Emulsion Polymerization of Ethylene.   II. Effect of Recipe on Particle Size and Distribution

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Synopsis

Particle diameters were measured in electron photomicrographs of polyethylene latexes prepared with a potassium soap, a polyethyoxylated *p*-alkyl phenol, or a sodium alkyl sulfate.   The volume-surface average diameters calculated from these values compare well with those obtained independently by soap adsorption.   Plots of the diameters on log probability paper indicate that the diameters follow a log-normal distribution.   The width of the distributions is given, and its effect on the difference between the number-average and volume-surface average diameters is discussed.   A study of the effect of the recipe shows that the diameter of the average particle produced in the emulsion polymerization of ethylene decreases as the amount of emulsifier is increased, but the addition of *tert*-butyl alcohol increases particle diameter.   Particle diameter is not affected by the initiator within the concentration range normally used.   During the course of polymerization, the number of particles slowly increases in the presence of *tert*-butyl alcohol, but in its absence the number of particles decreases.   In the absence of *tert*-butyl alcohol, the number of particles increases as the 1.1 power of the emulsifier concentration.

INTRODUCTION

Since World War II, many investigators have studied the emulsion polymerization of vinyl monomers.   However, the generally accepted mechanism applies only to monomers that are slightly soluble in water, because the properties of latexes prepared with water-soluble monomers change during preparation in ways that prevent a quantitative description of latex formation and growth.   These changes generally alter the number of particles, owing to coalescence and coagulation of polymer molecules or particles and to formation of oligomers which function as surfactants or as polymerization centers that do not arise from micelles. In addition to its importance in describing the kinetics of emulsion polymerization, the particle number also influences properties that contribute to the usefulness of the emulsion in fabricated products such as emulsion floor polishes, latex paints, and coated papers and fabrics.   Hence a study of the factors affecting particle number not only places the behavior of the monomer in relation to others, but also generates data of practical and theoretical importance.

According to Rupar and Mitchell,[1] electron microscopy is the most accurate way to measure the size of latex particles, but Maron's[2] method, which is based on the adsorption of soap on the polymer surface, is well established as a measure of particle diameter in many kinds of latexes. For example, Orr and Breitman[3] established agreement between these methods on latexes of butadiene–styrene, butadiene–acrylonitrile, and butadiene–methyl methacrylate polymers. In addition, Wilson, Miller, and Rowe[4] found that the two methods agreed on the size of particles in monodisperse latexes prepared by seeding with a poly(butadiene–styrene) latex, and Brodnyan and Brown[5] showed that diameters of particles in acrylic latexes measured by soap adsorption agreed with those measured by ultracentrifugation.

The first paper[6] of this series describes the preparation of stable latexes by the emulsion polymerization of ethylene. This report gives for some of these latexes the size and distribution of particle diameters based on measurements by soap adsorption and by electron microscopy and describes the effect on particle number of various components of the recipe used in the emulsion polymerization of ethylene.

EXPERIMENTAL AND RESULTS

Latexes

The latexes were prepared by the process of emulsion polymerization for ethylene described by Helin and co-workers[6] and contained as emulsifier the potassium salt of lauric, myristic, or stearic acid. The latexes containing *tert*-butyl alcohol were concentrated in a rotating flask evaporator at a temperature of about 70°C. under a reduced pressure controlled to keep the latex from foaming into the condensate receiver. The polymer concentration in the latexes generally lay between 20 and 40%, and their surface tensions usually exceeded 40 dynes/cm. The recipes by which these latexes were made appear in Table I.

Soap Adsorption

Maron computes the average diameter of latex particles from the moles of soap needed to saturate the surface of 1 g. of polymer and from the apparent area occupied by a molecule of the soap. The moles of adsorbed soap per gram of polymer is composed of the initial soap (S_i) and the added soap (S_a). A conductometric titration of the latex gives the concentration of initial soap, and a tensiometric or other conductometric titration shows how much soap must be added to bring the latex to its critical micelle concentration (CMC). At this point, the concentration of soap C in moles per liter of latex exceeds the concentration of added and adsorbed soap C_a by the amount dissolved in the aqueous phase C_f. There are two ways to find S_a. The basic one is to determine C at different initial concentrations of polymer and to plot the value C against the

concentration of polymer m at the CMC. The slope of the line is S_a; its intercept is C_f, the concentration of dissolved soap at zero solids. However, if C_f is known, the expression

$$S_a = (C - C_f)/m \qquad (1)$$

gives the added soap after a single titration determines C. We found, however, that if eq. (1) is used, C_f should be multiplied by the factor $(V - V_m)/V$, where V is the volume of the sample at its CMC and V_m is the volume of polymer in the sample. This correction is necessary because C_f is measured in moles per liter of latex, which contains less than a liter of aqueous phase. In our work, we used Maron's method, but applied this factor, which can be large if the soap has a high CMC and the latex is concentrated. In addition, we titrated with a soap solution of potassium myristate, used the apparent areas for the soaps as given by Maron, and computed the initial soap from data on the polymerization recipe and product.

Electron Microscopy

The particles were shadowed with platinum for the electron micrographs. As a check on calibration, some of the samples contained particles from a monodisperse latex furnished by the Dow Chemical Company. From measurements made on glossy enlargements of the micrographs, we calculated the number-average diameter (D_n), the volume-surface average
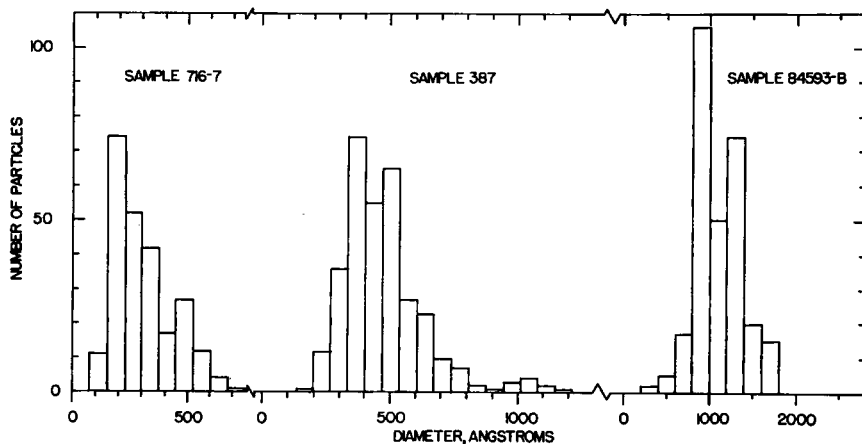

Fig. 1. Distribution of diameters of particles in polyethylene latexes.

diameter (D_s), and the coefficient of variation C_v of the particle diameters. These values appear in Table II. In addition, the distribution of diameters is shown in Figure 1 for the three latexes with the largest number of measured particles.

TABLE I
Dependence of Particle Size on Recipe

Run	Recipe[a]			Conditions[b]			Solids concentration, %		Particle diameter, A.°	Particle number × 10^{-11 e,d}
	Fatty acid parts[e]	Potassium persulfate, parts	tert-Butyl alcohol, parts	Temperature, °C.	Pressure, psig.	Time, hr.: min.	Terminal	Concentrated		
383	1.77 M	0.25	7.5	80	3000	1:46	27.0	31.8	460	6.3
384	1.23 L	0.20	10	80	3000	2:52	25.0	27.7	410	9.6
385	2.13 M	0.20	5	80	3000	3:06	25.4	32.8	450	7.2
386	1.76 S	0.20	10	80	3000	3:57	24.2	37.8	710	1.7
387	1.42 M	0.30	10	80	3000	1:45	26.4	36.6	540	4.3
388	1.42 M	0.30	5	80	3000	2:47	24.4	34.0	390	10.6
391	1.86 L	0.20	10	80	3000	3:54	24.8	32.0	370	12.1
392	1.77 M	0.25	7.5	80	3000	5:04	23.2	31.6	340	14.9
394	1.23 L	0.30	10	80	3000	2:10	24.0	29.0	610	2.6
395	1.86 L	0.30	5	80	3000	4:03	24.6	30.8	330	17.4
396	1.76 S	0.30	5	80	3000	5:15	23.8	36.0	480	5.2
401	2.65 S	0.30	10	80	3000	1:57	25.8	36.4	450	7.0
402	1.76 S	0.20	5	80	3000	4:37	26.4	32.8	490	5.8
403	1.77 M	0.25	7.5	80	3000	2:40	24.8	34.0	430	7.6
404	1.42 M	0.20	10	80	3000	5:42	25.6	34.2	520	4.6
405	1.76 S	0.30	10	80	3000	2:13	27.8	40.0	730	1.9
406	2.65 S	0.30	5	80	3000	4:39	25.8	34.2	440	7.7
407	2.65 S	0.20	5	80	3000	4:05	25.4	32.0	380	11.6
408	1.86 L	0.30	10	80	3000	3:10	26.5	34.0	480	6.1
410	1.86 L	0.20	5	80	3000	6:36	24.6	32.0	300	22.5
411	2.13 M	0.20	10	80	3000	5:10	24.4	29.8	390	10.1
412	2.65 S	0.20	10	80	3000	3:04	25.6	31.0	440	7.1
414	1.77 M	0.25	7.5	80	3000	4:06	26.8	35.4	500	5.7
415	2.13 M	0.30	5	80	3000	5:35	25.0	32.0	340	15.9

416	1.23 L	5	80	3000	3:47	27.2	35.2	510	5.5
417	1.42 M	5	80	3000	6:54	25.2	32.0	490	5.4
418	1.23 L	5	80	3000	4:30	26.0	30.2	490	5.5
419	2.13 M	10	80	3000	4:10	24.4	29.9	380	11.2
723	0.22 M	—	85	4500	2:08	18.0	—	620	1.8
724	0.43 M	—	85	4500	1:40	26.5	—	620	3.0
725	1.07 M	—	85	4500	4:35	19.2	—	280	20.6
726	1.50 M	—	85	4500	1:30	22.0	—	260	29.9
727	0.64 M	—	85	4500	1:15	24.0	—	420	8.2
732	2.90 M	—	85	4500	3:00	29.6	—	340	13.6
733	2.90 M	—	85	4500	2:00	32.4	—	340	15.9
735	2.90 M	0.016	85	4500	5:10	17.0	—	180	45.4
93f	1.77 M	12.5	80	3000	1:00	21.0	38.4	360	10.9
94f	2.90 M	9.5	80	3000	1:46	25.4	36.2	280	27.5
95f	1.09 M	15.5	80	3000	2:00	26.4	36.4	790	1.7

[a] The concentration of ingredients is expressed as parts per 100 parts of aqueous medium (water plus tert-butyl alcohol). Each run through number 419 contained 0.50 parts of K_3PO_4, but subsequent runs contained only 0.42 parts. In addition, each run contained an amount of KOH stoichiometrically equivalent to the fatty acid charged.

[b] Polymerizations were conducted in a 1-gal. stainless steel autoclave.

[c] Based on soap adsorption.

[d] Per cubic centimeter of aqueous phase.

[e] Abbreviations: L = lauric; M = myristic; S = stearic.

[f] Conducted in an 18-gal. stainless steel autoclave.

TABLE II

Size and Distribution of Particles in Polyethylene Latexes

Sample	Number of particles measured	Coefficient of variation	Number-average diameter D_n, A.	Volume-surface average diameter D_v, A.	Soap adsorption diameter, A.[a]
84593B	289	0.259	1070	1210	1050
84583S	120	0.198	484	522	517
84586C	90	0.189	1138	1212	1210
387	326	0.343	516	655	540
405	45	0.147	723	753	730
410	185	0.176	340	361	300
415	168	0.173	392	414	340
394	120	0.174	621	655	610
407	180	0.214	420	458	380
716–7	247	0.473	277	405	475
92254[b]	184	0.239	1309	1439	—
92207[c]	162	0.211	875	948	—
84586A[d]	164	0.243	1000	1125	—

[a] The polymerization and the titration were made with the potassium salt of fatty acids.

[b] Polyethoxylated p-nonylphenol was used as emulsifier.

[c] Sodium alkyl sulfate was used as emulsifier.

[d] Polyethoxylated p-octylphenol was used as emulsifier.

Effect of Recipe

The average diameter of the particles in each latex was measured by Maron's method of soap adsorption. The number of particles was computed from the average particle diameter and the solids content of the latex as determined on a moisture balance. The data for the following experiments (I–V) appear in Tables I and III.

Experiment I. This experiment was designed to show the differences among the potassium soaps of lauric, myristic, and stearic acid at two concentrations, as well as those between two concentrations each of initiator and tert-butyl alcohol in their effect on particle size. All combinations of a 3×2^3 factorial arrangement[7] were tested, including four center points with potassium myristate as the emulsifier, in a randomized block[7] of 28 runs—those first to appear in Table I—conducted at a temperature of 80°C. and a pressure of 3000 psig in a 1-gal. autoclave. The values for the average particle diameter were subjected to an analysis of variance to determine which effects were statistically significant compared with a standard error of 6.35 A. derived from replication of the center point and the three-factor interactions (Table IV).

This experiment can be summarized as follows. (a) An increase in the emulsifier of one part decreases the particle size by 135 A. (This is equivalent to increasing the number of particles by a factor of 2.4.) (b) An increase in the alcohol by 5 parts increases the particle size by 78 A. (This
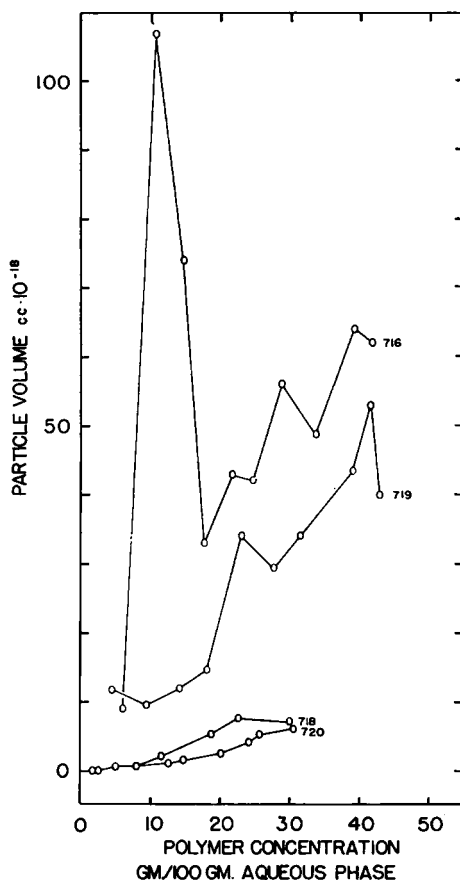
Fig. 2.   Effect of conversion on particle size.   Conditions: temperature, 85°C.; pressure, 4000–4500 psig; initiator, 0.16 part; K_3PO_4, 0.42 part; parts of other components as follows: (run 716) potassium myristate 3.72 parts, *tert*-butyl alcohol 10 parts; (run 718) potassium myristate 3.72 parts, *tert*-butyl alcohol 0; (run 719) potassium myristate 5.58 parts, *tert*-butyl alcohol 10 parts; (run 720) potassium myristate 5.58 parts, *tert*-butyl alcohol 0.

is equivalent to decreasing the number of particles by a factor of 1.7.) (c) Potassium stearate produces a particle that is 77 A. larger than that produced by either potassium laurate or potassium myristate. (This is equivalent to decreasing the number of particles by a factor of 0.6.)   (d) An increase in the initiator concentration of 0.1 part causes no significant change in particle size.   (e) The change in particle size due to one factor is not dependent on the level of another factor, i.e., the 2-factor interactions are not important.

Experiment II.   Runs 93, 94, and 95, conducted in an 18-gal. reactor show how the combined effect of changes in concentration of *tert*-butyl alcohol and potassium myristate affect the average particle diameter.

TABLE III
Dependence of Particle Size on Time and Recipe

| Run | Recipe[a] | | | Time, min.[b] | Solids, % | Polymer, g.[c] | Particle diameter, A.[d,e] | Particle, number × 10^{-18d,f} |
	Myristic acid, parts	Potassium persulfate, parts	tert-Butyl alcohol, parts					
716-1	2.90	0.16	10	15	9.4	6.1	260	7.4
-2				30	13.0	10.6	590	1.1
-3				45	15.7	14.3	520	2.1
-4				60	17.9	17.5	400	5.6
-5				80	20.5	21.5	435	5.4
-6				100	22.4	24.5	430	6.4
-7				120	24.6	28.4	475	5.5
-8				150	27.5	33.6	455	7.4
-9				180	29.6	37.7	495	6.4
-10				210	31.4	41.6	505	6.7
718-1	2.90	0.16	0	10	5.5	1.5	30	1280
-2				20	6.6	2.7	50	450
-3				40	8.6	5.1	90	155
-4				60	11.7	8.9	125	92
-5				80	13.6	11.5	155	65
-6				100	15.0	13.4	150	81
-7				140	19.6	18.8	210	41
-8				180	21.8	22.4	240	34
-9				220	25.7	30.3	285	27
719-1	4.35	0.16	10	15	6.6	0.9	—	—
-2				30	9.7	4.7	285	4.2
-3				45	13.7	9.7	265	11.2
-4				60	16.8	14.0	285	12.1

-5			75	19.4	17.8	305	13.2
-6			105	22.7	23.2	400	7.4
-7			135	24.8	26.8	385	9.9
-8			165	27.4	31.6	410	9.5
-9			225	31.0	38.9	435	9.7
-10			285	32.3	41.6	470	8.5
-11			305	33.0	43.0	425	11.7
720-1	4.35	0.16	0	10	6.7	1.0	—	—
-2			20	8.7	3.4	45	828
-3			40	12.1	8.0	84	252
-4			60	16.0	13.0	130	129
-5			80	17.2	14.6	140	106
-6			110	20.8	20.2	170	87
-7			170	23.3	24.2	200	65
-8			230	24.7	25.3	215	32
-9			290	27.2	31.1	235	50

a The concentration of ingredients is expressed as parts per 100 parts of aqueous medium (water plus *tert*-butyl alcohol). Each run contained 0.42 parts of potassium phosphate and a quantity of potassium hydroxide stoichiometrically equivalent to the acid used.

b Polymerizations were conducted in a 1-gal. stainless steel autoclave at a temperature of 85°C. and a pressure of 4000-4500 psig.

c Per 100 g. of aqueous phase.

d Determined by soap adsorption.

e Values less than 100 A., which no doubt have a large relative error, are reported merely to show that there is a measurable increase in polymer surface early in the reaction.

f Per cubic centimeter of aqueous phase.

TABLE IV
Effect of Various Factors on Particle Diameter

Factor	Average particle diameter, A.
Potassium laurate	438 ± 49
Potassium myristate	438 ± 49
Potassium stearate	515 ± 49
tert-Butyl alcohol	
5 parts[a]	424 ± 40
10 parts	502 ± 40
Emulsifier[b]	
2 parts[a]	531 ± 40
3 parts	396 ± 40
Initiator[b]	
0.2 parts[a]	455 ± 40
0.3 parts	472 ± 40

[a] These are parts per 100 parts of aqueous phase (water plus tert-butyl alcohol).

[b] These parts are nominal; 2 parts in equivalent to 7.75 and 3 parts to 9.32 mmoles of the fatty acid salt/l. of aqueous phase.

The anticipated and observed particle diameters and the concentrations of myristic acid and of tert-butyl alcohol appear in Table V.

The expected diameter from run 93 was based on a duplicate run made earlier, but the expected diameters from the others were predicted by a regression equation[7,8] derived from the data in experiment I and centered around run 93. Although the observed diameters were less than expected, the agreement with expected order demonstrates a reasonable control of particle diameter by adjustments in recipe.

Experiment III. The effect of the concentration of soap and the role of tert-butyl alcohol were examined in runs 716, 718, 719, and 720 by determining the particle size not only at the end of each run, but also at frequent intervals during the polymerizations which were conducted at a temperature of 85°C. and a pressure of 4500 psig in a 1-gal. autoclave. The diameters are plotted in Figure 2 against the concentration of polymer (here used as a measure of conversion, because the monomer concentration is constant) in the latex expressed as grams of polymer per 100 g. of aqueous phase. The average particle diameters were larger with tert-butyl alcohol

TABLE V
Effect of Recipe on Particle Size

	Run 93	Run 94	Run 95
tert-Butyl alcohol, parts	12.5	9.5	15.5
Myristic acid, parts	1.77	2.90	1.09
Particle diameter, A.			
Expected	700	400	1000
Observed	360	280	790

than without. Furthermore, with or without the alcohol, the greater concentration of soap gave the smaller average particle diameter.

The variation in number of particles as the amount of polymer increases is shown in Figure 3. It is interesting to observe that without alcohol the particle number decreases during the run, especially during its early part, but with alcohol, the number increases slightly during the course of the run.
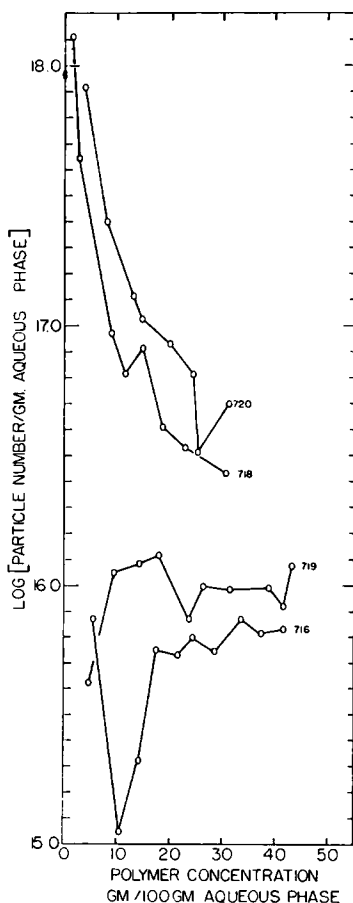

Fig. 3.   Effect of conversion on particle number.   Conditions as in Figure 2.

Experiment IV.   In this series of runs, which includes 718, 720, and 723–27, only the particle diameter at the final conditions is considered. The polymerizations were made in a 1-gal. autoclave at a temperature of 85°C. and a pressure of 4500 psig. The log-particle number plotted in Figure 4 against the log-soap concentration yields a reasonably straight line having a slope of 1.1; so the number of particles is a function of the soap concentration to the 1.1 power.
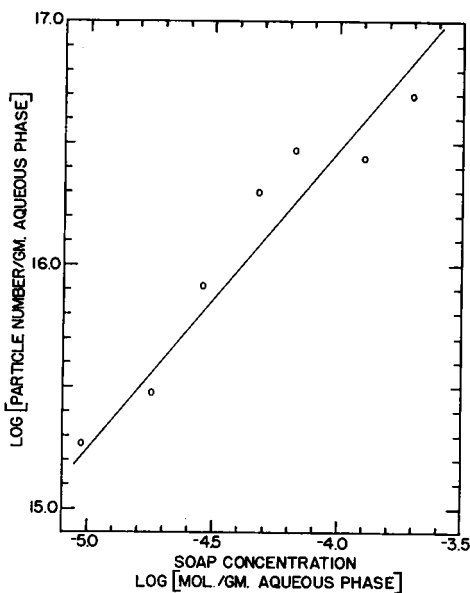
Fig. 4.   Effect of soap concentration on particle number in the absence of *tert*-butyl alcohol.   Particle number was measured at terminal solids concentration of 18–25%.

Experiment V.   In several runs conducted in a 1-gal. autoclave at a temperature of 85°C. and a pressure of 4500 psig, the initiator concentration was varied from 0.016 to 0.32 parts.   As can be seen in Table VI, the particle diameter did not respond in any systematic manner to the amount of initiator employed.

TABLE VI
Effect of Initiator Concentration on Average Particle Diameter

Run	Initiator concn., parts	Avg. particle diameter, A.
735	0.016	180
732	0.08	340
718	0.16	280
733	0.32	340

DISCUSSION

Dow polystyrene latex, run number LS-057-A, having an average particle diameter of 2640 A. and a standard deviation of 60 A. was used in the electron micrographs as an internal dimensional check on the routine calibration of the microscope.   The average diameter for these particles by the routine calibration was 2487 A., a value about 6% less than the expected diameter.   Shadowing causes an error in the opposite direction, as particle diameters can appear larger[9] than they really are by as much

as 230 A.   The values in Table I are based on the routine calibration of the electron microscope and are not corrected for shadowing errors.

The diameter by soap titration—it is a volume-surface average diameter—agrees acceptably with the volume-surface value calculated from electron micrographs, although the titration value is about 7.5% less than that given by electron microscopy.   The number average diameter
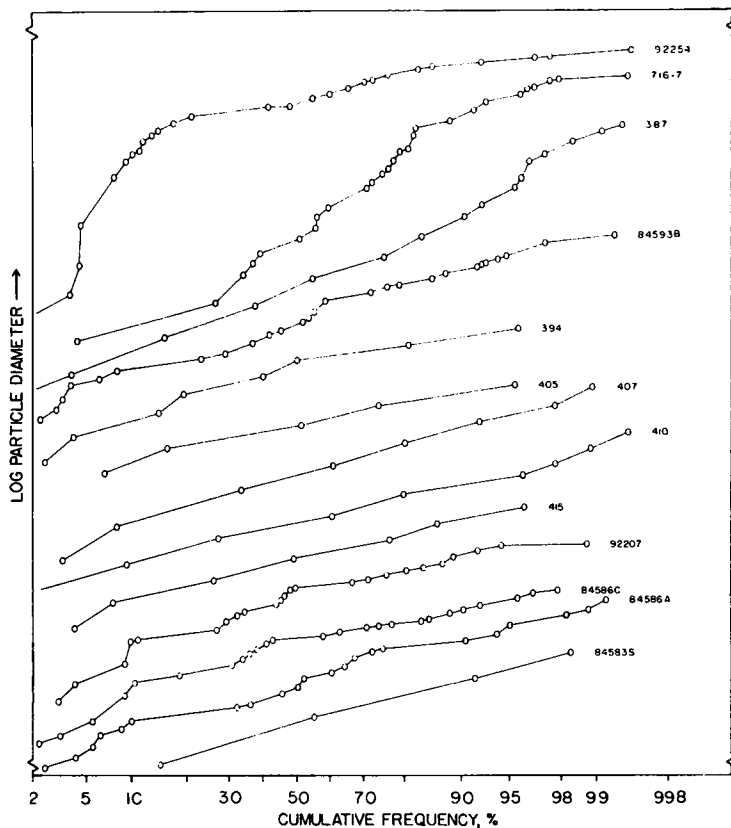

Fig. 5.   Cumulative distribution of log particle diameter.

D_n also is less than the volume-surface average diameter, but it should be; for the difference between them depends on the distribution of D_n. Orr and Breitman[3] show for a symmetrical distribution that the volume-surface average diameter is given by

$$D_v = D_n(D_n^2 + 3\sigma^2)/(D_n + \sigma^2) \qquad (2)$$

where σ is the standard deviation given by the product $C_v D_n$.   For the samples in Figure 1, the volume-surface average diameters are, by eq. (2), 378, 624, and 1026 A., values in reasonable agreement with those based on the electron micrographs.

Actually, in a monodisperse latex, D_s equals D_n because the standard deviation of such a distribution is zero; so, as the coefficient of variation increases, the distribution of particle diameters broadens. The pattern that this broadening follows is called the distribution function of the diameters. According to Brodnyan,[10] the distribution of diameters can be normal, log-normal, or intermediate. The cumulative distributions of the diameters are plotted in Figure 5 on log-normal probability paper. In order to present the data in one plot, the log-diameter scale was not fixed. Because the points seem to fall on straight lines between cumulative counts of 15–85%, the diameters follow a log-normal distribution.

Although the particle diameter of latexes prepared with potassium stearate is larger than if either laurate or myristate were used, the emulsifier concentration [E] has a much greater influence than the emulsifier type. However, its effect varies from monomer to monomer. Smith and Ewart[12] report that the number of particles N is proportional to $[E]^{0.6}$, but Medvedev[11] considers it to depend on $[E]^{0.5}$. However, Brodnyan et al.[10] report that particle number with methyl methacrylate and n-butyl methacrylate depends on $[E]^{3.0}$. Our relation for the dependence is $N \propto [E]^{1.1}$, which is much closer to the results of Medvedev and Smith-Ewart than to those of Brodnyan. There is some uncertainty in the terminal particle number, owing to the way the number changes during polymerization (Fig. 3). However, most of the change seems to occur early in the run, and by the time the conversion has reached 25% solids, the particle number is relatively stable. In any event, the number of particles increases as the concentration of emulsifier is raised.

Experiments I and II clearly show that larger and fewer particles are produced in a run made with *tert*-butyl alcohol than without it. Because the alcohol increases the solubility of the emulsifier, it is reasonable to assume that there is an attendant decrease in the amount of soap available to form micelles. As micelles are believed to be the source of particles, a reduction in their number is reflected in the number of polymer particles. In addition, *tert*-butyl alcohol seems to prevent the formation of the extremely small particles observed early in runs 716 and 719.

Varying the concentration of initiator I from 0.016 to 0.32 parts produced no significant change in the average particle number. This result agrees with Brodnyan's relation of $N \propto [I]^{0.0}$ for methyl methacrylate and n-butyl methacrylate, but not with the Smith-Ewart and Medvedev dependencies of $N \propto [I]^{0.4}$ and $N \propto [I]^{0.5}$, respectively.

CONCLUSION

The latexes described here as a group contain particles with diameters from less than 100 A. to more than 1500 A. In size and in distribution, which seems to be log-normal, the particle diameters of these new polyethylene latexes are much like those of other emulsion polymerized vinyl monomers. Maron's method of soap adsorption is satisfactory for measur-

ing the average particle diameters of these polyethylene latexes made with a potassium soap.

The number of particles formed at a conversion of about 20–25% solids in the batch polymerization of ethylene in an emulsion system increases as the 1.1 power in the emulsifier concentration, but the addition of *tert*-butyl alcohol reduces the number of particles that form.   In addition, the number of particles that form during polymerization in the presence of *tert*-butyl alcohol increases slightly with conversion, but in the absence of *tert*-butyl alcohol the number of particles decreases.   The number of particles is independent of the initiator between the limits of 0.016 to 0.32 parts.

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Résumé

On a mesuré par microphotographie électronique le diamètre de particules de poly-éthylène préparé par émulsion au moyen d'un savon potassique d'un *p*-alcoyl phénol polyéthoxylé ou d'un sulfate d'alcoyle sodium. Les diamètres moyens volume-surface, calculés à partir de ces valeurs, sont bien comparables à ceux obtenus indépendamment par adsorption de savon. Le graphique des diamètres en fonction du logarithme de la probabilité indique que les diamètres suivant une distribution logarithmique normale. La largeur de la distribution est donnée et on discute de la différence entre les diamètres moyens en nombre et en volume-surface. Une étude, effectuée sur l'influence du mode de fabrication, montre que le diamètre de la particule moyenne produit dans la polymérisation par émulsion de l'éthylène diminue par augmentation de la quantité d'émulsifiant et augmente par addition d'alcool *t*-butylique. Le diamètre de la particule n'est pas affecté par l'initiateur dans le domaine de concentration normalement employé. Durant la polymérisation, le nombre de particules augmente lentement en présence d'alcool *t*-butylique, tandis qu'il diminue sans alcool *t*-butylique proportionnellement à la concentration en émulsificant à la puissance 1.1.

Zusammenfassung

Teilchendurchmesser wurden an elektronenmikroskopischen Aufnahmen von Poly-äthylenlatices gemessen, welche mit einer Kaliumseife, einem polyäthoxylierten *p*-Alkylphenol oder einem Natriumalkylsufate hergestellt worden waren. Der Volums-oberflächenmittelwert des Durchmessers, der aus diesen Werten berechnet wurde, stimmt

mit den unabhängig durch Seifenadsorption erhaltenen Werten überein. Die Auftragung der Durchmesser auf einem log-Wahrscheinlichkeitspapier ergibt, dass die Durchmesser einer log-Normalverteilung gehorchen. Die Breite der Verteilung wird angegeben, und ihr Einfluss auf den Unterschied zwischen Zahlenmittel und Volums-Oberflächenmittel der Durchmesser wird diskutiert. Eine Untersuchung des Einflusses des Rezepts zeigt, dass der Durchmesser des mittleren bei der Emulsionspolymerisation von Äthylen erzeugten Teilchens mit steigender Emulgatormenge abnimmt, dass jedoch der Zusatz von t-Butylalkohol den Teilchendurchmesser erhöht. Innerhalb des normalerweise verwendeten Konzentrationsbereichs wird der Teilchendurchmesser durch den Starter nicht beeinflusst. Während des Verlaufs der Polymerisation nimmt in Gegenwart von t-Butylalkohol die Teilchenzahl langsam zu, bei Abwesenheit von t-Butylalkohol nimmt sie jedoch ab. In Abwesenheit von t-Butylalkohol nimmt die Teilchenzahl mit der Potenz 1.1 der Emulgatorkonzentration zu.