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# A Study of Medium and High Internal Phase Ratio Water/Polymer Emulsions

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Medium and high internal phase ratio water/polymer emulsions were studied utilizing scanning electron microscope techniques. Results are reported for the geometry and distribution of droplets for water/polymer ratios from 1/1 to 9/1. Electron micrographs confirm those models which predicts polyhedral droplet formation at high internal phase ratios.

## INTRODUCTION

The properties of high internal-phase ratio emulsions have been studied and reported (1-3). Although these studies have proven usefully predictive in some cases, (4) it has not been possible to examine the geometry of the emulsion particles. Photomicrographs are of little value since normal microscopic examination lacks sufficient resolution and depth of focus to reveal details of the microstructure. This paper presents a scanning electron microscope (SEM) study of solid-polymer-water emulsions for different water/polymer ratios in the medium internal-phase and high internal-phase emulsion ranges.

## EXPERIMENTAL

Recently, a styrene-based resin system was developed for the production of inexpensive castings where water (which acts as a filler) is emulsified in the resin prior to curing. A sample of this type of resin, designated WEP 661-P, was obtained from Ashland Chemicals Co. for use in this study.

Usually a ratio of about equal parts of water and resin is recommended in preparing acceptable castings. However, it was found that as much as 4 parts of water could be added per part of resin prior to curing, and in some instances ratios as high as 7/1 were obtained. The initial emulsion series was prepared as follows:

The apparatus consisted of a ring stand, a beaker clamp, a variable speed stirrer and controller, and a stainless steel split-disk stirrer. A 400-ml, tall-form (dye pot) beaker was clamped in position with a split-disk stirrer just clearing the bottom of the beaker.

Sixty milliliters of WEP 661-P resin (Ashland Chemical Co.) were placed in the beaker and 60 ml of tap water were added slowly while stirring. When all the water appeared to be taken up by the resin, stirring was stopped and a 31-ml sample was withdrawn into an aluminum weighing dish, labeled (1/1). Two drops of Lupersol DDM (Wallace and Tiernan Co.) were added, the resin and catalyst mixed, and the sample was then allowed to cure.

An additional 45 ml of water was added to the mixture in the beaker with stirring. A second 30-ml sample was withdrawn, labeled (2/1), catalyzed and cured.

Similarly 35 ml more of tap water was added and sample (3/1) (28 ml) was withdrawn and treated as before. Then 28 ml of tap water was added and sample (4/1) withdrawn. Only about 12 ml more water could now be mixed in before the emulsion became unstable.

Samples 1/1, 2/1, 3/1, and 4/1 cured to tough, opaque solids in 24 hr. They contained 50, 66.6, 75, and 80% water by volume, respectively.

The use of a dye-pot beaker and a split-disk stirrer to produce emulsions of this kind is a useful technique where small quantities of emulsion are required. However, as the emulsions become more viscous, it is necessary to vary the position of the stirrer within the dye pot and occasionally to work the stirrer up and down so that all portions of the samples are thoroughly mixed. Care must be taken in adjusting the speed of the stirrer so that the emulsion is not subjected to excessive shear since high shear may tend to break the emulsion.

A convenient technique for producing high internal-phase ratio emulsions in the laboratory makes use of a planetary type mixer (Hobart Kitchen Aid Mixer). This apparatus mixes the emulsion thoroughly without subjecting it to locally excessive shear. Emulsions containing 4/1 and 5/1 water/resin ratios were prepared as follows:

Twenty ml of WEP 661-P were placed in the mixer bowl and 100 ml of water were added slowly over a period of about 5 min while stirring. When all the water had been added, catalyst was introduced, the mixture was stirred, and a sample taken and allowed to cure for 24 hr at room temperature.

After curing, all samples were fractured transversely and further fractured so that a roughly cubical sample, approximately 3 mm on a side, could be obtained from near the center of the cured piece. Each sample was

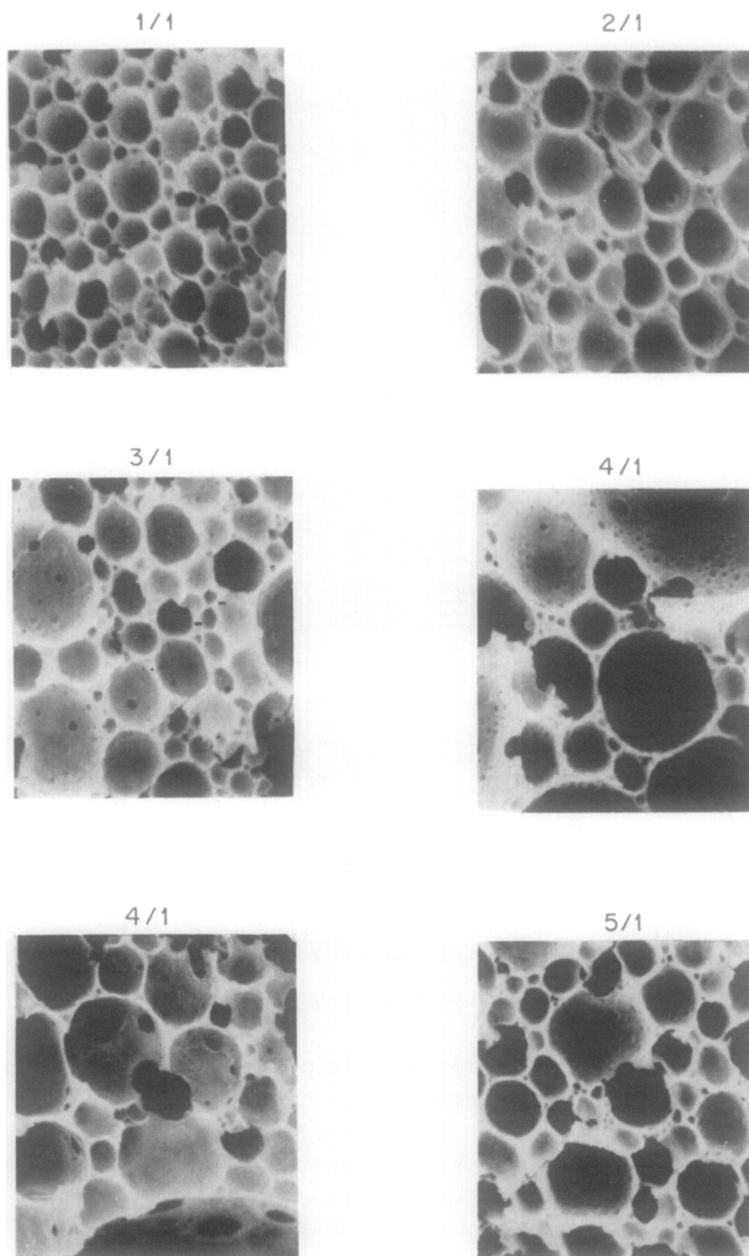
cemented to a copper mount and metallized utilizing standard techniques. The metallized fractured surfaces were examined using JEOLCO JSM-2 scanning electron microscope.

## RESULTS AND DISCUSSION

Figure 1 shows representative micrographs of the six samples described above. As expected the emulsion droplets in the 1/1 sample are essentially spherical and the walls between the droplets are quite thick. As the water ratio increased to 5/1 the geometry changes and the droplets are observed to approach a polyhedral configuration.

Prints of the micrographs from Fig. 1 were prepared and particle size counts made (Zeiss T6Z-3 Analyzer) in an attempt to obtain particle size distributions. The distributions were found to be bi- or trimodal rather than Gaussian. There were no obvious correlations between distributions and properties. Upon further study, a behavioral pattern became evident. A comparison of Figs. 1 and 2 assists in highlighting this development. Figure 2 shows a schematic representation of progressive changes in droplet geometry as a function of increased water content in the emulsion.

The emulsions were made by adding successive portions of water to an already prepared emulsion with a period of stirring after each water addition. The 1/1 samples, therefore, show a relatively monodisperse pattern similar to perhaps A or B in Fig. 2. In the micrograph of the 2/1 sample, one can see large droplets resulting from the recent additions of water and an array of small droplets from the previous additions. This same effect appears in the 3/1 samples. They resemble C, D, and E of Fig. 2. However, as more water is added, a point is reached where the emulsifier system will no longer accept it. At this point, droplets begin to recombine resulting in a polymodal distribution of large recombined droplets and smaller, as yet uncombined, droplets. This process proceeds until virtually total breaking of the emulsion has occurred. This is diagrammed in F and G of Fig. 2 and the beginning



of such a process can be seen in the 4/1 micrographs of Fig. 1. At higher phase ratios, the crowding of the droplets results in polyhedral shapes but the general coalescing mechanism still holds as seen in H and J of Fig. 2 and in the 5/1 micrograph of Fig. 1.

In order to investigate these phenomena somewhat more completely, a new series of emulsions was prepared. Some results, both at high and low magnifications, are shown in Fig. 3. The two top micrographs are of a 1/1 emulsion where the left sample was cured im-

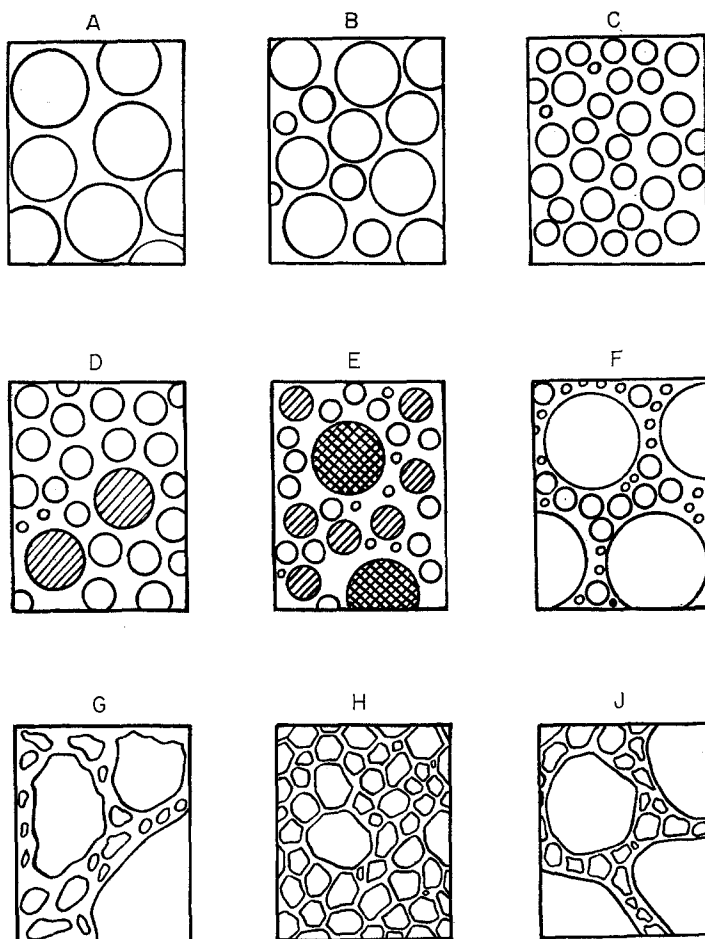


Fig. 2. Progressive changes in droplet geometry.

mediately and the right sample was allowed to stand for 1 hr before curing. Indications are that this emulsion is stable for at least this period of time and no particular differences can be noted. The middle left micrograph shows a  $780\times$  magnification of the portion of the above sample and demonstrates that the emulsion droplets were essentially spherical and the walls between droplets quite thick. The right hand middle micrograph is a  $780\times$  shot taken of a sample of the same emulsion which was stirred vigorously for at least 5 min before being catalyzed and cured. Note that small droplets are trapped in the walls between the large droplets indicating that some recoalescence has occurred and that this sample was

perhaps overstirred. The effect is even more pronounced in a 2/1 emulsion made at the same time. The difference in magnification shows that the drops are much larger and there is extensive recoalescence similar to sketch F or G in Fig. 2.

An experimental matrix was employed to investigate the effect of amount and type of agitation. Six additional emulsion samples were made, scattered through the matrix to yield as much information as possible. The object of this group of tests was to determine the difference in behavior of the emulsion system when made with the split-disk stirrer or when made with the Kitchen Aid Mixer, and also to determine the optimum amount of

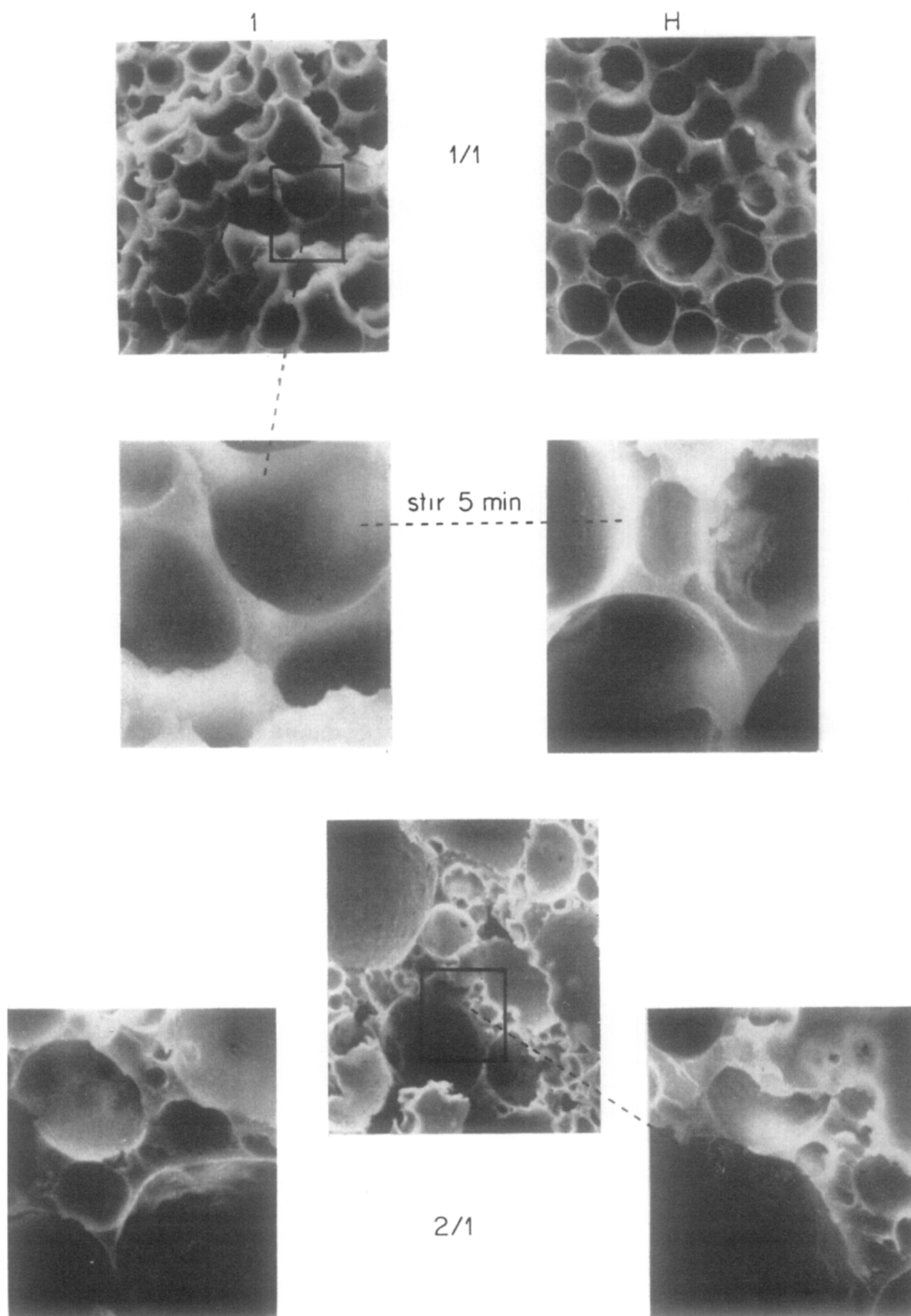


FIG. 3. Effect of time and stirring. Top  $\times 234$ ; middle  $\times 780$ ; bottom left  $\times 234$ ; bottom middle  $\times 780$ ; bottom right  $\times 234$ .

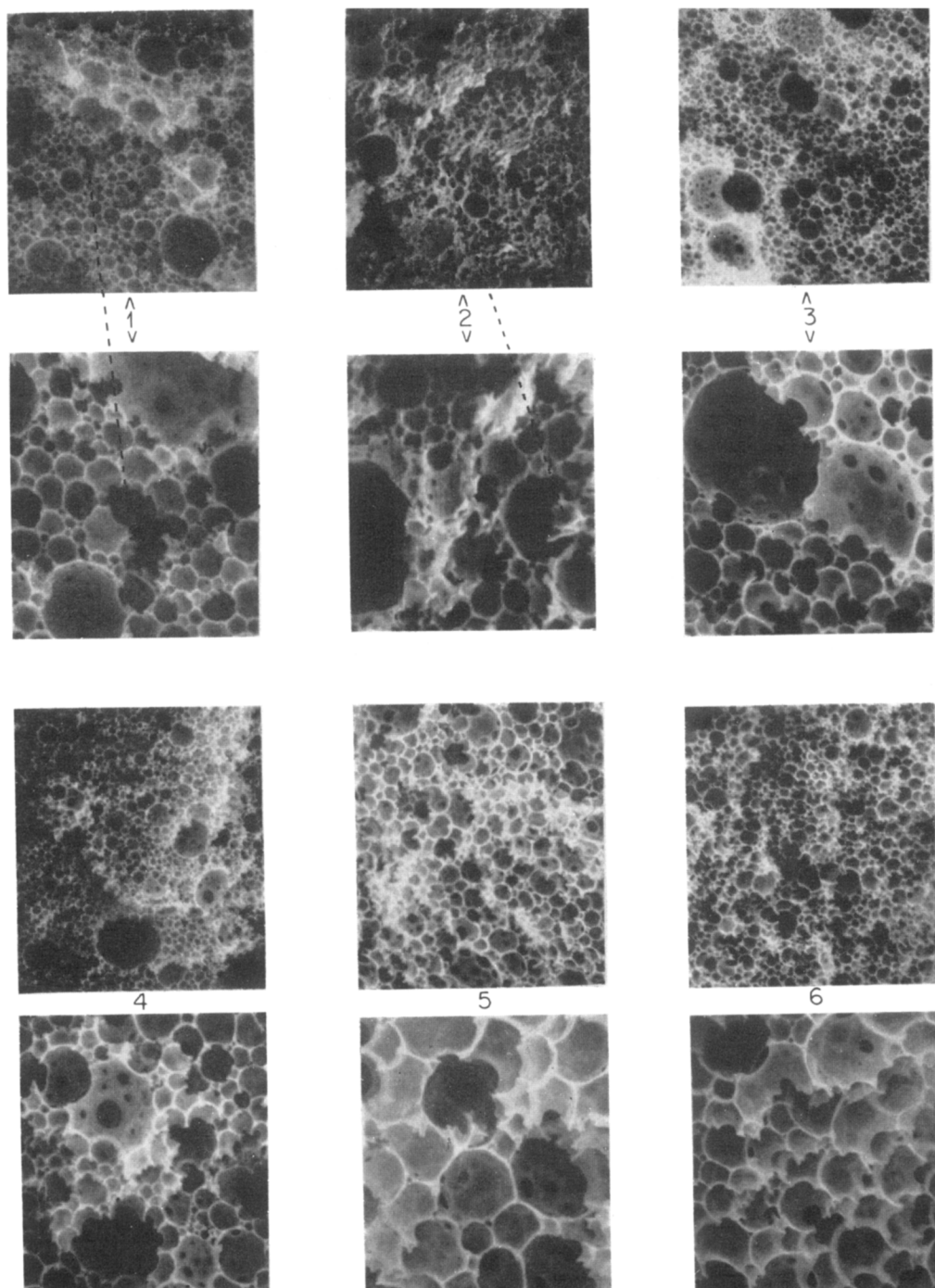


FIG. 4. Effect of emulsification method and phase ratio. First row (Top)  $\times 213$ ; second row  $\times 710$ ; third row  $\times 213$ ; fourth row  $\times 710$ .

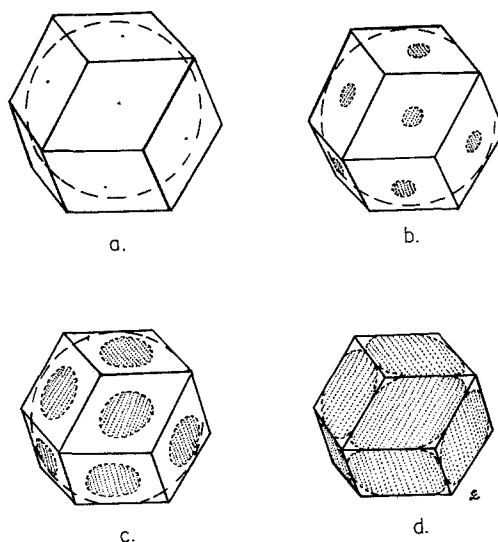


FIG. 5. Transition forms from sphere to polyhedron.

stirring with each device. It was necessary to add an auxiliary emulsifier [Y-4119, Petrolite Corp.) to the resin system, as well as a small amount of monomeric styrene to the WEP 661-P, in order to achieve higher ratios of water to resin. By using this modified system, 9/1 ratios were obtained. Figure 4 shows micrographs of the resin samples at 213 and 710 $\times$ . Samples 1 and 2 show the effect of additional stirring at a 6/1 ratio using the dye-pot mixer. The resin in Sample 2 was stirred for 5 min more than in Sample 1. It can be seen that recoalescence of droplets has started in Sample 2, and may even be beginning in Sample 1.

Samples 3 and 4 show the same resin water systems mixed with the Kitchen Aid mixer. This is a considerably lower shear operation. In Sample 3 the emulsion is definitely undermixed with a number of large droplets. Sample 4 shows a much more homogeneous mixture but still reveals the presence of large droplets. There is no evidence of recoalescence in Samples 3 and 4. Note that Sample 2 resembles F or G of Fig. 2 while Samples 3 and 4 resemble D or E or perhaps H.

Samples 5 and 6 were made with the Kitchen Aid mixer, Sample 6 being stirred for 5 min more than Sample 5. These two pictures are

particularly interesting since they show an emulsion which contains 90% internal phase (9/1). Here again, Sample 5 seems to be a trifle undermixed and Sample six nearly optimum. Note that the droplets are definitely polyhedral and seem to follow the general shape trends postulated in a previous article (2).

#### CONCLUSIONS

The SEM provides a technique for studying the geometry and distribution of droplets in crosslinked water-polymer emulsions. Information can be obtained which can be useful in optimizing a given mixing procedure. The results of this study are consistent with those models that predict polyhedral droplet geometries in high internal-phase ratio emulsions.

Classical emulsion theory stated that emulsions would either invert at or near the spherical close packing ratio of 74 + % or emulsions with higher ratios would have to be highly polydisperse. In a previous article, a theoretical analysis was given which showed that polyhedral, monodisperse droplets would require less total energy in the system than highly polydisperse spherical configurations (2). The mathematical analysis of the monodisperse,



polyhedral systems showed that emulsion properties could be expected to change critically at certain values of the phase ratio,  $\phi$ . Experimental work has tended to confirm at least the general outlines of this theory (2, 4). These SEM micrographs are, we believe, the first time anyone has been able to actually see the structure of an high-internal-phase ratio emulsion. The structures shown in these micrographs appears to confirm the mathematical theory amazingly well. It will be noted that the most stable emulsions are the most nearly monodisperse and that polydispersity occurs only in the early stages of mixing or after coalescence has begun. Illustration 6 of Fig. 4 is particularly revealing in that it shows an emulsion with 96% internal phase. This emulsion, while it is not completely monodisperse, approaches monodispersity quite closely and the higher magnification shows that the droplets are indeed approaching a polyhedral shape and resemble the predicted transition shapes illustrated in Fig. 2 of Ref. (2). This figure is reproduced here as Fig. 5.

If one visualizes Fig. 5c as viewed from the inside, one gets a picture of a spherical cavity

with 12 circular flattened areas. Since the rhomboidal dodecahedron has two kinds of vertices, one where three edges come together and one where four edges come together, the flattened spots will tend to group themselves into groups of three, four, or five depending on the point of view of the observer. The five spot configuration is illustrated in Fig. 5. One can also pick out the three- and four-spot configurations from the same illustration. Looking at Fig. 4 (6), one can see on the inside of a number of the droplets typical three four- and five-spot configurations. Similar configurations can also be seen in Fig. 4(5).

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