PROCEEDINGS
1976 CONTROLLED RELEASE PESTICIDE SYMPOSIUM

September 13, 14, 15, 1976

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Engineering and Science Division
Community and Technical College
The University of Akron
Akron, Ohio

PREFACE

The papers and abstracts bound herein were presented at the 1976 International Controlled Release Pesticide Symposium held at The University of Akron in Akron, Ohio on September 13, 14 and 15, 1976. The Symposium was sponsored by the Engineering and Science Division of the Community and Technical College (The University of Akron) and the Controlled Release Pesticide Committee. Other than pagination the papers and abstracts were duplicated as received. This allowed the rapid printing of the proceedings and availability to the participants at the time of registration.

A number of individuals generously contributed time, talent and funds in the planning and operation of this symposium. We are grateful to Mr. William Rushing of the U. S. Army Corps of Engineers. Waterways Experiment Station, Vicksburg, Mississippi, was instrumental in the provision of a sizeable grant used in providing monetary assistance to various authors. Several concerns donated the funds used in providing "free" coffee breaks for the attendees.

I wish to thank members of the Controlled Release Pesticide Committee for their assistance and advice. The Institute for Civic Education of The University of Akron handled many of the planning and operation details. I wish to acknowledge Mr. Marvin Phillips, Mrs. Linda Petticord and Mrs. Mary Elizabeth Chesrown of that group. Lastly, I extend my appreciation to Professor Michael Bezbatchenko, Chairman of the Engineering and Science Division, and those members of my staff; Miss Katherine Walker, Mr. William Evans, Mr. Thomas Quick, Miss Debra Pfeifer and Miss Katherine Krotzer who assisted in the various aspects of putting together this symposium.

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Criteria and Evaluation Division, U.S. Environmental
Protection Agency, Washington, D.C.

N. F. Cardarelli
Secretary

PARTICIPANTS

Approximately 300 members of the scientific community participated in this symposium. The welcoming address was delivered by Dr. D. J. Guzzetta, President of The University of Akron. Mr. Earl R. Glover, Deputy Administrator for the North Central Region, U.S. Department of Agriculture, gave the keynote address entitled "Food Production in an Environment of Reason." Four panel discussions were held:

Environmental Impact	Chairman- M. Kovacs, Environmental Protection Agency
Molluscicides	Chairman- K. Walker, The University of Akron
Environmental Analysis	Chairman- F. Brinckman, National Bureau of Standards
Field Evaluations	Chairman- J. Nelson, U. S. Army

Sessions were chaired by the following individuals:

Antifouling	J. Engelhart, M & T Chemical Co., Rahway, New Jersey
Molluscicides	C. J. Shiff, Blair Research Laboratory, Salisbury, Rhodesia
Herbicides	W. Rushing, U.S. Army Corps of Engineers, Vicksburg, Mississippi
Insecticides and Nematicides	J. Feldmesser, U.S. Department of Agriculture, Beltsville, Maryland
Insect Attractants	J. Peacock, U.S. Forest Service, Delaware, Ohio
Materials	H. Lonsdale, Bend Research Inc., Bend, Oregon
General	F. Harris, Wright State University, Dayton, Ohio

Downstream Carriage of Pesticides
P. Gingo, The University of Akron, Akron, Ohio

Evaluation of New Controlled Release Herbicides
G. A. Janes, Creative Biology Laboratory, Norton, Ohio

The Use of Kraft Lignin as a Carrier System
H. T. Dellicolli, Westvaco Corp., North Charleston, South Carolina

* * * * *

EXHIBITORS

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NCR, Appleton Papers Division, Dayton, OH

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CONTROLLED RELEASE PESTICIDES VIA MICROENCAPSULATION

Plenary Lecture

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I. INTRODUCTION

Controlled release probably means many things to many people. Webster does not define it explicitly, however, I believe we all have a basic understanding of what the term means. One might describe it as techniques or methods to make available within limits, quantities of materials to a specified area to accomplish only the intended effect by the presence of the material over a desirable time frame.

There are many ways in which this can be accomplished. In the pharmaceutical field, Theeuwes and Higuchi[13] have published on the elementry osmotic pump. (Figure 1)

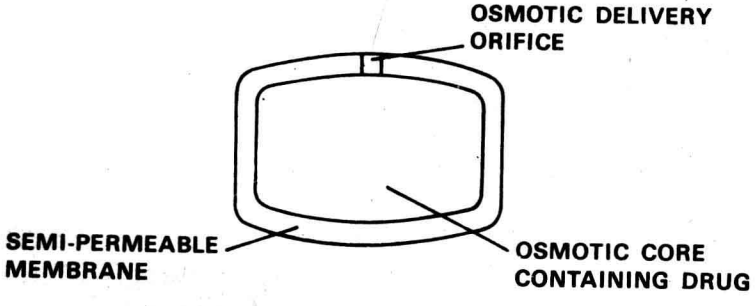

Figure 1. Elementry osmotic pump cross section (from Theeuwes, J. Pharm. Sc., Dec. 1975)

The structure is comprised on an osmotic core enveloped by a semi-permeable membrane having a sized delivery orifice. The delivery rate of solute by the system is constant as long as excess solid is present inside the device. The rate declines parabolically towards zero once the concentration falls below saturation.

Other researchers at F.R.L. Albany International Company[47] are investigating hollow fibers. (Figure 2)

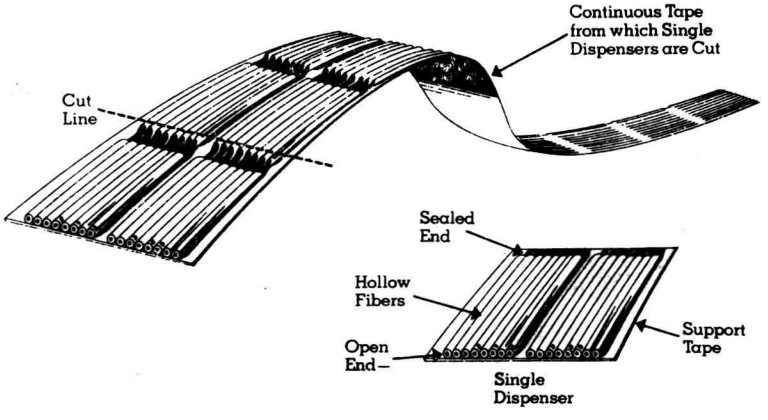

Figure 2. Conrel Vapor Dispenser

The dispenser is composed of a parallel array of hollow polymeric fibers adhered to an adhesive tape surface. The fibers are filled with the material to be delivered and sealed at uniform intervals along the length of the tape. If the tape is cut, vapor is released from the cut ends. The vaporizable liquid does not flow out because of capillary forces, but evaporation allows the material to be dispensed into the atmosphere.

Health Chem[47] scientists have developed the Hercon dispenser. (Figure 3) The special inner layer, contains dissolved pesticide which continually migrates to the surface rendering it bioactive. As the pesticidal material is removed from the surface, the strip is continually regenerated until the dissolved pesticide reservoir is depleted.

Montemarano and Dyckman[47] have synthesized a series of antifouling polymers with pendent organometallic substituents. (Figure 4) The addition of two or more organometallic groups along the polymer backbone broadens the antifouling activity of the polymer.

Thus, there are numerous approaches to controlled release or broading the effectiveness of a material.

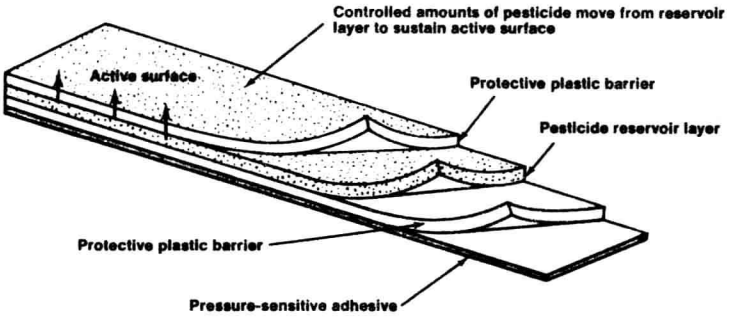

Figure 3. Hercon Insecticidal Plastic Structure

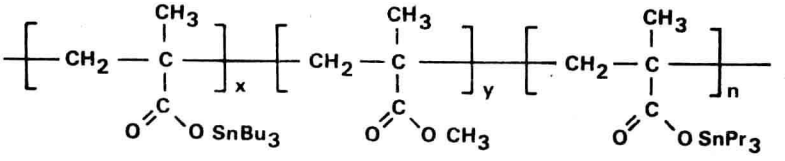

Figure 4. Polymers Containing Pesticides as Pendant Substituents. (from Montemarano and Dyckman)

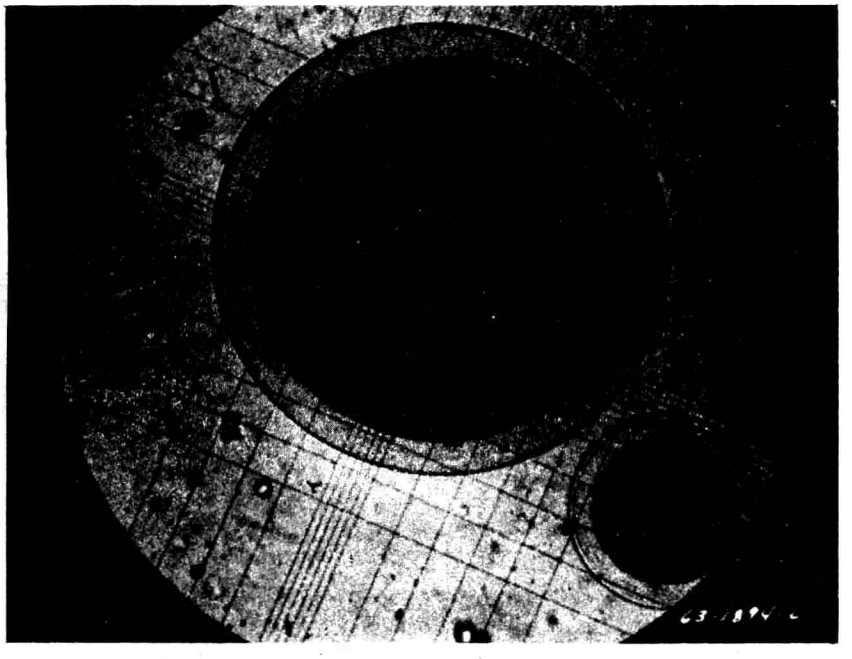

Figure 5. Photo of Microcapsule (courtesy NCR Corporation)

Turning to the subject of microencapsulation, how might it be utilized in pesticidal formulations?

The microencapsulation processes (Figure 5) can be described as techniques to reproducibly apply uniformly thin, polymeric coatings to small particles of solids, droplets of pure liquids or solutions, and dispersions. Microcapsules, the result of the processes, range in size from several tenths of a micron to a few thousand microns. The core material (syn.: fill, internal phase, I.P.) is the particulate mass to be microencapsulated. The coating material has also been referred to as the shell or wall material in numerous publications.

Microencapsulation processes can be effectively used to convert liquids to solids, separate reactive materials, reduce material toxicity, provide environmental protection to compounds or formulations, alter surface properties, control the release of materials, reduce the volatility or flammability of liquids, and for taste-masking bitter compounds. These are attributes more commonly derived from the microencapsulation of materials; however, they should not be considered the only contributions microcapsules can make to agricultural products.

A variety of core materials can be microencapsulated including liquids, solids, dispersions of solids in liquids as well as complex emulsions (Figures 6, 7 and 8). The composition of the core material can be varied in that it can contain dissolved material if liquid, and if solid, it can be a mixture of chemical moieties.

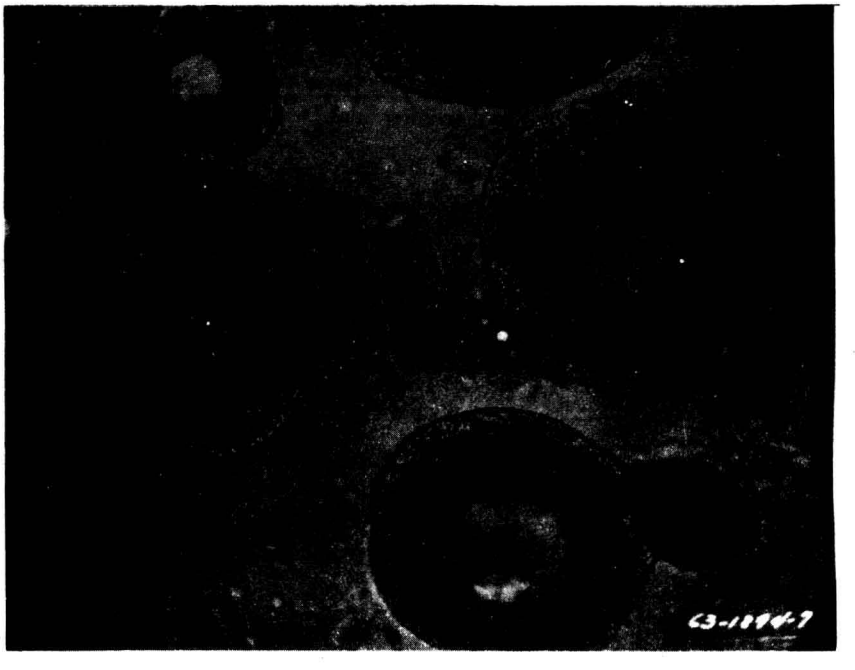

Figure 6. Microencapsulated Liquid (Courtesy of NCR Corporation)

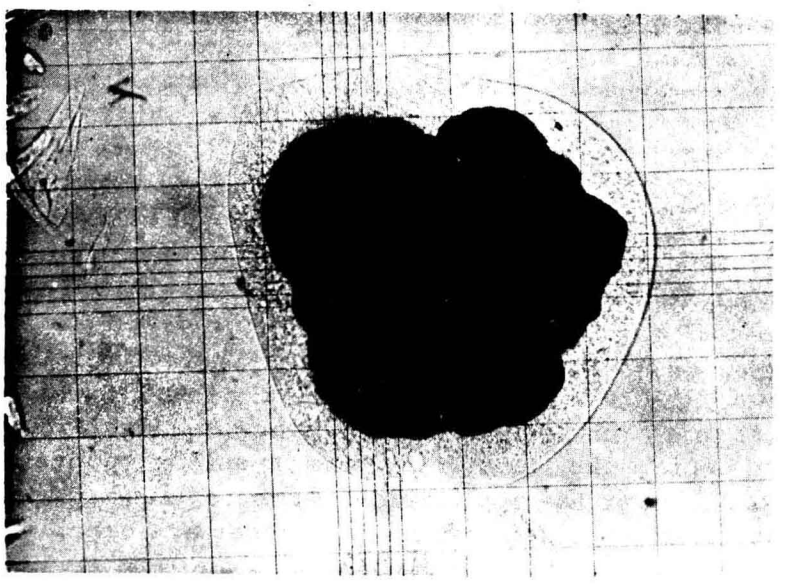

Figure 7. Microencapsulated Solids (Courtesy of NCR Corporation)

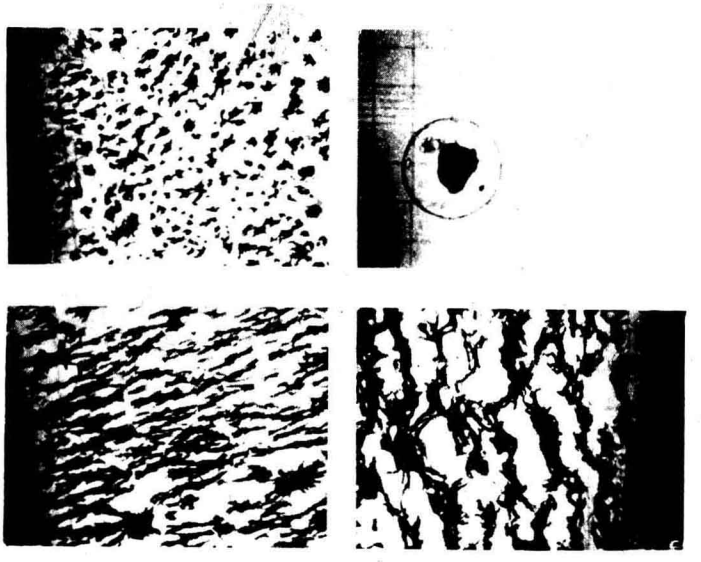

Figure 8. Microencapsulated Dispersion (Courtesy of NCR Corporation)

Microencapsulation Process	Applicable Core Material	Approximate Particle Size (Microns)
Air Suspension	Solids	35-5000 *
Coacervation-Phase Separation	Solids & Liquids	2-5000 *
Electrostatic Deposition	Solids & Liquids	1-50
Interfacial Polymerization	Solids & Liquids	2-5000 *
Multiorifice-Centrifugal	Solids & Liquids	1-5000 *
Pan Coating	Solids	600-5000 *
Spray Drying & Congealing	Solids & Liquids	5-600

* Capable of Coating Larger Particles

Table I. Microcapsule Processes and Their Applications

There are many microencapsulation processes described in the literature. Table I depicts the various microencapsulation processes that will be described. It shows the applicable core materials and the approximate size of the resultant capsules that the processes are capable of producing.

II. AIR SUSPENSION PROCESS

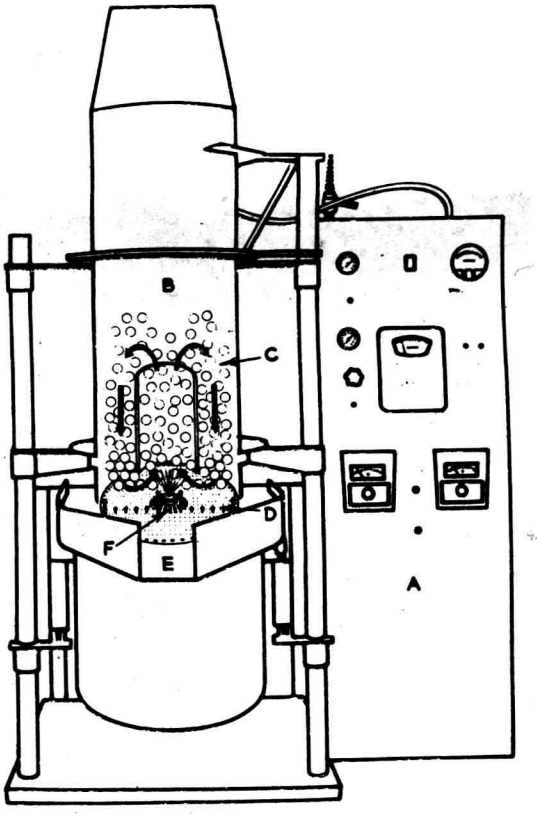

Figure 9. Schematic Drawing of Air Suspension Apparatus (Courtesy of WARF)

The air suspension process (Figure 9) to produce microcapsules was pioneered by Wisconsin Alumni Research Foundation (WARF). The process can be used to microencapsulate a wide variety of solid core materials. Some liquids can be microencapsulated by imbibing them in porous solids and then coating them as described below.

The air suspension batch type process involves dispersing solid, particulate core materials in a supporting air stream and spray-coating the suspended particles. The particles are suspended on an upward moving air stream within the coating chamber. The flow direction of the core material is controlled, producing a cyclic pattern as the coating material is sprayed onto the moving particles. During each pass through the coating zone, the core material receives an incremental amount of coating, and the process is continued until the desired coating level is achieved. The supporting air stream also serves to dry or solidify the coating while the material is being microencapsulated.

III. COACERVATION - PHASE SEPARATION PROCESSES

The coacervation-phase separation processes (Figure 10) to produce microcapsules were pioneered by the NCR Corporation[4]. The processes are capable of microencapsulating a large number of liquids, solids, solutions and dispersions of solids in liquids.

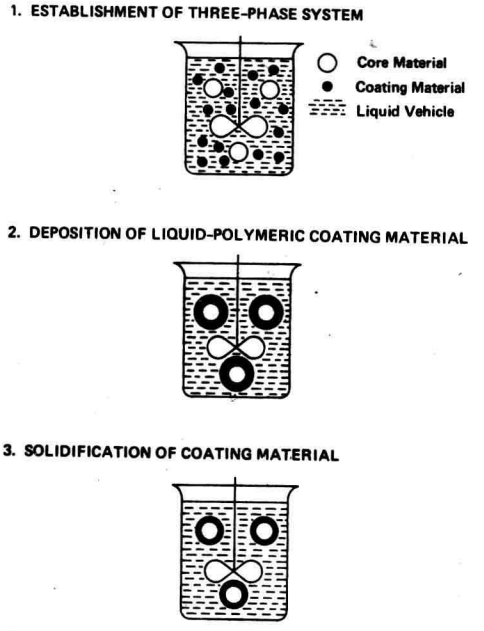

Figure 10. Schematic of Coacervation-Phase Separation Process (Courtesy of NCR Corporation).

The batch type processes consists of three steps which are carried out with controlled physical mixing. Step One of the process involves the formation of three imiscible chemical phases: a liquid manufacturing vehicle, core material and the coating material (the coacervate). Step Two of the process consists of depositing the liquid polymer coating upon the core material. This is accomplished by controlled, physical mixing of the liquid coating material and the core material in the manufacturing vehicle and by chemical driving forces, such as sorption and spreading of the coating material at the core material-vehicle interface. Step Three of the process involves solidifying the coating, usually by thermal, cross-linking or dissolvent techniques, to form a self-sustaining microcapsule. If the microcapsules are to be used in powder form, subsequent drying operations such as spray, freeze, fluid bed, solvent or tray drying techniques are required.

IV. ELECTROSTATIC DEPOSITION

Microencapsulation utilizing electrostatic principles (Figure 11) have been accomplished by a process described by the Illinois Institute of Technology Research Institute (IITRI)[3]. The process is capable of coating small particulate solids and liquids.

The process employs an atomizing device which discharges a mist of liquid coating material into a chamber. The mist is given an electric charge as it leaves the atomizing device and is then deposited by electrostatic

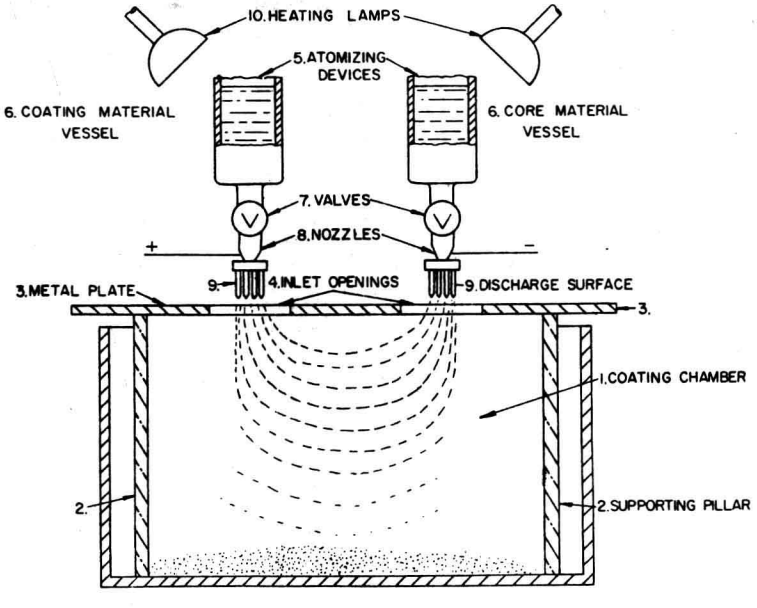

Figure 11. Schematic Diagram of Electrostatic Microencapsulation Apparatus.

attraction upon the core material to be coated. The mist of coating liquid is electrically charged by projecting it into an electrostatic field. The respective charges are imparted to the core material and the coating material by the action of a corona discharger device operating at high voltage.

V. INTERFACIAL POLYMERIZATION

A number of companies are producing microcapsules by using in situ interfacial polymerization techniques. The processes are capable of handling liquids and solids. The methods (Figure 12) involve the reaction of chemical moieties located at the interface existing between a core material substance and a continuous phase in which the core material is dispersed. The continuous or core material support phase is usually a liquid. Both addition and condensation polymerization reactions can be used to produce the microcapsules.

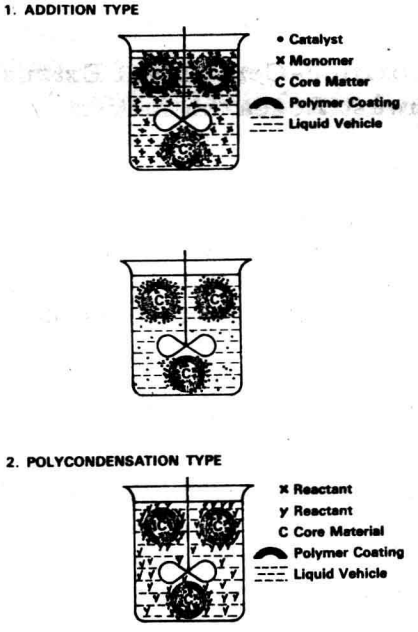

Figure 12. Interfacial Polymerization Techniques

VI. MULTIORIFICE-CENTRIFUGAL EXTRUSION PROCESS

The multiorifice-centrifugal extrusion process to microencapsulate materials is one of several physical methods developed by the Southwest Research Institute (SWRI)[8]. Although the processes are designed to primarily microencapsulate a host of liquid core materials with various coatings, selected solids can be microencapsulated as dispersions in liquids

provided the resultant dispersions have reasonable flow properties.

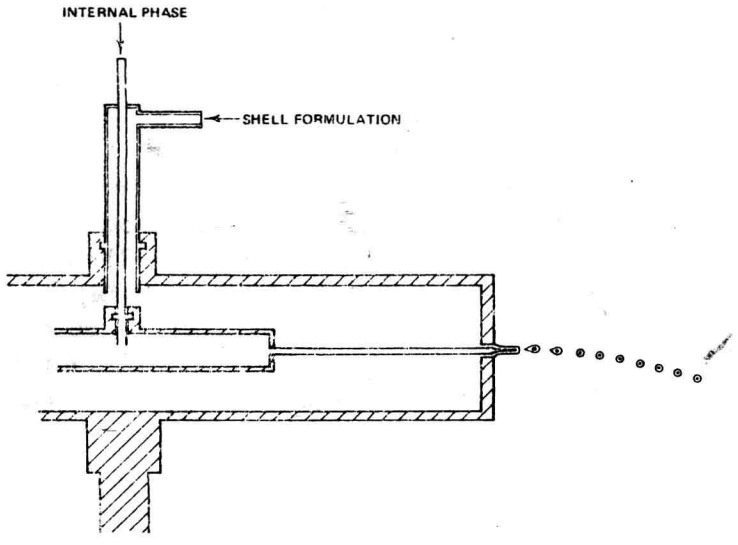

Figure 13. Multiorifice-Centrifugal Extrusion Head (Courtesy of Southwest Research Institute)

In the equipment diagramed in Figure 13, concentric feed tubes enter a seal assembly at the center of a rotary head. The liquid core material flows through the inner tubes and enters a central chamber from which tubes radiate outward and pass through orifices about the periphery of the head. The liquid coating formulation flows through the annulus of the concentric feed tubes, into the rotating head, and finally through the annuli created by the radial tubes and orifices. As the head rotates, a compound fluid rod of core and coating material emerges from each orifice, continually breaking up at the end to form a series of individual microcapsules. The microcapsules can then be solidified thermally or by use of a hardening bath to crosslink the microcapsules. If a hardening bath is used and dry capsules are desired, the drying methods referenced under the coacervation-phase separation process would be applicable.

VII. PAN COATING

Pan coating (Figure 14) of solid particles has been practiced by the pharmaceutical industry for many years.[14] The process can microencapsulate numerous solids with film forming polymers.

The material to be microencapsulated is normally deposited onto various spherical substrates such as non-pareil sugar seeds and then coated with various layers of film forming polymers. The coating is applied by

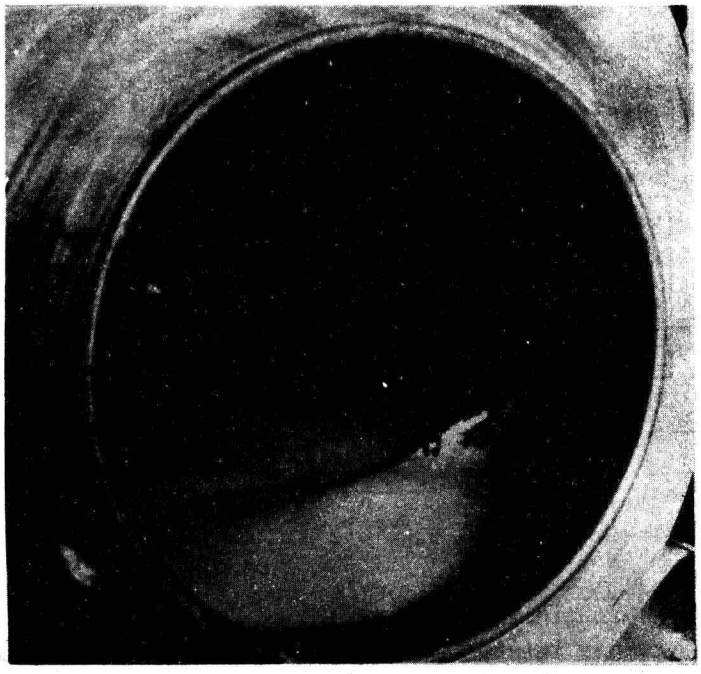

Figure 14. Pan Coating of Non-Pareil Sugar Seeds (Courtesy of Smith, Kline Corporation)

pouring or spraying a coating solution onto the tumbling particulate solid in the coating pan while the pan is rotated on a shaft. The coating solvent is removed through evaporation which may be accelerated by the passage of air at the desired temperature over the tumbling particles of core material.

VIII. SPRAY DRYING AND SPRAY CONGEALING

Spray drying and spray congealing methods of producing microcapsules have been practiced for many years in the food industry.[8] The primary use has been in the production of the so called "locked-in" flavors. Many coating materials can be applied to liquid and solid core materials. Normally these processes are conducted in the various type of commercially available spray drying equipment (Figure 15) readily obtainable in the marketplace.

Both spray drying and spray congealing involve dispersion of the core material in a coating solution or polymer melt and atomizing the dispersion into air or a liquid media which rapidly solidifies the coating. In spray drying this normally involves solvent (primarily water) removal from the coat-solution thus resulting in a dry microcapsule product. In the case of spray congealing, no solvent is present as the coating is a polymer melt (such as a wax) and a simple coating temperature change congeals the mass, thus