Particle Size in Suspension Polymerization

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Control of size and geometrical form of densely cross-linked hydrocarbon polymers yields fluid spherical powders useful as dielectrics and in rheological studies. Such studies also bear on polymer forms important in ion exchange resins.

Several significant factors influencing the preparation of polymer spheroids have been established on a semiquantitative basis: Polyvinyl alcohol proved to be a highly efficient stabilizer for polymer spheroid preparations. Under comparable conditions, (*a*) high molecular weight grades, (*b*) partially hydrolyzed grades, and (*c*) high concentrations of stabilizer were associated with spheroids of lower mean diameters. These generalizations cover suspension stabilization down to roughly 0.1% stabilizer. The concentration limits where suspending action begins are, however, of special interest. Here it was found that the number of polyvinyl alcohol molecules present became important—that is, for equal weight concentrations in the vicinity of 0.005%, low molecular weight polymer (19,000) produced stabilized (although large) spheres whereas usual high molecular weight polymer (95,000) was ineffective.

Close to the maximum possible yield of well-formed spheroids was reproducibly obtained in narrow size distribution and with average spheroid diameters ranging from 5 microns to several millimeters in diameter—a thousand-fold variation in dimensions.

MECHANICAL agitation, suspendants, viscosities, and interfacial tension exert a pronounced effect on the ultimate particle size distribution, average particle size, and extent of agglomeration in a suspension polymerization product. The object of this study was to separate effects of some of these variables. Several dispersants or suspension stabilizers, as they are commonly called, were examined with particular emphasis on their effectiveness in providing discrete spherical particles of 0.3 to 0.4 mm. average diameter. Polyvinyl alcohol was studied in greatest detail, as the various grades available allowed considerable latitude in the regulation of particle size.

The mechanics of forming suspensions (*15*) of insoluble polymerizable "oils" in an aqueous system is illustrated schematically in Figure 1. Mechanical agitation subjects the monomeric substance to a viscous drag causing elongation to a threadlike form with subsequent degeneration into drops (*16*). Simultaneously, *through the reverse process of coalescence, the drops tend to revert to the original monomeric mass.* In a simple mechanical suspension under a constant overall rate of shear, a dynamic equilibrium is quickly established. Clusters of globules held together by weak residual forces, but not fused, tend to disperse under the disruptive stress of an agitated system. Effective surface-active agents also will deflocculate these aggregates (*2*). With the onset of polymerization and the accompanying increase in viscosity there is greater resistance to distortion of droplets due to viscous drag but unfortunately a greater tendency toward aggregation through collisions with neighboring globules. The latter phenomenon is minimized by suspension stabilizers which are selectively adsorbed at the interface, serving as protective [illegible] of [illegible] particles. This is illustrated schematically in the [illegible] enlarged droplet in Figure 1 supporting an adsorbed [illegible] of polyvinyl alcohol.

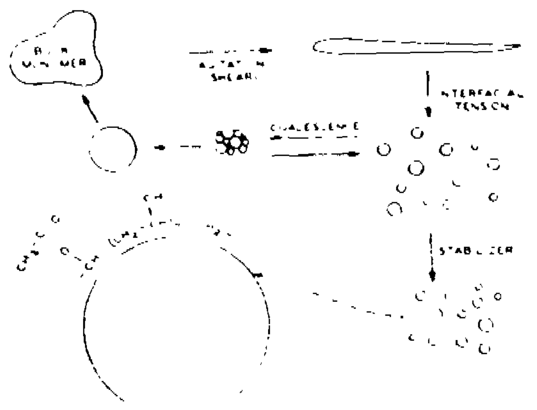

Figure 1. Schematic Diagram of States of Dispersion in Suspension Polymerization of Technical Divinylbenzene (*16*)

Only a limited number of monomers, most vinyl compounds, possess properties *suitable* for suspension polymerization (*1*). Methyl methacrylate, styrene, and some styrene derivatives were examined casually in this study, but the data presented were obtained from a mixture of isomers of ethylvinylbenzene and divinylbenzene. This was supplied by the Dow Chemical Co. under their code number, Q302.1. It consisted of over 40% divinylbenzene as determined by total unsaturation. Except in a few trial runs, the inhibitor, *t*-butyl catechol, was not extracted before polymerization, since it had little effect on the end result. It did, however, cause an appreciable induction period at moderate reaction temperatures (*5*) as shown in Figure 2.

The principal stages in the polymerization of a suspended globule of divinylbenzene mixture are illustrated schematically in Figure 3. The first and most critical phase is characterized by rapid viscosity increase due to the developing polymer chains. Here, *the conditions favorable for globular clustering are* [illegible] prominent, and the need for some sort of stabilization is [illegible] urgent. The intermediate phase is reached when the growing polymer chains have permeated throughout the globule [illegible] resulting in a gelatinous structure of polymer swollen by monomer. In the final stage [illegible] [illegible] has extended to a compact cross-linked [illegible] network manifested by [illegible] polymer. The level of the [illegible] in Figure 2 represents the [illegible] initial stage, the gelatinous phase is the steep portion, the upper end of the curve coincides with setting into a [illegible] polymer.

Previous investigators [illegible] have observed that suspension polymerization is merely [illegible] polymerization on a reduced scale. In this respect it differs sharply from typical emulsion polymerization where the [illegible] initiation are considered to be situated at the interface [illegible] in the aqueous phase ([illegible]). Hence, presumably [illegible]

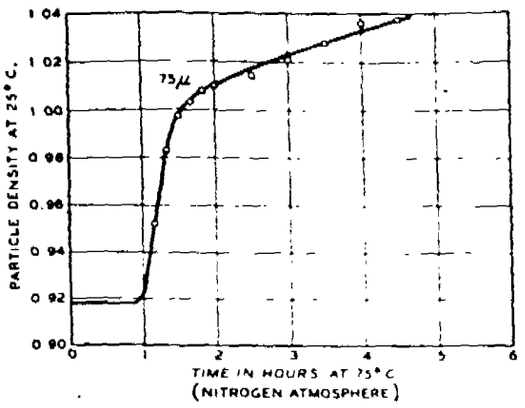

Figure 2. Rate of Polymerization of Divinylbenzene Mixture as Determined by Particle Density Change

An induction period of approximately 1 hour is indicated by horizontal portion of particle density curve

sensitivity (rate and modification of emulsion systems to the scope of stabilizer is absent in suspension polymerizations

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Factors that do, however, influence the rate of polymerization of the divinylbenzene mixture are given in Figures 4 and 5. They are self-explanatory. Retardation due to atmospheric oxygen varies according to the degree of agitation as exhibited by its correlation with particle size in Figure 5. The densities were determined by flotation.

The kind of reactor shown in Figure 6 was used throughout. It comprised a spherical flask fitted with a *condenser*, *centered* centrifugal impeller, and a thermometer for measuring the suspension temperature. Heat was furnished by a water bath. With reactors of 2 liters or more capacity and centered stirring it was necessary to resort to a centrifugal impeller since the monomer (density 0.92) had a tendency to collect in the vortex. This design of reactor was certainly not suited for optimum efficiency (*1*) in forming dispersions, but it proved convenient and entirely *adequate for the purpose of evaluating relative effectiveness of* stabilizers.

The ratio of water to monomer was maintained at approximately 12 to 1 by volume. Although greater ratios of water to monomer favor increased yields of discrete spheroids, it was possible to work with equal amounts of each without encountering excessive clustering in the product.

Both inorganic and organic classes of suspension stabilizers were examined. The inorganic materials such as bentonite and tricalcium phosphate were associated with opaque polymer products, partly due to surface roughness. They were considered undesirable contaminates that were difficult to remove and did not permit the range of average particle sizes possible with organic materials. A partial list of the organic dispersants that were investigated is as follows:

Methyl cellulose	Carboxymethyl cellulose
Polyvinyl methyl ether	Starch
Polyvinyl alcohol	Gelatin
Polyethylene glycol	Apple and citrus pectins
Polymethacrylic acid	Sodium alginate

All are typical *hydrophilic polymers*. They were tested qualitatively at several concentrations. Data on some of the more effective, presented in Table I, were obtained using 100-ml. aliquots of 1% by weight of stabilizer solution with 250 ml. of the divinylbenzene mixture. Yields derived from runs, each differing only by the stabilizer, were weighed and sieved. Average sphere diameters represent given sieve fractions. The 1.7-mm. fraction, for example, represents that portion of the product caught on a standard 12-mesh screen, the 0.3-mm. fraction is that portion passing a standard 40-mesh screen but caught on the 60 (figure 7). Counts of spherical particles in each sieve fraction were made with an optical micrometer and occasionally checked with a sphericity grader. These counts were expressed in per cent of the total number of particles in each size range. The clustered material was concentrated in the larger size ranges, accounting for the lower sphere counts in this region. Marked variations in particle size distribution are apparent. Apple pectin showed a particularly broad range of particle sizes. Polyvinyl alcohol (medium solution viscosity, completely saponified) not only gave the narrowest size distribution but also led to a product with a greater degree of sphericity. It should be emphasized that, with the exception of polyvinyl alcohol, only limited tests were made on these materials, and although the results were inferior to those obtained with polyvinyl alcohol, other samples might prove more effective particularly when they are used with monomers other than the divinylbenzene mixture. Under the circumstances polyvinyl alcohol appeared to merit further examination.

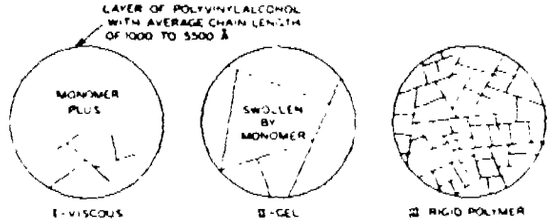

Figure 3. Schematic Representation of Stages in Suspension Polymerization of Technical Divinylbenzene

Much information is available in the literature on the structure (*3, 7, 7a*) and properties (*2, 12*) of polyvinyl alcohol. Surface tension measurements on its solutions as well as those of polyethylene glycol suggest (*6*) that molecules of water-soluble polymers in solution exhibit definite orientation at surfaces or interfaces. The evidence supports the assumption that adsorbed molecules at the water interface are arranged horizontally rather than in the perpendicular fashion exemplified by the fatty acids. Bohn and Ernsberger (*2*) have reported that the presence of polyvinyl alcohol may reduce the interfacial tension of Nujol in aqueous suspension as much as 50% or more. In addition, they found a considerable variation in surface activity between different grades. In general the partially hydrolyzed grades lower the interfacial tension most. Others (*4, 12*) have found erratic re-

TABLE I. COMPARISON OF STABILIZER EFFICIENCY

	No. spheres, % of Total Particles in Each Size Range, Av. Sphere Diam., Mm.					Weight % of Each Size Range Based on Total Sample Weight, Av. Sphere Diam., Mm.				
	Over 1.7	1.7–0.6	0.6–0.3	0.3–0.2	Less than 0.2	Over 1.7	1.7–0.6	0.6–0.3	0.3–0.2	Less than 0.2
Stabilizer		43	80	93	98		0.8	31	59.6	7.9
Polymethacrylic acid		0	60	90	95		1.1	23.1	66.8	8.1
Gelatin		0	30	90	95		4.0	11.1	71.2	13.8
Citrus pectin	0	20	70	90	97	21.0	20.1	38.2	13.8	
Apple pectin	0	50	60	100	100	0.2	3.2	12.1	81.5	2.8
Polyvinyl alcohol										

TABLE II. RELATIVE STABILIZING PROPERTIES OF VARIOUS GRADES OF POLYVINYL ALCOHOL

Stabilizer Grade	No. Spheres, % of Total Particles in Each Size Range — Av. Sphere Diam., Mm — Over 1.7	1.3	0.6	0.3	Less than 0.2	Weight, % of Each Size Range (Based on Total Sample Weight) — Av. Sphere Diam., Mm — Over 1.7	1.3	0.6	0.3	Less than 0.2
77–0.99			0	10	95	0	0	0.9	8.4	90.7
100–0.92	15	40	30	90	95	1.6	9.6	19.1	57.9	11.9
98–0.98	5	40	75	95	95	0.5	6.3	26.1	65.4	1.8
100–1.13	10	30	40	90	98	0.9	7.9	15.9	55.1	20.4
78–0.78	0	0	0	10	95	0.1	0.7	7.2	19.0	73.2
90–0.65	0	0	5	50	95	0.4	1.6	2.9	17.5	77.6
98–0.83	0	50	80	99	99	0.5	4.5	16.5	76.3	2.1
80–0.35	0	0	0	5	95	3.3	8.7	12.2	53.2	22.6
98–0.34	30	40	90	80	95	4.8	21.6	34.8	36.0	2.9

and had to be filtered out of solutions of the higher viscosity grades. This insoluble material was actually irrelevant since polyvinyl alcohol concentration and viscosity measurements were made on the final solution after filtration.

Runs were made in 5-liter capacity reactors of the type shown in Figure 6. The reactor was charged with an aliquot portion of stabilizer solution and sufficient distilled water to provide a volume of 3200 ml. This was stirred at 250 r.p.m. as 250 ml. of the divinylbenzene mixture containing 1% by weight of benzoyl peroxide were added. The reaction was carried out at 80° C. for 3 hours. Stirring was then discontinued, the product separated, washed several times with methanol, and dried. High static charges, accumulated by the dry spherical product, necessitated use of either high humidities, radioactive static-eliminators, or graphite dusting in order to ensure trouble free size analyses. The spheroids of fully polymerized divinylbenzene mixture are hard, infusible, and easily fractured. Moreover, swelling in benzene either at room temperature or at 80° C. does not exceed 2%. These properties indicate the high degree of cross linkage which constitutes the framework of the molecular structure of the polymer.

The relative effectiveness, as suspension stabilizers, of various grades of polyvinyl alcohol is given in Table II and Figure 8. They are arranged according to their solution viscosity and degree of hydrolysis. Data were obtained using 0.5% stabilizer based on the weight of divinylbenzene mixture present. Sieve fractions are expressed as weight in per cent based on the total sample weight. Each of the six bar graphs in Figure 8 represents average yields obtained with a single grade of stabilizer. Reproducibility of individual runs varied as much as ±5% in respect to the mean fraction. The numbers in the upper left-hand corner of each graph represent the per cent hydrolysis and intrinsic viscosity of the stabilizer used. For example, the number 98-0.82 signifies a polyvinyl alcohol grade, 98% hydrolyzed, with an intrinsic viscosity in aqueous solution of 0.82. According to Flory (7) the intrinsic viscosity of 0.82 corresponds to a number-average molecular weight of approximately 54,000. Separation of this grade into fractions by solubility differentials would presumably show the typical broad distribution of molecular weights.

High viscosity and partially hydrolyzed grades of polyvinyl alcohol were associated with products of fewer aggregates and smaller average particle diameters. Lower yields of spheroids were provided by the low viscosity grades. However, the latter were effective at lower concentrations than were permissible with other grades. Concentrations of as low as 0.005% (based on weight of monomer) of low molecular weight stabilizer were reached before aggregation in products became appreciable. Figure 9 shows the effect on size distribution when concentrations of three different stabilizer grades were varied. With a concentration of 2% of 90-0.82 stabilizer, based on the divinylbenzene mixture, a 90% yield of the desired 0.3-mm. spheroids was obtained. As might be suspected, higher concentrations of stabilizer led to smaller average particle diameters.

To avoid possible inaccuracies due to gradual deterioration in efficiency of the stabilizer, fresh solutions were used with each preparation. The suspension pH at the end of typical polymerizations with divinylbenzene mixture varied between 4.8 and 5.0. Presumably inhibitor and perhaps catalyst fragments caused this. The desirable pH range was found to be 3 to 7. Below pH = 3, clustering becomes a considerable problem. Increasing the pH to 10 appeared to have little effect on the sphericity, but opaque products from alkaline runs suggested occluded impurities and possible surface roughness.

Many materials act as precipitants for polyvinyl alcohol. Most acids can be tolerated in fair concentrations but solutions are quite sensitive to alkalies with the possible exception of ammonium hydroxide. Low molecular weight grades are reported to be surprisingly sensitive (2) to electrolytes associated with hard water. Higher molecular weight, partially hydrolyzed grades are less affected.

As shown in Figures 8 and 9, it is entirely possible to achieve sharp size distributions through a remarkable range of particle sizes by simply varying the intrinsic viscosity, degree of hydrolysis, and concentration of polyvinyl alcohol stabilizer. Controlled agitation has a similarly pronounced effect. Combination of these factors permits the preparation of sphere size ranges averaging from two microns to several millimeters in diameter using the type apparatus shown in Figure 6. It is now difficult to predict

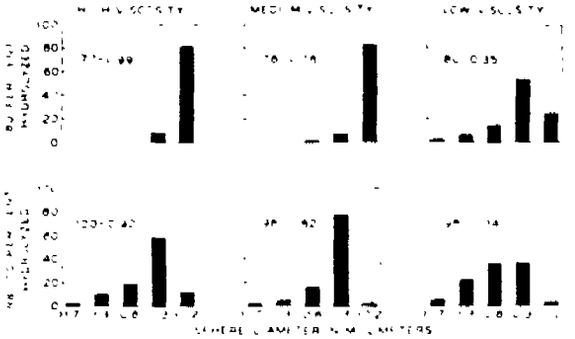

Figure 8. Relative Stabilizing Properties of Polyvinyl Alcohol of Varying Molecular Weight and Degree of Hydrolysis

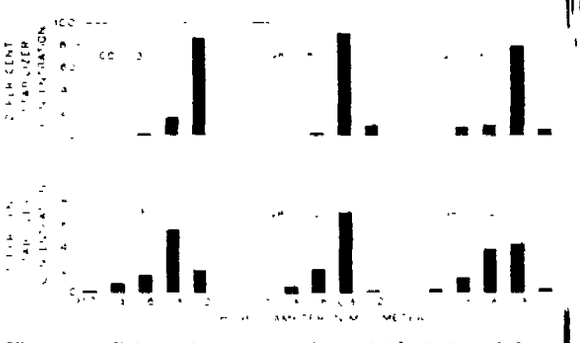

Figure 9. Effect of Varying Polyvinyl Alcohol Stabilizer Concentration on Sphere Size Distribution

Stabilizer concentration, % based on weight of monomer

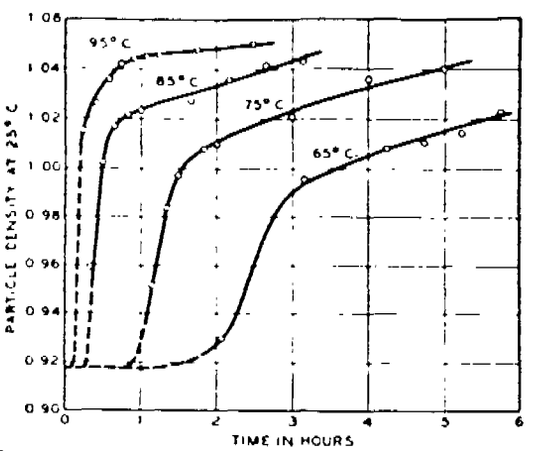

Figure 4. Rate of Polymerization of Technical Divinylbenzene

Various reaction temperatures determined by particle density change

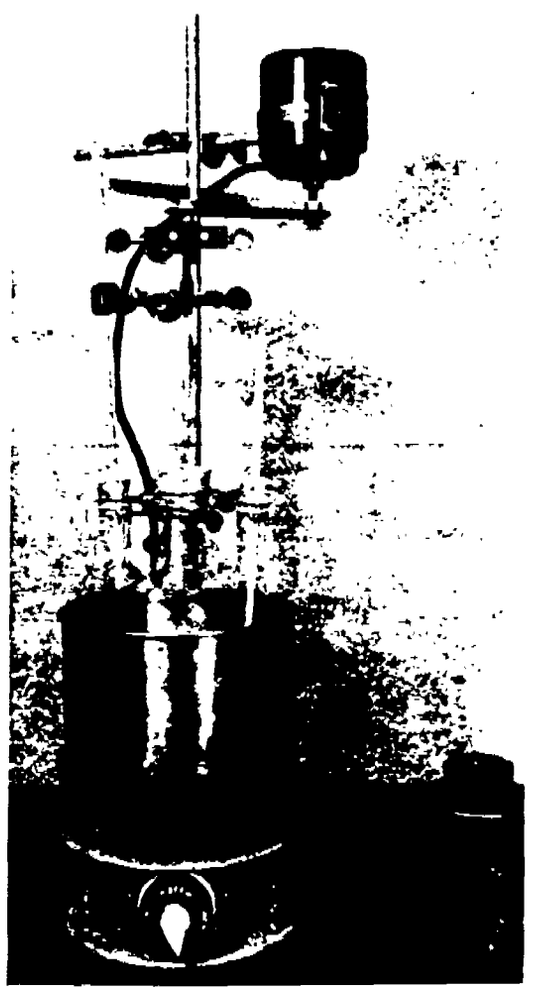

Figure 6. Suspension Polymerization Reactor Used with Technical Divinylbenzene

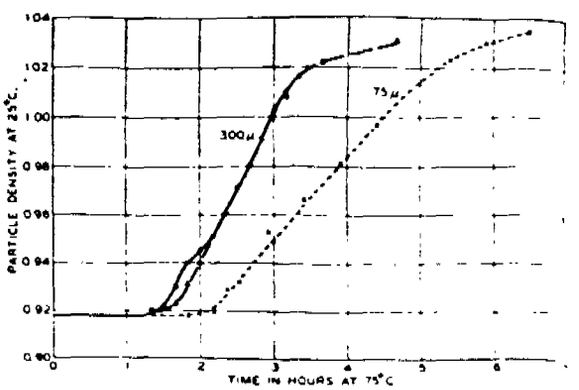

Figure 5. Rate of Polymerization of Technical Divinylbenzene Determined by Particle Density Change

Retardation for different particle sizes is due to presence of atmospheric oxygen

sults with polyvinyl alcohol solutions. Clarke and Blout investigated aging phenomena and found carbonyl functionality to be inherent in polyvinyl alcohol. They postulated that ketal formation was responsible for much of the observed aging and offered, in support of this, the fact that stable polyvinyl alcohol solutions could be prepared by heating for several hours with 0.02 *N* hydrochloric acid. Light scattering studies have shown that molecular aggregation occurs with the partially hydrolyzed polyvinyl alcohols (*17*) whose solubilities in aqueous solutions decrease with an increase in temperature. In spite of this reactivity, Flory and Leutner (*7*) checked the correlation between intrinsic viscosity of polyvinyl alcohol solution and number-average molecular weight while examining its molecular structure.

A series of polyvinyl alcohols was tested for suspension stabilizer function. Intrinsic viscosities of their aqueous solutions at 25° C. ranged from 0.35 to 1.13, or a viscosity-average molecular weight range from 19,000 to 95,000 (*7*). A 1% solution of each grade was prepared. Low viscosity grades gave clear solutions. A very small quantity of insoluble material was present

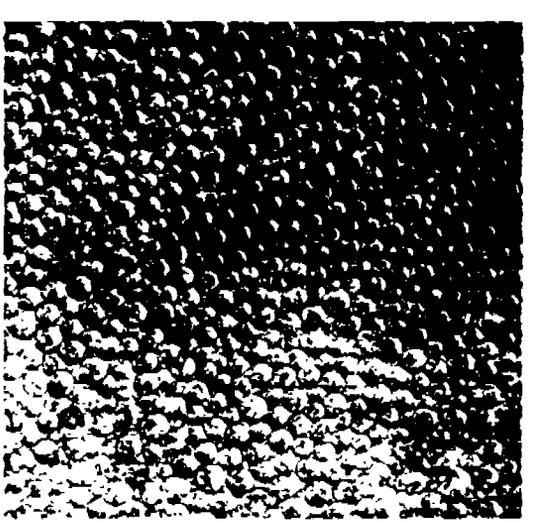

Figure 7. Technical Divinylbenzene Polymer Spheres Illustrating Geometrical Perfection Attributed to Spherical Fractions in Tables I and II

This is typical 0.3-mm. fraction. Presence of few small spheres is due to accumulation of static charge by product during screening; graphite dusting, which reduces this charge, was used for all sieve analyses

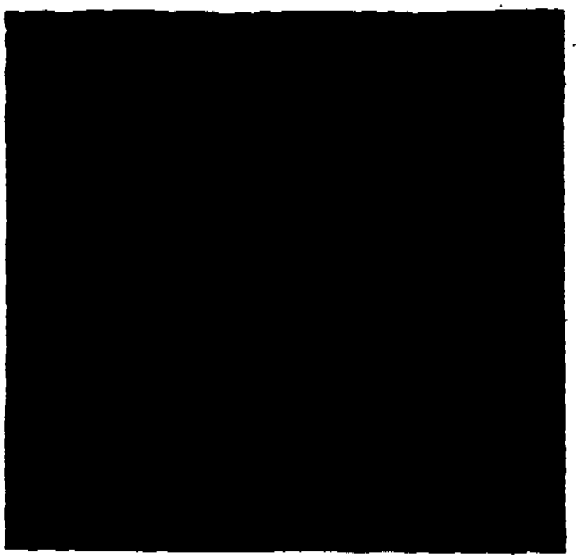

Figure 10. Polymer Globules from Technical Divinylbenzene (4–20 Microns)

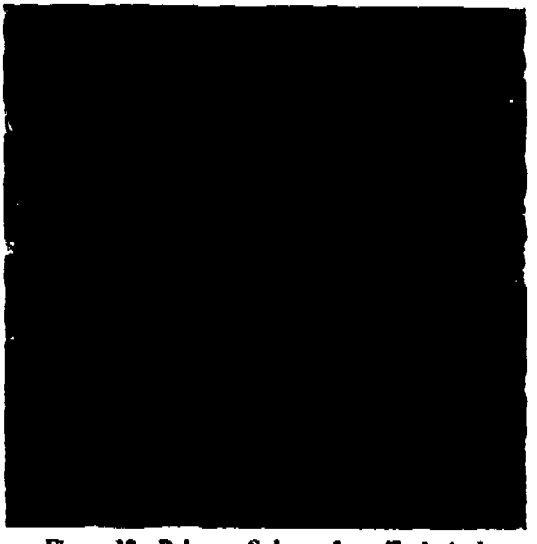

Figure 12. Polymer Spheres from Technical Divinylbenzene (Rolled Sample)

definite size distributions in the extremes of the above ranges. This is especially true of the small spheroids. Judging from styrene (*10*), the divinylbenzene mixture should have an interfacial tension with water of approximately 35 dynes per cm. Besides considerable energy in the form of high speed stirring, viscous aqueous solutions coupled with appreciable surface activity of partially hydrolyzed polyvinyl alcohols are required to reduce the average droplet size to the 20-micron range. In a typical reaction, a 2-liter spherical flask (Figure 6) was charged with 1200 ml. of 2% stabilizer (77-0.99) and 92 grams of divinylbenzene mixture catalyzed with 1% benzoyl peroxide. The suspension was stirred at 740 r.p.m. for 5 hours at 80° C. Foaming was not severe (*8*). Foam that did form was unstable and controllable. Removal of the stabilizer and other impurities from the product was accomplished with repeated washings and centrifugal separations. The dried product consisted of spheroids

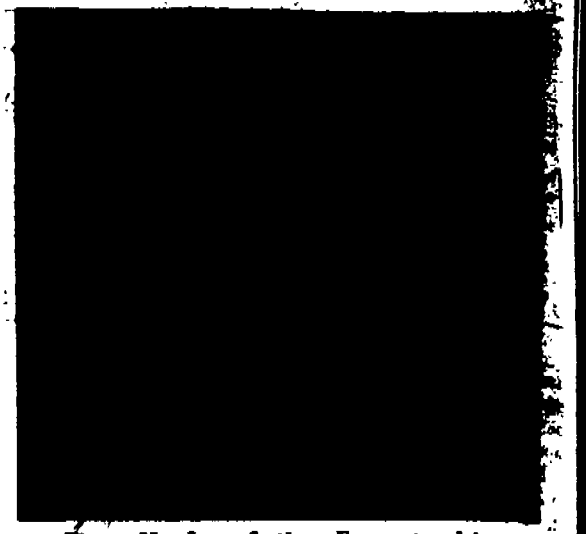

Figure 11. Imperfections Encountered in Suspension Polymerization Products

ranging from 7 to 38 microns in diameter (Figure 10). The physical behavior of this powder closely resembled that of a fluid. These particles can be regarded as huge microgel molecules (*1*), which, however, sediment from solution quite completely under gravity. Reduction of the stirring rate to 365 r.p.m. resulted in a product varying between 14 and 63 microns average particle diameter. Use of a homogenizing mixer gave a particle size range of 3 to 8 microns with the same suspension.

Various defects commonly found in suspension polymerization products are shown in Figure 11. These were the attributes to be minimized by this study. Scrutiny of the individual particles reveals twinned and clustered spheroids throughout. A few cenospheroids, some of which are cracked, appear as the lighter particles, and occluded bubbles can be seen in a few others. Most of the sample is composed of well-formed spheres as shown in the rolled sample, Figure 12. Tear-shaped spheroids, not illustrated, are frequently found among products with an average diameter of several millimeters.

ACKNOWLEDGMENT

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