Spray Drying of Emulsions Containing Volatile Oils

by

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SUMMARY

Although spray dry encapsulation is a widely used method for preparing dry powdered flavors from liquid flavor oils, few studies have been made on the comparative retention of different oils. Little information is available in the published literature on how the oil is lost or how this loss can be prevented. Fundamental studies of the structure of the spray dried particles have not been made.

The objective of this study was to investigate the structure of the dry particles containing oil and the retention of various oils under spray drying conditions using "Mor-rex 1918", a hydrolyzed cereal product, as the solid encapsulant. The drying of emulsions containing benzyl alcohol, benzene, methyl benzoate, and a mixture of benzyl alcohol and methyl benzoate were studied. Some emulsions were prepared with small amounts of gum arabic to see how this stabilizer effected the structure of the dry particles and the retention of oil.

Emulsions were prepared from a mixture of the soluble solids, water and oil by emulsifying the oil in a high speed blender. The emulsions were then spray dried and the dry powders consisting of the solids and encapsulated oils were analyzed for oil retention. A number of observations were made concerning the retention of the oils; e.g.: 1) under similar drying conditions, the retention of the various oils showed that benzyl alcohol was retained better than benzene

which was retained better than methyl benzoate, indicating that volatility of the oil is not the only factor in oil retention, 2) doubling the amount of solids in the aqueous solution did not improve the retention of benzene but did improve benzyl alcohol retention, 3) adding gum arabic did not effect the methyl benzoate retention but lowered the benzyl alcohol retention, 4) both oils in an emulsion with a 50/50 mixture of benzyl alcohol and methyl benzoate as the emulsified phase were evaporated in approximately the same amounts, and the total oil loss for this preparation was between the oil loss observed from emulsions of each of the oils separately, indicating that the oil loss is due to exposure of the drops to the drying air, and 5) the size of the spray dried particles effects the retention of oil.

The major structural differences observed in the dry powders were between particles containing benzene, which had thick walls and a small central void, and the particles obtained from emulsions with oil with low volatility, which had thin walls and large central voids. When no gum arabic was added to the emulsion, the walls had only very small voids and were substantially solid. With gum arabic, the walls of the particles contained numerous large voids.

1. INTRODUCTION

During the past fifty years or so, microencapsulation has found many applications. One area where microencapsulation is commonly used is in the flavor and aroma industry, where encapsulation of volatile oils has seen considerable commercialization. A number of companies in the United States and Europe prepare dry encapsulated flavors. Many more companies extract and prepare the oils and still other companies manufacture the solids which form the protective capsular wall (9).

The primary use for these encapsulated flavors is in instant pudding and pie filling mixes. However, encapsulated flavors are also used in candy, toothpastes and even in advertising promotions (2). Although encapsulated flavors are much more expensive than in the liquid form, their cost is justified because they are irreplaceable in powdered mixes. An additional benefit is that encapsulated oils are protected from oxidation and evaporation.

There are several ways to prepare microcapsuls, including liquid-liquid coacervation, interfacial polymerization, and molding and grinding processes (10). One of the most widely used methods is spray dry encapsulation. Spray dry encapsulation has several advantages over the other commonly used methods of which the two most important are relatively low cost and the ability to operate the process continuously.

Spray dry encapsulation involves preparing a stable emulsion of a volatile oil in a solution or colloidal suspension of water and a suitable solid material and subsequently spray drying this emulsion to evaporate the water. In this way the oil is retained in the dry solid which acts as the encapsulant or wall material. Although the oils to be encapsulated are often quite volatile and the spray dryer is operated at temperatures much higher than 100°C to promote rapid evaporation of the water, the retention of the oil can be quite high. Several factors combine to maintain the droplets at a reduced temperature and prevent vaporization and loss of the volatile oil. First, during the early stages of drying, rapid evaporation from the surface of the droplet removes heat from the drop and helps maintain the drop at a low temperature. Secondly, the residence time within the spray dryer is only a few seconds in most cases (11), and finally in normal co-current drying equipment a temperature gradient exists in the tower so the droplets are exposed to decreasingly severe temperatures during the drying. These factors also help prevent pyrolysis of the wall material.

Choice of the proper wall material is one of the most important considerations in spray dry encapsulation. Balassa and Fanger (3) summarized the desirable characteristics of the wall material as follows:

(a) Solutions should have low viscosity at high solids content.

(b) Solutions should form stable emulsions with oil.

(c) Wall material should not react with the oil.

(d) Dry wall material must be impermeable to oil.

(e) Dry wall material should be impermeable to air and humidity.

(f) Wall material should be edible.

Although a number of different solids have been tried, the most commonly used are naturally occurring polymeric materials.

Thijssen and Rulkens (13) have shown that with coffee extract solids as the wall material, retention of flavor oils during spray drying was increased as dissolved solids content in the original emulsion was increased for all flavoring materials tested. Work by Ban (4) indicated that retention of peppermint oil was increased with increased solids in the emulsion when using gum arabic as the encapsulant. But as McKernan (9) suggests, the maximum solids content is limited by the properties of the emulsion. Emulsions which have gum arabic concentrations greater than 20 weight percent are difficult to spray dry because they do not flow easily through either pressure nozzles or disk atomizers. Gelatins are viscosity limited at lower concentrations and do not spray easily at concentrations much above 10 weight percent. In addition they must be kept warm to prevent gelling. Of the commonly used wall materials, only solutions of starches and hydrolyzed starches are still sprayable at concentrations of 50 weight percent in aqueous solutions.

Both gum arabic and proteinaceous gelatins form stable emulsions with many oils. Adamson (1) explains that this is due to preferential adsorption of these polymers along the oil-water interface in the emulsion. The adsorption prevents coalescence by raising the local viscosity around the drop surface. Starches do not provide emulsion stabilization.

While none of the commonly used wall materials react with flavor oils, some are permeable to certain oils (12), and others allow penetration of oxygen and humidity into the encased oil (14). For most oils oxidation means loss of flavor, off tastes, or loss of nutritional value. Considerable loss of oil upon standing can result if the wall material is permeable to the oil.

The wall material should be edible. In almost all applications for flavors and aromas, the capsular material is consumed with the flavor. Most wall materials are designed to pass through the digestive system so as to be neither nutritious nor poisonous, but some wall materials, especially the proteins and gelatins, can actually be nutritious. Usually wall materials will have a bland taste so as not to interfere with the flavor oil taste.

Combinations of wall materials are sometimes used to overcome the shortcomings of a single material. For example, gum arabic is often used with starch derivatives so that good emulsion stabilization can be coupled with the low solution viscosity of the starches. Invert sugars have been used as fillers for gelatin wall materials. Sometimes antioxidants are mixed with the wall materials to retard destruction of the oil by oxidation. McKernan (9) gives a complete list of commonly used wall materials.

Loss of the valuable flavor oils during drying is the most serious problem involved in spray dry encapsulation. Few studies have been made on the cause of flavor oil loss and specific causes are as yet unclear. Although high drying temperatures and low boiling oils have been suggested as major contributors to flavor losses during spray drying, Brooks (6) has shown that retention of flavor oil can actually be increased by raising the inlet air temperature of the spray dryer. Ban (4) did not find a significant difference in retention of peppermint oil with inlet temperatures ranging from 180 to 210°C. Thijssen and Rulkens (13) showed that retention was not related to the volatility of the aroma when materials were spray dried in coffee extract. Some of the most volatile materials were actually retained the best.

Several investigators have suggested that flavor oils are retained because a semipermeable membrane forms around a droplet during the early stages of drying. This membrane permits the passage of water as drying progresses but retards the passage of oily materials such as flavors. In this way the particle is depleted of water while it retains a large portion of oil. Thijssen (13) has made measurements on acetone diffusion which show that the diffusivity of acetone is retarded greatly in solutions with high solids contents. Marshall (7) states that almost all materials will form a dry "skin" if drying conditions are correct.

1.1 Purpose

Since very few studies have been made on losses of oils during spray drying this study was designed to answer some fundamental questions about spray drying. The following questions were considered for these experiments:

1. What is the role of the volatility of the oil in how well it is retained?
2. How does solids content of the original emulsion affect retention?
3. How well are hydrophilic flavor oils retained compared to hydrophobic materials?
4. How does emulsion stabilization with gum arabic affect oil retention?
5. How are mixtures of oils retained as compared to single oils?

6. How do the above factors change the microscopic structure of the spray dried particles?

Hopefully with the answers to these questions a better understanding of the causes of flavor oil losses during spray drying can be attained.

2. EXPERIMENTAL WORK

2.1 Chemicals

"Mor-rex 1918" - The encapsulating solid used in this study was "Mor-rex 1918", a hydrolyzed cereal product of CPC International, Englewood Cliffs, New Jersey. This material is a white crystalline powder, readily pourable and non-hydroscopic. It is easily dispersable in water.

Gum arabic - The gum arabic used as a stabilizer in a number of experiments was from the Fisher Scientific Company. The gum arabic was ground in this laboratory with a mortar and pestle to assist in dissolution.

Benzyl alcohol - The benzyl alcohol used in this study is a product of the Aldrich Chemical Company Incorporated, Milwaukee, Wisconsin. Benzyl alcohol is a clear thick liquid with a distinct "fruity" odor.

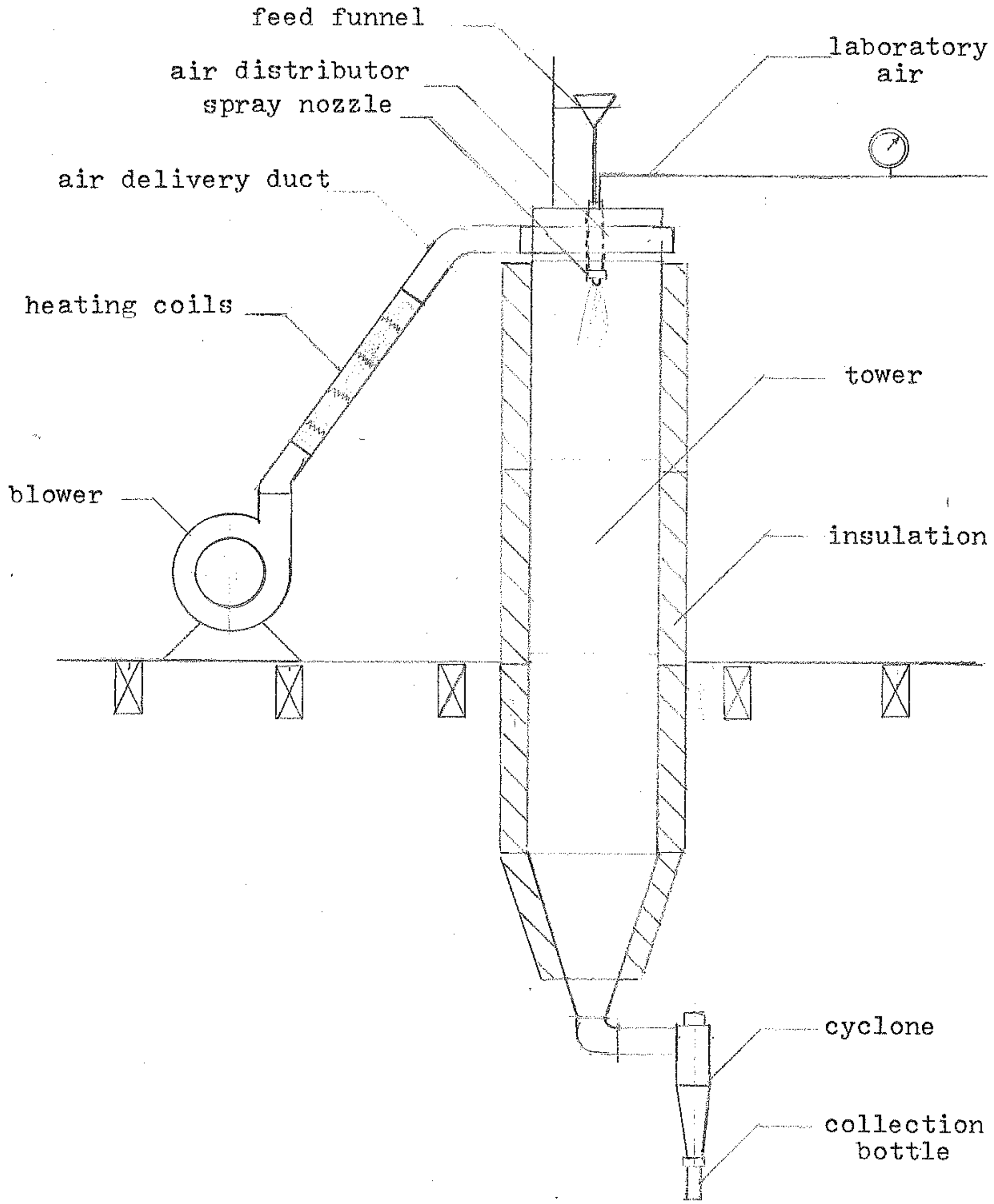
Methyl benzoate - The methyl benzoate used in this study is manufactured and distributed by Eastman Organic Chemicals. It is a clear liquid, with a strong "minty" odor.

Benzene and 95% ethanol - Both the benzene and the 95% ethanol were obtained from the University of Wisconsin Chemical Engineering Department.

2.2 Equipment

Spray dryer - A skematic representation of the spray dryer used in these experiments is shown in Figure 1. The

Figure 1. Spray Dryer

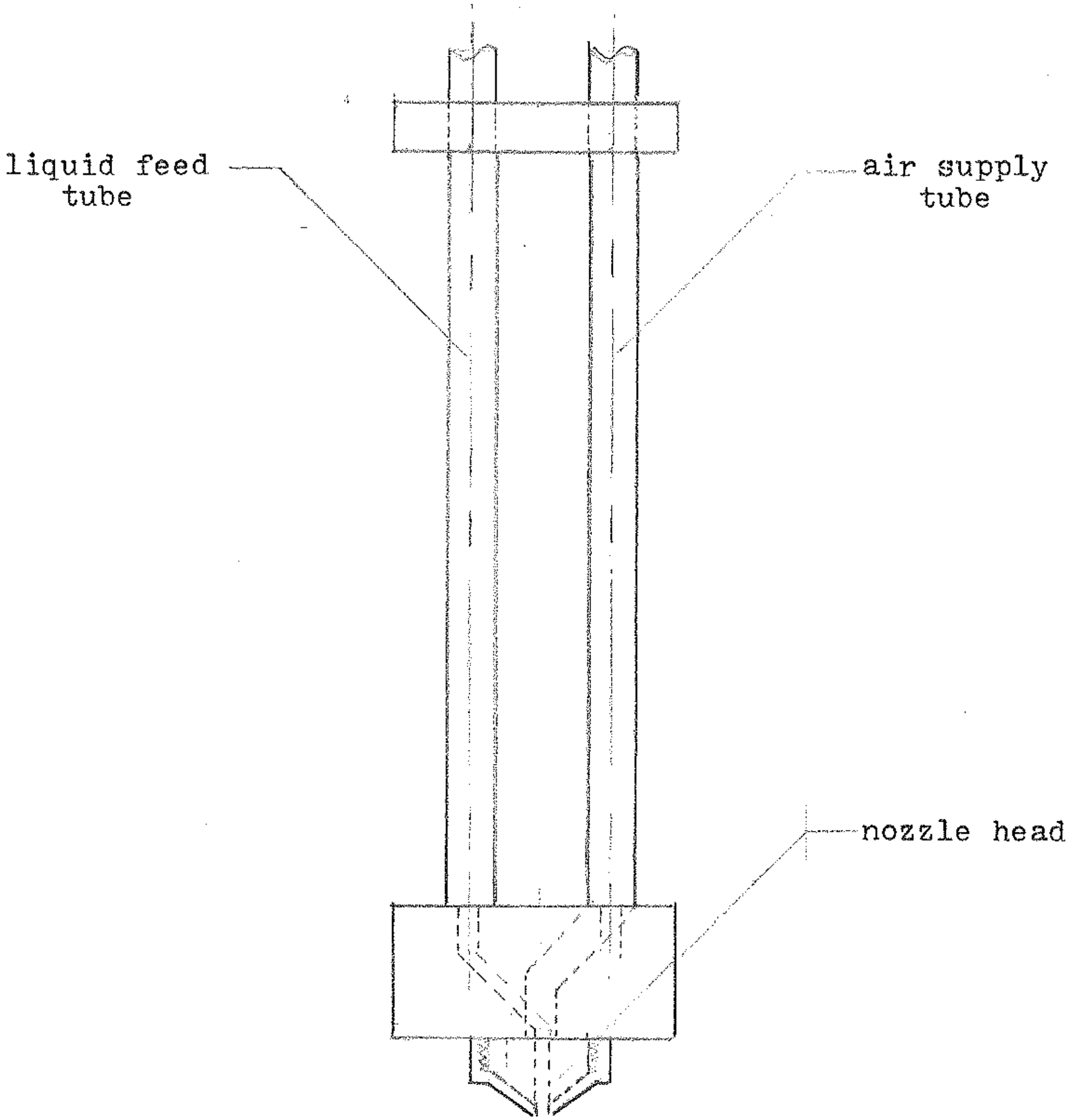


equipment consists of a blower, air delivery duct and heating coils, air distribution system, tower, and cyclone collection system. The material to be spray dried is fed through a pneumatic atomizer nozzle which uses compressed laboratory air to help atomize the liquids.

When the spray dryer is in operation, the drying air is supplied by the blower from laboratory air. The air is heated by electrical heating coils as it passes up a 5 inch duct leading to the tower top. At the tower top the air enters at right angles to the tower axis through a ring arrangement. The air is then directed downward along the axis of the tower to provide the co-current air flow. The air passes down through the tower which measures 7'5" in length and 20" in diameter. As the air exits from the tower, it passes through two conical sections which reduce the diameter of the air flow area to 4". The air is then passed through the cyclone separator where entrained solids in the air are settled out and collected in a glass collection jar at the bottom of the cyclone. The air, now substantially free of solids, passes out the top of the cyclone.

The feed emulsions were atomized with a pneumatic air nozzle at the top of the tower. Fresh liquid feed was supplied from a funnel which was connected to one side of the atomizer (Figure 2). Pressurized air was connected to the other side of the atomizer. The action of this pressurized air flowing out of the nozzle served to draw the feed liquids through the orifice of the nozzle and to aid

Figure 2. Pneumatic Nozzle



in atomizing them.

Benzene distillation apparatus - In Figure 3 is shown the benzene distillation apparatus used to determine the benzene contents of the spray dried powders. The apparatus consists of a boiling flask for dissolving the dry powders containing benzene, a heating mantle and variac system to heat the boiling flask and contents, a condensing-collecting system to collect and measure the benzene once it had been separated from a solution, and a beaker of water to monitor escaping gases.

Vapors arising from the heated flask are condensed in the condensing apparatus shown skematically in Figure 5. This vaporization-condensation cycle effectively separated the emulsified benzene from the water and "Mor-rex" of the solution. The condensed vapors dripped down into the collection tube where any liquid water sank to the bottom and liquid benzene floated to the top due to their difference in density. As more benzene condensed,water was returned to the flask through the return tube. The beaker on the right hand side of the apparatus prevented pressure build-up during the heating of the apparatus. Bubbles passing through the water indicated gases were escaping.

Blender - A "Waring Commercial Blendor, Model 5011" was used to dissolve the "Mor-rex" and emulsify the oils used in this study. The blender, shown in Figure 4 had a two speed motor system, with push buttons for "off", "low"

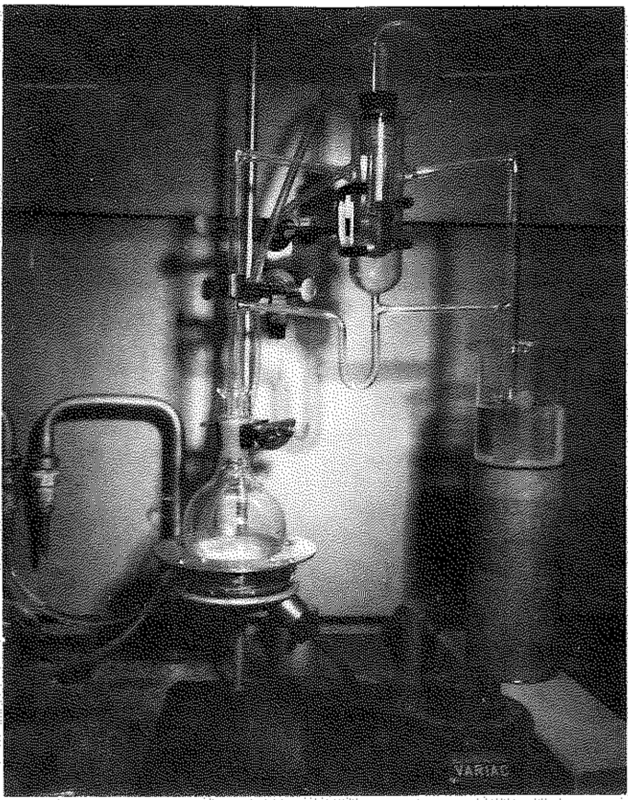
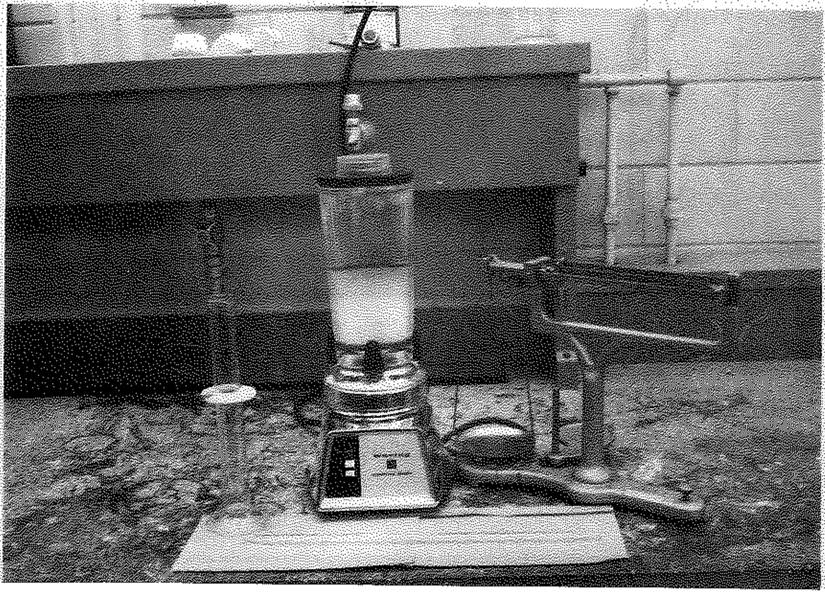


Figure 3. The Benzene Distillation Apparatus

Figure 4. Blender and Other Equipment for Making Emulsions



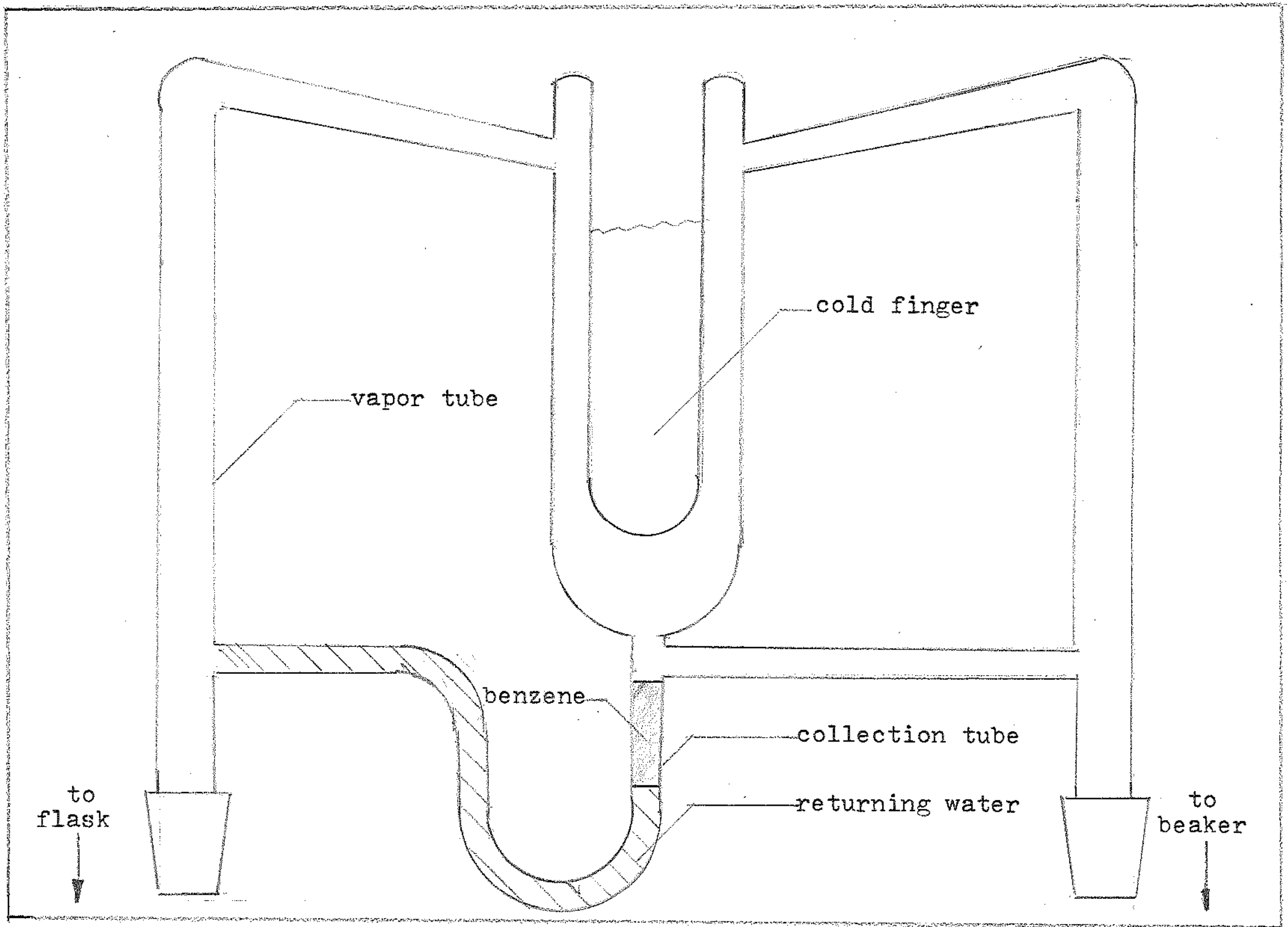


Figure 5. Benzene Condensing Apparatus

and "high", and a glass mixing bowl into which the liquids and solids were blended. For these experiments a rubber baffle which fitted tightly into the bowl was made to cut down the effective bowl volume to 1/3 its original volume. This baffle prevented undo splashing of the bowl contents during mixing.

2.3 Experimental Procedure

2.3.1 Emulsion Preparation

The spray dried emulsions were prepared with a "Waring Blendor". For the emulsions which incorporated no gum arabic, the desired amount of "Mor-rex" was first weighed on the triple beam balance with the correct weight determined from the desired water: "Mor-rex" ratio. In all emulsion formulations 100 ml of distilled water were used. The "Mor-rex"was placed in the mixing bowl of the blender and the water was then added. The rubber baffle was put into place and the blender was run at low speed for about 10 sec. to dissolve the "Mor-rex" and thoroughly mix the solution. This procedure always entrapped a certain amount of air as minute bubbles, so the solution was allowed to set for 3 min. while these bubbles creamed out. When all the entrapped air had been removed, the solution became clear.

Next, the specified volume of oil was added to the mixing bowl with a pipette. The rubber baffle was again reinstated to prevent splashing and the blender was operated at high speed for exactly 30 sec. This treatment was sufficient to emulsify the oil droplets to less than 10 μm in diameter. After completion of the high speed blending, the emulsion was allowed to set for 5 min. to remove the newly entrapped air bubbles. Microscopic examination of the emulsion before and after the 5 min. waiting period showed only minimal coalescence of the oil during this time and the droplets remained smaller than 10 μm. After the latter deaeration period, the emulsions were charged to the spray dryer.

For the emulsions which contained gum arabic, all the procedures described above were followed with the exception that before the water was added to the "Morrex", the correct amount of gum arabic was dissolved in the water by stirring with a spoon.

2.3.2 Spray dryer operation

Before a series of runs was begun, the inside wall of the dryer was scrubbed clean - especially the lower conical sections where maximum wall buildup occurred.

To prevent burnout of the heating elements, the air flow was first established by starting the blower. Next both heaters were turned on and the variac was set at ca. 45 percent of full scale. The dryer was then allowed to come to thermal equilibrium which took about two hours. The variac was adjusted slightly as needed to fix the inlet temperature at 180 ± 2°C and the corresponding outlet temperature to 107 ± 3°C. After the inlet and outlet temperatures were stabilized, the nozzle air pressure was turned on to the correct predetermined setting as read on the pressure gauge. This setting was 15 psig for solutions with a 4:1 water:solids ratio and 20 psig for solutions with a 2:1 water:solids ratio. The feed funnel was then connected.

Just before feeding the emulsion to the spray dryer, 75 ml of distilled water was fed to the dryer. This had the effect of lowering the nozzle temperature which in turn prevented the emulsion from clogging the nozzle because of rapid evaporation of the liquids in the orifices of the nozzle. The emulsion was added to the feed funnel just as the water level reached the neck of the funnel.

While the emulsion was being fed into the spray dryer, some creaming of the oil was evident. As the last portion of the emulsion passed through the funnel neck, special note was taken of the volume of creamed oil since this could not be encapsulated. For retention calculations this amount of oil was subtracted from the original amount in the emulsion.

Immediately after the last portion of emulsion passed into the spray nozzle, the funnel and nozzle were cleaned by feeding another 75 ml of water to prevent the nozzle from clogging. The spray dried products were then collected from the glass collection bottle at the bottom of the cyclone.

To shut down the dryer, the heaters were first shut off and the inlet temperature was allowed to fall to 60°C before turning off the blower. This procedure prevented the heating coils from burning out or their insulation from being degradated.

2.3.3 Analysis of samples

Samples containing benzene

The amount of benzene retained was determined by distilling an emulsion reconstituted from a known weight of the dry powder containing benzene.

Before attempting to analyze the samples prepared in the spray dryer, several emulsions with known benzene contents were prepared. These emulsions were made by dissolving 4 gm of "Mor-rex" into 20 ml of distilled water and mixing in a certain volume of benzene.

The emulsion was poured into the flask of the distillation-separation apparatus (Fig. 5). The heating mantle was put into place, and dry ice and water added to the cold finger. The heating mantle variac was set to deliver about 80 volts and insulation was wrapped around the glassware to prevent condensing of the vapors before entering the cold finger area.

After 5 - 10 min. the solution began to boil and vapor was seen condensing in the cold portion of the apparatus. Much of the vapor became frozen to the cold finger, the rest turned to liquid and dripped into the collection loop. When it was apparent that the condensing vapors no longer contained benzene (30 - 45 min.), the heating mantle was turned off and warm water was added slowly to the cold finger to sublime the remaining dry ice and thaw the frozen benzene and water which had collected. When all the ice and benzene had been thawed, the depth of the benzene in the collection loop was measured. From data taken on known samples, the calibration curve shown in Fig. 6 was plotted. The linearity and zero intercept of this curve indicate that nearly all the benzene was being recovered with this method.

For the spray dried samples, a known weight of powder containing benzene, usually 3 - 4 gm, was added directly to the flask together with 20 ml of water and the emulsion reconstituted by mild stirring. Any powder left undissolved after stirring, quickly dissolved when the apparatus was reassembled and heat was applied. The procedure for unknown samples from this point was identical to that for the known samples as previously described. When all of the benzene had been collected, the volume of benzene was determined by referring the measured depth to the calibration curve. Typically two measurements of each dry powder sample were taken. In all cases, excellent agreement was seen from sample to sample.

With the known density of benzene, the data taken in this way was put on a dry solids basis.

Samples containing benzyl alcohol and methyl benzoate

Ultraviolet spectrophotometry was used to analyze for both of these oils. Samples of spray dried particles containing benzyl alcohol and methyl benzoate were washed with benzene to remove oils exposed on the exterior particle surface. After removal of the excess benzene by filtration, the particles were allowed to air dry and then were placed in an oven for 15-20 min. at 95°C to evaporate any residual benzene and to reduce the moisture content. Microscopic examination of the particles before and after this washing revealed that the particles had not changed, although the powder lost its clinging tendency and its wet appearance since the surface oil was removed. Benzene did not penetrate the particles.

The dry particles were dissolved in an aqueous ethanol solution containing 47.5 volume percent ethanol in a volumetric flask. This not only dissolved the wall material but also was effective in dissolving the entrapped oils. One ml of this solution was volumetrically transferred to a test tube containing 9 ml of 95 weight percent ethanol. The tube was shaken vigorously and a precipitate of the wall material was formed. The test tube was sealed and centrifuged at 2,000 rpm for 30 min. to effect complete precipitation of the "Mor-rex" or mixture of "Mor-rex" and gum arabic. The supernate from this solution was either analyzed in the spectrophotometer directly or diluted by a factor of 10 and then analyzed to determine the amount of oil in the solution.

A series of known samples were analyzed and the results were plotted to be used as a calibration curve. The curves for benzyl alcohol and methyl benzoate are shown in Figs. 7 and 8 respectively. As in the calibration curve for benzene, good linearity and zero intercepts indicated that the analysis procedure accounted for all of the oil. As a check to determine if any oil was trapped in the precipitated "Mor-rex", the pellets from the bottom of the centrifuge tubes were redissolved and reprecipitated. None of the tested precipitates were found to contain any oils.

For the samples containing both benzyl alcohol and methyl benzoate, a graphical subtraction procedure was used to determine the amount of benzyl alcohol in the

Figure 6. Benzene Determination Calibration Curve

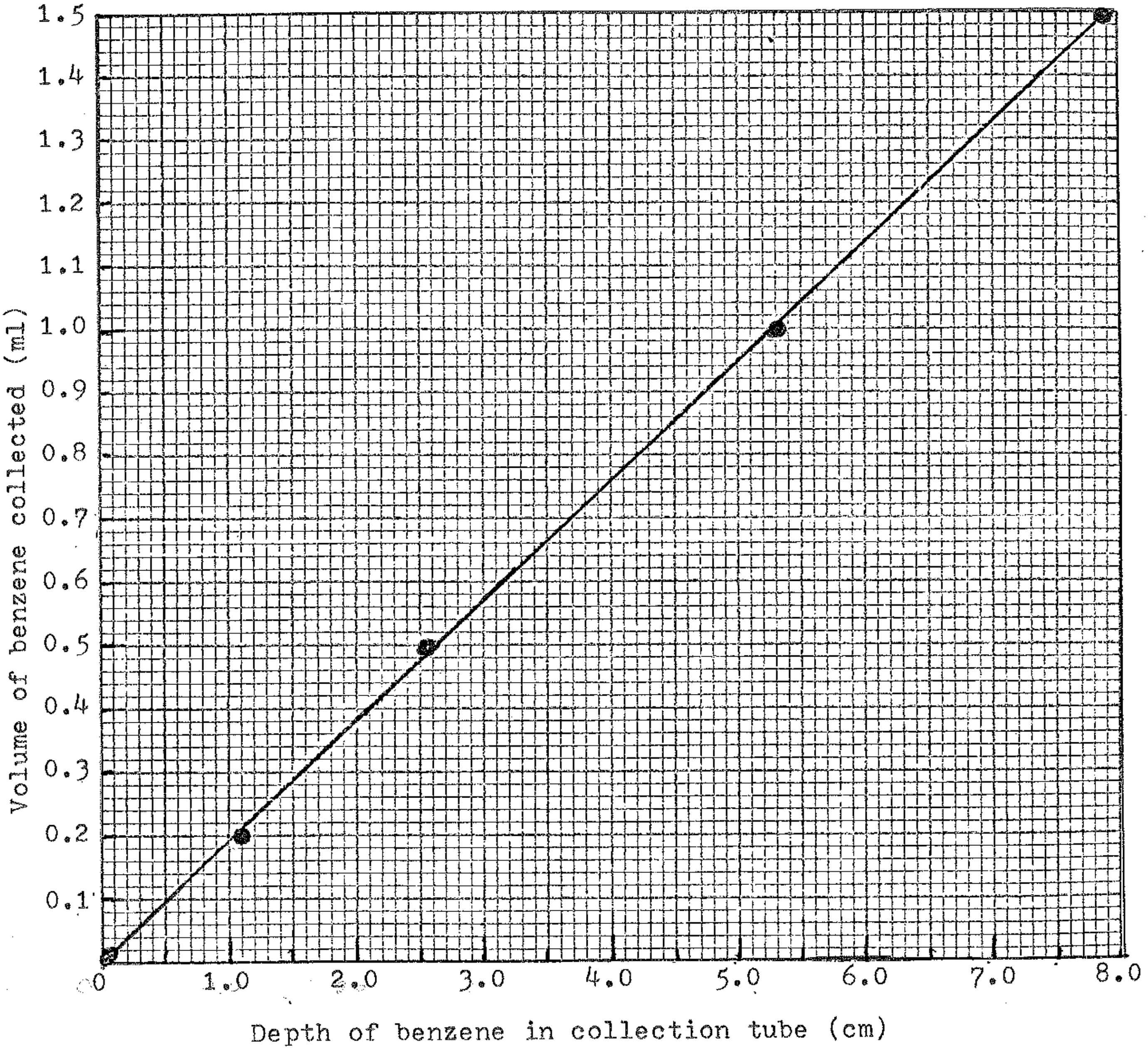


Figure 7. Benzyl Alcohol Determination Calibration Curve

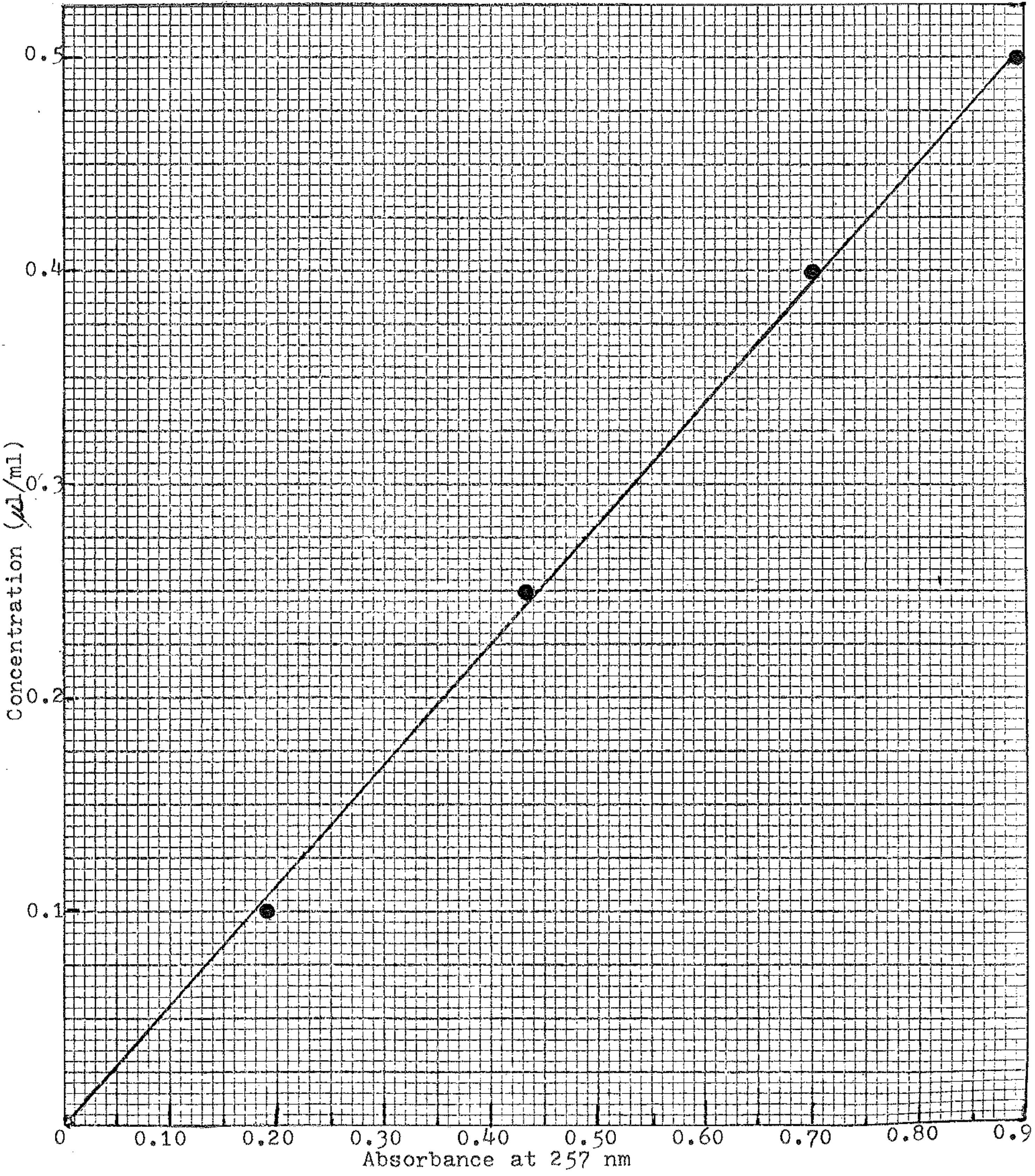
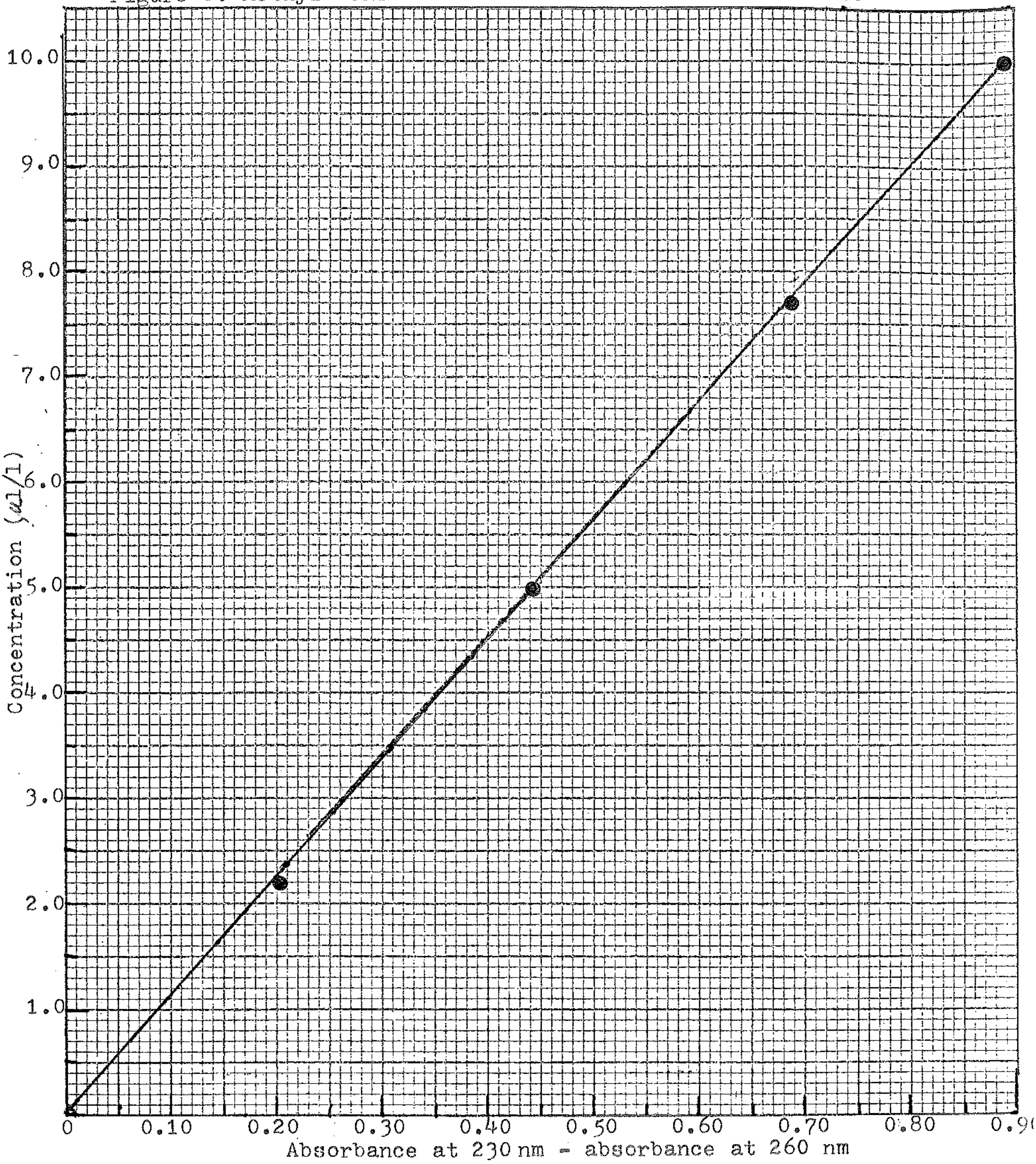


Figure 8. Methyl Benzoate Determination Calibration Curve



sample. This procedure is illustrated in Fig. 9. Methyl benzoate has a much stronger absorption spectra than benzyl alcohol - so much so, in fact, that methyl benzoate absorption is not effected by benzyl alcohol or small amounts of "Mor-rex" in solution.

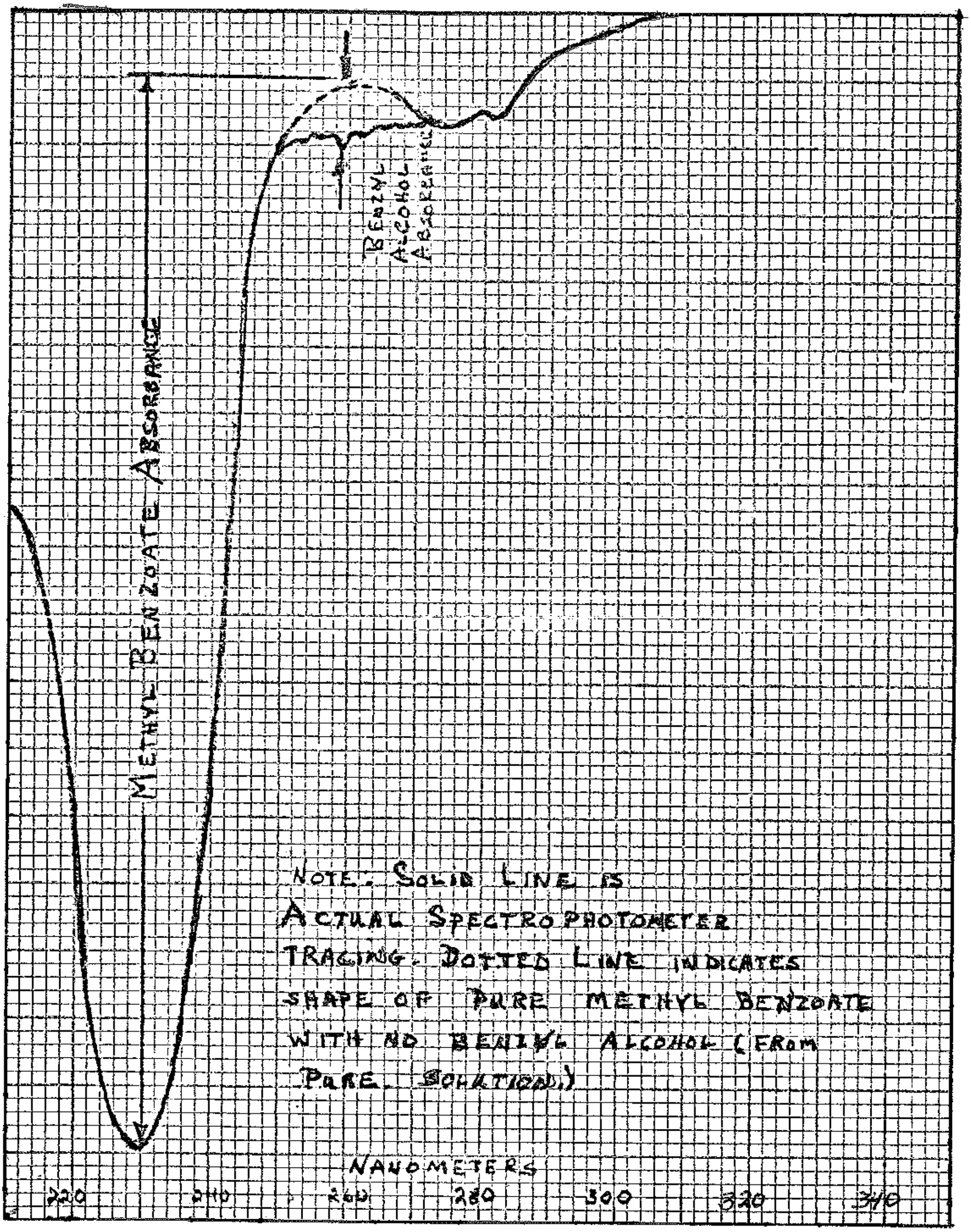
2.3.4 Electron microscopy

The samples viewed under the scanning electron microscope were mounted on a viewing pedestal with "double stick" tape. The sample was sprinkled on the tape and the excess was blown and lightly brushed off. A portion of the particles were lightly crushed with a knife point to assure some broken particles could be found under the field of view.

Before viewing, the samples were subjected to a vacuum and chromium was electrically sublimed onto the particle surface. This treatment improved the conductivity of the particles and prevented electrical charging from the electron beam. The total time for coating with chromium was varied from 20 to 60 sec. and the best results were obtained with the longer coating times. The particles were not heated significantly under these conditions.

The coated sample was then removed from the sublimation chamber and placed into the viewing chamber of the electron microscope. The pressure in the viewing chamber was reduced to 5×10^{-6} atms and viewing was

Figure 9. Method for Determining Benzyl Alcohol Content in a Solution with a Mixture of Oils



NOTE: SOLID LINE IS ACTUAL SPECTROPHOTOMETER TRACING. DOTTED LINE INDICATES SHAPE OF PURE METHYL BENZOATE WITH NO BENZYL ALCOHOL (FROM PURE SOLUTION.)

begun as machine instructions directed. Photography was carried out with Polaroid 52 black-and-white film.

2.3.5 Size separation

Some of the samples as taken from the spray dryer cyclone were separated according to size by screening. The screen sizes used in these separations were Tyler mesh sizes 120 (nominal 125 μm), 200 (nominal 74 μm), and 325 (nominal 44 μm). The particles which passed the 325 screen were collected in a tray. The screens were shaken on the Roto-tap seive shaker for 15 min. Generally, separations were accomplished easily but some of the samples with high oil contents tended to clog the screens. In these cases, the Roto-tap was periodically stopped during the 15 min. screening period and the screens cleaned with a soft brush.

3. RESULTS

3.1 Benzene

In Fig. 10 is shown a partially broken particle of encapsulated benzene produced from an emulsion with a "Mor-rex" content of 0.25 gm/ml-water and an original benzene content of 0.6 ml/gm-"Mor-rex". The spray drying conditions used to prepare this particle were an inlet temperature of 180°C and an outlet temperature of 110°C. The particle contains one large central void about 55 μm in diameter, and a large number of smaller voids ranging from 1 to 10 μm in diameter. The outer surfaces of particles prepared in this way have an "orange peel" appearance as shown.

The particles obtained from emulsions containing 0.5 gm-"Mor-rex"/ml-water were different from their counterparts with lower "Mor-rex" contents. Intact particles from these emulsions were not observable under the electron microscope. Eighty percent of the particles were already broken when taken from the cyclone of the spray dryer and the remainder apparently underwent fracture during the vacuum treatment or when chromium was sublimed onto them before viewing. The particles appeared as broken egg shells under the electron microscope.

In Fig. 12 the benzene contents of particles from emulsions of varying oil contents for high and low "Mor-rex" contents are compared. As indicated, little difference can be seen between the benzene contents of emulsions with high

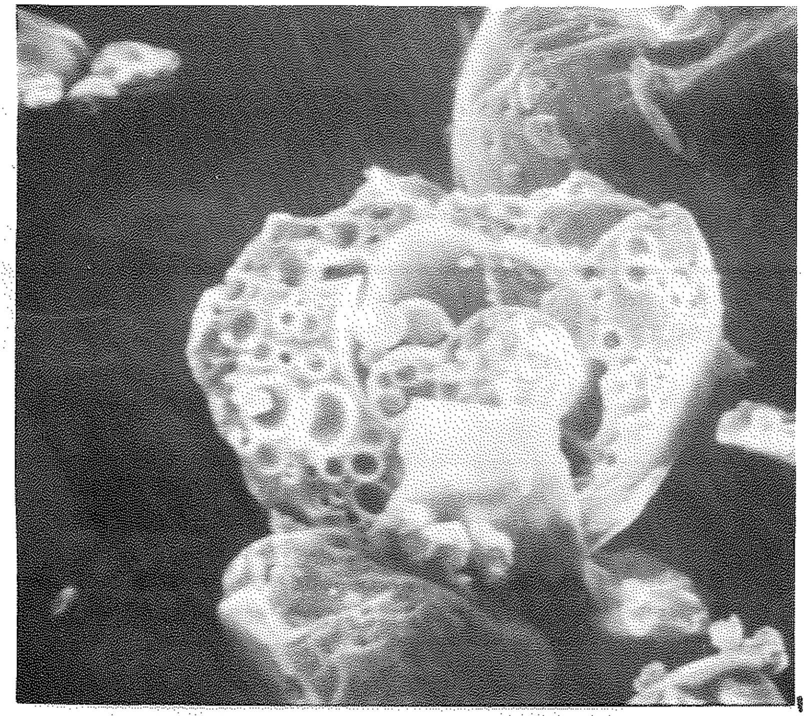


Figure 10. Partially Broken Particle from Benzene Emulsion (500x)

Figure 11. Partially Broken Particle from Benzyl Alcohol Emulsion with Low Solids Content (500x)

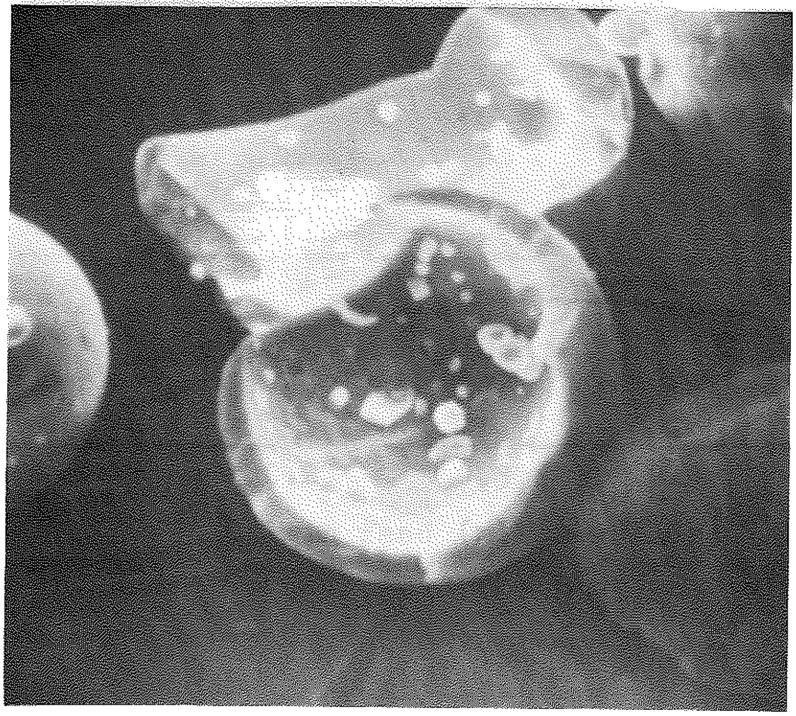
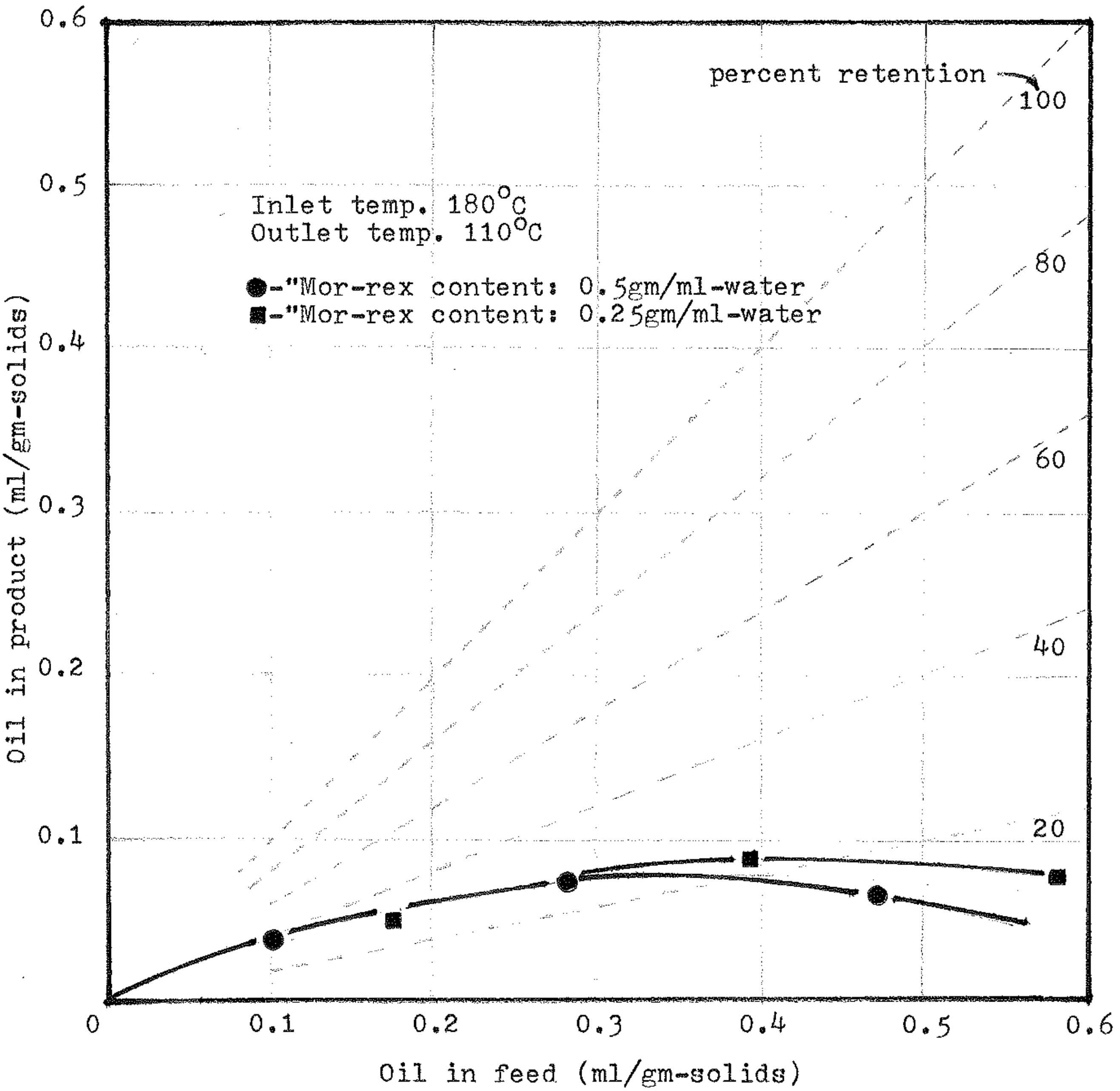


Figure 12. Retention Curves for Benzene Emulsions with High and Low "Mor-rex" Contents



and low "Mor-rex" content. The maximum retention in both cases is about 10 ml-benzene/100 gm-"Mor-rex" under the drying conditions used here. Absolute retention dropped off for emulsions with high oil contents.

3.2 Benzyl alcohol

Although dried under conditions identical to those for the benzene containing particle shown in Fig. 10, a broken particle from a spray-dried sample containing benzyl alcohol has a vastly different structure (Fig. 11). No large voids were seen in the wall and the central void was much larger than in the benzene case. The central void in this particle accounts for about 50 percent of the total volume. In the benzene containing particle, the central void represented only 7 percent of the total volume.

For emulsions containing a greater amount of "Mor-rex", (0.5 gm/ml-water) the collected particles were not fractured as in the benzene containing particles. These particles, shown in Fig. 13, were very similar to the particles from lower "Mor-rex" containing emulsions, with a large central void and thin walls. The walls were somewhat thicker with higher "Mor-rex" contents and the large central void represented only 40 percent of the total volume. A close examination of the wall of one of these particles, as shown in Fig. 14, reveals tiny voids 0.5 - 1 μm in diameter.

When gum arabic was added to the emulsions of benzyl alcohol, the appearance of the particles was changed con-

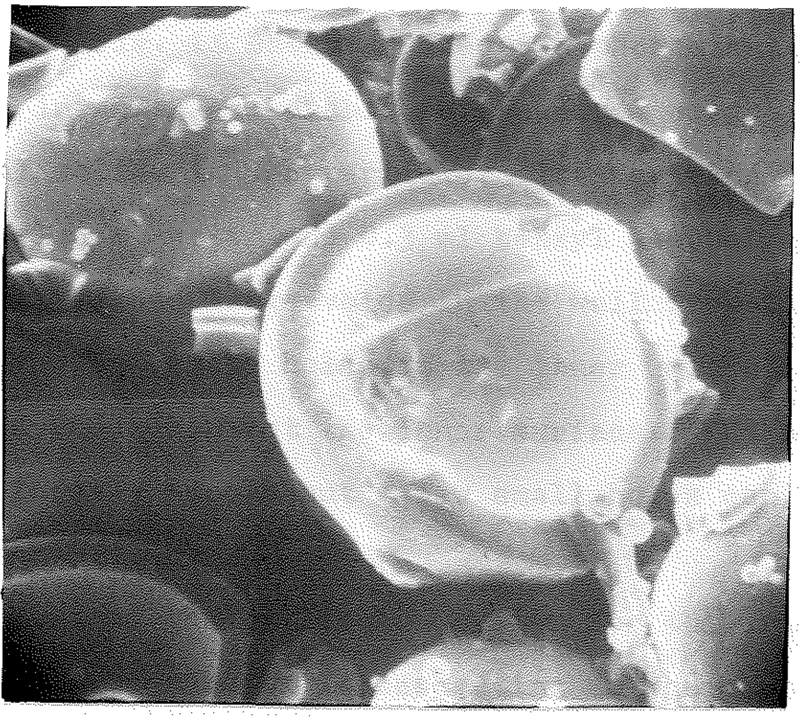
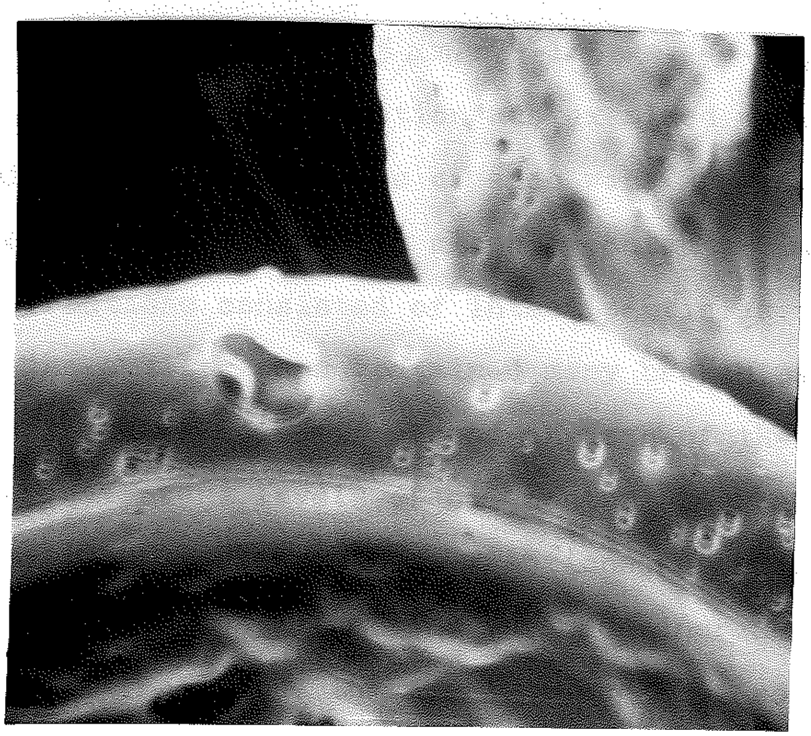


Figure 13. Partially Broken Particle from Benzyl Alcohol Emulsion with High Solids Content (500x)

Figure 14. Wall of Spray Dried Particle Showing Small Voids (2500x)



siderably. Fig. 15 shows an electron photomicrograph of a particle in which gum arabic represents 2 weight percent of the total solids in the particle. The emulsion formula was 0.5 gm-solid/ml-water and 0.3 ml benzyl alcohol/gm solids. This particle has large voids in the wall from 1 to 10 μm in diameter and small holes in the inner wall of the sphere where the voids contact the inner surface. The outer surface is largely smooth but a few small holes can be seen on close examination.

Because of the collection system for the dried particles and possibly because of forces acting on the particles during drying, a large number of broken particles were contained in the dry powder taken from the spray dryer. To separate out whole particles for analysis, the particles containing benzyl alcohol were seived into four nominal size fractions; greater than 125 μm, 74-125 μm, 44-74 μm and less than 44 μm. Each size fraction was examined under an optical microscope and samples of each were washed with benzene and analyzed for benzyl alcohol content. The two largest fractions consisted of intact particles to a large extent, the smaller ones contained many broken particles. Fig. 17 shows the retention found in each of the size fractions for different levels of oil content in the original emulsion. The two larger size fractions showed greater retention as oil content of the feed was increased. For the smaller size fractions, the absolute content dropped off

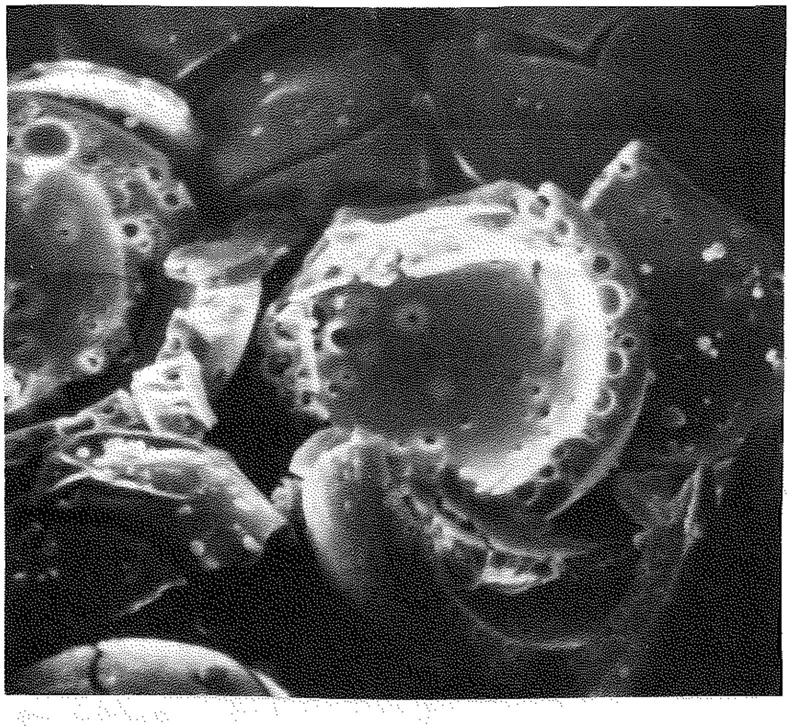


Figure 15. Particles Containing Benzyl Alcohol and Gum Arabic (500x)

Figure 16. Particle from Spray Dried Emulsion of Methyl Benzoate in "Mor-rex" (500x)

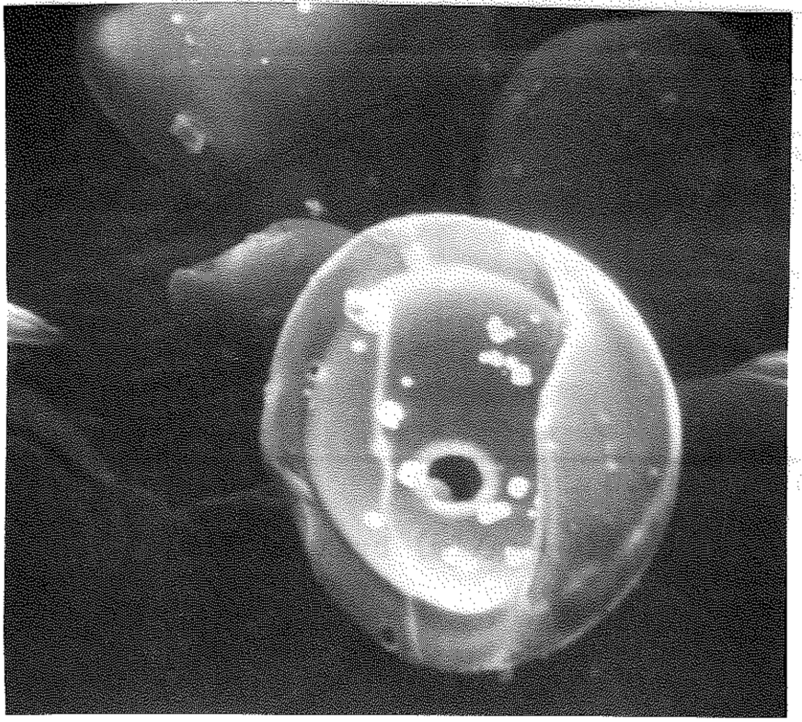
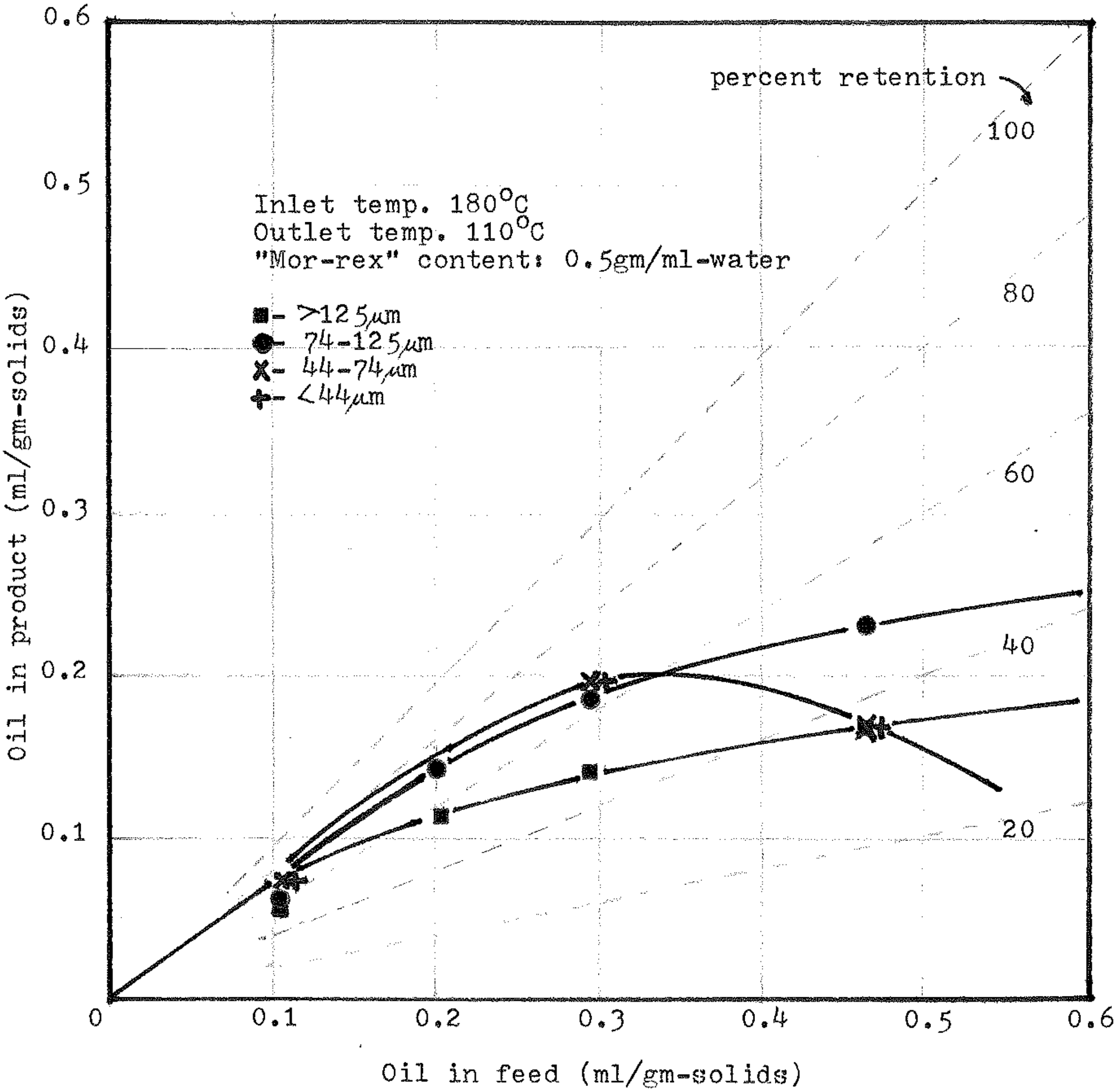


Figure 17. Retention of Benzyl Alcohol in "Mor-rex" for Different Size Fractions



considerably for emulsions with more oil in the original emulsion.

The higher content of the 74-125 μm particles compared to the greater-than-125 μm particles was due to a higher oil content within the central void of the particle. Table I shows the content of the wall material after crushing the particles and the total contents. The content of the central void was obtained by difference.

TABLE I

Benzyl Alcohol Content of Different Parts of Spray Dried Particles

Nominal Particle Size, μm	Total Oil Content ml/gm-solids	Oil Content of Wall ml/gm-solids	Oil Content of Center ml/gm-solids
125 μm	0.144	0.101	0.043
74-125 μm	0.198	0.094	0.104

Fig. 18 shows the comparative retention of benzyl alcohol at high and low "Mor-rex" concentrations for the particles in the size range of 74-125 μm. Better retention is seen at all levels of oil in the original emulsion at higher "Mor-rex" concentrations.

Addition of 2 weight percent gum arabic to the emulsion reduced the retention of oil at all levels as shown in Fig. 19. Higher oil contents in the emulsion resulted in a drop in the retention of oil.

Figure 18. Retention of Benzyl Alcohol from Emulsions with High and Low "Mor-rex" Contents

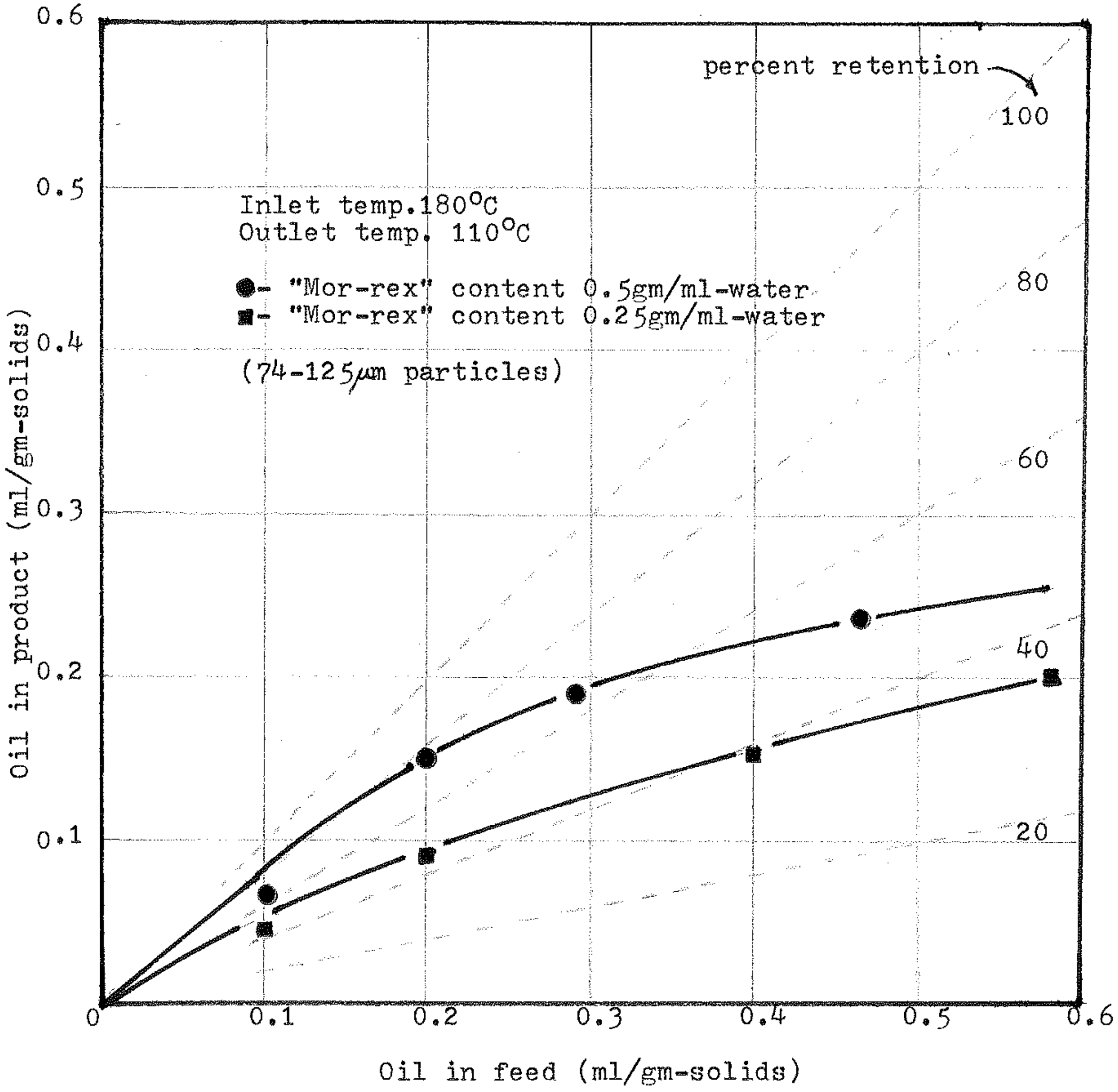
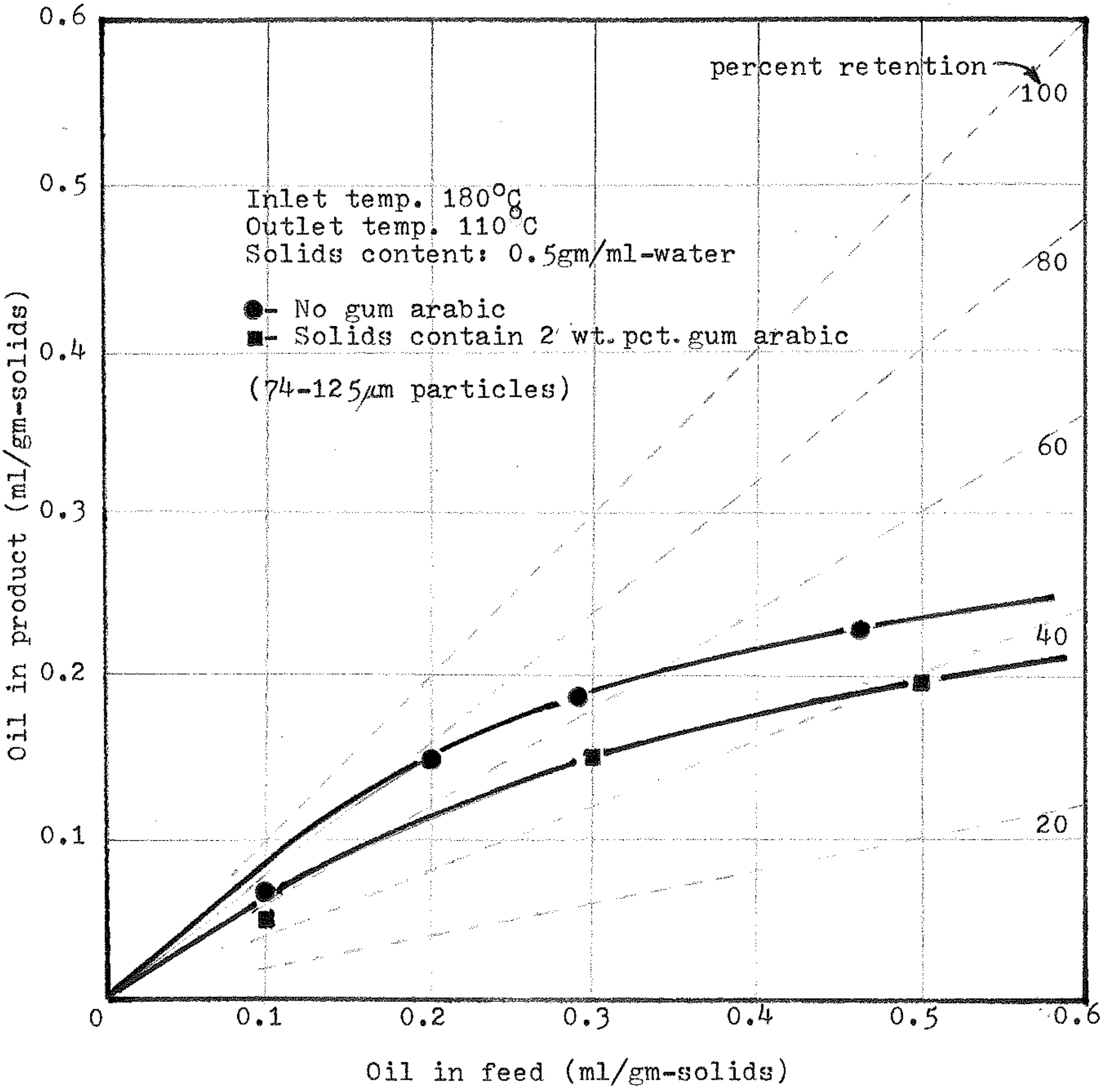


Figure 19. Retention of Benzyl Alcohol from Emulsions with and without Gum Arabic



3.3 Methyl benzoate

Emulsions of methyl benzoate were spray dried in a fashion similar to those of benzene and benzyl alcohol. Fig. 16 and Fig. 20 show particles from emulsions with and without gum arabic. The particles were very similar in appearance to particles from emulsions containing benzyl alcohol.

The retentions of methyl benzoate for emulsions with and without gum arabic are almost identical and very low as shown in Fig. 22.

3.4 Benzyl alcohol and methyl benzoate

A 50/50 mixture of benzyl alcohol and methyl benzoate was emulsified in the manner of the benzene, benzyl alcohol, and methyl benzoate containing emulsions and spray dried to show the effect of simultaneous evaporation of two oils and to simulate a flavor oil with more than one component. Electron photomicrographs of particles prepared from these emulsions with and without gum arabic are shown in Figs. 21 and 23 respectively. As is seen, these particles also have the appearance of the benzyl alcohol containing particles.

The total retention of oil for this mixture is shown in Fig. 24. Fig. 25 shows the retention of each of the oils when analyzed separately for emulsions with and without gum arabic. As in the case of the benzyl alcohol emulsions, addition of gum arabic caused a reduction of oil retention.

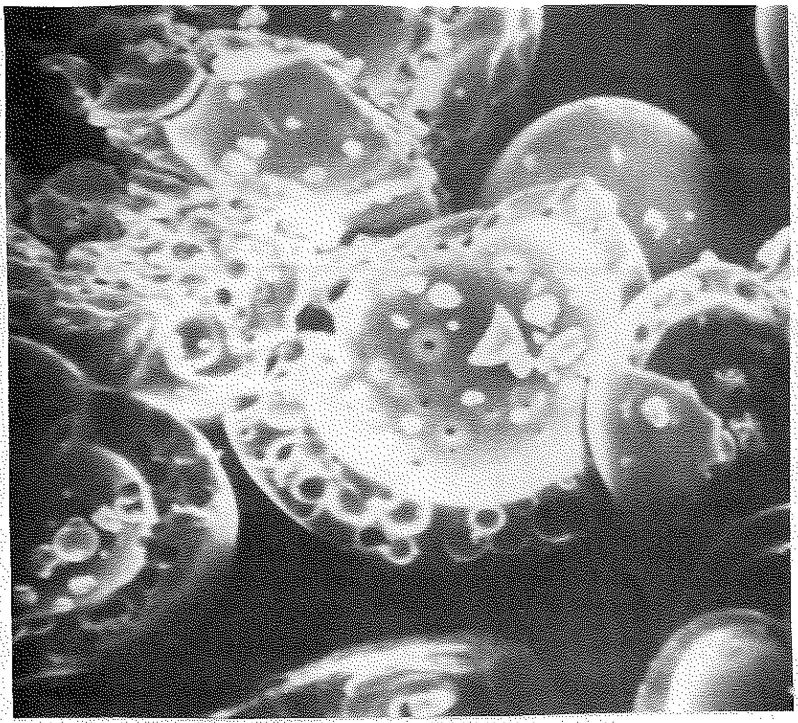


Figure 20. Particles Containing Methyl Benzoate and Gum Arabic (500x)

Figure 21. Particle Spray Dried from an Emulsion Containing a 50/50 Mixture of Benzyl Alcohol and Methyl Benzoate (500x)

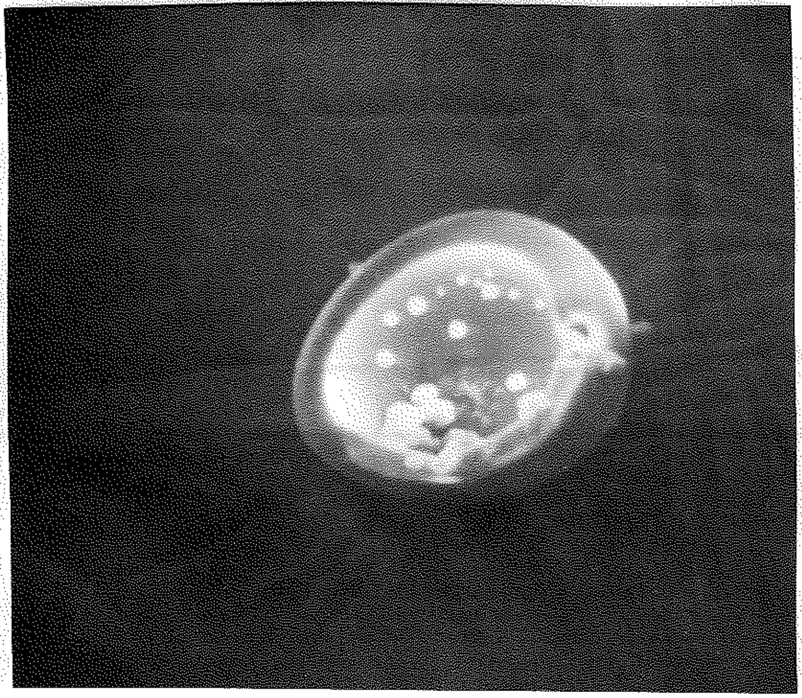
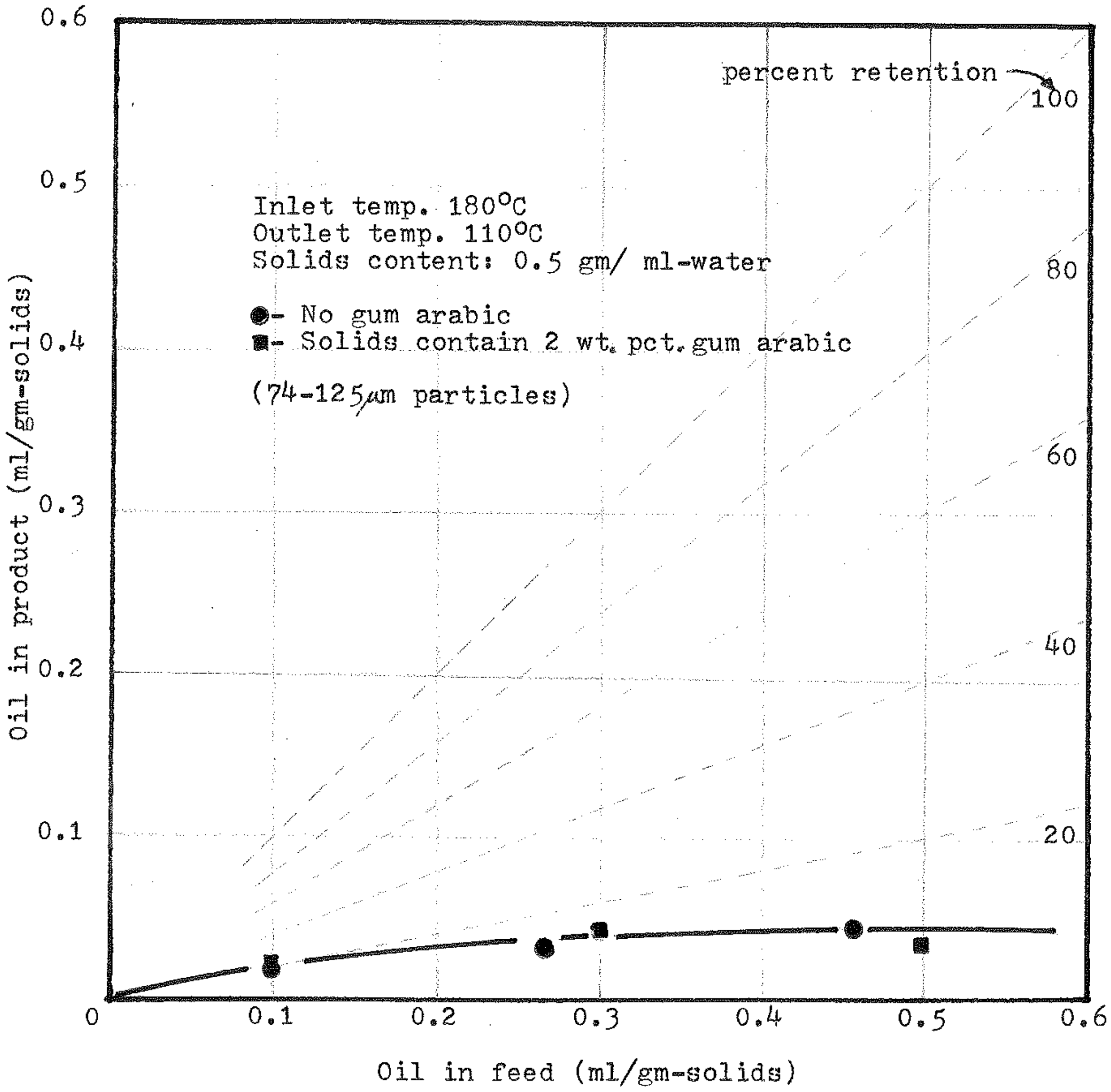


Figure 22. Retention of Methyl Benzoate from Emulsions with and without Gum Arabic



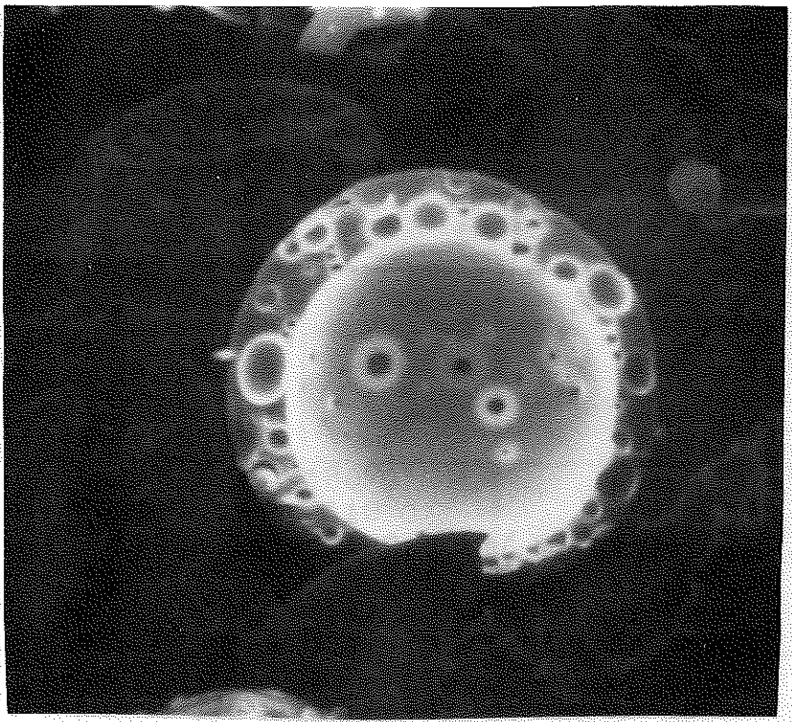


Figure 23. Particle from an Emulsion Containing a 50/50 Mixture of Benzyl Alcohol and Methyl Benzoate with Gum Arabic (500x)

Figure 24. Total Oil Retention from Emulsions Containing a 50/50 Mixture of Benzyl Alcohol and Methyl Benzoate with and without Gum Arabic

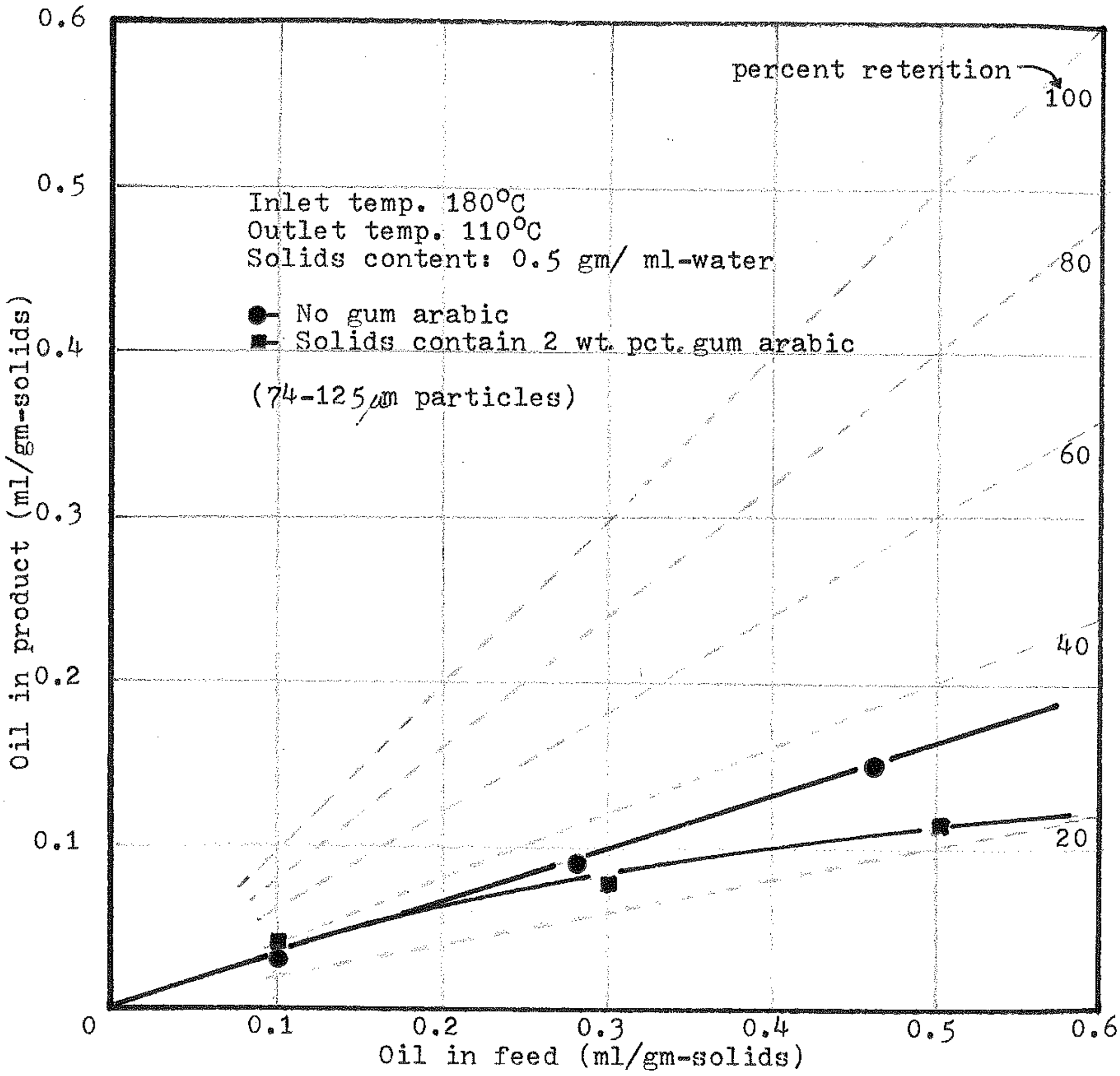
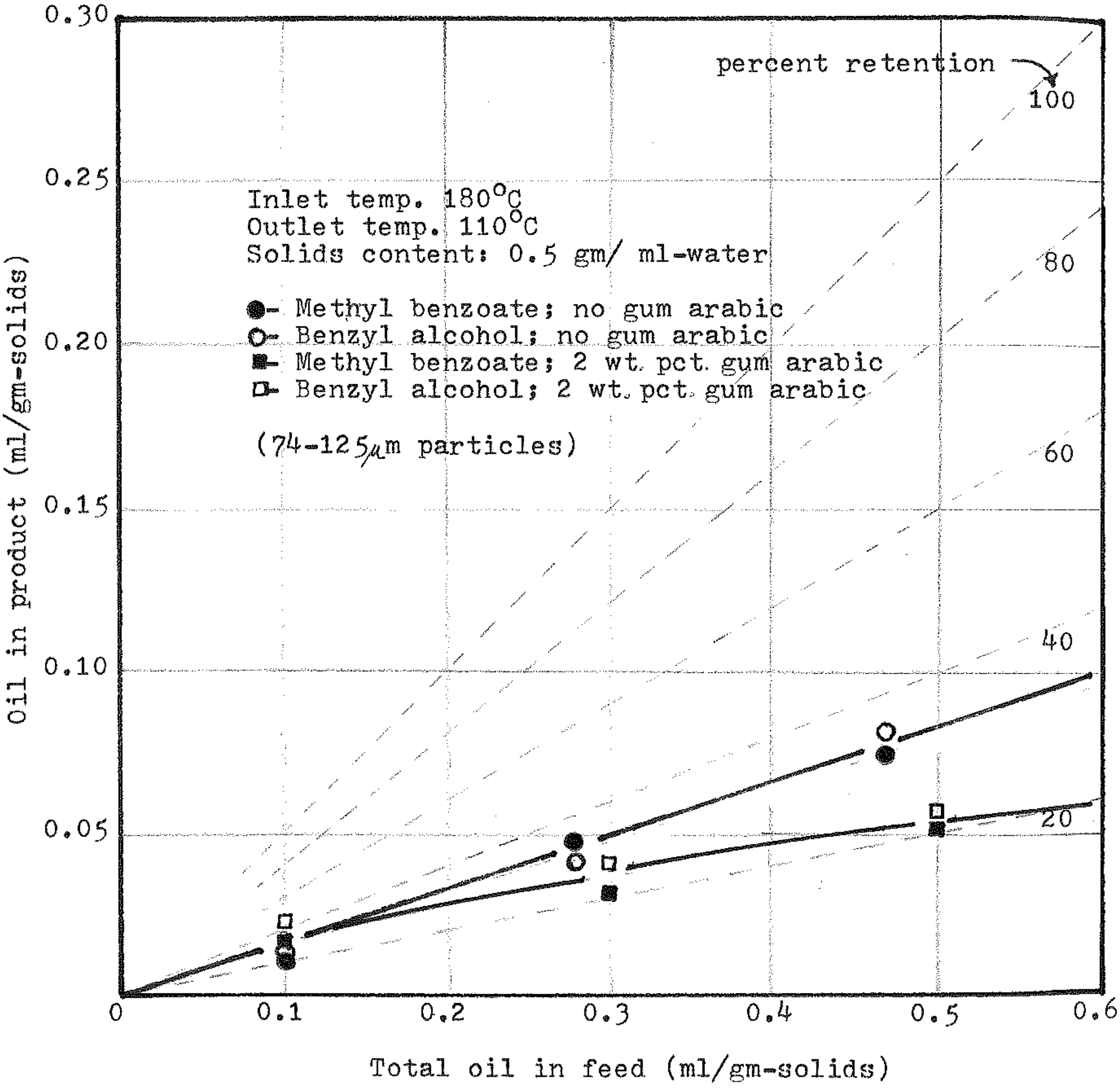


Figure 25. Retention of Each Oil from Emulsions Containing a 50/50 Mixture of Benzyl Alcohol and Methyl Benzoate with and without Gum Arabic



4. DISCUSSION OF RESULTS

4.1 Particle Structure

The four different particle structures, which resulted from the emulsions dried in this study, are a consequence of the drying conditions, wall material used, and the type and properties of the emulsified oils.

4.1.1 Drying Conditions

For a small dryer, such as the one used in these experiments, the number of different drying conditions possible is severely limited. Unless the particles are extremely small, either high drying temperatures, high solids contents, or long drying times are needed to ensure that the particles are dry when they reach the dryer exit. For photography purposes, and because the emulsion droplets were limited in size to 1 to 10 μm, it was necessary to prepare spray dried powders which had particles as large as 200 μm.

Trial runs with solutions having solids contents of 0.5 gm-"Mor-rex"/ml-water were dried at 160°C, 180°C and 220°C. At 160°C only a small amount of dry powder was recovered from the spray dried solution. The rest of the solids apparently remained in the tower as wall buildup because the solution had not completely dried. When the inlet temperature was 180°C, 60-80 percent of the solids was collected as dry powder. At 220°C, 80-90 percent of the solids were recovered but some charring of the solids was evident from the brown tint of the collected powder. For solutions having only 0.25 gm-"Mor-rex"/ml-water, drying at 180°C yielded from 20-30 percent of the total solids fed as dry product. Drying at 220°C raised the recovery in these solutions to 50 percent but again charring of the "Mor-rex" was was evident. It was decided to use the 180°C inlet and 110°C outlet temperatures for all drying runs.

Solutions of "Mor-rex" dried under these conditions gave hollow particles much like those shown in Fig. 11 of emulsions of benzyl alcohol and "Mor-rex". The larger particles showed evidence of puckering similar to the appearance of raisins but the smaller particles were generally spherical.

4.1.2 Wall material composition

Small additions of gum arabic to the emulsions greatly influenced the structure of the particles which resulted from spray drying. When "Mor-rex" was used as the sole wall material, no voids appeared in the walls of the particles from emulsions containing benzyl alcohol, methyl benzoate or a combination of these two oils. Apparently drying of the emulsions caused coalescence of the oil droplets contained in the drying particles.

The sequence of events during spray drying of these emulsions can be described as follows:

1. As drying occurs, water is removed from between emulsion droplets drawing them closer together.

2. This continues until the droplets are so close that the small amount of liquid and dissolved solids between the droplets is no longer a barrier to their coalescence.

3. Two droplets touch and immediately form a single larger droplet.

4. This continues until only one droplet remains where hundreds had been originally.

Microscopic examination of spray dried particles from benzyl alcohol emulsions clearly shows these large droplets entrapped in the central void of the particles.

When gum arabic is added to the emulsion, it is adsorbed along the oil-water interface of the emulsion droplets. Even when most of the water has been removed from between two droplets having this adsorbed gum arabic, it is unlikely that the two will coalesce because the gum represents an energy barrier to the two droplets actually touching. It is for this reason that gum arabic is effective as a stabilizer. The particles from emulsions with gum arabic have large voids in the wall where the still emulsified droplets are entrapped.

The rate of change in the average volume of an emulsified droplet due to coalescence can be represented by the following equation:*

$$\frac{d\bar{V}}{dt} = C \exp. (-E/RT) \qquad (1)$$

C is a constant given by:

$$C = (4/3)\phi \frac{kT}{\eta} \qquad (2)$$

$\bar{V}$ = average droplet volume

ϕ = fraction of emulsion which is oil

η = viscosity of the aqueous phase

E = "Activation energy" for coalescence

R = gas constant

T = absolute temperature

k = Boltzmann constant

At a given temperature, evaporation of water from an emulsion with dissolved solids increases ϕ and also η. If the effect of an increase in ϕ is greater than the viscosity effect, coalescence will take place more and more rapidly as water is removed. Addition of gum arabic has the effect of raising E and coalescence is retarded.

4.1.3 Type of oil

The spray dried particles of the benzene emulsions were very different in appearance from those particles from emulsions containing the higher boiling oils. For

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*This equation is from the author's personal class notes given by Professor M. Karel of M.I.T. in a 1973 course, in the department of Nutrition and Food Science entitled "Advanced Food Engineering".

emulsions with low "Mor-rex" contents, the particles from benzene containing emulsions had thick walls, small central voids and wall voids. None of these characteristics were seen in the particles from emulsions with high boiling oils. The particle structure is clearly related to the properties of the oil.

This structure of the benzene containing particles arises because during the drying process some of the emulsified benzene reaches the surface of the drop and is evaporated. This in turn tends to depress the temperature of the drop below that for removal of water only. At the lower temperature, water evaporates more slowly from the drop since the vapor pressure of water over the solution in the drop is lower. Decreasing the evaporation rate causes the drop to shrink as the surface of the drop recedes when the solids diffuse back into the drop. Finally the solution of the drop is so concentrated that further shrinkage no longer takes place and a surface skin is then formed. This description of the drying drop suggests why the drop has thick walls and a small central void. The wall voids are due to entrapped benzene. In this case, even without gum arabic, the emulsified drops do not coalesce because the solution is so concentrated by the time the surface film forms and water is drawn from between the drops that the drops do not draw very close together.

Early in the drying period, the high boiling oils are also exposed to the surface of the drop. However, since they vaporize rapidly only at high temperatures, they do not depress the drop temperature or water evaporation. This leads to a surface film quickly forming and the emulsion droplets coalescing as described above.

When the "Mor-rex" content is high, drops formed from emulsions of benzene experience ballooning and rupturing during drying; the higher boiling oils form the cenospheres seen with lower "Mor-rex" contents. The particles rupture because benzene is entrapped within the higher, more concentrated emulsions, and, as the temperature rises, it vaporizes, expands and, consequently causes the particles to balloon. The higher boiling oils are not vaporized by the temperatures reached by the drying drops.

4.2 Retention

Why some oils are retained much better than other oils remains somewhat unclear. Several possibilities can be suggested; e.g.:

1. Volatility determines the tendency of the oil to escape.
2. Solubility in the wall material influences how well the oil is retained.
3. Surface and interfacial properties of the oil

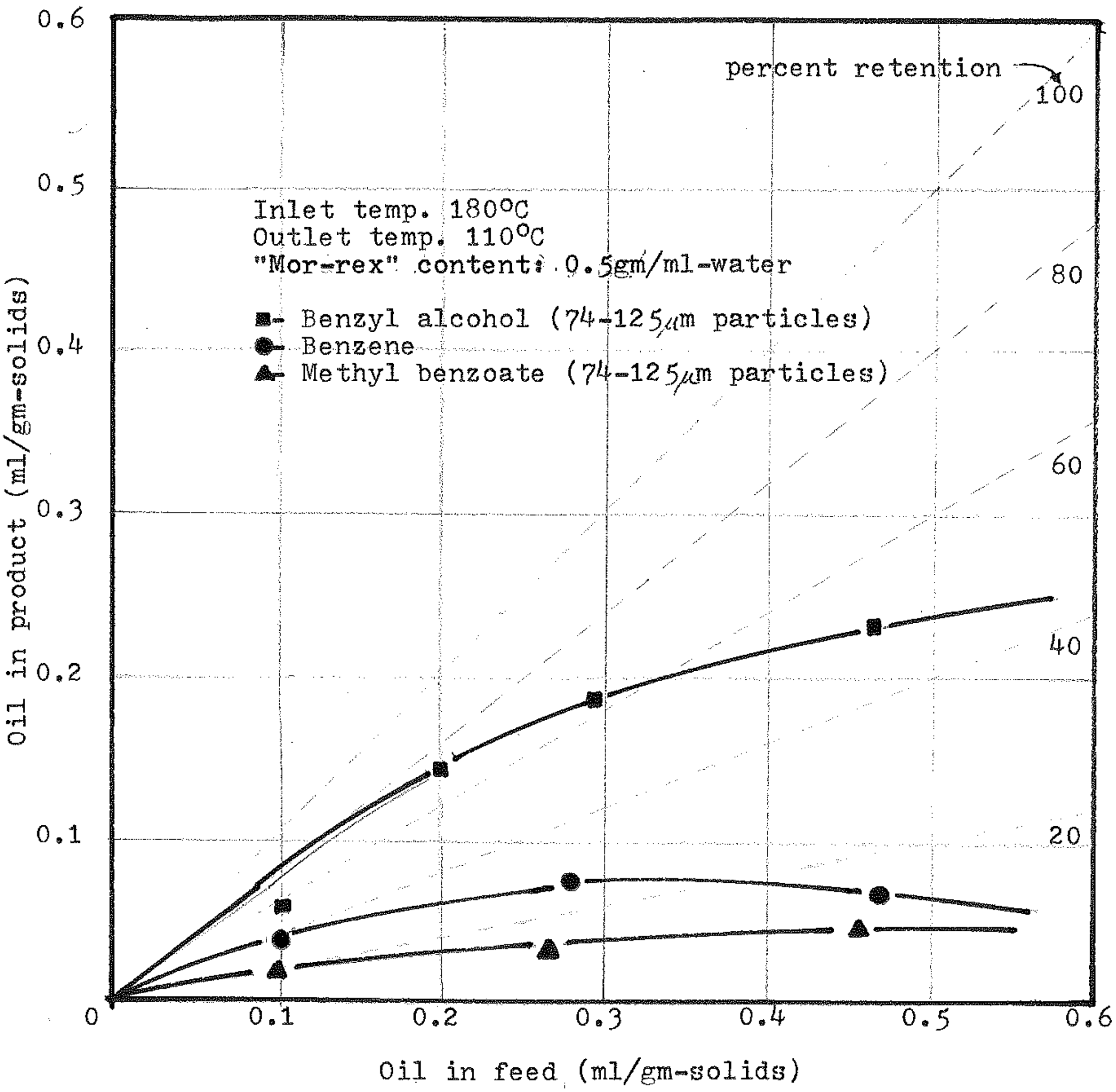
and aqueous solution affect oil loss during spray drying.

4.2.1 Volatility

It seems intuitively evident that highly volatile oils would be difficult to spray encapsulate because they would boil away at the temperatures necessary to evaporate the water in such a system. To some extent this is true, but Thijssen and Rulkens (13) have clearly shown that retention of an oil is not solely dependent on volatility They demonstrated for coffee extract solids, that volatility bore no relationship to the retention of various aroma oils.

The findings of the present study indicate that volatility does not explain why oils are lost during spray dry encapsulation. In Fig. 26 a comparison between the retention of methyl benzoate, benzene, and benzyl alcohol is made. Despite the fact that methyl benzoate boils more than 100°C higher than benzene, the recovery of methyl benzoate oil was lower. The reason for this difference is not entirely clear. However, the manner in which the particles dry may offer the explanation. During the drying of drops containing benzene, benzene is surely evaporating and perhaps, even boiling. Since the rapidly evaporating benzene removes heat quickly, the particles are cooled and the rest of the benzene contained in them does not vaporize

Figure 26. Comparative Oil Retention from Spray Dried Emulsions Containing Benzyl Alcohol, Benzene, and Methyl Benzoate



and is therefore retained. This would help account for relatively high benzene retention.

It is also apparent that, if volatility were the only consideration in oil retention during spray dry encapsulation, there would not be a drastic difference in benzyl alcohol and methyl benzoate losses since both boil at approximately 200°C. However, Fig. 26 shows how differently the two oils are actually retained.

4.2.2 Solubility

The solubility of the oil in the wall material can also influence retention. If the oil is not soluble in the wall material and if the semipermeable membrane which forms around the drying droplet is not pervious, then diffusion of the oil through the membrane cannot take place readily. This follows since the permeance of a nonporous membrane for a diffusing species is the product of the solubility and the diffusivity of that species.

The solubility parameter can give an indication of the relative solubility of a liquid in a polymeric material, see Billmeyer (5). Thijssen's (13) data seems to show a relationship between an aroma's solubility parameter and how well it is retained in spray dried coffee extract solids as shown in Table II.

TABLE II

Relationship Between Retention and Solubility Parameter for Various Aromas in Spray Dried Coffee Extract Solids

Aroma	Percent Retained	Solubility Parameter (cal/cm^3)$^{\frac{1}{2}}$
Ethylene	75	6.0*
Pinakolin	72	7.1ǂ
Acetone	65	9.7+
Methanol	50	14.5+
Water	3	22.5

* - Parameter for ethane

ǂ - Calculated value

\+ - From Billmeyer (15)

High solubility parameters seem to indicate that the material is not retained well.

The aromas in Thijssens (13) study, however, were only dissolved in parts per million and a similar relationship between solubility parameter and retention was not found for the oils investigated in this study. Where a combination of oils was used, both appeared to be lost to the same extent.

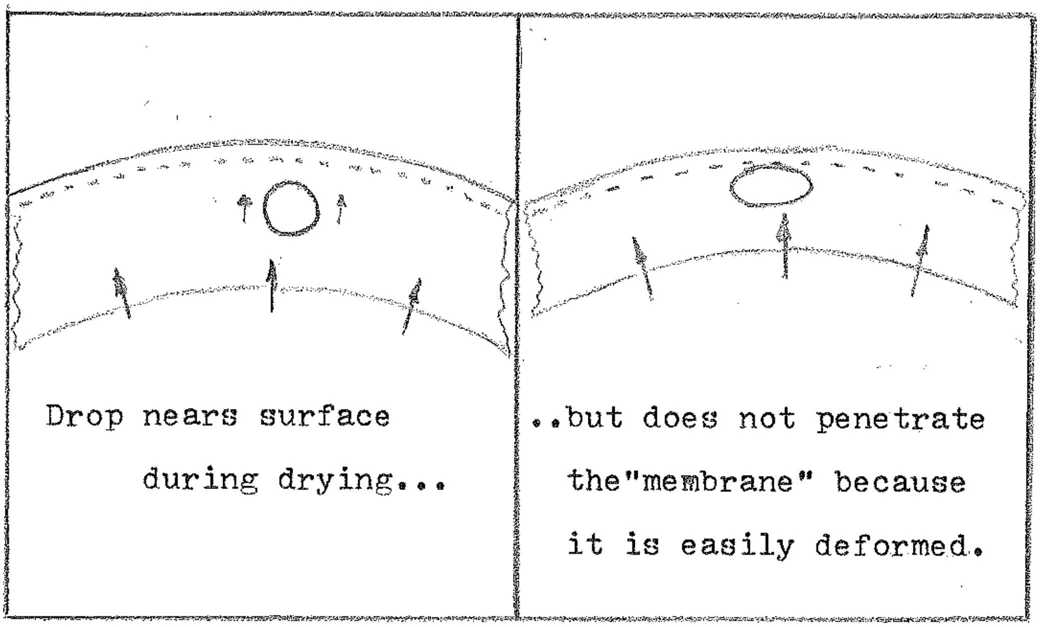
4.2.3 Surface properties of the oil

A third possibility is that the surface properties of the oil are the primary cause of loss in these emulsions. During the drying process, the emulsion undergoes considerable change. Once the surface film is formed, there is a flux of water, dissolved solids and emulsion droplets toward that surface as a result of the formation of the central void. What happens to the oil when it nears the surface of the drop may depend on its interfacial tension with the water.

Oils which have low interfacial tensions with aqueous solutions can be deformed from a strictly spherical shape easily because the deformation does not represent a large rise in energy of the system. When a droplet of such an oil nears the film-like surface of a drying drop, it will tend to deform rather than penetrate the film surface. For this reason oils of this type should be retained well. This is shown schematically in Fig. 27. On the other hand, oils which have a high interfacial surface tension will not deform as easily and have a much better chance of penetrating the surface film and being evaporated. This situation is shown in Fig. 28.

Benzyl alcohol emulsions likely have low interfacial tensions because this oil is partially miscible with water. Methyl benzoate should have a high interfacial tension with water because of its immiscibility. A mixture of these oils likely has an interfacial tension approximating an average of the two.

This theory can be used to explain why benzyl alcohol is retained better than methyl benzoate and

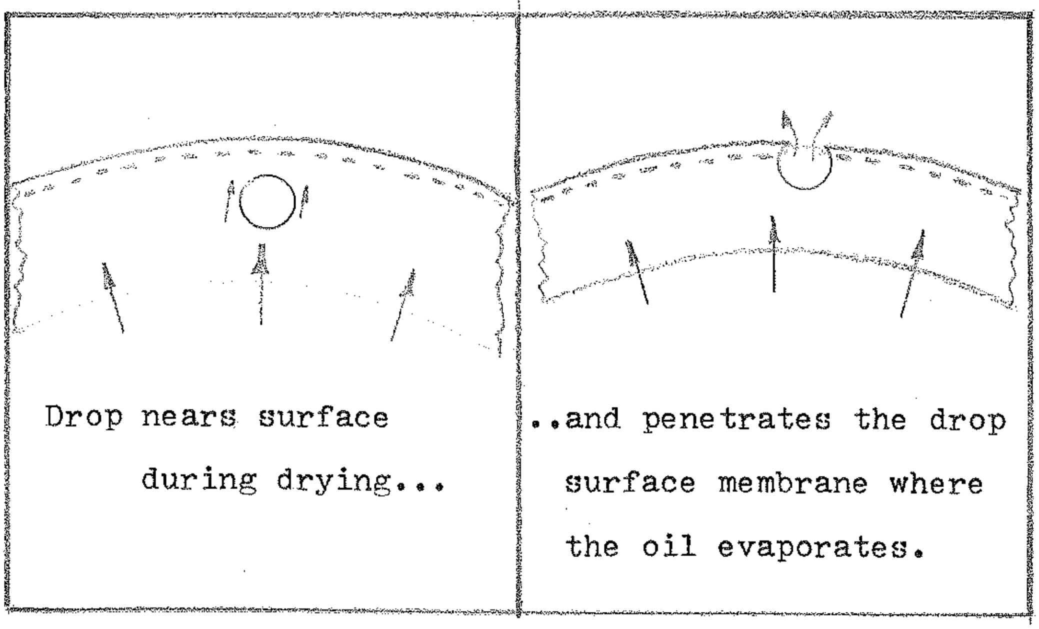


Drop nears surface during drying...

..but does not penetrate the "membrane" because it is easily deformed.

Figure 27. Proposed Mechanism Accounting for Relatively High Retention of Oils with Low Interfacial Tension

Figure 28. Proposed Mechanism for High Loss of Oils with High Interfacial Tension



Drop nears surface during drying...

..and penetrates the drop surface membrane where the oil evaporates.

also why a combination of the two oils is retained somewhere between the two as shown in Fig. 29.

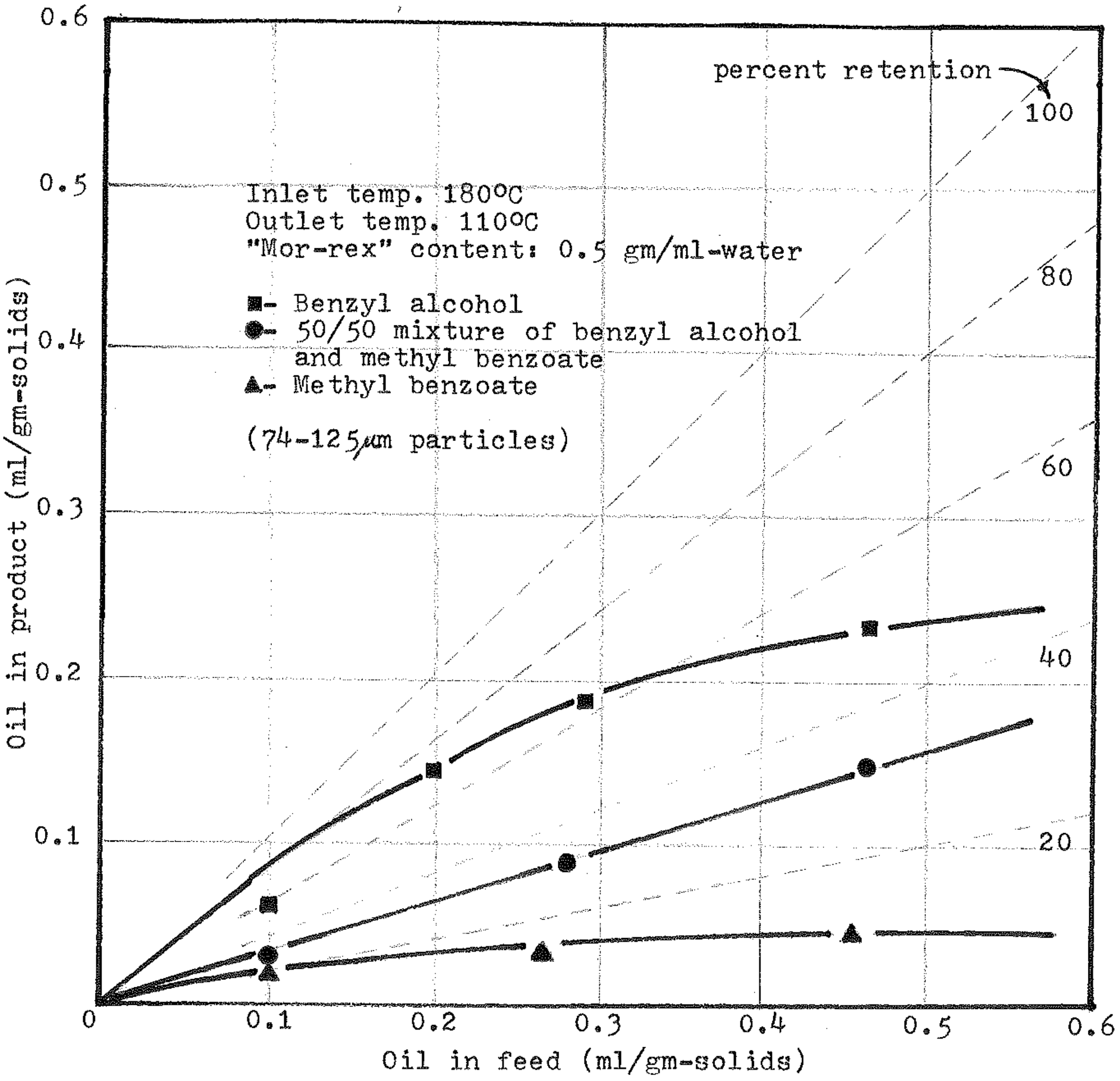
Since emulsion droplets are either exposed or not exposed at the drying drop's surface, this theory also predicts that the retained oil should have the same composition as the original oil when a miscible mixture of oils is encapsulated.

4.3 Size effects

It is worth explaining the observation shown in Fig. 17 of how the size of the particles affected the retention of oil.

Brooks (6) found that slowing the disk speed of an atomizer, and thereby increasing the drop size in the atomized spray, increased the retention of ethyl caprylate in gum arabic during spray drying. Ban's (4) results seem to indicate that disk speed did not greatly effect retention of peppermint oil in gum arabic. The results of the present study show that larger particles retained less benzyl alcohol than smaller particles from the same drying runs, as long as the particles were not broken. This is probably due to the fact that larger particles dry more slowly and therefore lose more oil before a surface film is formed. The very small particles consist largely of broken particles and therefore cannot be expected to show better retention. More concentrated emulsions probably result in more broken particles. Brooks (6) has also shown that addition of more oil

Figure 29. Comparative Oil Retention from Spray Dried Emulsions Containing Benzyl Alcohol, Methyl Benzoate, and a 50/50 Mixture of Benzyl Alcohol and Methyl Benzoate



to the emulsions resulted in spray dried particles which had lower oil retention. His findings are probably due to an increase in broken particles.

4.4 Solids content

The most thoroughly documented effect on retention is the effect of increased solids in the emulsion. The results of this study show, for benzyl alcohol, that increasing the solids content in the original emulsion increases the retention as shown in Fig. 18. Several other investigators have also shown that increasing the solids in the feed increases the retention of the oil; e.g. Ban (4), Brooks (6), Thijssen (13). This is presumably due to the fact that in the more concentrated solutions, the surface film which is responsible for retaining the oil is established earlier (8).

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results of this study the following conclusions were drawn:

1. The losses of oil incurred during spray drying of emulsions are not solely dependent on the volatility of the oil.
2. The solubility of the oil in the wall material is not an important factor in the loss of oil.
3. Gum arabic stabilizes the emulsions and prevents coalescence of the emulsion droplets during drying, but does not necessarily improve the oil retention, and actually reduces the retention of benzyl alcohol.
4. Higher solids contents in the feed solution improve benzyl alcohol retention, but do not improve benzene retention.

5.2 Recommendations

This study can only be considered a first step in determining the reason for loss of oil during spray drying. The following recommendations are made concerning future studies which may be helpful in understanding the oil loss phenomena.

1. A more complete series of oils with a wide

variety of volatilities should be encapsulated and the particles should be examined with an electron microscope to determine how volatility of the oil affects their structure.

2. More oils with differing solubilities in water should be spray encapsulated in this method and comparisons of their retentions should be made.
3. Different solid materials should be used as the encapsulant to determine how each affects the retention.
4. Additions of surfactants should be made to determine how these affect oil retention.
5. A homogenizer should be used to prepare emulsions with finer droplet size, and to see how this affects retention.

APPENDIX

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Sample Calculation of Benzene Retention

An emulsion which had an oil content of 0.3 ml-benzene/gm-"Mor-rex" was spray dried. Before entering the spray dryer 0.02 ml of benzene/gm-"Mor-rex" was observed to have spontaneously separated out. The original oil content was therefore determined to be 0.28 ml/gm-"Mor-rex".

20 ml of water was added to the boiling flask of the distillation apparatus, and 3.23 gms of the spray dried powder was added. After reassembling the apparatus and distilling the benzene over, the observed depth of benzene in the collection tube was 1.10 cm. Figure 6 was used to determine that this corresponded to 0.21 ml of benzene. The benzene content calculated on a benzene free basis is then given by the following equation:

$$\frac{\text{ml benzene}}{\text{gm "Mor-rex"}} =$$

$$\frac{\text{observed volume of benzene (ml)}}{\text{gm of original sample} - (\text{density of benzene (gm/ml)} \cdot \text{volume of benzene (ml)})}$$

In this case;

$$= \frac{0.21}{3.23 - (0.88 \cdot 0.21)}$$

$$= 0.069 \text{ ml/gm}$$

On a percent retained basis;

$$\text{percent retained} = 100\% \; (0.069 / 0.28)$$

$$= 24.6\ \%$$

Sample Calculation of Benzyl Alcohol Retention

An emulsion containing 0.30 ml-benzyl alcohol/gm-

"Mor-rex" was spray dried, no oil was observed to have separated out. The spray dried powder containing benzyl alcohol was seive-separated into various size fractions, and then a small amount of the 74-125 μm particles were stirred in a beaker of benzene and subsequently filtered out of the benzene. After 15 minutes of air drying, the particles were placed in an oven at 95°C for 15 minutes. The washed and dried particles were then weighed and dissolved in a volumetric flask containing 25 ml of 47.5 weight percent ethyl alcohol and water. The particles weighed 1.64 gms., they were assumed free of moisture.

One ml of the solution was volumetrically mixed with 9 ml of 95 weight percent ethanol in a test tube, the test tube was thoroughly shaken, stoppered and centrifuged. Following centrifugation, exactly one ml of the supernate was transferred to another test tube containing 9 ml of 95 weight percent ethanol. This tube was thoroughly shaken, and an analysis was taken of this liquid using the ultraviolet spectrophotometer. The reference solution was prepared from "Mor-rex" in a manner identical to the sample. The absorbance as indicated by the peak height from 280-257nm was determined to be 0.185 absorbance units. Using Figure 7 it was determined this corresponded to 0.00011 ml benzyl alcohol/ml solution. Since the original solution was diluted 100 fold before analysis this corresponded to 0.011 ml benzyl alcohol/ml of original solution, and since there was

25 ml of original solution 25 x 0.011 or 0.275 ml benzyl alcohol were contained in the dry powder.

The content of benzyl alcohol on a dry solids basis was determined by using the following equation:

$$\frac{\text{ml benzyl alcohol}}{\text{gm "Mor-rex"}} =$$

$$\frac{\text{observed volume of benzyl alcohol (ml)}}{\text{gm of original sample} - \left(\begin{array}{l} \text{density of benzyl alcohol(gm/ml)} \\ \text{volume of benzyl alcohol(ml)} \end{array} \right)}$$

In this case;

$$= \frac{0.275}{1.64-(1.04 \cdot 0.275)}$$

$$= 0.203 \text{ ml/gm}$$

On a percent retained basis;

$$\text{percent retained} = 100\% \; (0.203 / 0.30)$$

$$= 67.7 \%$$

The determination of methyl benzoate was done exactly like that for benzyl alcohol above.

APPROVED:

E. J. Crosby

Dr. E. J. CROSBY

Professor of Chemical Engineering

DATE:

26 August 1976