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Microencapsulation Techniques, Applications and Problems

HERMAN NACK, B.Ch.E.*

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Synopsis—A number of techniques have been developed for encapsulating small particles ranging in size from a few microns or less to about 2000 μ. In addition, there are other factors which must be given careful consideration in the development of suitable microencapsulated products, such as: physical and chemical properties of the core material and wall material; post-treatment of capsules; interaction of capsules and substrate; storage conditions; release mechanisms; and economics.

MICROENCAPSULATION processes of interest in the cosmetics field include: aqueous phase separation, nonaqueous phase separation, interfacial polymerization, multiorifice rotating cylinder, fluidized-bed spray-coating, melt prilling in a fluidized bed, spray drying, diffusional exchange, and meltable dispersion.

INTRODUCTION

Interest in the application of microencapsulation technology in a wide variety of fields continues to run high. Recent research activities and commercial applications publicly disclosed include: detoxicants for treatment of uremia (1); flavor and aroma constituents in foods (2); dye precursors for graphic products (3); slow-release pharmaceuticals (4, 5); slow-release fertilizers (6); and perfumes (7). Undoubtedly, there are many applications that have not been disclosed, but have been and are being studied in laboratories all over the world.

This paper has been prepared with the objective of providing information on some of the significant elements and physical and chemical factors of concern in microencapsulation processes and systems. Descriptions of selected processes and discussion of some of the problems and potentials of this technology are presented.

* Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio.

There are numerous reasons for considering microencapsulation for a given problem and some of these are: to change the physical characteristics of a core material (for example from liquid to "powder"); to provide controlled release of capsule contents; to permit mixing and storage of reactive or incompatible materials; to mask taste or color; and to reduce volatility.

Major Elements of Microcapsule Systems

Core

The core phase, and consequently the capsule itself, may represent a wide range of possible configurations. Some of these are shown in Fig. 1. Operations that may be required in preparation of suitable cores include: spheroidization, prilling, emulsification, grinding, and atomization. Selection of the preferred technique of core preparation may be of considerable importance as the configuration of the resulting capsule may strongly influence the performance of the capsular product in the end use application.

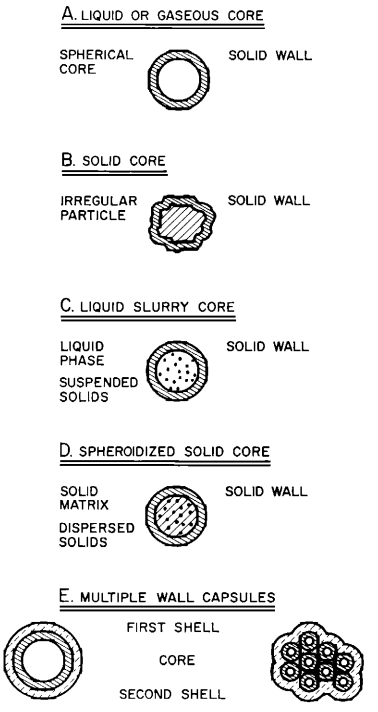

Figure 1. Capsule configurations

Wall

The selection of the proper wall material or materials for a given product application is often determined by the requirements of the system under consideration. For example, if the capsular product must resist the leaching action of an aqueous medium, the wall material selected should be hydrophobic in nature and provide a good water barrier. Since the wall deposited tends to follow the contour of the core (as indicated in Fig. 1), the final form of the capsular product is affected by the core configuration. Depending upon the encapsulation process employed, it may be more or less difficult to coat uniformly core particles whose surfaces possess sharp peaks and depressions much like the problems encountered in conventional painting or plating.

Microencapsulation Process Selection

The selection of the preferred microencapsulation process for a given application is not always a simple task for there are a large number of processes from which to choose. One must be concerned with such factors as: whether the core is solid or liquid; the solubility characteristics of the core; the reactivity of the core with candidate wall materials and solvents; the size of the desired capsule; the method of attaching the capsule to the desired substrate; the method of core release; and process and product economics.

A detailed discussion of the above factors is beyond the scope of this paper. Some of the more important aspects are discussed in a later section in which microencapsulation processes are described.

Capsule Post-Treatment

In many instances the capsules made by a given process require additional treatment to impact the desired properties. Post-treatment may involve chemical and/or physical methods. Hardening of gelatin capsule walls by treatment with formaldehyde is employed in capsules used for carbonless carbon paper. Polymer wall films deposited from organic solvent solutions may be hardened by treatment with a selected nonsolvent for the wall material. Heat-fusible wall materials deposited on core particles may be improved in barrier properties by a suitable heat treatment. Thin coatings of liquids and finely divided solids may be applied to the capsule wall surface to reduce the tendency of capsules to adhere to each other and to improve barrier properties in selected environments.

Capsule-Substrate Interaction

Although there are instances where capsules, as produced, are used directly in a product, in numerous cases the capsules must be fastened to a substrate or suspended in a medium for proper functioning in the end use. For example, encapsulated perfume is attached to paper tissues so that pressure release may be instigated when the tissue is crumpled in use. Food flavor capsules may be suspended in a matrix of jelly in a tart and must remain stable until release is effected by heating in the toaster or oven.

Here two problems are encountered: the need for a method of applying capsules to substrate and the need to avoid adverse effects of substrate on capsule stability in storage. The method selected for applying the capsules to the substrate must avoid the use of solvents that tend to leach core material through the capsule wall during the application period. In addition, the presence of the binder employed to fasten capsule to substrate should not significantly interfere with subsequent capsular release. Products which require suspension of capsules in a matrix must be designed so that the capsule contents and wall remain intact during the time the product is stored prior to consumption. If the capsule is surrounded by an aqueous medium (for example, in a food product) the wall material (which may be a fatty material) must limit the rate of leaching of core so that sufficient active core material remains at the time release is desired.

Storage

Conditions under which capsules and products containing capsules are stored vary widely. Factors of concern include temperature, humidity, pressure, light, or other forms of radiation and air pollutants. Capsules containing volatile materials or certain reactive chemicals must be protected from excess temperature to avoid premature evaporation or decomposition of the core contents. If the core is hygroscopic, capsules may absorb water from a high humidity atmosphere to the point of wall rupture, in some cases. Conversely, capsules containing some water in the core may lose water by evaporation in a low humidity environment, thereby reducing the reactivity of the capsular system. Excessive pressure on capsules in storage, such as certain slow release fertilizers, may cause blocking or welding together of the capsules so that the product is no longer free-flowing. Stacking of capsule-containing

products may cause premature rupture of capsules in the bottom layers of the stack.

Release and Reaction

Capsular core release may be instigated by such methods as: pressure and shear to rupture the wall, heat to melt wall material, dissolution of the wall by a solvent, and extraction of the core contents by leaching through the wall. The mechanism selected is governed by the end use application of the product.

Release of core contents is usually followed by some chemical reaction with a material adjacent to the capsule, or a physical effect such as evaporation or wetting. The efficiency of release and mixing with a co-reactant is important to minimize the quantity of capsules required, hence cost. If speed of reaction is important, release should involve intimate contact with a co-reactant and avoid losses of core material to substrate or surroundings.

Product Performance

Perhaps the most important criterion for judging the over-all performance of a capsular product relates to economics. As usual, one must come to grips with the question: "Is the consumer willing to pay for the extra cost of microencapsulation?" Here one must take into consideration not only the product novelty aspects of the problem, but also such marketing factors as consumer education, distribution patterns, and price consciousness. Unfortunately, there are no pat answers to this problem especially since there may not be a similar established product to serve as a point of reference. It is evident that such a situation calls for careful product development and market studies.

Microencapsulation Processes

There are a large number of microencapsulation processes and modifications of processes that have been disclosed in the literature and patents. Processes of potential interest in the cosmetics field were selected for discussion in this paper.

Aqueous Phase Separation

In aqueous phase separation processes a polymeric or macromolecular wall material is dissolved, or dispersed as a sol, in water. The core material to be encapsulated, which must be immiscible with water, is dispersed in particulate form throughout the aqueous phase by stirring.

Wall formation occurs when the dissolved wall material is caused to "phase out" and "wrap" around the core particles by a suitable system change. Possible system changes include: reduction in temperature, addition of chemical precipitating agent, or pH alteration.

A highly successful adaptation of aqueous phase separation is called aqueous phase coacervation, which has been applied to the encapsulation of such materials as carbonless carbon paper reactants, flavor oils, and perfumes (3). In this process the macromolecular wall material (i.e., gelatin) is phased out of aqueous solution as a concentrated liquid phase (coacervate) which forms a uniform liquid coating around the core particle. On further processing a hardened solid (gelatin) wall is formed around the core material. The method is outlined in Fig. 2.

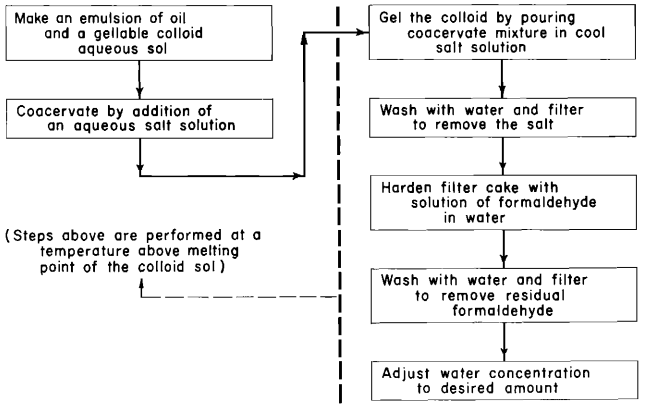

Figure 2. Aqueous phase separation

Aqueous phase separation processes have been applied to both liquid and solid cores. Capsule sizes may vary from a few microns to several millimeters. The capsule wall may be treated to present a good barrier to oily or hydrophobic materials, but it is usually a poor barrier to water or hydrophilic materials.

Nonaqueous Phase Separation

Nonaqueous phase separation is the inverse of the aqueous phase process in that the continuous wall-containing phase is organic or hydrophobic in nature, and the core material is usually water-miscible (hydrophilic). In the process shown in Fig. 3, the core liquid (called polar solvent solution) is suspended in droplet form by stirring in polymer solution (wall material). Phasing out and core wrapping of the

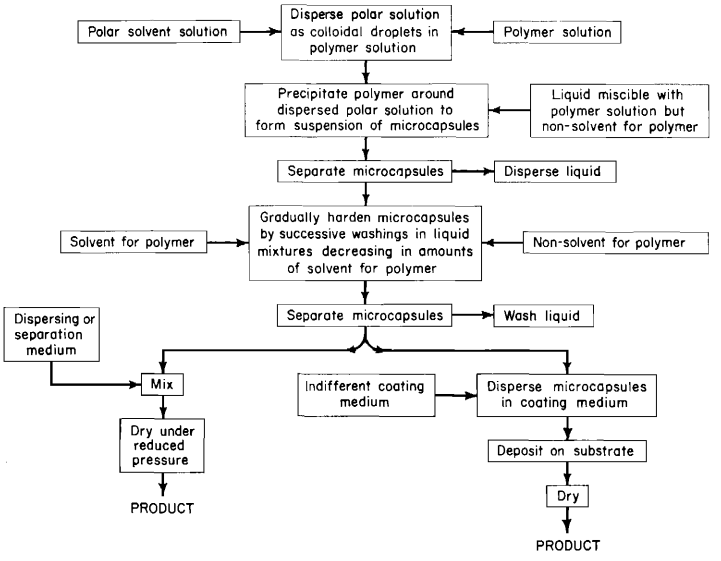

Figure 3. Nonaqueous phase separation

wall material is caused by the addition of a liquid (nonsolvent) that is miscible with the organic solvent but immiscible with both the core particle and the polymeric wall material. The process may be modified to include a coacervation step and suitable measures for hardening the capsule walls (8).

Both liquid and solid core particles may be encapsulated by nonaqueous phase techniques. Capsule sizes may be varied over a wide range from a few microns to millimeters, and a variety of wall materials may be employed. This process has been applied to such diverse core materials as reactive chemicals, glycerine, urea, and pigments.

Interfacial Polymerization

The formation of a polymer at the interface between two liquid phases is known as interfacial polymerization. This film-forming technique has been used to make capsules with either hydrophilic or hydrophobic cores. Capsules with polyamide (nylon) walls can be made by a process in which an aqueous core liquid containing an aliphatic diamine (i.e., hexamethylenediamine) is dispersed in droplet form in an organic solvent (i.e., chloroform-cyclohexane, 1:4). When a solution of a dicarboxylic acid halide (i.e., sebacoyl chloride in the above mixed solvent) is

added with stirring, the nylon walls of the capsules are formed. The reaction can take place at room temperature and depends on the fact that acid halides of this kind are nearly insoluble in water, while the proper diamines have an appreciable partition coefficient towards the organic phase. The polymer is formed in the organic phase, and since the rate of polymer formation exceeds the rate of diffusion of the diamine out of the aqueous phase, the nylon wall is deposited almost entirely at the interface (9). Product applications have included core materials such as dye precursors, oils, proteins, and enzymes.

Multiorifice Rotating Cylinder

A multiorifice encapsulation device utilizes centrifugal force to form capsules from fluid wall formulations. The wall formulation is hardened by appropriate means after the capsules are formed.

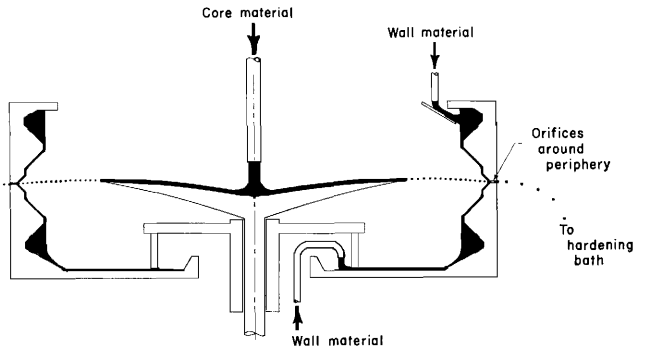

Figure 4. Multiorifice rotating cylinder device

The apparatus consists of a rotating cylinder having orifices located about its periphery. As shown in Fig. 4, the wall material is fed to two internal grooves from which it flows by centrifugal force to the individual encapsulating orifices where membranes are formed. The core material is fed onto a concentrically rotating disc and is projected onto the membranes. When the combined mass of core and wall material is such that centrifugal force overcomes the cohesive force of the wall material, individual capsules break loose and are projected outward. The membranes re-form, and the next capsules are formed. Capsule size is inversely proportional to rotational speed. Good size uniformity is claimed, since the capsules do not break loose from the orifices until a given mass is reached (10).

The walls of the formed capsules may be hardened by various means including chemical reaction, evaporation of a solvent, and cooling. The process would appear to be suitable for making a variety of products involving primarily liquid cores. It may have limitations when capsules below about 100 μ are required. It is expected that scale-up of the process might have some mechanical limitations. However, high production rates are claimed for some products. Applications include capsules containing water, solvents, wax solutions, and pesticides.

Fluidized-Bed Spray-Coating

Microencapsulation of core particles that can be fluidized by a gas may be accomplished by spraying a coating agent (wall) onto the surface of the particles. The wall may be formed by congealing of a molten material, by chemical reaction on the surface, or by evaporation of a solvent from a coating solution. The solvent is removed with the gas leaving the bed. Coating thickness may be easily controlled by the amount of wall material applied. A conventional fluidized-bed spray-coating unit is shown on the left in Fig. 5 (11).

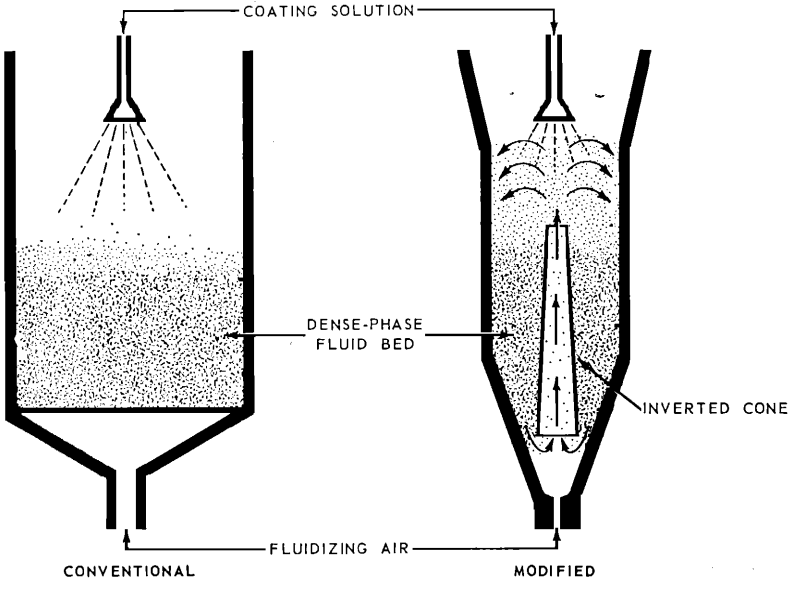

Figure 5. Fluidized-bed spray-coating units

Conventional fluidized-bed spray-coating methods are generally employed in the encapsulation of solid particles, and a minimum capsule size of about 100 μ is the usual rule. Liquids may be encapsulated if they can be frozen in particulate form and coated at temperatures below their freezing point (12). Fluidized-bed encapsulation has yielded such products as: slow release fertilizer, coated iron particles, seeds, salts, and clays.

Deagglomerating-Jet Spray-Coating

Numerous modifications of the conventional fluidized-bed microencapsulation concept have been developed to satisfy the needs of particular problems. A deagglomerating jet unit was created to coat core particles of small size (less than about 100 μ) which tend to agglomerate in a conventional fluidized bed. Here the key feature is the use of a high velocity gas jet and a conical conduit in a fluidized bed to deagglomerate the partially coated particles before additional coating material is applied from the coating spray nozzle. This method is shown on the right in Fig. 5 and may be employed to encapsulate solid particles down in the 10-μ size range. It does not lend itself to liquid cores nor to solid core particles larger than about 300 μ (5). Products include pharmaceuticals, resin catalysts, inorganic salts, and pigmented plastics.

Melt Prilling in a Fluidized Bed

This process is illustrated in Fig. 6. Here the wall material must be in solid particle form so that it can be fluidized by a gas. The core material is heated and is in liquid form for atomization from a nozzle to yield droplets of the desired size. The droplets of core material fall into the fluidized bed and are simultaneously cooled and coated with the wall material particles. The heat liberated from the core droplets is transferred to the wall material particles causing them to melt, adhere to the core surface, and flow together to form a coherent capsule wall structure. A mixture of capsules and bed material is removed from the fluidizing column and the capsules are separated by screening. The excess bed material is returned to the system. The process has been made continuous by providing for continuous capsule removal and bed material make-up (13).

Capsule sizes possible by this process range from about 300 to 3000 μ. Both liquid and solid core capsules can be made; however, the core material must be able to withstand the temperature required to provide the

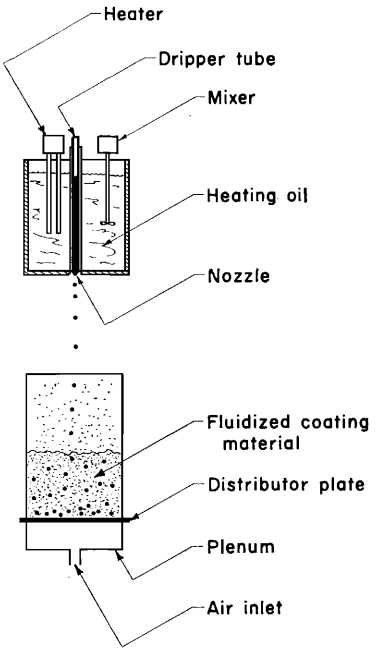

Figure 6. Melt prilling in fluidized bed

energy for fusing the wall material particles together. Applications of this process have yielded slow-release fertilizers, glycerine capsules, and biologically active encapsulated products.

Miscellaneous Processes

There are a number of additional microencapsulation processes that might be included in this paper but, in the interest of brevity, can only be mentioned here.

"Spray drying" encapsulation is an old process that has received new interest in recent years (14). It involves the atomization and spray drying of an emulsion in which the core is the discontinuous phase and the wall material is a constituent of the continuous liquid phase.

In a process known as "meltable-dispersion," the wall material in a molten state and the core material are dispersed in a medium (in which both are insoluble) at a temperature high enough to maintain the wall material in liquid form. By means of agitation and use of wetting agents, the wall material is caused to envelop the core particles, and solidifies on cooling to complete capsule formation (15).

In the "diffusional exchange" processes, a previously formed capsule with a porous coating is immersed in a preferred liquid so that the original core contents are diffused out of the capsule and the liquid diffused in. The resulting encapsulated liquid is then overcoated or subjected to a treatment that imparts the desired degree of wall impermeability (16).

Another aqueous phase separation process employs a process fluid such as mineral oil. An emulsion of a flavor oil, for example, in an aqueous gelatin solution is dispersed in the process fluid and the mixture is cooled to phase out the gelatin. The capsules may be hardened by dehydration of the water with anhydrous alcohol (17).

Problems

As in many areas of science and technology, practical or applied developments have outrun an understanding of the fundamental factors of microencapsulation. This situation has probably been accentuated by the proprietary aspects of many of the applications of interest. It is not surprising, therefore, that the literature in this field is primarily concerned with methodology and products rather than with underlying principles. It is a truism in the field of microencapsulation that experience is the best teacher, and that even the most proficient practitioner learns something almost every time he goes into the laboratory.

Perhaps one of the most difficult technical problems is to control the properties of the capsule wall. Here one tries to extrapolate the available knowledge on formation and properties of polymer films and organic and inorganic coatings to the encapsulation process of interest. The results of such attempts often leave much to be desired, since there is usually only a slight resemblance between the conventional film forming operations and those in microencapsulation. In general, some of the factors that should be considered include: formulation of wall material, solvents and nonsolvents employed, temperature, and rate of deposition.

A problem that is common to many microencapsulation processes is the agglomeration of capsules during wall formation. As the wall materials change from liquid to solid form they often go through a sticky stage which makes agglomeration difficult to avoid. The problem becomes more pronounced as particle size is reduced. Various methods which may be employed to minimize this difficulty include the use of chemical hardening agents, careful selection of wall materials and of solvents, addition of parting agents, and application of mechanical devices to physically separate capsules.

The evaluation of capsules and capsular products is sometimes as much of a problem as is the making of a product. In the early stages, one usually employs relatively simple and rapid screening methods which hopefully relate to the eventual real world situation. If satisfactory progress is made, the evaluatory methods tend to become more complex until, finally, actual use conditions must be employed. This phase of testing may be quite time consuming and costly. Thus, the design of the evaluation procedures can be critical as regards the over-all progress of a given program.

Summary

The potential applications of microencapsulation fall into widely different areas such as the biomedical, agricultural, food, and pharmaceutical fields. Successful product development requires careful attention to many factors both technical and economic. There are a wide variety of microencapsulation processes available for use in specific problems, and no single process can be applicable to all types of situations. Most processes are subject to certain common problems such as agglomeration of capsules during wall deposition.

At times it is difficult to see what the future holds for microencapsulation. Certainly, there is a need for additional basic and applied knowledge on the phenomena involved and, if this knowledge is forthcoming, one might expect an upsurge in practical applications. Undoubtedly, novel microencapsulation processes will be developed, which may also increase the scope of commercial products. In addition, as competence is increased in existing processes, costs should be reduced and the competitive position of encapsulated products improved. Already, the technique has yielded some rather unique solutions to complex problems. Perhaps a concise assessment of the picture is one of cautious optimism, that is, progress, but not without hard work.

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