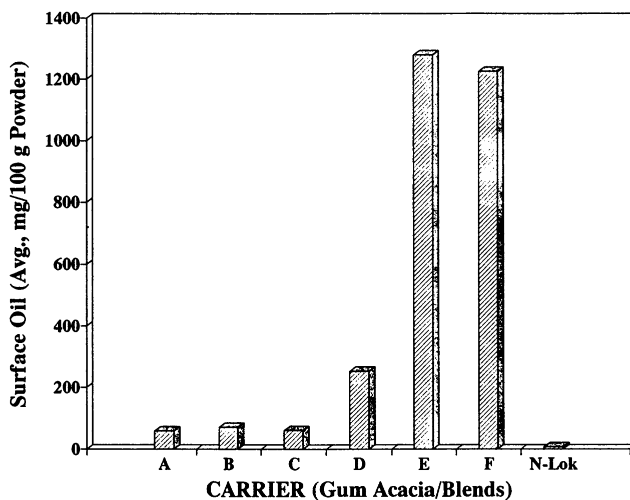

Figure 3. The average extractable oil content of orange oil spray dried in various carrier materials.

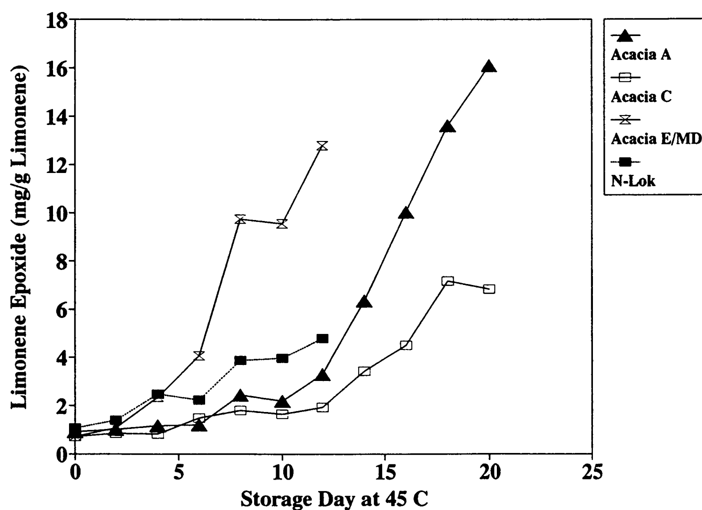

Figure 4. Oxidative deterioration of orange oil during the storage -- influence of carrier type.

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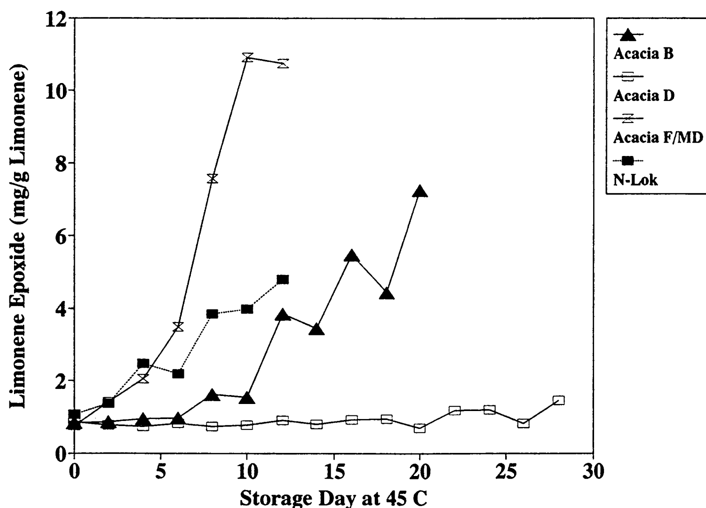

Figure 5. Oxidative deterioration of orange oil during the storage -- influence of carrier type.

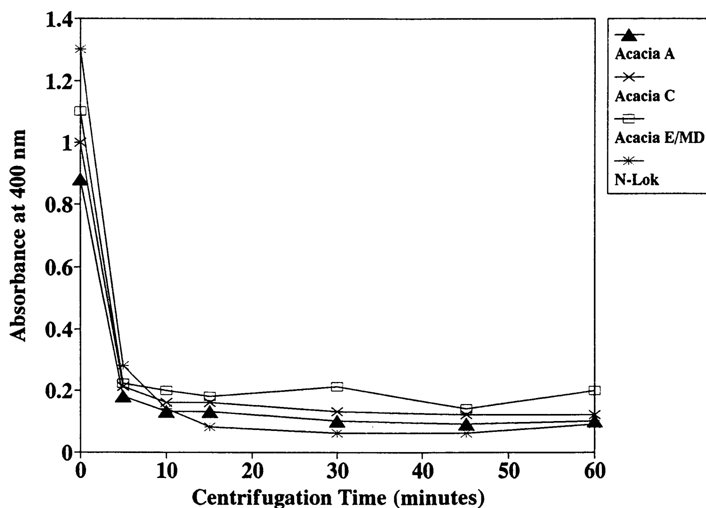

Figure 6. Optical density of reconstituted spray dried orange oil during centrifugation.

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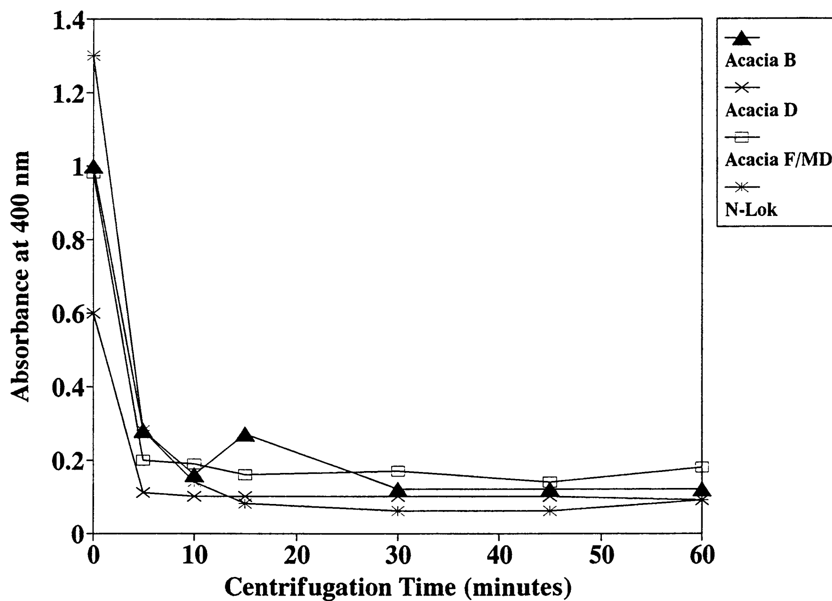

Figure 7. Optical density of reconstituted spray dried orange oil during centrifugation.

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Chapter 15

Flavor Encapsulation

Influence of Encapsulation Media on Aroma Retention During Drying

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Flavoring of food products needs agents in liquid or powder forms ; to obtain the latter, encapsulation techniques can be used. One way is to dry an emulsion composed of volatiles and food grade material like sugars or proteins. We have studied the behavior of a mixture of aroma compounds fixed on carbohydrates to simulate strawberry flavor. The carriers are glucose syrups of different mean molecular weight, in the presence of a stabilizer, gum arabic or modified starch. This mixture was freeze-dried in standard conditions. Aroma analysis was carried out by gas chromatography and sensory analysis to study the influence of the other constituents on the retention. The aromatic quality (evaluated by judges) is not the same as the relative proportions of each compound change. To interpret the results, we developped simple model systems and demonstrated that volatile retention depends on physico-chemical interactions, which can reduce the diffusion rate, and also on partition coefficients between phases in the encapsulating media.

Flavoring of food products to increase or modify the aroma or to mask an undesirable flavor needs flavoring agents in liquid or powder forms. To obtain the latter many encapsulation techniques can be used, of which the most common is spray-drying. Much work has been done on the development of others techniques like extrusion, coacervation or molecular inclusion (*1*, *2*) and recently papers concerning the microencapsulation of volatile compounds and natural essential oils have been published (*3*). The influence of process variables and composition on retention of volatile aromas during drying has been extensively studied over many years (*4, 5, 6, 7*), and theories have been developed to explain the retention of volatiles during drying of food materials. Several review papers are available on mechanisms of aroma losses (*8, 9*). Volatile losses are often less than would be expected from volatility data and two basic mechanisms have been proposed to explain the retention of homogeneously dissolved aroma components during drying.
- The micro-region concept (*10*).

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Table I : Composition of the artificial strawberry flavor

Aroma compound	Concentration (%) m/m	Aroma compound	Concentration (%) m/m
ethyl propionate	2.5	benzylic alcohol	1.7
ethyl butyrate	1.6	2-methyl-2-pentenoic	
trans-2-hexanal	2.5	acid	33
isoamyl butyrate	2.5	ethyl maltol	6.6
2-butanol-3-one	0.8	heliotropin	2.2
n-butyl pentanoate	2.5	ethyl phenyl glycidate	16.5
butyric acid	0.8	γ-n-heptyl	
caproic acid	1.7	butyrolactone	16.5
lactic acid	6.6	ethyl vanillin	6.6

Table II : Composition of the aqueous solution containing 6% of flavor content (for 100g).

Carrier	Concentration (m/m)	Emulsifier	Concentration (m/m)
Glucose	40	modified corn starch	3
Maltose	40	modified corn starch	3
Corn syrup solids :			
- DE 41.5	40	modified corn starch	3
- DE 28.5	40	modified corn starch	3
- DE 28.5	60	modified corn starch	3
- DE 28.5	40	arabic gum	3

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- The concept of selective diffusion in which it was proposed that the diffusion coefficient of water and volatiles are reduced as water concentration decreases due to drying (*11*). As the diffusion coefficients of the volatiles decrease more rapidly than that of water, the trapping of flavor compounds is greatly influenced by the rate of drying and of the formation of a dry skin around the products. Somewhat more complicated is the loss of aroma compounds which are present in the form of a dispersion (*12-14*). Various carbohydrates were initially tested for encapsulation properties.

We first prepared an artificial strawberry flavoring composed of 16 pure aroma compounds (Table I) ; this mixture was added at 6 % concentration to an aqueous solution containing corn syrup solids and a stabilizer, gum arabic or modified corn starch (Table II). This solution was freeze-dried in conditions allowing no structural changes giving specific aroma losses. Analysis by sensory evaluation and by gas chromatography of products after drying allow us to study the influence of the carrier on the aroma fixation. The results were treated with statistical techniques.

Sensory evaluation : Following a flavor profile, tests to classify samples and a reference solution were carried out on the 4 characteristics best discerned by the judges ; the reference solution was an aqueous solution of glucose (40 %) with 6 % of aroma compound. In the experiment, 11 media were analysed. Table III only presents a part of the results obtained ; thus, the sum of the ranks varies according to the studied properties.

Table III : Sensory evaluation of the encapsulated strawberry flavor before and after drying (sums of the ranks).

	Flavor			
Carrier	"Strawberry"	Pungent	Green apple	Vanilla
before drying glucose	185**	163*	181**	90
after drying				
maltose	126	98	132	155
- DE 41.5	90	100	92	172**
- DE 28.5	118	141	123	119
- DE 28.5 (60%)	96	113	147	101
- DE 28.5 (arabic gum)	141	137	112	113

* significant level 5% ** significant level 1%

The sums of the ranks show a significant difference between the reference solution (before drying) and the other samples (after drying), but even if the intensity differences are not significant, the overall assessments between these latters are not similar, as shown by factorial analysis. The sample containing DE 41.4 exhibits little fruit flavor in contrast to that with maltose which is fruity and fresh ; DE 28.5 gives a sweet flavor of intermediate fruitiness.

Gas chromatography : The results are expressed as the percentage of each volatil fixed on the carrier (figure 1), and show quantitative changes in the proportions of each volatile. The analysis of the results shows a group of 3 DE samples containing DE 28.5 corn syrup solids in which the volatiles are fixed in the same manner, while the aroma behavior differs with the more hydrolysed corn syrup solid (DE 41.4) and maltose. We can conclude that the behavior of the volatiles depends not only on the nature of these compounds but also of the carriers or substrates even in the same class. The quantitative changes in aroma proportions (measured by gas chromatography) give sensory modifications.

The objective of our work is to show from examples, with well-defined and simple systems, the role of physico-chemical interactions between volatiles and substrates in the retention of aroma components during drying.

Material and Methods

Material. Model systems composed of water, five volatiles and substrate were used. The volatiles were each dissolved in water at 1000 ppm (table IV). Two types of substrate were used :

- Carbohydrates of different molecular weight (table V).
- Casein, glycosylated or not (table VI).

. The bovine caseinate was prepared from frozen cakes (2 kg) given by "prospérite laitière", Arras, France, thawed at 4°C. After a series of solubilisations (at pH 7), rinsing and precipitations (at pH 4.6), the sodium caseinate (reajusted at pH 7) was freeze-dried and stored at 4°C in closed packaging ; its mean molecular weight was about 23000.

. Glycosylated caseins : The aldehyde group of sugars reacts by reduced alkylation on the amine group of lysine.

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Table IV : Physico-chemical properties of volatiles

Volatile	Formula	Molecular weight	Solubility in water (g/100g)	Vapor pressure (mmHg at 25°C)
Acetone	CH_3-CO-CH_3	58	∞	250
Ethyl Acetate	CH_3-COO-CH_2-CH_3	88	8.6 (20°C)	94
2-propanol	CH_3-CHOH-CH_3	60	∞	21
Diacetyl	CH_3-CO-CO-CH_3	86	25 (15°C)	58
n-hexanol	$CH_3(CH_2)_4$-CH_2OH	102	0.59 (20°C)	1

Table V : Origin and molecular weight of sugars

Sugar	Origin	DE	Molecular weight
Glucose	Merck	100	180
Maltose	Merck	50	342
Corn syrup solids			
- MD 63	Roquette	61.5	291
- MD 33	Roquette	31	560
- MD 05	Roquette	20	868

Table VI : Physico-chemical characteristics of caseins

	Modification rate[a] (%)	Water content (%)	NaCl (g/100g d.m)
Bovine caseinate	0	6.1	3.5
Glycosilated caseinates :			
- Glucose	45	7.8	13.5
- Maltose	54	6.3	13.0

[a] The modification rate is the proportion of substituted lysyl groups in casein.

This reaction was maximal after 180 hours at pH 8. The glycosylated caseins then were dialysed, dissolved at pH 7 and freeze-dried. The modification rate was determined using 2, 4, 6-trinitrobenzene sulfonic acid (T.N.B.S.).

Methods. Air-drying : all the solutions were dried in the same experimental conditions in a laboratory drier.

* air temperature : 60 ± 0.5°C
* air relative humidity : 65 %
* air rate : 2 $m.s^{-1}$

Every ten minutes, a sample was weighed and analysed by gas chromatography after rehydration.

The retention of aroma compounds is expressed as the ratio of the quantity of volatile after and before drying multiplied by 100.

• Volatile diffusivity : the technique of concentration profile was used (15).

• Activity coefficients of the volatiles were measured at infinite dilution by an inert gas stripping method (16). Another technique, equilibrium dialysis, was used to find the extent of interaction between casein and volatiles (17).

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Table VII : Physico-chemical properties and retention of acetone in aqueous solutions of sugars

Substrates	Retention (%) after drying of a solution at 40% *	Diffusivity ($x10^{10}m^2.s^{-1}$) 25°C		a_w=0.75 (25°C) water content (%)
		50 % *	30 % *	
Glucose	38.5	1.21	14.7	37
Maltose	71.0	1.25	11.7	15
Corn syrup solids :				
DE 61.5	66.0	1.32	12.1	28
DE 31	74.5	1.17	-	20
DE 20	78.7	0.97	10.9	16.5

* Water content

• Infra-red Spectrophotometry. This technique was used to measure interactions between volatiles and non volatiles by the displacement of absorption bands of chemical groups implied in the interactions (18). Analysis was carried out after sorption of each pure aroma compound on a caseinate film.

Results and Discussion

The behavior of volatiles during drying is modified by the presence of carbohydrates and caseins. The retention of volatiles is not negligible at the end of drying (15).
- **With Sugar Solutions** (Figure 2). All the results are approximately explained by the diffusivities of the volatiles which depend strongly on the water content (Figure 3) and the water activity at the surface of the product during air-drying : for a given relative humidity of the air, a_w at the interface is the same, for example 0.75, and the molar fraction of the substrate is constant. If the molecular weight of the substrate increases, its mass fraction increases, the mass fraction of water decreases, aroma diffusivity decreases and obviously its retention increases as shown in table VII.
- **with Caseins.** The rate of water loss during drying is very similar for all the solutions (Figure 4). Some small differences appear between glycosylated caseinates and caseinate with free sugar wich are significant only at the end of drying (0.2 grams water per gram of dry matter) (19). Below a critical value (3 g/g dry matter) the loss of aroma compounds becomes very low, as shown for ethyl acetate.
* In the presence of bovine caseinate, the percentage retention increases linearly with initial dry matter between 2.5 and 10 % ; above this latter concentration, the value levels towards a constant (Figure 5), this retention depends on the nature of the volatile and decreases in the order n-hexanol, 2-propanol, diacetyl, ethyl acetate and acetone, (Figure 6). As shown by many authors, this order cannot be explained only by the variation in volatility, (expressed by the Henry constant (table VIII) : ethyl acetate and diacetyl are more volatile than acetone but have higher retention rates, while n-hexanol is least volatile and has the highest retention. The lowest diffusion coefficient is given by n-hexanol and there is no relation between diffusivity, volatility and retention rate for the other compounds.

Measurements of activity and diffusion coefficients do not entirely explain the observed retention rates (except for alcohols) and physico-chemical binding data are

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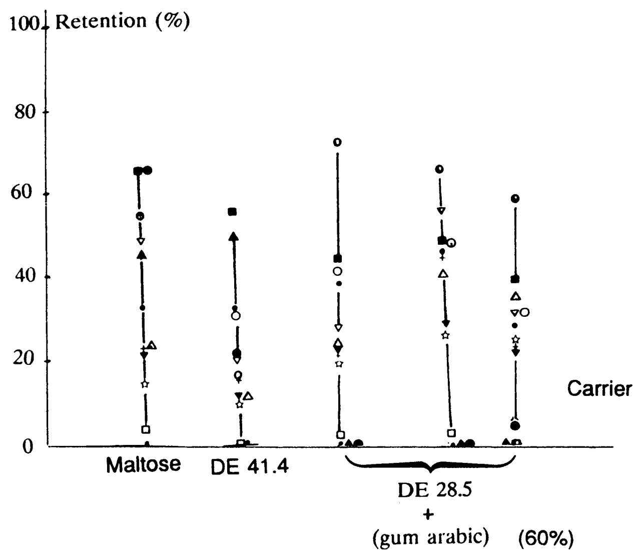

Figure 1 : Strawberry aroma recovery after drying (measured by gas chromatography).

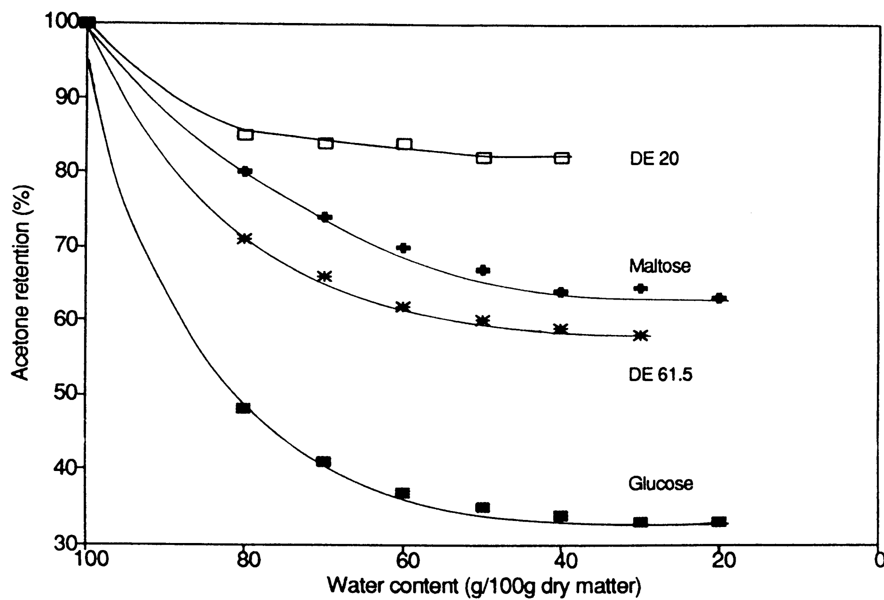

Figure 2 : Effect of sugars on acetone retention during drying.

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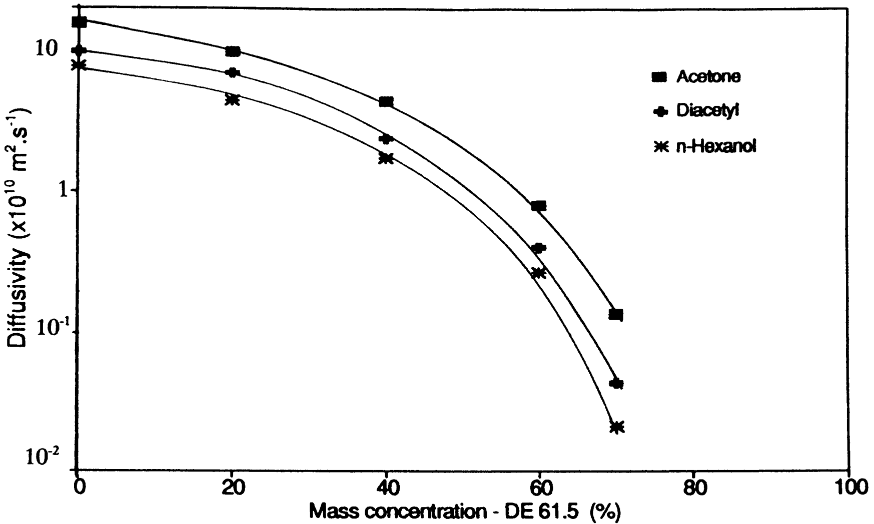

Figure 3 : Effect of mass concentration of glucose syrup on the aroma diffusivity (25°C).

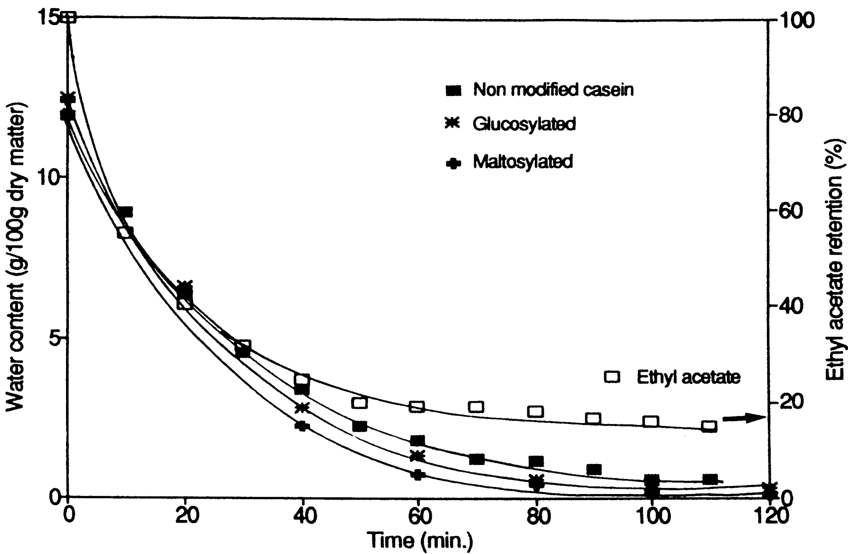

Figure 4 : Water content and ethyl acetate retention as a function of drying.

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In Encapsulation and Controlled Release of Food Ingredients; Risch, S., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1995.

Table VIII : Physico-chemical properties and retention of volatiles in aqueous solutions of bovine caseinate

Volatiles	H_w (atm)	H_c	D_w ($\times 10^{10}$ $m^2.s^{-1}$)	D_c	Moles fixed/mole casein	retention (%) *	**
Acetone	2.3	2.3	12.7	4.8	0	36.7	16
Ethyl acetate	7.9	8.3	11.7	3.3	0	41.6	19
Diacetyl	1.1	7.1	8.5	5.1	3.4	43.1	22
2-propanol	0.2	0.5	10.2	4.9	0	50.7	35
n-hexanol	0.8	0.4	5.6	2.5	0	55.0	38

H_w, H_c : Henry's constant (γ^{∞}_1 P^S_1) - 25°C
D_w, D_c : Diffusivity in 5% bovine caseinate solution at 25°C
* after 20 min of drying (water content 6.4 g/g dry matter)
** after 60 min of drying (water content 1.8 g/g dry matter)

therefore essential. Diacetyl has a greater volatility and diffusivity than acetone, but has a distinctly higher retention due to strong interactions with casein (measured by an equilbrium dialysis technique). Ethyl acetate has a low diffusivity but is very volatile and binds only weakly to casein ; its retention rate is low.

Measurements by Infra-Red Spectrophometry have shown the existence of hydrogen bonds between bovine caseinate and both acetone and ethyl acetate ; in fact, this type of interaction decreases the frequency of the C=0 vibration (Table IX) for diacetyl, no hydrogen bonds are apparent but other binding is present which may be due to bonds between the C=0 groups of diacetyl and the amine groups of lysine in the casein. The 2 carbonyl groups are implicated as the signal at 1714 cm^{-1} is no longer observed. The conjugated double bonds favor interaction with the protein.

* Chemical modification of caseins does not in general alter the order of retention of volatiles. However it appears that whatever the water content (between 0.5 and 97.5 %) glycosylated caseins have a lower retention capacity than unmodified caseins (Figure 7).

This negative aspect of chemical modification should be due to the effects of interactions. For diacetyl, the diffusivity is increased, because fixation is hindered by blocking of the ϵ-amine sites. For acetone, volatility and diffusivity are only slightly reduced ; glycosylation creates a steric barrier which reduces acetone-casein interactions and facilitates its loss during drying.

The negative effect of chemical modification is supported by retention rates in reference solutions containing unmodified casein and free glucides. The retention is higher than observed with unmodified casein.

Measurement of activity and diffusion coefficients, and physico-chemical interactions can explain the retention of aroma compounds during drying. However it is also necessary to consider the effect of drying temperature on proteins : beyond a certain temperature, the structure is modified (denaturation and aggregation of peptide chains), and Maillard reaction between ϵ-NH_2 groups of lysine and sugars in the medium are favored. An increase in temperature increases the proportion of α-helices in β-casein ; it might be thought that such a situation would be favor

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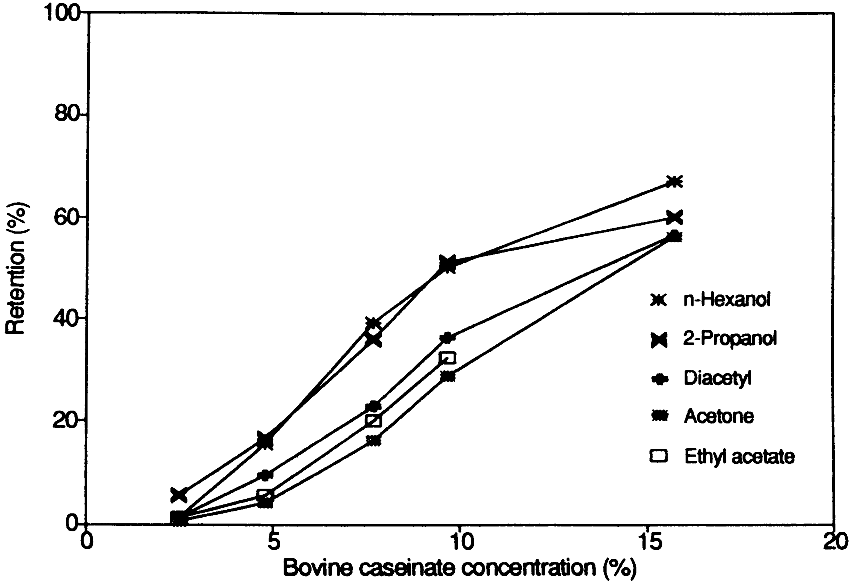

Figure 5 : Effect of the initial caseinate concentration on the aroma retention during drying.

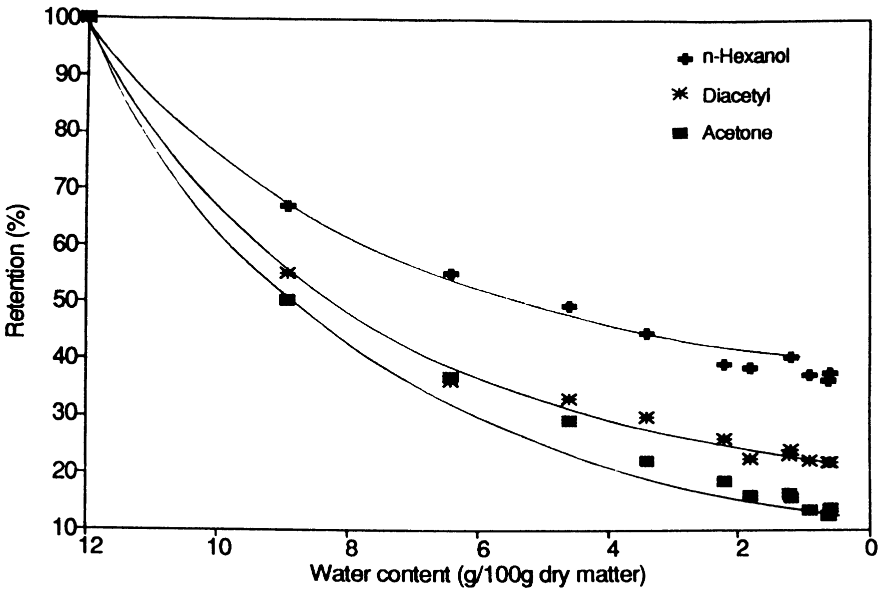

Figure 6 : Retention of aroma compounds during drying of bovine caseinate solution as a function of water content.

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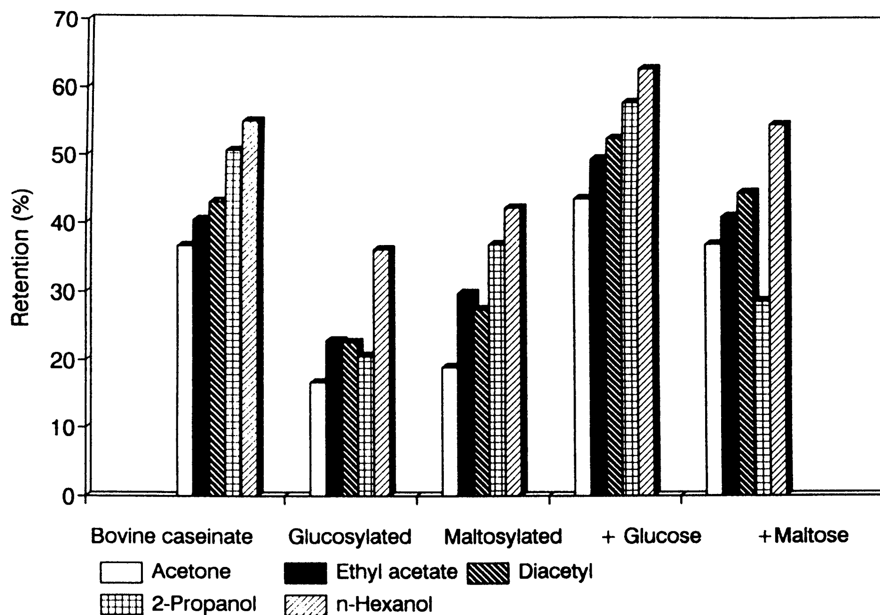

Figure 7 : Retention of aroma compounds during drying of caseinate solutions (at 6.5 g water/g dry matter).

Table IX : Infra-Red Spectrophotometry of aroma compounds sorbed or not on bovine caseinate

Volatile	Wavenumber (cm^{-1}) of carbonyl group in	
	pure compound	sorbed on caseinate
- C=O		
Acetone	1714.6	1707.9
Diacetyl	1714.6	1721.3
-O-C=O		
Ethyl acetate	1738.2	1731.6

entrapment of aroma compounds. However, Chirife and Karel (1974) showed that thermal denaturation of BSA (65.5°C/120 min) and pepsin (82°C/120 min) did not significantly affect the retention.

Conclusion

Retention of aroma compounds during drying depends strongly on the diffusivity in simple mixtures of sugars. This retention is higher with caseinates and the interactions between volatiles and non-volatiles can have a much greater effect than diffusivity alone. Much more work remains to be done ; at this stage we should note the lack of physical data of aroma compounds such as activity and diffusion coefficients, and pay attention to physico-chemical interactions in complex media.

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Chapter 16

Protection of Artificial Blueberry Flavor in Microwave Frozen Pancakes by Spray Drying and Secondary Fat Coating Processes

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While spray dried flavors were retained at about the same level as liquid flavors, fat coating of the spray dried flavor resulted in substantially better retention in pancakes. The improved retention of coated flavors during frying and microwave reheating is attributed to the delayed release of the flavor during heating. Flavor release from coated flavorings into water ranged from 23 to 68% when temperatures did not exceed the melting point of the coating fats, but increased to 80-98% when temperatures exceeded the melting points of the coating fats. This was dependent upon the material being coated (e.g. gum acacia vs maltodextrin) and type of coating fat. Flavor loss during frying and microwave reheating of pancakes ranged from 0-15% for coated flavorings as compared to 17-95% when liquid flavorings were used.

The market for microwave foods appeared to be unlimited a few years ago. However, sales never reached the predicted levels and in fact, have been declining in recent years. The main problem with microwave foods has been the lack of quality relative to their traditional counterparts. An important aspect of quality is flavor.

The major flavor problems associated with microwavable foods are a lack of typical flavor development during heating and substantial losses of any flavors added to the product (1). The first problem in attempting to increase the thermal generation of aromas during microwave heating has been addressed in several ways including the addition of precursor systems (2), the use of active packaging (metalized films) and/or formulation modification to improve absorption of microwave energy. The second problem, that of flavor loss during microwave

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heating, is relevant since whatever flavor is formed during heating or added in an attempt to overcome a lack of flavor development is typically lost due to steam distillation. Studies have shown 95% or more of a given flavor compound can be lost from model food systems during microwave cooking (3). Steiken *et al.* (4,5) has investigated the influence of microwave heating on flavors. He found that the formation of Strecker aldehydes and the loss of flavor components were much greater during microwave heating than conventional heating.

There are several techniques which may be used to improve the retention of flavor compounds during the microwaving process. Sadafian *et al* (6) have studied the retention of encapsulated aroma compounds during extrusion-cooking. Spray dry encapsulation and β-cyclodextrin inclusion were found to increase the aroma retention during extrusion. Reineccius (7) has discussed the potential for using secondary coating of already encapsulated materials in microwave food applications. Theoretically, this approach offers excellent protection to the flavoring during storage (little evaporative losses and oxidation) and would delay release until the flavoring is well into the microwave process thereby decreasing flavor losses. The secondary coating can be accomplished in several ways. Preferred methods include fluidized-bed coating (8) and centrifugal coating (9).

The objectives of this research were to evaluate the effectiveness of spray dried flavorings and secondary coated spray dried flavorings in improving flavor retention during the initial frying and subsequent microwave reheating of pancakes.

Experimental

Model blueberry flavor. The blueberry model flavor system was composed of equal parts of ethyl methyl butyrate, α-terpineol, ethyl valerate, phenylenthanol, *t*-2-hexenal, anethole, linalool, methyl anthranilate, maltol and γ-decalactone. These chemicals were obtained from Aldrich (Milwaukee, WI).

Spray drying. Gum arabic and maltodextrin-100 (M-100) were the two carrier materials used for spray drying. Solutions of gum arabic (30% w/w) and M-100 (50% w/w) were gently heated over a steam bath to facilitate solubilization. The solutions were cooled to room temperature and refrigerated (4°C) overnight. Model blueberry flavor was emulsified into the hydrated carriers (20% w/w of solids) using a high shear blender (Greerco Corp. model 1L.81, Hudson, NH). Each emulsion was immediately spray dried using a Niro Utility Drier with a centrifugal wheel atomizer. The inlet and outlet temperatures were controlled at 200 and 100°C, respectively.

Secondary coating. The spray dried flavorings produced above were put into a fluidized bed agglomerator (Glatt Hlatgen WSG-5, Winchester, KY.) and coated with liquid fat by Zumbro Inc. (Owatonna, MN). Two commercial powdered vegetable stearins were used for coating: Dri-Tex and Stereotex (Karlshamns USA, Inc., Columbus, OH). Dri-Tex is a hydrogenated cottonseed oil with a melting point of 145°F (62.8°C) and Stereotex is a hydrogenated soybean oil with a melting point of 165°F (73.9°C) . These powdered fats were melted prior to applying in the fluidized-bed. The desired coating of fat was ca. 30% by weight.

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Determination of flavor release from coated flavors. 1 g of secondary coated powder was weighed into a headspace vial, and 9 m*l* of distilled water was added. The vial was sealed with a Teflon cap and then incubated at two controlled temperatures for 1 hr before manually sampling the headspace for flavor compounds by GC. For Dri-Tex coated powder, the incubation temperatures were 45 and 74°C. The Stereotex coated powders were incubated at 52 and 85°C. Values for a complete release (100%) were based adding 0.3 g coating fat and 0.7 g spray dried powder into a headspace vial and following the same procedure as outlined above for the coated samples.

Determination of coating amount. 2 g of secondary coated powder were placed in an extraction thimble (Whatman, 22×80 mm) and covered with glass wool. The thimble had been predried and weighed. Extraction was done in a Soxhlet extractor with 150 m*l* petroleum ether for 6 hr. The thimble was removed and dried in an air oven at 100°C for 1 hr. The thimble was placed in a desiccator with Drierite and allow to cool. The thimble and its contents were weighed to calculate the fat content in the sample and the percent fat in the sample was calculated.

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Determination of flavor retention in batter and fried pancakes. 20 g of spray dried flavoring were mixed with 300 g of commercial pancake mix. The flavored pancake mix was then combined with 300 g distilled water to make pancake batter. The flavored pancake batter was then fried on a Teflon coated griddle at 190°C until the color was golden brown. Samples of batter and fried pancakes were taken for the determination of blueberry flavor compounds and the remainder of the pancakes were frozen at -20°C overnight in Zip Lock bags. The following day, the frozen pancakes were reheated in a microwave oven and then analyzed for blueberry flavor compounds.

Flavor isolation was done by solvent extraction. The procedure involved adding 30 m*l* acetone (containing ethyl hexanoate as internal standard, 0.045mg/m*l*) to 15 g batter, (15-x_1) g fried pancakes, or (15-x_2) g microwave reheated pancakes. x_1 and x_2 were corrections for water loss in the fried pancakes and microwave reheated pancakes, respectively. These amounts of water were added back to the sample prior to adding acetone. The extraction was completed on a magnetic stirplate. The resultant mixture was filtered and the filtrate frozen at -70°C for 90 min to solidify the fat. The liquid portion was recovered by filtering. The extract was then dried with anhydrous magnesium sulfate, filtered again, and concentrated to approximately 2 m*l* under nitrogen and analyzed by GC.

The GC, column and operating conditions were as follows: Hewlett Packard model 5880 with FID detector; DB-5 column (length:30m, i.d.:0.32mm, film thickness:1 *u*, J&W Scientific, Folsom, CA). The GC temperature program started at 40°C and then increased at 5°C/min to 200°C. The carrier gas was helium at a column head pressure of 15 psig.

Results and discussion

Efficiency of secondary coating. Table I shows the percentage of fat coated on the spray dried flavorings. The fat contents of the secondary coated powders were

all ca. 30% which was the coating target. The standard deviations of four coated powders were low ranging from 0.7% to 3.7% for G-165 (Stereotex coating on gum arabic spray dried flavor) and M-145 (Dri-Tex coating on maltodextrin-100 spray dried powder), respectively.

Table I. Percentages of fat on secondary coated spray dried flavorings*

G-165**	G-145	M-145***	M-165
	-------- % --------		
30.88±0.21	28.06±0.64	27.61±1.02	28.79±0.22

*: all experiments have four replicates.
**: indicates gum acacia carrier and 165°F coating.
***: Indicates maltodextrin carrier and 165°F coating.

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Thermal release. Due to the nature of the analytical headspace procedure, results were most accurate and reproducible with only the more volatile flavor compounds. Volatility of many of the flavor compounds in the model was too low to be detected by the static headspace procedure. Thus, data on flavor release from the secondary coated flavorings was based only on the release of the most volatile compounds, ethyl methyl butyrate(EMB) and *t*-2-hexenal, which provided more reproducible data. It is expected that the release of all volatiles would be represented by these compounds.

The percentages of flavor release of Dri-Tex coated flavoring at 45 and 74°C incubation are shown in Table II. The results show that when the incubation temperature is lower than the melting point of Dri-Tex (63°C), release of the flavoring is retarded compared to the data from incubation at a temperature higher than that of the Dri-Tex melting point. It is, however, obvious that over a period of 1 hr at 45°C, a substantial amount of flavoring was released even at the lower incubation temperature. This shows that the coating was not perfect but allowed some of the spray dried particle to dissolve and release its flavor upon contact with with water.

When the incubation temperature was higher than the melting point of Dri-Tex, the coating fat melted and the secondary coated powder dissolved in water to release flavor compounds quickly. If the incubation time is long enough, the flavor release of the dissolved powder should theoretically reach 100%. In this experiment, about 86% the of flavor release was obtained from both G-145 and M-145 samples. However, G-145 samples showed a better thermal flavor release than M-145. The percent changes between two incubation temperatures (45°C & 74°C) were ca. 62 and 35 for G-145 and M-145, respectively.

Flavor release from Stereotex coated flavorings (Table III) was similar to that from Dri-Tex coated flavorings. The coated gum acacia powder released less flavor when held below the melting point of Stereotex than the maltodextrin coated powder. The percent changes between the two controlled temperatured samples (52°C and 85°C) were ca. 52 and 41 for G-165 and M-165, respectively.

Flavor protection. Data for the losses of added blueberry flavor compounds during the frying of pancakes are presented in Table IV. When flavor was added

before the frying process, compounds which are more volatile, such as ethylmethyl butyrate, ethyl valerate and *t*-2-hexenal, should have greater losses than other less volatile compounds. Little loss was observed for fat soluble flavor compounds such as α-terpineol, maltol, anethole and γ-decalactone. Results of spray dried powder samples were mixed. The increases of ethylmethyl butyrate, ethyl valerate and γ-decalactone were not expected. A possible explanation for this abnormal phenomenon might be that the lipid oxidation products of the aged pancake mix and new volatiles formed during frying might coelute with these three compounds making chromatographic separation difficult. The higher flavor losses observed in spray dried samples vs. flavor solution samples was considered the result of longer frying time which caused greater volatilization of flavor compounds.

Table II. Percentages of flavor release of Dri-Tex coated powder incubated at 45 and 74°C*

	% release			
	M-145		G-145	
	45°C	74°C	45°C	74°C
EMB	54.15	84.25	22.90	88.63
t-2-hexenal	68.73	88.11	26.76	80.31

*: all experiments have four replicates.

Table III. Percentages of flavor release of Stereotex coated powder incubated at 52 and 85°C*

	% release			
	M-165		G-165	
	52°C	85°C	52°C	85°C
EMB	49.31	91.03	32.50	88.35
t-2-hexenal	55.49	98.50	39.11	88.09

*: all experiments have four replicates.

With Stereotex coated powder samples, all the flavor compounds showed an increased after the frying process. The increases are reasonable because after the temperature of pancakes reached the melting point of Stereotex, the flavor compounds started to release into fried pancakes. During the frying process, the holding time at high temperature was just enough for the coating fat to melt and release the flavor compounds, but not long enough for flavor compounds to volatilize. Thus few flavor compounds were detected in the G-165 batter samples, but increased amounts of flavor compound were observed in G-165 fried pancakes.

When frozen pancakes undergo microwave reheating, the flavor compounds typically flash out by steam distillation. Table V shows the losses of added blueberry flavor compounds in microwave reheated pancakes. Severe losses of flavor compounds were observed from both flavor solution and spray dried powder samples, particularly for EMB, ethyl valerate and *t*-2-hexenal. In G-165 samples, the losses of these three compounds were significantly reduced.

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Table IV. Changes of added blueberry flavor compounds in fried pancakes*

	solution**	G-spray**	G-165**
	------------	%	--------------
EMB	-69.0	+13.4	+117.0
ethyl valerate	-86.0	+27.1	+97.8
t-2-hexenal	-51.0	-53.3	+135.6
linalool	-21.0	-56.1	+94.5
phenylethanol	--	-15.3	+137.3
α-terpineol	-2.0	-47.9	+113.2
anethole	-8.0	-58.6	+119.7
methyl anthranilate	--	-22.2	+85.6
γ-decalactone	-11.0	+25.0	+122.4

*: compared to batter samples.
**: all experiments have four replicates.

Table V. Changes of added blueberry flavor compounds in microwave reheated pancakes*

	solution**	G-spray**	G-165**
	------------	%	-------------
EMB	-93.6	-94.6	-41.6
ethyl valerate	-92.9	-94.9	-49.2
t-2-hexenal	-81.6	-57.5	-10.0
linalool	-55.7	-62.0	-19.5
phenylethanol	--	-61.3	-14.2
α-terpineol	-30.6	-16.7	-21.8
anethole	-32.6	-33.3	-31.5
methyl anthranilate	--	-28.4	-7.1
γ-decalactone	-24.7	-25.2	-14.3

*: compared to fried pancakes.
**: All experiments have four replicates.

One interesting observation was the performance of methyl anthranilate in liquid flavor samples and encapsulated samples. Osnabrugge (9) has pointed out that alcohols, aldehydes and ketones will interact with proteins to varied degrees. With no protection, the amino group of methyl anthranilate reacted with the aldehyde group of the sugars in the pancake mix to form Schiff's bases. This binding of methyl anthranilate prevented extraction by acetone, so there was no peak observed for methyl anthranilate in flavor-solution samples. With protection by encapsulation, methyl anthranilate was separated from the sugars by the carrier wall material. The interaction was blocked, and we could again detect the peak of methyl anthranilate in G-spray and G-165 samples.

Conclusion

Thermally controlled release of flavor compounds is a characteristic property of secondary fat coated flavored powders, and can be applied in microwave frozen food products to protect against flavor loss from distillation (flash-out). The initial wall materials used as the spray dry carrier will affect the performance of secondary fat coated powders. In this study, the secondary coated gum arabic powder was observed to exhibit a better thermally controlled release property than the maltodextrin secondary coated powder. Many factors still need to be evaluated in the future, such as the protective effect of maltodextrin spray dried powders and secondary coated powders, as well as the physical properties of these encapsulated powders. All of these factors should be more thoroughly investigated before applying the theory to commercial food products.

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Chapter 17

Vitamin A Fortification in a High Stress Environment

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Vitamin A deficiency is a primary cause of blindness in 500,000 children per year worldwide. Fortification requires a foodstuff that is widely used by the target population, is centrally processed (or packaged). The fortified foodstuff must be acceptable to the consumer. In Indonesia monosodium glutamate (MSG) was selected for fortification. MSG is a white crystalline material, vitamin A is bright yellow. The fortified product must retain potency and have a white appearance in the market. In 1983 work was initiated to develop an acceptable form of vitamin A for this application.

The project started out simply to make vitamin A beadlets white so they would blend into the MSG. High ambient humidity and temperature, combined with MSG's tendency to absorb water create a stressful environment. A discussion of problems encountered, how they have been addressed and current status of the project will be presented.

The need to improve vitamin A consumption in many parts of the world is well documented (1, 2). World Health Organization (WHO) has estimated that more than 500,000 children per year become partially or totally blind due to a deficiency of Vitamin A in their diet. Several million have less severe health problems associated with vitamin A deficiency (3).

In 1983 USDA/AID approached Coating Place to develop a "whitened" form of vitamin A beadlets. Vitamin A fortification of monosodium glutamate (MSG) had previously been tried with limited success. Hoffman

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LaRoche vitamin A palmitate beadlets (250CWS) had been used in previous work in the Philippines but the small round beadlets segregated from the larger MSG crystals. This created problems in content uniformity and appearance. Appearance was also a problem because MSG is advertized and promoted as "pure, white crystals" much as Americans expect sugar or salt to be clean and white. Vitamin A is bright yellow. When the particles segregated the presence of a "foreign" material was obvious.

Early Results:

The initial work was directed at devising a simple way to whiten the beads and to keep them from segregating from the MSG. This was accomplished by placing vitamin A beads in a Littleford mixer, wetting them with a titanium dioxide (TiO_2) pigmented solution of hydroxypropyl cellulose (Klucel EF, Aqualon) dissolved in ethanol, mixing briefly, then adding a fine powdered form of MSG which was adhered to the whitened beads by the damp Klucel. This coated, agglomerated product was then dried. A more complete description of the procedure is provided given by Muhilal, et. al. (4).

By this method the vitamin A beads were covered with a thin white coating to which small white MSG crystals were adhered. The resulting particles were much lighter in color than the starting beads and also were slightly agglomerated, more closely approaching the particle size of the MSG to be fortified (Table I).

Table I. Particle Size Comparison: Beadlets, Coated Beadlets, MSG

U.S. Mesh	*μ Size*	*Vit A*	*Coated Vit A*	*MSG Crystals*[1]
>18 mesh	>1000μ	--	trace	trace
-18/+25	710-1000	<1%	2-10%	0-10%
-25/+45	350-710	23%	50-65%	65-70%
<45	<350	77%	<35%	24-44%

[1]Range of MSG crystal sizes from all three vendors

Three primary vendors of MSG were involved in this work, each with a slightly different crystal size range. The coated particles were easily mixed with dry MSG from all three vendors and did not segregate during filling and handling. Segregation tests were performed at Iowa State University (6). MSG was fortified with Vitamin A (target 3,000 IU/g),

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filled into packages and shaken to simulate handling. Samples were removed from the top, middle and bottom of the test packages and tested for potency (Table II).

Table II. Results of Segregation In Handling Tests

MSG Product	*Vitamin A Form*	*Sample Position*	*Vitamin A Assay (IU/g)*
Company A MSG	Coated	Top	2865 IU/g
		Middle	2752
		Bottom	2680
Company B MSG	Coated	Top	2595
		Middle	2675
		Bottom	2645
Company C MSG	Coated	Top	2967
		Middle	2840
		Bottom	2765
Company C MSG	Uncoated	Top	1750
		Middle	2300
		Bottom	5100

Whitened vitamin A prepared as above was used in field trials in Indonesia with excellent results (4). Muhilal et. al. report marked decrease (>85%) in the incidence of eye disease (Bitot's Spots) and significant decrease (over 50% in 1 - 5 year age group) in child mortality in the pilot area (Tables III and IV).

Table III. Prevalence of Bitot's Spots in Children

Time in Months	Initial	5 Months	11 Months
Fortified MSG	1.24%	0.32%	0.15%
Unfortified MSG	0.77	0.90%	0.80

Adapted from ref. 4

Table IV. Mortality in Children

Deaths/1000 - by age	*<12 Months*	*12-60 Months*
Fortified MSG	91	17
Unfortified MSG	102	31

Adapted from ref. 4

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This work was very encouraging and plans were made to expand the project. As larger scale activity commenced and fortified MSG began to be distributed over a wider area it became apparent that the fortified MSG was discoloring in certain areas. This had not been noted in the pilot study and it was imperative to determine the cause. The expanded project was delayed pending resolution of this issue.

Two problems were identified as a result of this and subsequent work:

1. Field stability is less than desired for commercial distribution.

2. Less than desired level of color masking (whiteness).

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Appearance/Stability:

When the above product is mixed with MSG at lower levels of fortification ($\leq$2500 IU/g) it is very difficult to detect visually. At higher levels ($\geq$3,000 IU/g) the MSG takes on a perceptible yellowish cast.

The degree of whiteness was the first concern dealt with because it was apparent even before the above field trials that if the level of fortification was to be raised a whiter product was needed. The above method of manufacture was developed to be relatively easy to use and not require expensive or unusual equipment. In order to achieve a whiter product it was necessary to use higher pigment levels (TiO_2) and to apply a more uniform coating. Because of its well established ability to apply uniform coatings of any desired thickness the Wurster fluid bed process was used to develop a second generation product with improved whiteness.

The goal of improved whiteness was easily achieved and the process was adjusted to allow a controlled amount of agglomeration. The resulting white particles have a size distribution similar to that of the MSG crystals. Field trials in 1989 indicated that this product did not have the necessary chemical stability in the field (figure 1).

This coating was also based on hydroxypropyl cellulose and TiO_2. Further investigation indicated that this "improved" product was comparable in stability to the earlier product. It is believed that other factors are responsible for failure to note the stability problem during earlier trials. In particular, the test site for the previous fortification study was at an elevation of 400 - 800 meters, with cooler temperatures and lower humidity than areas at sea level (5) and it is also believed that

faster turnover of product within the test area compared to larger scale distribution prevented observation of any stability problems in the earlier field trials.

The vitamin A with the white hydroxypropyl cellulose coating above lacked the necessary extended shelf stability. Under field conditions at sea level it lost potency and discolored in less than 3 months. Other forms of vitamin A (in pork gelatin beadlets) are believed to be more stable, however these are not acceptable under regional dietary restrictions.

Field stability is a major concern as MSG is typically sold to the target population in very small packets. The consumer expects to purchase a free flowing white crystalline material and associates whiteness and free-flow characteristics with quality. It is therefore important that these properties be retained to the maximum degree possible.

Monosodium glutamate (MSG) is somewhat hygroscopic, particularly at very high humidity. Over a wide range of humidities below 85% RH MSG absorbs only moderate amounts of water, but above 85% RH the equilibrium water content rises dramatically (figure 2).

Unfortunately Indonesia has very high ambient temperature and humidity, particularly at sea level where most of the population is located. Daytime temperatures often rise above 30° C (95° F) in the daytime, and storage areas may go as high as 50 - 60° C (122 - 140° F). At night the ambient temperatures drop to about 24° C (75° F) and the air is saturated. When vitamin A is present with moist MSG it reacts to yield a dark yellow or brown stain that spreads over the MSG, resulting in a muddy color that is not acceptable to the consumer.

In many areas MSG is purchased at small stands. These stands are open air and therefor not air conditioned. They may be located in the sun with the roof providing the only shade. As the sun's position changes different parts of the stand may be in the sun throughout the day. Although MSG there is relatively high turnover of MSG packets in populous areas, in the more remote areas it is possible for packets to be exposed to ambient humidity and sunlight for 6 months or more.

Under field conditions of high temperature and humidity (>80% RH @ >80° F) moisture is able to permeate the packaging materials and attack the vitamin A beadlets. The packaging materials used are of good quality (MVTR = 5g/m^2/24 hr @ 40°C, 90% RH), but due to the high surface

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area of the package to mass of contents (26-35 mm^2/gram) water vapor transmission is significant. The smallest package contains approximately 600 mg product and may take up 0.1 mg/day (7).

The Klucel coating used above is not, and was not intended to be, a good moisture barrier. The 1989 trials made clear that we did not have a product that would meet all requirements under "real life" conditions. As a result of these findings additional development work was initiated, and changes were made in the test conditions. Samples are now tested at 35° C, 75% RH. Accelerated testing is now done at 35° C, 85% RH.

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Further developments:

At one time it was felt that simply applying a water resistant coating onto the vitamin A beadlets would suffice to provide 6 month stability. The above field data showed that the product would retain potency ($\geq$50%) and appearance for 6 weeks in the market place and longer in storage. Pharmaceutical applications have a long history of using water resistant coatings for controlled release, i.e. controlling water permeation rates. In these applications it is common to extend release by a factor of 5 or 10 (see figure 3). It was hoped that by using a water resistant coating a factor of 4 or 5 improvement in stability could be achieved.

A major flaw in this concept is that the original coating never did provide 6 weeks stability. A significant portion of the stability was due to the time required for sufficient water to permeate the package and increase the water content of the MSG. Once the moisture content of the MSG reaches a significant level moisture is available to attack the coated beadlet. The time for the original beadlet alone to fail when water is available is very short.

Once water is inside the packet and available even a good moisture barrier is somewhat permeable and will fail eventually. It turned out that even doubling the shelf life of the fortified MSG by improved coating composition alone was very difficult. The coating that has currently been developed is a good moisture barrier within the limitations imposed by the following criteria:

1) Must be food approved and not violate dietary restrictions.
2) Must be water resistant.
3) Must be stable up to 60° C.
4) Must be bioavailable.
5) Must be white or near white.

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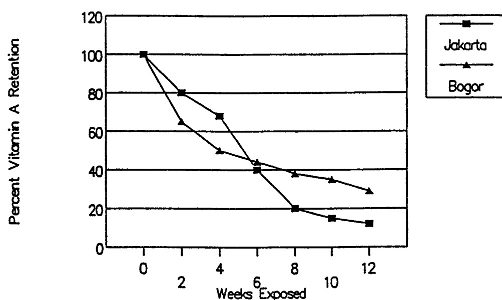

Figure 1. Chemical stability of vitamin A.

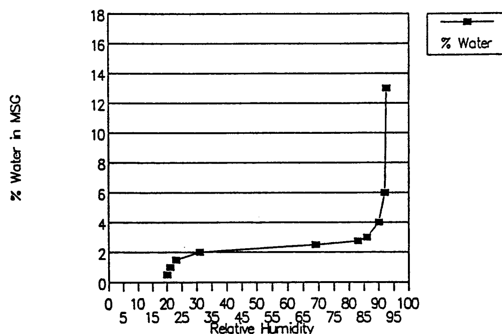

Figure 2. Water absorption isotherm for MSG.

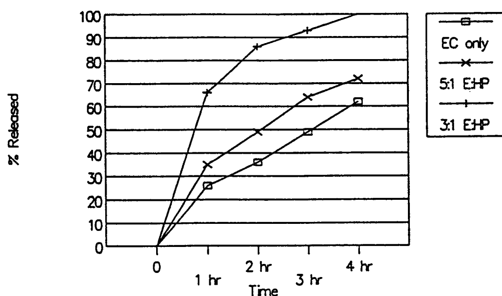

Figure 3. Change in release of soluble salt vs. coating composition.

This work has resulted in a white coating that can be applied onto commercially available vitamin A palmitate beadlets and provides improved moisture barrier properties as well as whiteness. Further improvement in stability has been achieved by development of an improved bead by Hoffman La Roche. Both visual and chemical stability are vital to a successful product. It is possible to have either chemical or visual stability without the other. A product that has good chemical stability but is discolored is unacceptable to the consumer; a product with good cosmetic properties but little potency has no value.

The white coating presently in trial was developed after it was determined that improved barrier properties were required. This turned out to be a very difficult problem. The vitamin A beadlets are approximately 250μ in size. For purposes of achieving high potency and of controlling cost it is desirable to keep the coating level relatively low, however maximum barrier properties require higher coating levels (greater film thickness). 30% coating levels result in an approximate film thickness of 15μ. Although this improved barrier coating does improve the stability of the product, it actually works in concert with the packaging materials to provide the necessary stability.

The current whitened beads made using the improved barrier coating and the improved beadlets are currently in test in the field. At three months the visual properties are good. Analytical results regarding potency retention are not available at this time. Resumption of large scale fortification trials are dependent upon current product remaining field stable for at least 6 months, a determination that the improved beadlet can be made commercially, and a determination by the Indonesian government and other funding agencies to continue the work.

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Chapter 18

Review of Patents for Encapsulation and Controlled Release of Food Ingredients

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Extensive work is being conducted in the area of encapsulation particularly as it applies to the food industry. Many specific applications are now appearing in the patent literature. Some patents detail ingredients and the ways to most efficiently encapsulate them while other patents discuss methods or materials to be used in the encapsulation of other components. One major area in the patent literature is for the sustained or controlled release of sweeteners and flavors for chewing gum. A number of these patents will be described. Recently issued patents that apply to food ingredients will be discussed.

Encapsulation and controlled release of food ingredients is important in developing new food products and in improving the quality of existing products. There is ongoing research to develop new techniques and materials for encapsulation. Some of the work focuses on general techniques or materials which can have broad application while there is also emphasis on specific applications. A considerable amount of the work is being patented to protect the rights of the inventors and to make the investment in the research more profitable for those supporting it. While a review of the scientific literature will give insight into some of the advancements in encapsulation and controlled release, it is important to review the patent literature as well. This chapter is not intended to be a comprehensive review of all patents in the field; however, it will discuss some specific areas which have recently received increased attention. These areas include controlled and sustained release, encapsulation of sweeteners, new carrier materials and new methods of encapsulation.

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Two of the early areas encapsulation where commercially significant patents were issued were for extrusion and coacervation. Two of the patents for extrusion were issued to Swisher in 1957 and 1962 (*1, 2*). The first patent covered the concept of mixing a flavor system into a corn syrup melt and extruding it into pellets or into a hot imiscible liquid which could be rapidly cooled to harden the pellets. The pellets were washed with isopropanol to remove surface oil and then dried under a vacuum. The second patent recommended the addition of glycerol to the corn syrup and heating it to 110 to 130 C. The patent also disclosed the extrusion of the molten mass through a die into a cold isopropanol bath to solidify the strands which could then be broken into the desired size by agitation.

A patent on a similar process was issued to Beck in 1972 (*3*) except that the desired wall material was a combination of sucrose and hydrolyzed cereal solids. Further changes in the desired wall material to include maltodextrin and a modified food starch in place of sucrose were patented by Barnes and Steinke (*4*). Development has continued on this process with two patents issued to Miller and Mutka in 1985 and 1986 (*5, 6*). The first patent used a process similar to that of Swisher (*1*) to encapsulate juice solids. The second patent also used the same process as the previous extrusion patents but revealed the control of the emulsifier content and emulsification pressure to optomize the encapsulation efficiency.

The other early commercially significant patent was for carbonless paper (*7*) using a coacervation encapsulation technique. The work that led to the patent was started in the late 1930's and continued for several decades (*8*). The back of one sheet of paper is coated is coated with capsules that contain a colorless dye base in oil and the front of the other sheet is coated with an acidic clay that reacts with the dye base and produces the color. The pressure of a pen on the surface of the paper causes the capsules to rupture to release the dye base.

Controlled Release

Controlled release of materials is becoming increasingly important in a wide variety of fields including pharmaceuticals and agrochemicals and is covered in another chapter in this book by Reineccius entitled "Controlled Release in the Food Industry". Within the food industry, one of the major areas where a number of patents have been issued for products with controlled release is for chewing gum. Traditional methods of encapsulation (i.e. spray drying or extrusion) will protect added flavors or sweeteners in the product until time of consumption or mastication. One of the ongoing challenges is to provide a chewing gum in which the flavor and/or sweetener will be released at a constant intensity over a long period of time. This can be referred to more specifically as sustained release. Two of the most active companies have been Wm. Wrigley Jr.,Co. and Warner-Lambert Company.

One patent (*9*) assigned to Wrigley involves mixing an ingredient such as an intense sweetener with a molten wax which is then cooled to solidify the mixture.

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The mass is ground to produce the desired particle size for incorporation into chewing gum. The wax coating protects the sweetener and will slow the release as the gum is chewed.

Another patent (*10*) that also provides for delayed release involves formation of coated particles by meltspinning techniques. A more recent patent specifically addresses the incorporation of encapsulated alitame into chewing gum (*11*). Ingredients in the gum base can induce degradation of the Alitame and it is desirable to have a delayed release of the sweetener. The Alitame can be encapsulated by any of the traditional means to produce a product in which the Alitame degradation will be slowed. The gum can also be made in such a way that the sweetener is incorporated into a separate portion of the gum such as a liquid center.

A patent assigned to Warner-Lambert Company discloses a composition and method for making either hard candies or particles that contain flavors (*12*). In this patent, a mixture of mannitol, saccharin and sorbitol is heated to about 200 C, cooled and then seed particles containing sorbitol are added to induce solidification. The solid mass can then be ground to produce small particles for incorporation into chewing gum. Another patent covers the use of a hydrophobic polymer with film forming characteristics togehter with a hydrophobic plasticizer as the encapsulating materials for a sweetener (*13*). The wall materials used allow for gradual release of the sweetener for up to 30 minutes during mastication of a chewing gum. Three other patents disclose the use of low molecular weight polyvinyl acetate as a first coating material (*14 - 16*). Two of the patents use a secondary coating of a hydrophilic material (*14, 16*). These patents all result in a prolonged release of sweeteners and/or flavors into a chewing gum system.

Danochemo A/S filed a European application for controlled release of materials to be used in chewing gum (*17*). The aqueous solution or emulsion containing the flavoring material is sprayed into an air stream that has a temperature of 50 - 120 C. The product is then coated in a fluidized bed system. The application claims that the particles formed are more dense and larger than those disclosed in prior art which helps reduce loss of flavoring and minimizes exposure to oxygen. When incorporated into chewing gum, the flavor material exhibited an extended release.

A method for the production of controlled release flavor particles is disclosed in a patent assigned to International Flavors & Fragrances (IFF) (*18*). In this patent, flavor materials along with a texturizer are mixed into a molten system consisting of a fat or wax with a melting point in the range of 130 to 195 F and at least one emulsifier. This can then be either spray chilled or drum chilled to solidify the particles. Another IFF patent describes the use of a mixture of low density polyethylene and polyethylene glycol as the encapsulating agents for 2-methyl-2-pentenoic acid to give a strawberry flavor for use in a chewing gum (*19*). The combination of the water soluble and water insoluble polymers give a sustained release of the flavoring material.

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One other patent describes the encapsulation of butylated hydroxyanisole (BHA) that allows for controlled release of the anitoxidant into vegetable oil or molten fat (*20*). The particles are formed by combining molten BHA droplets with an edible film-forming polymer that is in a liquid dispersion. The mixture is cooled below the melting point of the BHA so that the the edible polymer forms a film around the solidified BHA. The droplets are then surface dried.

A European application assigned to Kelco International Ltd. discloses the use of a gel matrix for controlled release (*21*). A protein with an ingredient that will bind to it is trapped within the gel matrix. The release of the ingredient is triggered by contact of the capsule with a proteolytic enzyme which degrades the protein. This could be used in food applications as well as for assays for specific chemicals.

There has been considerable activity in the past couple of years in the area of sustained release of sweeteners and flavors in chewing gums. Many of these patents are continuations in part of earlier patents and build on the existing technology. These will not be discussed in detail but some are included here as references for the reader that wants further information. A large number of these patents have been assigned to Wm. J. Wrigley Company (*22 - 31*).

The patents in the area of controlled release tend to cover specific applications. They include wall materials that will perform the desired functions and processes that will allow films to form around droplets of the food ingredients. Most of them rely on either temperature or mastication for release of the active ingredient which is typically a sweetener or flavor.

Carrier Materials

The carrier materials used for encapsulation and controlled release can have a significant impact on the retention of the core material as well as the performance and functionality of the final product. This is particularly true for encapsulation of flavors. A Canadian application for a patent on starch hydrolysate dicarboxylic acid esters was filed by Morehouse of Grain Processing Corporation (*32*). The application reveals a process for making the starch hydrolysate by combining a 50% maltodextrin solution in water at pH 8 with n-octenylsuccinic anhydride. After one hour of mixing, a 1% aluminum sulfate solution was added. The material was then freeze-dried and oven dried to yield a free-flowing powder which could be used for spray drying of flavors. This carrier also was shown to give good emulsion stability.

A patent application assigned to Griffith Laboratories Worldwide, Inc. reveals the use of a denatured protein coating (*33*). The ingredients to be encapsulated are mixed into a protein solution which is either heated to denature the protein or subjected to proteolysis to insolubilize the protein. The coagulated material is then comminuted to produce microcapsules. An alternative process involves the addition of polysaccharides to the mixture to yield a coating that is partially water soluble.

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Boskovic et al (*34*) developed a carrier system comprised of maltose, maltodextrin and a gum or other film-forming polysaccharide. When flavoring materials such as a single-fold lemon oil were spray dried with this carrier using a rotary atomizer, the powder showed no signs of off-flavor development when held at 70 F for up to one year. No antioxidants were added to the system. The oil load was reported to be 15.7% with 0.9% surface oil.

Fuji Capsule K.K. patented a carrier system which also discloses a method of manufacturing capsules (*35*). The carrier system consists of a solution of gelatin or other water soluble polymers that are mixed with the core materials. The capsules can be produced by disk, punching or drop methods. The capsules produced are soft and can be used in jelly type products. Plasticizers can be added to further soften the wall material.

A European patent application was filed by Alko, Ltd. which discloses the use of polysaccharides that have been either chemically or enzymatically depolymerized and hydrophilic colloids either alone or with crosslinking agents as the wall material for encapsulation (*36*). The technique used for encapsulation using these materials appears to be coacervation as a change in pH is used to form the capsules which are then hardened by the addition of glutaraldehyde.

Method Patents

Many of the patents for controlled release and new carrier systems also reveal methods for the production of the encapsulated material. There are some new patents which use existing materials and focus solely on new methods or processes. One process was revealed in a patent assigned to SCM Corporation for the production of a food acidulant in particulate form (*37*). The acidulant is first plated onto calcium lactate followed by coating with a molten edible lipid. This process could yield a product that would have a controlled release at a higher temperature.

Another method patent discloses a series of steps to produce an encapsulated flavor with delayed release (*38*). The primary method is to first prepare an emulsion containing the flavoring material and a partially hydrophilic wall material consisting of gelatin, a natural gum and a plasticizer. This mixture is dried to form a solid matrix which is then milled into small particles followed by coating with a water insoluble material.

A relatively new technique for encapsulation is centrifugal suspension-separation. This method was described in a patent by Sparks and Mason (*39*). In this process, core particles are suspended in the coating liquid and then introduced onto a rotating disk. With the proper conditions, the coating material will form a film around the core material. The coated particles are spun off into a tower that the disk is contained in where they are dried. This method and further

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applications of the process are discussed in detail in another chapter in this book entitled "Centrifugal Suspension-Separation for Coating Food Ingredients" by Sparks et al.

Other Patents

Protection of specific ingredients is one important application for encapsulated materials. Aspartame can be degraded by heat and several recent patents have tried to address this issue. In one of the patents, the aspartame is encapsulated in a material such as ethylcellulose or methylcellulose (*40*). This shell can protect the aspartame during baking so that the finished goods retain the desired sweetness level. Another patent discloses the use of a matrix of lecithins, fatty acids and waxes, glycerides and a silicone-based antifoam agent to encapsulate the sweetener (*41*). This mixture should have a melting point between 20 and 90 C and will provide for a particle that will have increased temperature tolerance.

A patent describing the use of liposome encapsulated ingredients was assigned to Nabisco Brands, Inc. (*42*). In this patent, a mixture consisting of at least flour and shortening are heated to 150 F in an extruder and then water and the liposome entrapped ingredients are added in a manner so that the liposomes are not ruptured and a dough is formed. The mixture is cooled slightly before extruding at low pressure and forming pieces which are then baked to obtain the desired texture.

Another liposome patent assigned to Nabisco is for the encapsulation of a highly unsaturated lipid (*43*) for incorporation into margarine. In this patent, an aqueous material is entrapped in a liposome with at least one polar lipid bilayer in which the unsaturated lipid is dissolved.

A patent assigned to Warner Lambert descibes the making a microcapsule by coacervation (*44*). The core is comprised of the flavoring agent and a resin. The coating material consists of gelatin, gum arabic and glutaraldehyde. The flavor is mixed into the molten resin, then this is homogenized into an aqueous solution of gelatin. Another aqueous solution containing gum arabic is added to the emulsion which is then diluted with water and the pH adjusted to cause coacervation. The temperature is lowered to cause gelation of the gelatin and gum arabic. An aqueous solution of glutaraldehyde is added and the microcapsules recovered.

As indicated at the beginning of the chapter, this is not intended to be a comprehensive review of all patents on encapsulation and controlled release. There are numerous other patents that are concerned with materials other than food ingredient. As can be seen, a wide variety of work is being carried out that is being patented. Some of the patents cover simple applications of certain materials while others cover in detail materials and methods to manufacture microcapsules with the desired properties. The area that seems to be receiving the most attention is for controlled and sustained release. We have found a number of ways to encapsulate

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flavors and other ingredients to protect them from the atmosphere and surrounding materials. The work is now concentrating on ways to design systems where active materials are released at the desired time. This work will provide for improved food products and new applications for encapsulated materials.

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