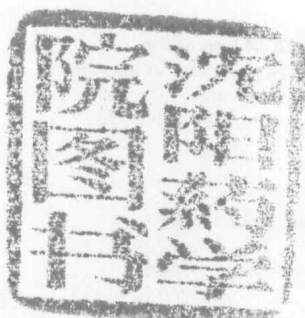


**Microcapsules and
Microencapsulation
Techniques**

ndc

MICROCAPSULES AND MICROENCAPSULATION TECHNIQUES

M.H. Gutcho



Y074619

NOYES DATA CORPORATION

Park Ridge, New Jersey, U.S.A.

1976

Copyright © 1976 by Noyes Data Corporation

No part of this book may be reproduced in any form
without permission in writing from the Publisher.

Library of Congress Catalog Card Number: 76-9494

ISBN: 0-8155-0625-2

Printed in the United States

Published in the United States of America by

Noyes Data Corporation

Noyes Building, Park Ridge, New Jersey 07656

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.....	1
MICROENCAPSULATION TECHNIQUES USING GELATIN.....	3
Simple Coacervate Systems.....	3
Salt Coacervation with Sodium or Ammonium Sulfate.....	3
Use of Negative Gelatin Derivatives.....	5
Low-Temperature Dispersion of Polymeric Materials.....	6
Complex Coacervation—Gelatin plus Natural Polymers.....	8
Two Oppositely Charged Colloids—Coacervation by Dilution and pH Adjustment.....	8
Dual-Walled Microcapsules—Use of Acid-Releasing, Protein-Insolubilizing Agent.....	12
Dual-Walled Microcapsules—Precoat of Interfacially Produced Polymer of Siloxane and Silanolate.....	14
Polymers Purified by Passage Through Mixed Bed Ion Exchanger.....	15
Both Colloids Having Negative Charge.....	17
Complex Coacervation—Gelatin plus Natural Polymers—Use of Shock-Preventing Agents.....	18
Polyelectrolytes Having Anionic Functional Groups.....	18
Gelatin of Lower Isoelectric Point.....	20
Complex Coacervation—Gelatin plus Natural Polymers—Shock Preventers with Synergist.....	21
Additive Is Maleic Anhydride, Acrylic or Methacrylic Acid Polymers.....	21
Additive Is Phenolic Monomer or Resin.....	23
Polyacrylic Acid as Coacervate Inducing Agent.....	25
Vinyl Acetate-Maleic Acid Copolymer as Coacervate Inducing Agent.....	26
Addition of Polyisocyanates or Polyisothiocyanates to Hydrophobic Oil Solutions.....	28
Condensation Product of Naphthalenesulfonic Acid and Formaldehyde to Strengthen Colloid Interaction.....	29
Complex Coacervation—Gelatin plus Inorganic Polymer.....	33
Polysilicate as Complexing, Phase Separation Inducing Polymer.....	33
Polyphosphate as Complexing, Phase Separation Inducing Polymer.....	34

Complex Coacervation—Gelatin plus Synthetic Polymer	35
Induced by Methyl Vinyl Ether-Maleic Anhydride Copolymer	35
Charged Autogenously Polymerizable Material Used with Polymers of Opposite Charge	37
Opaque Capsule Walls via Incorporation of Carbon Black	39
Simple and Complex Coacervation Using Natural or Synthetic Polymers . . .	41
Encapsulation of Oil-in-Water Emulsion—Aqueous Phase Contains Thickening Agent	41
Encapsulation of Water-in-Oil Emulsions—Oil Phase Contains Anti- Inversion Agent.	43
Improved Hardening of Coacervates—Gelable Colloid Dissolved in Thiocyanate Solution	45
Exchange of Encapsulated Material Through Capsule Wall by Diffusion . . .	46
Replacing Oily Material with Liquid Water-Miscible Materials.	46
Pretreatment of Capsules Containing Highly Polar Liquid.	48
Encapsulation of Basic Nitrogen Compounds with Gelatin	50
Use of Acid Precursor Gelatin	50
Use of Alkali Precursor Gelatin	53
Weighted Encapsulated Nitrogen Compounds.	54
Continuous Encapsulation Using Liquid-Liquid Phase Separation.	57
Single Material Entrance and Exit Ends.	57
Multiple Entrance Ports, Single Exit Port	60

MICROENCAPSULATION WITH SYNTHETIC POLYMERIC FILM

FORMERS	65
Liquid-Liquid Phase Separation.	65
Halogenated Rubber, Poly(Ethylene-Co-Vinyl Acetate)	65
Polyvinyl Alcohol-Alkylene Glycol Cyclic Borate Ester Complex	67
Phase Separation of Polymeric Nitrile Wall from Salt Solution	70
Three Phase System Using Poly(Ethylene-Co-Vinyl Acetate) Wall.	71
Polymerization Reactions	73
Polymerization of a Monomer Around a Nucleus	73
Hydrophobic Polymer Graft Polymerized onto Gelled Irradiated Hydrophilic Polymer.	74
Encapsulation with Polymerizable Epoxy Monomer	77
In Situ Polymerization of Polyhydroxy Phenolic Materials with Aldehyde.	78
Interfacial Polycondensation Reactions.	79
First Intermediate Injected into Portion of Nonreactive Liquid	79
One Intermediate Includes Polyfunctional Reactant for Crosslinking . . .	83
Finely Divided Solid Dispersing Agent	86
Phosphorus-Containing Polymer	88
Polyamide Structure from Diacid Chloride and Amino Acids	89
Other Interfacial Reactions.	91
Walls of Polyvinyl Alcohol-Cyclic Borate Ester Complex	91
Formaldehyde Condensation Product with Polymeric Wall Former- Emulsifier	93
Between Polymeric Emulsifier and Nonpolymeric Crosslinking Agent . .	94
Nonprotein Emulsifier-Wall Former plus Crosslinking Agent.	95
Polyaddition Polymerizate at Interface from Epichlorohydrin and Polyamine	97
Polymerization of Urethane Elastomer plus Epichlorohydrin with Polyamine	98

Precipitation at Interface Between Particles and Manufacturing Vehicle . . .	99
Encapsulation of Water-Soluble Substances in Preformed Film-Forming Polymer.	100
Solvent for Polymeric Material Removed by Evaporation	100
Solvent for Polymeric Material Removed by Solvent Extraction.	101
Water-Soluble Substance Added to Second Aqueous Phase.	101
Thermoreversible Coacervating Acrylic Acid-Acrylate Copolymers.	103
Preparation	103
Use	104
Aminoplasts	105
Aminoplast Shell from Urea-Formaldehyde Precondensate.	105
Surface Active, Crosslinkable Aminoplasts	109
Reactive Tenside plus Aminoplast Precondensate	111
Other Processes	114
Film Formers That React to Form High MW Material.	114
Polyvalent Polyisocyanate plus Second Wall Former.	116
Evaporation of Solvent from Polymer Solution.	117
Single Step Atomizing and Spray Drying.	119
Encapsulation of Very Reactive Substance Using Polyurethane Resin. . .	121
Water-Sensitive Core Encapsulated in Two Layered Wall.	123
Dual Walled Microcapsules Containing Water	124
Hydrophobic Polymer Dissolved in Low BP Solvent	126
Isocyanate Encapsulated by Synthetic Polymers.	128
CELLULOSE ESTERS AND OTHER WALL FORMERS.	131
Methylcellulose Wall	131
Phase Separation Induced by Raising Temperature and Adding Complementary Polymer.	131
Phase Separation Induced by Raising Temperature and Adding Polyelectrolyte	132
Ethylcellulose Wall	133
Phase Separation Induced by Adding Complementary Polymer	133
Polymer Deposited by Cooling Below Critical Liquid-Liquid Phase Separation Temperature	135
Liquid-Liquid Phase Separation by Evaporation of Solvent.	137
Controlled Transfer of Solvent from Organic into Aqueous Phase.	138
Other Cellulose Wall Formers	140
Outer Film of Ethylcellulose Around Gelable Lipophobic Polymer	140
Saponification Reaction of Alkali Substance with Cellulose Ester.	142
Spherules from Ethylcellulose Preliminary Capsules Using Desiccation Techniques	143
Other Shell Materials.	145
Capsule Walls of Waxy Materials	145
Heat Coagulation of Albumin Utilizing Infrared Absorber and Infrared Radiation	146
Liquid Cores Encapsulated with Metals.	148
Biliquid Column of Shell Material Around Fill Liquid.	149
Soluble Surfactant in Shell Composition for Liquid Fills	153
CAPSULE WALL TREATMENT	156
Chemical Wall Sealing Processes	156
Inhibiting Clustering with Cationic Surfactant	156
Dewatering with Sulfonate	158

Dewatering with Sulfosuccinate or Phosphate Ester	159
Dewatering with 2-Methyl-2,4-Pentanediol	161
Walls Hardened with Metallic Chelating Salts	162
Use of Transition Metal plus Graft Polymerization	164
Decreasing Sensitivity to Humidity by Uranyl or Vanadyl Ion Complexing.	166
Decreasing Sensitivity to Humidity by Vanadyl Ion Complexing	167
Use of Waxy Materials.	169
Decreasing Permeability via Metal Coating	170
Interstitial Condensation-Polymerization Reaction	173
Apparatus for Hardening by Cooling or Chemical Action	173
PIGMENTS AND PAINTS	178
Encapsulated Pigments	178
Pigment Encapsulated with Acrylic Interpolymers	178
Azo Organic Pigments Encapsulated with Vinylpyrrolidone Polymer ...	180
Polymer Treated Pigment Encapsulated with Hydrated Metal Oxide. ...	181
Aqueous Emulsion Polymerization for Encapsulation of Pigment Particles.	183
Cationic Charge on Pigment Prior to Polymerization.	185
Dispersion Polymerization of Polymer Treated Pigment Particles	188
Additives for Improving Paints	189
Thermoplastic Polymeric Walled, Air-Filled Microcapsular Opacifier ...	189
Filler and Texturizing Agent for Nonaqueous Paints.	191
Cellular Polymeric Material for Obtaining Hiding Power	192
PAPERMAKING.	194
Air-Containing Microcapsular Opacifiers	194
Pigmented Air-Containing Microcapsular Opacifiers	194
Polymeric Resin Walled Air-Containing Microcapsular Opacifiers	197
Air-Containing Microcapsular Opacifiers in Dry Pressure-Sensitive Copy Paper.	200
Microcapsular Opacifiers Having Polymeric Core Grafted to Polymeric Shell	202
Preparation of Grafted Polymeric Core Microcapsules.	202
Grafted Polymeric Core Microcapsules Used with Dye-Containing Microcapsules	204
Grafted Polymeric Core Microcapsules Containing Inorganic Pigment. ...	206
Use of Expanded Microspheres in Papermaking.	207
Vinylidene Chloride-Acrylonitrile Copolymer Shell	207
Outer Coating of Soluble Metal Salt	209
Other Papermaking Applications.	210
Coating Solution of Coacervate Forming Materials Containing Microcapsules	210
Microcapsule-Cellulose Fiber Units	211
Urea-Formaldehyde Microspheres for Paper Filler.	212
FOOD PRODUCTS.	215
Animal Feed	215
Encapsulated Polyhydrogenated Hydrocarbon Feed Additive.	215
Edible Microglobule for Mariculture	217
Ruminant Medicinal Compositions.	218
Encapsulated Methionine for Ruminants.	219

Flavors and Aromas	220
Encapsulation in Gelatin or Vegetable Gum	220
Encapsulated Alliacious Flavoring Composition	223
Flavoring Compositions Containing Encapsulated Volatile Components	225
Encapsulation of Volatile Flavoring Agents with Dry Nonfriable Films	226
Dextrinized Starch Acid Esters of Substituted Dicarboxylic Acids for Encapsulation of Volatile Oils	227
Gluten Encapsulated Delayed Release Products	229
Capsule Composition Sprayed Through Gaseous Medium into Polyglycol	230
Polyglycol Used to Desolventize Shell Composition	232
Encapsulated Additive for Removing Buttery Flavor in Beer	234
PHARMACEUTICALS	236
Vitamins	236
Ethylcellulose Encapsulated Nutrients	236
Centrifugal Encapsulation Process for Fat-Soluble Vitamins	237
Amylose Products as Encapsulating Agents	240
Phase Inversion in Presence of Surface Active Agent	242
Aspirin	244
Stomach-Insoluble, Intestine-Soluble Aspirin Composition	244
Water-Soluble Aspirin Composition	245
Sustained Release Ethylcellulose Encapsulated Aspirin	246
Encapsulation of Heat Sensitive Materials	247
Phase Separation by Dispersion in Aqueous Solution of Inorganic Salt	247
Organic Solvent of Dielectric Constant 15 to 34, Poorly Compatible with Liquid Paraffin Vehicle	249
Organic Solvent of Dielectric Constant Below 10, Poorly Miscible with Polyhydric Alcohol Vehicle	250
Controlled Release Pharmaceuticals	252
Enterically Active Controlled Release Microcapsules	252
Controlled Release Ophthalmic Dosage Form	253
Layered Tablets with Medial Layer of Controlled Release Microcapsules	254
Amino Acids	256
Encapsulation in Hardened Fat	256
Encapsulation in Oil and Fat Mixture	257
Other Processes	258
Nonthrombogenic Microcapsules of Controlled Permeability	258
Encapsulated Indomethacin	259
Encapsulated Erythromycin	261
Biodegradable, Parenteral, Radioactive Microspheres	262
Albumin Encapsulated Radionuclides	263
BEAUTY AIDS	265
Encapsulated Perfumes	265
Perfume Coated Sheets	265
Coating with Pressure Rupturable Capsules of Odoriferous Material	266
Aqueous Printing Ink with Perfume-Containing Microcapsules	268
Capsule Wall of Polymerized Polyisocyanate Monomer	269
Cosmetic Aids	271
Cosmetic Makeup Removing or Treating Composition	271
Microencapsulated Solvents for Nail Enamel Removal	273

Aerosol Composition Containing Self-Releasable Encapsulated Hair Dye	275
Sanitary Napkin Containing Encapsulated Deodorant	276
ADDITIONAL USES FOR ENCAPSULATED PRODUCTS	278
Anaerobic Adhesive and Sealant Compounds	278
Redox Catalyst System to Coact with Peroxy Initiator	278
Monomeric Core in Shell of Its Own Homopolymer	280
Curing Agents for Resins	281
Alginate Capsule Containing Aliphatic Amine Curing Agent and Alkyl Monophenol	281
Alginate Capsule Containing Amine Curing Agent, Alkyl Monophenol and Polyhydric Phenol	283
Adsorbed Curing Agent with Shielding Secondary Adsorbate	284
Autogenously Reactive Capsule with Curing Agent on Outer Surface	286
Aerosol Mixture of Encapsulated Amine Curing Agent plus Epoxy Resin	287
Dentistry	289
Dental Amalgam Containing Encapsulated Mercury	289
Marking Material for Indicating Areas of Varying Pressure	291
Laundry and Cleaning Products	292
Case Hardened Capsules of Brighteners	292
Two Stage Polymerization of Optical Brighteners	294
Detergents with Chlorine Donors and Encapsulated Fluorescent Whiteners	295
Encapsulated Chlorine Releasing Agent	296
Aerosol Stain Remover with Encapsulated Stain Remover and/or Encapsulated Adsorbent	299
Encapsulated Fabric Softener	300
Photographic Materials	301
Polymer Encapsulated Silver Halide Grains	301
Silver Halide Present in Walls of Capsule	303
Encapsulated Processing Solutions	304
Temperature Sensitive Visual Display Devices	307
Encapsulated Cholesteric Liquid Crystal Material	307
Encapsulated Mixtures of Cholesteric and Nematic Liquid Crystal Materials	310
Tobacco	313
Microencapsulated Syththetic Clove Flavoring for Tobacco	313
Reconstituted Tobacco Sheet Containing Encapsulated Flavoring Materials	314
Weather Modification	316
Use of Microencapsulated Hygroscopic Seeding Agents	316
Encapsulation of Urea or Sodium Chloride	318
Other Applications	319
Microencapsulated Alkalis or Acids for Use as Buffer Solutions	319
Microporous Encapsulating Particles for Controlled Release or Immobilization of Reactants	321
Apparatus for Producing Radioisotope Microspheres	323
Disposable Reserve Electrochemical Cell with Encapsulated Electrolyte	326
Encapsulated Flame Abating Compounds for Shaped Polystyrene Foam	328

Corrosion Inhibitor Encapsulated in Cellulose Acetate or Hydroxyethylcellulose	330
Encapsulation of Alkali-Sensitive Dimerisophthalic Acid	332
Encapsulated Electroscopic Marking Material (Toner).	334
Polymeric Web Structures Containing Encapsulated Components.	336
Lamp for Dispensing Vapors from Encapsulated Materials	337
Durable Press Fabrics—Encapsulated Catalyst or Resin	339
Artificial Fibers Containing Encapsulated Fiber Modifiers	342
COMPANY INDEX	344
INVENTOR INDEX	346
U.S. PATENT NUMBER INDEX	349

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

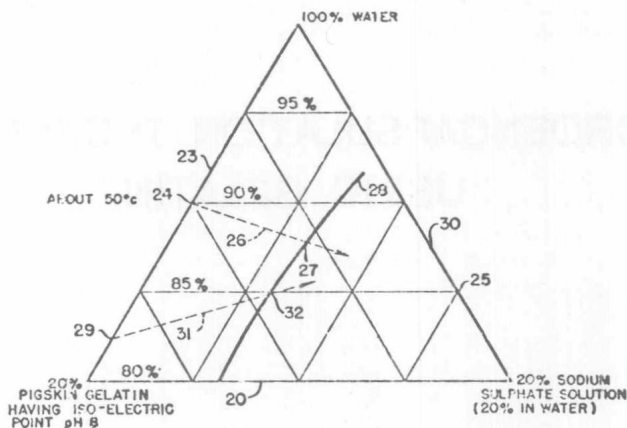
A fundamental simple coacervate system, often referred to in this book, is that described by *B.K. Green; U.S. Patent Reissue 24,899; November 29, 1960; assigned to The National Cash Register Company* for the preparation of oil-containing microcapsules by salt coacervation. The encapsulating material 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 $\text{Na} > \text{K} > \text{Rb} > \text{Cs} > \text{NH}_4 > \text{Li}$ and the anions $\text{SO}_4 > \text{citrate} > \text{tartrate} > \text{acetate} > \text{Cl}$ 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 attapulgate, 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, $\frac{4}{10}$ 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."