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Microcapsules and Microencapsulation Techniques

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MICROCAPSULES AND MICROENCAPSULATION TECHNIQUES

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents issued since 1967 that deal with microcapsules and microencapsulation techniques. To round out the complete technological picture, one earlier patent and one reissue were included.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of microcapsule manufacture and microencapsulation techniques.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring our new durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

15 Reasons Why the U.S. Patent Office Literature Is Important to You –

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.

2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.

4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.

5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.

6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.

7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.

8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.

9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.

10. Obtain licenses — many U.S. chemical patents have not been developed commercially.

11. Patents provide an excellent starting point for the next investigator.

12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.

13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.

14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.

15. It is a creative source of ideas for those with imagination.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

Microencapsulation, which has already proven useful for a variety of commercial purposes, can be expected to find further application in new and exciting areas.

Microcapsules are composed of a polymeric skin or wall enclosing a liquid core or other body of material. The capsule wall is inert to the substance it contains, possesses enough strength to allow for normal handling without rupture, and is sufficiently thin to permit a high core volume to wall volume ratio. The contents of the capsule are contained within the wall until released by some means that serve to break, crush, melt, dissolve, rupture or remove the capsule shell, or until the internal phase is caused to diffuse out through the capsule wall.

With the use of microencapsulated compositions, handling problems are facilitated. Materials which would react with one another on contact, can be individually encapsulated and then mixed without premature reaction. Liquid-filled microcapsules have low vapor pressure thereby eliminating any toxicity hazard during handling.

Microcapsules can be uniformly distributed on a matrix body or coating. They can also be used to fill macrocapsules. Since encapsulated fills are protected from air, moisture, microorganisms and other contaminants, spoilage is reduced and shelf life increased.

Thus, microcapsules can be advantageously used in a wide range of applications to contain dyes, inks, chemical reagents, pharmaceuticals, flavors, pesticides, cleaners, adhesives, perfumes, light and heat sensitive materials etc.

The encapsulation of volatile aromas and flavors protects them from chemical or physical oxidation and from thermal decomposition. For medicinals, encapsulation serves to mask unpleasant odor and taste and to protect against oxidation and spoilage. In addition, encapsulation can be such that the medicant will be selectively absorbed in the intestine rather than the stomach, or released gradually to provide relief over a prolonged period of time. Encapsulated perfumes can be coated on paper to make fragrance sheets. The polymeric shell of the capsule can

be made susceptible to decomposition in certain environments, or of a kind that permits diffusion through the capsule wall to allow for the slow, prolonged release of fungicide, herbicide, insecticide and fertilizer. And of course, a common use of microcapsules today is in pressure sensitive, mark-forming sheet material systems to substitute for typewriter ribbons or carbon paper.

This book deals with microcapsules having a variety of natural or synthetic materials as wall-formers. Included are some new, relatively inexpensive shell materials. The techniques for microencapsulation which are detailed encompass phase separation and polymerization, as well as physical, interfacial and other methods. Procedures for strengthening capsule walls and avoiding capsular aggregation are also covered, as are continuous encapsulation processes.

The preparation and use of microencapsulated products for paints, papermaking, food products, pharmaceuticals, perfumes, cosmetics, adhesives, amine curing agents, cleaning products, etc., are among those described.

MICROENCAPSULATION TECHNIQUES USING GELATIN

SIMPLE COACERVATE SYSTEMS

Salt Coacervation with Sodium or Ammonium Sulfate

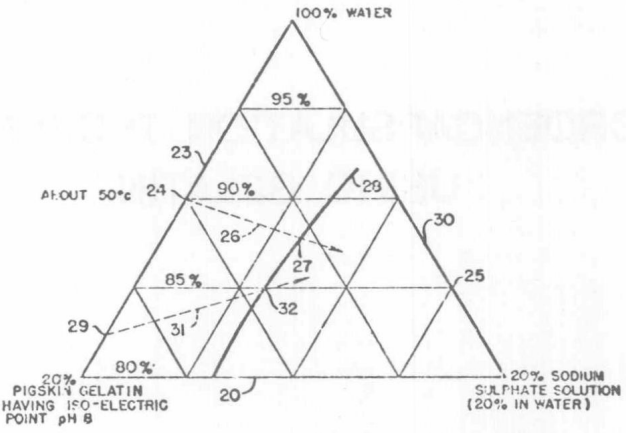
A fundamental simple coacervate system, often referred to in this book, is that described by *B.K. Green; U.S. Patent Reissue 24,899; November 29, 1960; assigned to The National Cash Register Company* for the preparation of oil-containing microcapsules by salt coacervation. The encapsulating material is gelatin (isoelectric point at pH 8).

Determining Conditions for Coacervation: In determining under what conditions with particular materials coacervation takes place, resort may be had to the formation of a ternary diagram such as Figure 1.1 resulting from a testing of various amounts of pigskin gelatin and sodium sulfate solution. In the causation of coacervation by use of a salt, the salt attracts water away from the colloid material causing the colloid material to separate or unmix, forming, in the vessel in which this step is taken, after they are allowed to separate by gravity, a colloid-rich fluid in the bottom and a layer extremely poor in colloid material on top.

The tests which are made to determine the coacervate region as far as amounts of material are concerned can be done with the colloid sol and the salt solution without the oil. Inasmuch as it is impractical to work with solutions of gelatin in which there is less than 80% water, because of viscosity, the diagram deals in that portion of the ternary scale above 80% water. The line **20** represents 80% water, the horizontal lines being indexed with the intermediate percentages of water. Coacervation is noticed by a clouding effect appearing in the sol which transmits less light than normal.

This may be noted by passing a beam of light through the sol as the salt solution is added and estimating by eye the change towards a cloudiness, or an electric photometer may be used. A particular sol is made of the pigskin gelatin and various solutions of sodium sulfate in water are added thereto. With a starting point of any place on line **23**, that is to say any sol of gelatin and water having less

FIGURE 1.1: TERNARY DIAGRAM SHOWING COACERVATION REGION OF GELATION IN WATER USING SODIUM SULFATE AS THE SALT



Source: U.S. Patent Reissue 24,899

than 20% gelatin content, by weight, the aqueous sodium sulfate solution is added. For instance, if a 10% gelatin in water sol is used, the starting point would be **24** on line **23**. If now a 15% solution of sodium sulfate in water, as would be plotted at point **25**, is added slowly which would be plotted along the dotted line **27** a clouding effect will be noticed which means that the gelatin in water sol is changing so that the entire mass of gelatin in a liquid phase is contracted because of the increased interaction between the gelatin molecules.

This clouding effect, first noticed at point **27**, will continue as more of the sodium sulfate solution is added. During the experiments to determine the coacervate line **28** by various experiments with different concentrations of sol and salt solution, the ingredients are kept at 50°C. As another example in determining the line **28**, a 17½% sol of gelatin in water, represented by point **29**, is treated with a 12½% solution of sodium sulfate in water as represented by point **30**.

As this sodium sulfate solution is added to the aqueous gelatin sol, the addition takes the mixture along the line **31** toward point **30**, the clouding effect of coacervation becoming apparent at point **32**.

By making a number of such experimental additions of the sodium sulfate solution to various sol concentrations, the contour of line **28** may be ascertained and the ranges within which coacervation occurs by the addition of sodium sulfate solution to the gelatin sol may be ascertained. The region to the right of line **28** is the coacervate region of the mixture but the addition of salt solution should not be carried far past the line **28** in actual practice, the more salt solution added the more aggregation occurring until a lumpy mass is formed. Useful salts for coacervation may be made from the cations $Na>K>Rb>Cs>NH_4>Li$ and the anions SO_4>citrate>tartrate>acetate>Cl such being arranged in the order of their effectiveness in this process.

Inasmuch as the finished encapsulated material will find an important use in the making of coating compositions which will form a transfer film on record material, such as paper, the preferred oil used is trichlorodiphenyl which is relatively nonvolatile, inert, and which can be obtained in a colorless and pure form. Into this trichlorodiphenyl may be dissolved a colorless color reactant as crystal violet lactone which is 3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide.

This phthalide compound has a white crystalline structure and, when dissolved to the extent of 3% by weight, in the trichlorodiphenyl and placed in contact with a sheet of paper sensitized with attapulgite, will turn to a dark blue color similar to crystal violet. When fluid-dispersed capsular material containing this oil is applied to a sheet and dried to form a transfer film, the capsules may be ruptured locally at points of printing and marking pressures to release the oil which will come in contact with the sensitized undersheet.

Example: 1 gal of an oil-in-water emulsion of 20 parts, by weight, of trichlorodiphenyl containing the phthalide and 100 parts, by weight, of a sol of 10%, by weight, of pigskin gelatin in water, is prepared, the emulsifying continuing until the drop size of the oil is from 2 to 5 microns. This material is kept at 50°C to prevent the gelatin from gelling.

With the temperature of the ingredient still kept at 50°C, the coacervation then is induced by adding, slowly and uniformly, 4/10 of a gallon of 20%, by weight, of sodium sulfate in water. During coacervation, the gelatin molecules are deposited uniformly about each oil droplet as a nucleus. The uniform addition of this material is accomplished by continuous agitation.

To gel the coacervate, the heated coacervate mixture is poured into 10 gal of 7%, by weight, of sodium sulfate in water at 19°C, with agitation. This rapid cooling and gelation results in a pore size so small that the encapsulated oil cannot escape through the capsule wall. The material is filtered and washed with water, the temperature being kept below the melting point of the gelatin, to remove the salt. If desired, the filtered material is hardened by combining it with 2 gal of a 37% solution of formaldehyde in water.

This hardened mass then is filtered and washed to remove the residual formaldehyde. The resulting filter cake is adjusted to the proper water content by the addition of water or the removal thereof, by ordinary means such as centrifuging or spray drying, and the material is ready for use. If this material is intended for paper-coating composition it is kept in aqueous suspension and applied directly to the paper which is then dried leaving the capsules adherent to the paper and to each other in a film.

Use of Negative Gelatin Derivatives

By means of a process developed by *L.D. Taylor; U.S. Patent 3,369,900; Feb. 20, 1968; assigned to Polaroid Corporation* encapsulation of a water-immiscible solvent as the nuclei material may be achieved utilizing a single, negative colloid material. A solution of a negative hydrophilic colloid is prepared and, with constant stirring throughout, the temperature and pH of the system is adjusted to a level above the point at which the colloid will floc or precipitate out. A coacervate of the colloid is formed at this point which may be referred to as the "cloud point."