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Contractor: Stanford Research Institute

Contract No.: DA 18-108-405-CML-746

SRI Project: SU-1191

FIFTH QUARTERLY PROGRESS REPORT

Covering the Period

April 1 to June 30, 1961

Title: ENCAPSULATED AEROSOLS

Prepared by

Robert C. Robbins

Date: July 31, 1961

Prepared for

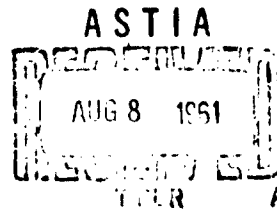
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CONTENTS

	<u>Page</u>
I SUMMARY	1
II INTRODUCTION	1
III CONDENSATION-POLYMERIZATION SYSTEMS	2
IV STRONG INERTIAL FORCE SYSTEMS	4
V CONCLUSIONS	9
VI CONTRIBUTING PERSONNEL	9
APPENDIX	10

FIGURES

	<u>Page</u>
Figure 1. Dibutyl Phosphite Droplets Encapsulated in Gelatin	5
Figure 2. Two-Stage Microcapsule Generator	7
Figure 3. Dibutyl Phosphite Droplets Encapsulated in Natural Rubber	8

Fifth Quarterly Progress Report*

ENCAPSULATED AEROSOLS

I Summary

An investigation was made of aerosol droplet encapsulation by the condensation-polymerization of vinyl acetate, methyl acrylate, and methyl methacrylate vapors with boron trifluoride or nitrogen dioxide. Vinyl acetate produced microcapsules with either boron trifluoride or nitrogen dioxide. Methyl acrylate produced microcapsules with boron trifluoride only. Under the conditions of these experiments, neither boron trifluoride nor nitrogen dioxide promoted sufficiently rapid polymerization of methyl methacrylate to produce microcapsules.

A two-stage microcapsule generator, designed to provide fairly large shearing forces between the core aerosol and the encapsulating liquid droplets, was assembled and operated. The behavior of a number of liquid pairs was investigated in this device. A simple liquid on liquid encapsulation, glycerine on dibutyl phosphite, was achieved, as demonstrated by the difference in the storage properties of the encapsulated and the unencapsulated dibutyl phosphite droplets.

Solutions of polyethylene, cellulose nitrate, and natural rubber were also used as candidate encapsulation liquids in the two-stage generator. The capsule yields for the polyethylene and cellulose nitrate were good and the rubber capsule yield was excellent.

II Introduction

This study is being made to investigate the basic principles involved in aerosol encapsulation. As aerosol particles of all combinations of liquids and solids are of potential interest, the scope is necessarily broad. New techniques for the production of encapsulated aerosols are being developed, as well as methods for evaluating the various approaches. The particle size range of interest is one to one hundred microns.

*NOTE: The Fourth Quarterly Report was included in the April 1, 1960 to March 31, 1961 Final Report.

III Condensation Polymerization Systems

In an earlier phase of this work,¹ microencapsulation of liquid droplets by polymer films, formed by the polymerization of vapor phase monomer, was found to be feasible. At that time, only diolefins with nitrogen dioxide were studied. In using nitrogen dioxide as a polymerization promoter, the possibility of its reacting with the core material must be considered. This can be minimized by mixing the aerosol with the monomer mixture. The homogeneous gas phase reaction proceeds much more rapidly than the reaction between the nitrogen dioxide gas and the liquid droplets; thus, by proper control of concentrations and reaction time, exposure of the core material to nitrogen dioxide can be minimized. Nevertheless, a less reactive polymerization promoter might be preferred for encapsulation of especially reactive droplets or particles. An example of such a promoter is sulfur dioxide. Sulfur dioxide and olefins will react to produce sulfone copolymers. The reaction is not considered to be a fast polymerization reaction but is of sufficient interest as a possible means of microencapsulation to be investigated.

A dibutyl phosphite aerosol was generated using a No. 40 De Vilbiss nebulizer. Nitrogen flow through the nebulizer was 7 liters/min. Five ml/min of isoprene vapor were added to and mixed with the aerosol stream; downstream 3 ml/min of sulfur dioxide were then added. The volume of reaction vessel was about 20 liters, thus providing a reaction time of nearly three minutes.

Samples were collected and analyzed for dibutyl phosphite. The analytical procedure is described in the appendix. Analysis of the collected samples compared with unencapsulated reference samples indicated a barely significant trace of encapsulation. Some encapsulation may have occurred, however, as the fresh sulfone polymer film may have been soluble in the alcohol used in the phosphite determination. No further work was carried out with this polymer system.

Rapid polymerization of a number of monomers, in the gas phase, can

1. Robbins, R. C. "Encapsulated Aerosols." Final Report, SRI Project SU-3191, Pg. 17 (April 1961).

be realized by the catalytic action of boron trifluoride. Three of the most reactive monomers were selected for study: methyl methacrylate, methyl acrylate, and vinyl acetate.² The fraction of core material encapsulated by the polymerization condensation of these monomers using boron fluoride catalysis was determined. Later, these same monomers were used with nitrogen dioxide replacing the boron trifluoride in a similar series of experiments. Details are described in the following paragraphs.

An attempt was made to encapsulate dibutyl phosphite droplets with polymethyl acrylate, using boron trifluoride. There was no evidence of encapsulation, based on dibutyl phosphite analysis, but a sample of the collected material, upon examination under the phase contrast microscope, appeared to contain microcapsules. This ambiguity was probably caused by polymer film solubility in the alcohol.

As no alcohol is used in the phosphoric acid titration, phosphoric acid was made the core material in a series of experiments to characterize the encapsulation behavior of the six possible combinations. Concentrations of core droplets, monomer, and promoter were kept at the same levels in all experiments. Again, about 7 liters/min of nitrogen were passed through the De Vilbiss nebulizer containing the phosphoric acid.

The appropriate monomer vapor was generated by passing nitrogen through the liquid monomer contained in a constant temperature bubbler (0°C). The nitrogen dioxide was generated in the same way. The bubble rate of the boron trifluoride gas, passing through carbon tetrachloride, was measured. The bubble volume was determined; this permitted the flow rate of boron trifluoride to be calculated. The monomer vapor and the promoter concentrations were both approximately 500 ppm in the entire series of experiments.

The following table shows the percentage of core material encapsulated by the different polymer films as judged by phosphoric acid analysis.

2. Burnett, C. M. Rate constants in radical polymerization reaction. Chemical Society Quarterly Review, 4, 308 (1950).

PERCENT ENCAPSULATION OF PHOSPHORIC ACID DROPLETS
BY POLYMERIZATION OF MONOMER-PROMOTER PAIRS

Promoter	Monomer		
	Vinyl Acetate	Methylacrylate	Methyl Methacrylate
Boron Trifluoride	35%	40%	None
Nitrogen Dioxide	35%	None	None

IV Strong Inertial Force Systems

Under ideal conditions two immiscible liquids can be mixed and atomized using a gas under pressure in a two-fluid nozzle to produce a large fraction of two-phase droplets, with one liquid phase encapsulating the other. This approach was used with some success when applied to mixtures of phosphoric acid and tung oil.³ When the two-phase droplets were reacted with nitrogen dioxide, 30% of the phosphoric acid was found to be encapsulated.

Mixing the two bulk liquids severely limits the number of possible pairs. They must be immiscible, they must have no tendency to react chemically, and the emulsion viscosity must not be too great. One interesting pair of liquids, which met these limitations, was investigated. Dibutyl phosphite and aqueous gelatin solution (3% gelatin by weight) were mixed and nebulized together. The droplets were collected and microscopically examined. Figure 1 is a photomicrograph of some of the large capsules which were formed.

The existence of capsules was also shown in a qualitative way by comparing the weight changes of core material in unencapsulated samples and encapsulated samples, both stored for the same length of time under identical conditions. To obtain this comparison two pairs of duplicate samples, one pair unencapsulated, the other pair encapsulated, were analyzed for dibutyl phosphite by titration; one sample of each pair was analyzed

3. Robbins, R. C. "Encapsulated Aerosols." Final Report, SRI Project SU-3191, Pg. 20 (April 1961).



RA-3151-13

FIG. 1
DIBUTYL PHOSPHITE DROPLETS ENCAPSULATED IN GELATIN
(Magnification Approx. 430X)

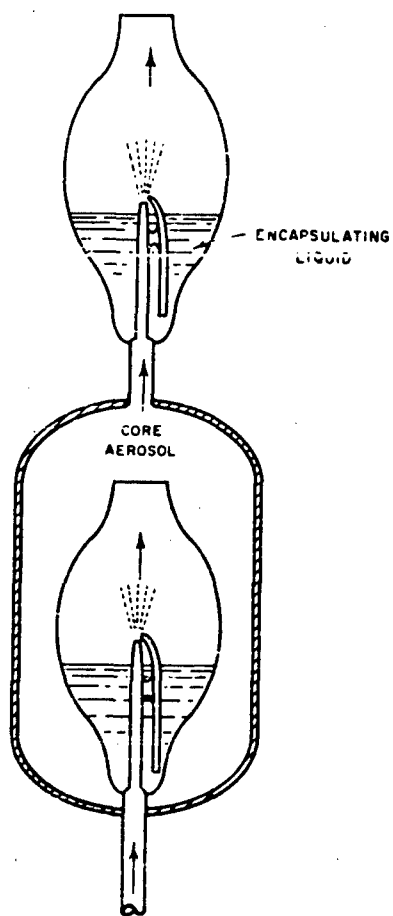
immediately, the other sample of each pair was analyzed after exposure. After 65 hours' dark-room exposure to clean filtered air at ambient temperature and humidity the bare dibutyl phosphite droplets lost 61% of their weight while the weight loss of the gelatin-encapsulated droplets was 52%.

Although earlier experiments with Venturi mixers and high velocity mixing tubes showed that these devices were not efficient promoters of aerosol encapsulation, a two-jet aerosol generator, with two pressure stages, was felt to be sufficiently different in operating principle and geometry to warrant a trial. De Vilbiss nebulizers were used for the two jets. The first stage nebulizer, containing the core droplet material, was encased in a pressure chamber. The aerosol discharge from the first stage was the pressurized medium used to disperse the encapsulating liquid in the second stage nebulizer. The second stage jet of the generator was operated at sonic velocity (critical flow) to provide large inertial forces between the aerosol containing the core droplets and the "encapsulating" droplets being generated. A diagram of the generator is shown in Fig. 2.

The first liquid pair investigated in the two-stage generator was glycerine on dibutyl phosphite. The weight change comparison after storage was used as an encapsulation indicator. After 65 hours' storage the weight changes differed by 54% (based on the initial weight of the unencapsulated material) and were interpreted to mean that encapsulation occurred;

Next, the encapsulating ability of three polymer solutions in the second stage of the microcapsule generator was investigated. The first solution was 1% polyethylene in toluene. No direct titrations were made, but collected samples were given the storage weight-loss tests. In 16 hours the blank sample lost 25% of its weight of dibutyl phosphite. The encapsulated sample did not lose any weight.

The second encapsulating solution was 5% cellulose nitrate in acetone. This solution was used with dibutyl phosphite in the two-stage microcapsule generator. Forty-eight percent encapsulation was produced on a mass basis as judged by chemical analysis and the capsules formed were not affected by the alcohol solvent used in the dibutyl phosphite analysis.



RA-5181-10

FIG. 2
TWO STAGE MICROCAPSULE GENERATOR

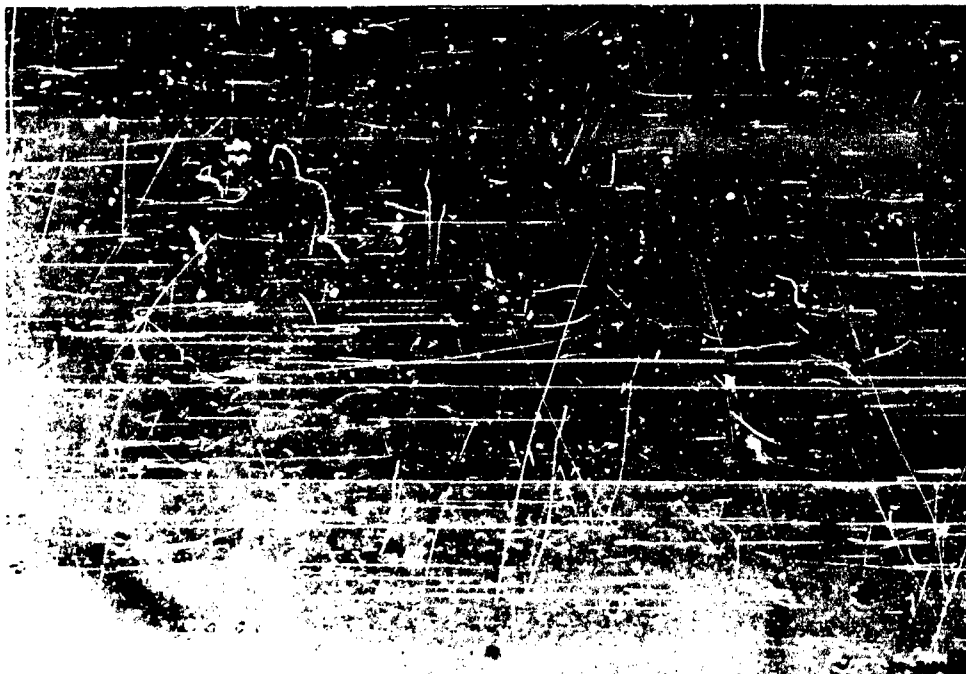


FIG. 3
DIBUTYL PHOSPHITE DROPLETS ENCAPSULATED IN NATURAL RUBBER
(Magnification Approx. 430X)

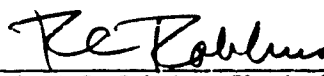
Natural rubber in carbon disulfide was the third encapsulating solution. The concentrations used were about one percent by weight rubber. Capsules were generated in good yields; they released liquid when scraped together and crushed. Hydrolysis of carbon disulfide solvent interfered with the quantitative determination of encapsulation. Figure 3 is a photomicrograph of the dibutyl phosphite droplets encapsulated in rubber. This system will be studied in detail in an attempt to correlate percent encapsulation, core-coat weight ratios, capsule permanence, water vapor permeability, and solvent effects on core material.

V Conclusions

Vinyl acetate polymerizes very rapidly in the vapor phase with boron trifluoride or nitrogen dioxide. Either combination has as great a potential application to the production of encapsulated aerosols as the diolefin vapor-nitrogen dioxide system. As the monomer reactivity decreases, the trend is reflected in the encapsulation capability. Methyl acrylate produced microcapsules with boron trifluoride but not with nitrogen dioxide. Methyl methacrylate produced no capsules with either promoter. The two-stage microcapsule generator appears to be generally capable of producing encapsulated aerosols of the type which are generated from a pair of liquids. In contrast to earlier devices investigated, the geometry of this generator is such that evaporation of the solvent aids the formation of capsule films when solutions of film-forming materials are used.

VI Contributing Personnel

Persons who contributed to the project were Dr. R. D. Cadle, Manager, Atmospheric Chemical Physics Department, Mr. C. E. Lapple, Senior Scientist, Dr. R. C. Robbins, Physical Chemist, and Mrs. Jill Thomas, Chemist.


Robert C. Robbins, Physical Chemist
Atmospheric Chemical Physics Department

RCR:ema

APPENDIX

MODIFIED DIALKYL PHOSPHITE DETERMINATION FOR ANALYSIS OF SMALL SAMPLES

A quantitative factor related to the extent of encapsulation occurring in aerosol droplets may be obtained if a quantitative analysis is made of the available core material in unencapsulated and encapsulated samples containing known quantities of core material. This may be done if the microcapsule coating is not penetrated or removed during the analysis.

A procedure for the volumetric determination of dialkyl phosphites has been developed by Bornhart and Rattenburg¹ based on neutralization of the phosphite with excess NaOH, then back titrating the HCl. One mole of NaOH is consumed for each mole of dialkyl phosphite. By reducing solution concentrations, and adjusting the volumes to accommodate small samples, sensitivity was increased to about 0.1 micromole of dialkyl phosphite.

It was found that it was necessary to have about 150% excess of NaOH at a minimum concentration of 0.1 N for quantitative phosphite neutralization. The back titration could be done with HCl as dilute as 0.007 N using phenolphthalein indicator.

When microcapsule films are encountered which are soluble in alcohol or water, an indirect approach is necessary.

Procedure

Five ml of 95% ethyl alcohol are used for dissolving the sample. One ml of 0.1N NaOH is added, followed by 2 drops of indicator, then the solution is back titrated to the endpoint with 0.007 N HCl.

Should the total phosphite in encapsulated material be required, after addition of the alcohol, 5 ml of solvent for the encapsulating material film may be added and shaken with the sample in alcohol before adding

1. Bornhart, D. N. and K. H. Rattenburg. Anal. Chem. 28, 1765 (1956).

the 0.1 N NaOH. This mixture may be treated in one of two ways: If the film solvent is nonpolar and immiscible in water, as is often the case, the two phases are separated after adding the NaOH solution and the sample is then back titrated in the normal way. If the film solvent is miscible with water, it may be disregarded during titration. The film solvent utilized must not react with the dibutyl phosphite or with water.