Factors Affecting the Promoted Aggregation and Coalescence of Synthetic Rubber Particles

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Synopsis

Small particles (ca. 700 A.) in an SB-R latex can be agglomerated (aggregation and coalescence) to the large size and heterogeneous distribution required for fluid high solids latex. This agglomeration is promoted by high molecular weight materials such as polyvinyl methyl ether (PVM). The mechanism of this agglomeration has been investigated. The effects of controlled variations in the amounts of PVM, electrolyte, soap and latex solids content were determined using statistically designed experiments. The agglomeration was found to differ from Smoluchowski kinetics in that it could best be described by the relationship: $(1/n) = (1/n_0) + at - bt^2$ where n = particle number, t = time and a and b are constants. The agglomeration rates were about 10^{11} to 10^{12} times slower than the theoretical Smoluchowski rapid coagulation rate. Increases in PVM, soap, and latex solids increased the agglomeration rate. The agglomerations were self-limiting and reached equilibria the level of which increased with increases in PVM and decreased with increases in soap. Regression equations relating the effects of the controlled variables on the agglomeration rate and the equilibria states are derived and presented graphically. The particle size distribution of the final latex was significantly correlated, with that expected from theoretical collision theory.

I. INTRODUCTION

It has been demonstrated by Howland, Chambers, and Aleksa[1] that the agglomeration (aggregation and coalescence) of small particles (ca. 700 A.) in SB-R latexes to the large size and heterogeneous distributions required for fluidity at high concentrations can be promoted by high molecular weight, water-soluble materials, in particular polyvinyl methyl ether (PVM).

It is interesting to note that the PVM used has the properties La Mer, Smellie, and Lee[2] have found to be required for an effective flocculating agent for a phosphate slime which is a very different colloidal system than the one studied here.

The base latexes employed are unique colloidal systems in that they are completely stable at particle concentrations as high as 2×10^{15} particles/cm.[3] and have particles in the submicronic region.

The mechanism of the PVM agglomeration whereby the colloidal stability factors (electrostatic, hydration, and adsorbed surface films) are overcome to allow agglomeration to occur is little understood. Of more

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interest for a practical process are the reasons for the termination of the agglomeration short of complete coagulation of the latex.

Statistically designed experiments were used to investigate the agglomeration mechanism. Factors studied were controlled variations in the amount of PVM, electrolyte, soap, and particle concentration.

II. EXPERIMENTAL

Materials

Two different SB-R type base latexes were used in this study. The polymerization recipes and latex physical properties are given in Table I. Both latexes were soap titrated to minimum surface tension[3] and the per cent coverage of the particle surfaces by the soap present from the polymerization recipe are included in the table. The size distributions of the particles of latex A are given in Figure 1. The size scale in this and subsequent figures showing particle size distributions is logarithmic for convenience in presentation, since the agglomerated latexes have quite broad size ranges.
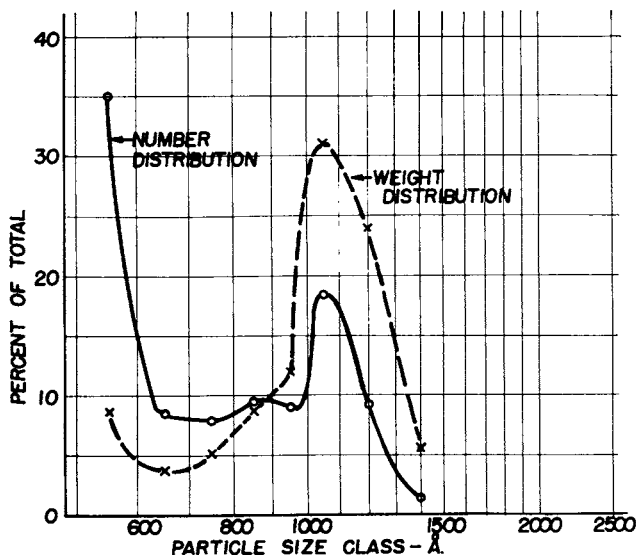

Fig. 1. Particle size distribution of base latex.

The polyvinyl methyl ether (PVM) was a commercial grade which had been treated[4] to increase its effectiveness as an agglomeration promoter. The soaps and sodium sulfate were technical grade and were added to the latex in aqueous solutions.

TABLE I
Polymerization Recipe of Base Latex

	Parts	
	Latex A	Latex B
Butadiene	72	73
Styrene	28	27
K-Rosin soap	1.50	1.75
Daxad 15	0.43	0.50
K_2SO_4	0.43	0.50
Diisopropylbenzene hydroperoxide	0.10	0.10
Sodium formaldehyde sulfoxylate	0.142	0.142
$FeSO_4 \cdot 7H_2O$	0.0079	0.0079
Tetrasodium tetraethylenediamine	0.0316	0.0316
Sodium hydrosulfite	0.03	0.025
Potassium oleate	2.00	2.75
Potassium dimethyl dithiocarbamate	0.20	0.20
Water	139	130
Conversion, %	80	80
Nominal temperature, °C.	5	5
Soap coverage, %	33.9	38.7

Procedure

The agglomeration procedure as conducted commercially uses a mixture of a treated PVM and potassium sulfate electrolyte as the promoter. The latex containing the agglomerants is concentrated by heat, and the agglomeration proceeds concurrently with the removal of water. Early experiments[12] showed that under certain conditions high solids could be obtained without an undue increase in viscosity. Under other conditions the latex would become very viscous before reaching the desired solids, but when left standing the viscosity would decrease and the latex could then be concentrated to high solids and low viscosity. These results indicate that the two processes, concentration and agglomeration, do not have to proceed simultaneously. To simplify this study the concentration step was eliminated, and agglomerations were conducted at various predetermined concentrations.

The agglomerating agents in the recipe were thoroughly mixed with the base latex. These mixtures were charged to 24 oz. soda bottles fitted with perforated caps containing self-sealing gaskets for sampling by hypodermic syringe. The bottles were rotated end over end in a water bath controlled at 50°C. Samples were removed at regular intervals for the determination of particle sizes and distribution.

The particle size distributions were determined by an alginate[5] creaming method. The average particle size and number of particles per unit volume were determined either by the alginate method or a turbidity[6,7] method calibrated against it. The turbidity method is much faster and less time-consuming than the alginate method, and so it was used more extensively.

III. RESULTS AND DISCUSSION

Basic Features

Before proceeding with an examination of the factors affecting the agglomeration several basic features need to be established.

Aggregation and Coalescence. A typical turbidity time curve for an agglomeration of latex A in Table I, conducted at one concentration is given in Figure 2. The corresponding surface tensions and Brookfield viscosities of the latex are also presented in this figure. Here it may be seen that the turbidity increase is very rapid in the early stages of the agglomeration, but the rate decreases with time, and the turbidity approaches a maximum level. The surface tension and Brookfield viscosity both decrease to minimum values as the agglomeration proceeds.

The results in Figure 2 show that agglomeration (both aggregation and coalescence) of the original latex particles does take place under the influence of PVM. The viscosity decrease does not distinguish between aggregation alone and both aggregation and coalescence, since the viscosity would decrease in either case. The concurrent decrease in surface tension, however, does establish that coalescence has taken place. That is, as coalescence occurs the amount of latex particle surface area is decreased. Consequently the distribution of soap between the particle surface and the
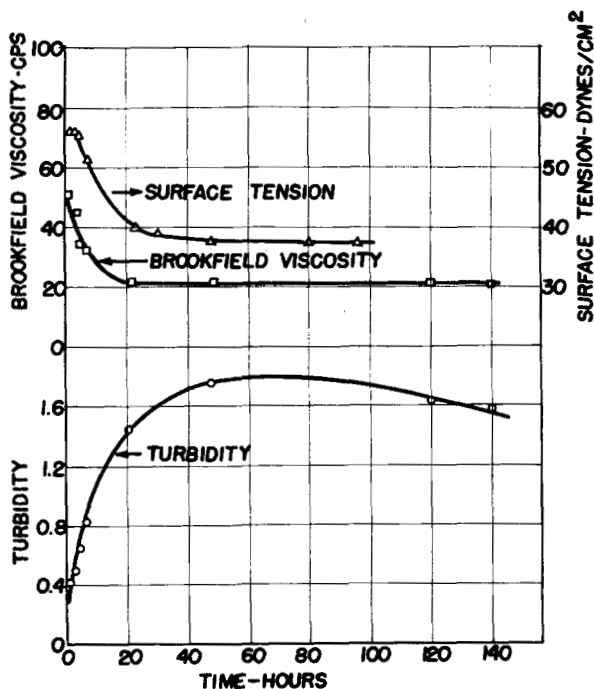

Fig. 2. Effects of agglomeration on latex properties.

aqueous solution is shifted toward the aqueous phase with a resulting decrease in surface tension.

Particle Size Distribution Changes. The weight frequency distributions of particles for this latex after agglomeration for various time intervals are presented in Figure 3. It is evident that as the agglomeration proceeds the weight fraction of larger particles increases at the expense of the smaller, and the distribution widens to include larger particle sizes. The base latex had essentially no particles over 1400 A. After $1/2$ hr. there was an appreciable fraction having sizes up to 4000 A. and after 7 and 72 hr. there were substantial weight fractions of particles having diameters of 10,000 A. and larger.
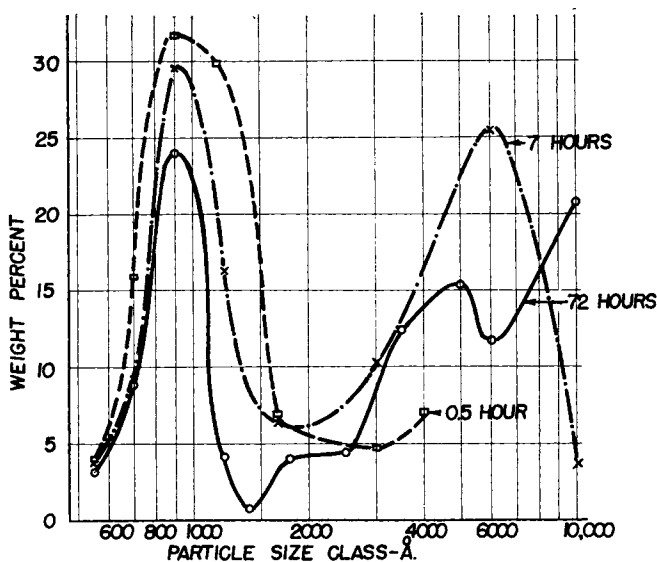

Fig 3. Weight distributions of particles at various times of agglomeration.

The number frequency distributions for these same samples are given in Figure 4. Here in contrast with the previous diagram, the large particles do not figure as conspicuously, as they contribute very little to the total number, although they contribute a large fraction of the total weight of the agglomerated sample.

It is apparent also in Figure 4 that the number of particles in all class ranges of the original latex is reduced. The number is even reduced in the intermediate- and large-size range, which would be gaining new particles from the agglomeration of particles of smaller size.

Collision of Latex Particles. Agglomeration must proceed by collision of particles followed by aggregation and coalescence. The frequency of collision of gas molecules is given by the equation[8]
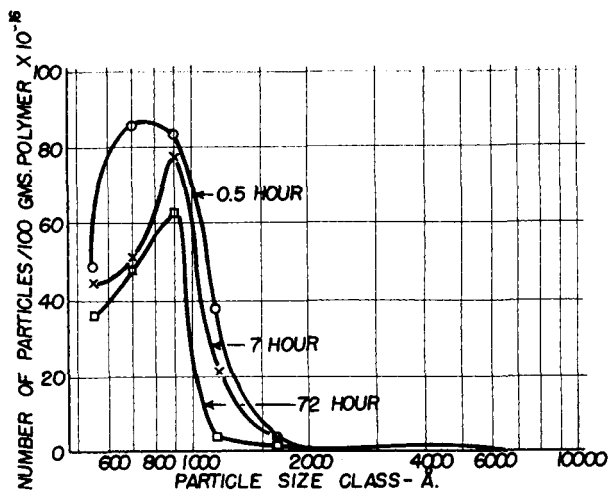
$$Z = Kn^2D^2 \qquad (1)$$

Fig. 4. Number distribution of particles at various times of agglomeration.

where Z is the frequency of collision, n is number, D is diameter, and K is a constant.

Davies and Rideal[9] have reported that in the coagulation of colloids the collision factor is of the same magnitude as that between gas molecules. If eq. (1) is valid for the present system it would be expected that the change in number of particles in a given size range should correlate with its n^2D^2 product.

The number distribution of a latex before and after agglomeration is given in Table II along with the calculated n^2D^2 products for the original

TABLE II
Number Frequency Distribution of Latex
Before and After Agglomeration

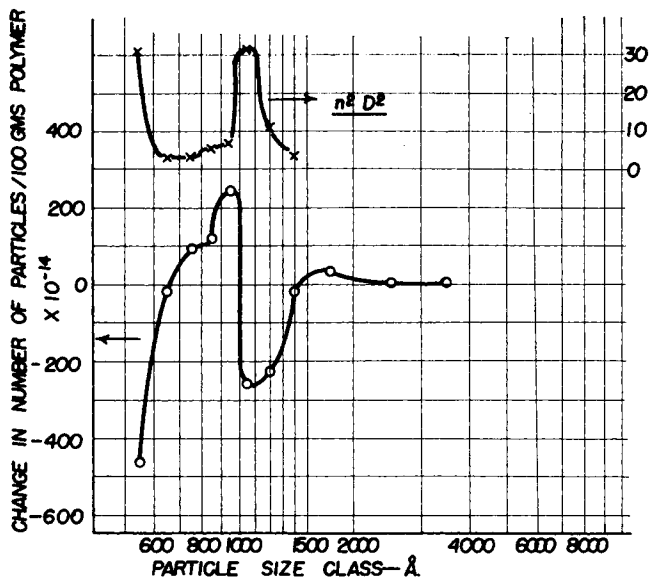|	Number of particles per unit weight $\times 10^{-14}$			
Diameter, A.	Original	After agglomeration	Difference (after-original)	n^2D^2
550	1010	448	−562	309
650	250	230	−20	26
750	231	326	95	30
850	277	398	121	55
950	265	508	243	63
1050	531	277	−254	311
1200	267	41	−226	103
1400	38	20	−18	28
1750		37	37	
2500		9	9	
3500		2	2	
500		1	1	
Total	2869	2297		

Fig. 5. Change in particle size distribution during agglomeration.

latex and the difference in number of particles (Δnp) before and after agglomeration. It is interesting to note that although the 1050 A. class has only one-half as many particles as the 550 A. class their n^2D^2 values are essentially equivalent. The change in particle number during agglomeration and the n^2D^2 values are presented in Figure 5. Here it is evident that a correlation exists in that the Δnp curve is close to an inverted image of the n^2D^2 curve. The regression coefficient of the effect of the n^2D^2 on particle number difference was calculated by the statistical method of linear regression and was found significant greatly beyond the 99% confidence limit.

It should be realized that the regression analysis as carried out is not completely accurate. This is because all classes above the smallest gain new particles by agglomeration of the classes below them at the same time as they are losing particles by agglomeration to larger sizes. This error should not be great, however, because as the smaller ones agglomerate they add a lesser number to the higher class than they lose. For example, about two 550 A. particles are required to form a 650 A. particle and to form an 850 A. particle four 550 A. particles are required. Furthermore, neglecting this effect would reduce the correlation found. Therefore, even greater confidence is warranted in the conclusion that the larger particles grow faster than the smaller ones and that the n^2D^2 relation is valid.

The substantiation of this relation between n^2D^2 and Δn has great practical as well as theoretical significance. Practically it illustrates the profound influence the size distribution of the base latex has on the final latex size distributions, which in turn control the fluidity,[5] the amount of macro particles (coagulum), as well as the performance of the latex in its final appli-

cation.   These results indicate that in mixtures of small and large particles the stability of the individual particles is independent of their size and that the agglomeration depends only on the frequency of collision of the particles. The finding is certainly in part the result of these studies being made under continuous agitation which exerts a greater influence on the larger particles.[10,13]

Statistically Designed Experiments

A statistically designed experiment was conducted to study the effects of controlled variations in the amounts of PVM, electrolyte, and soap in the recipe, as well as the latex solids concentration at which the agglomeration was carried out.

Latex B in Table I was used, and the levels of each of the factors studied are presented in Table III along with their coded values.   The maximum level of latex solids was limited because at concentrations above 48% its viscosity becomes too high for handling.   The lower soap level was established by the amount of soap present during the polymerization of the latex.   The highest soap level was held at 57.2% of saturation because early experiments had shown that as the soap coverage approached saturation little or no agglomeration occurred.   This could be expected in that as shown earlier in Figure 2 the surface tension drops during the process and agglomeration ceases as the surface tension reaches a minimum.

TABLE III
Levels of Variables Tested

		Code level			
Variable	-2	-1	0	1	2
X_1 PVM, phs[a]	0.015	0.030	0.045	0.060	0.075
X_2 Sodium sulfate, phs[a]	None	0.05	0.10	0.15	0.20
X_3 Total solids, %	30.1	34.9	39.7	44.5	49.3
X_4 Add soap, phs[a]	None	0.62	1.24	1.86	2.48

[a] phs = parts per hundred of latex solids.

The combination of each of the factors tested are given in Table IV along with the turbidity results after various times of agglomeration.   The coding system means for example that in the first sample coded -2, -1, -1, -2 the combination of ingredients were 0.015 PVM, 0.05 Na_2SO_4, 35% latex solids, and 0.62 parts of soap.

The last nine samples were also tested for particle size distribution by the alginate method with the results as given in Table V.   An empirical relationship between turbidity and total particle number was determined using these data.   This relationship was then used to calculate the total number of particles in all 25 sets of samples.   The particle numbers were then converted to their reciprocals for further analysis.

TABLE IV

Turbidity Results After Variable Agglomerating Times

	Treatment combination				Turbidity (1000 × absorbance/g.)										
	X_1	X_2	X_3	X_4	1 hr.	3 hr.	5 hr.	22 hr.	24 hr.	29 hr.	30 hr.	46 hr.	48 hr.	72 hr.	118 hr.
1	-2	-1	-1	-2	0.07	0.09	0.09		0.13		0.13		0.15	0.17	
2	-1	-1	-1	-2	0.12	0.11	0.13		0.22		0.23		0.26	0.31	
3	-2	1	-1	-2	0.10	0.15	0.09		0.13		0.14		0.16	0.20	
4	-1	1	-1	-2	0.14	0.14	0.17		0.30		0.28		0.39	0.50	
5	-2	-1	1	-2	0.12	0.12	0.14		0.25		0.27		0.31	0.39	
6	-1	1	1	-2	0.20	0.21	0.26		0.53		0.55		0.69	0.83	
7	-2	1	1	-2	0.14	0.15	0.19		0.35		0.37		0.47	0.59	
8	-1	1	1	-2	0.24	0.27	0.31		0.67		0.75		0.90	1.28	
9	-1	-1	1	-1	0.23	0.21	0.33		0.59		0.58		0.82	1.03	
10	-1	-1	1	1	0.31	0.30	0.37		0.97		0.98		1.41	1.60	
11	-1	1	1	-1	0.23	0.25	0.29		0.66		0.66		1.00	1.17	
12	-1	1	1	1	0.43	0.49	0.55		1.24		1.38		1.60	1.82	
13	1	-1	1	-1	0.32	0.37	0.42		0.96		1.08		1.40	1.86	
14	1	-1	1	1	0.53	0.62	0.67		1.41		1.44		1.54	1.69	
15	1	1	1	1	0.41	0.47	0.51		1.27		1.67		1.96	2.15	
16	1	1	1	1	0.69	0.72	0.87		1.43		1.33		1.53	1.63	
17	0	0	0	0	0.45	0.61	0.72	1.42		1.48		1.84			2.05
18	2	0	0	0	0.92	1.37	1.39	1.96		1.97		2.06			2.23
19	-2	0	0	0	0.20	0.25	0.30	0.54		0.50		0.66			0.88
20	0	2	0	0	0.61	0.76	0.92	1.71		1.91		1.78			2.07
21	0	-2	0	0	0.42	0.57	0.63	1.32		1.29		1.89			2.30
22	0	0	2	0	1.58	1.69	1.84	2.19		1.88		2.00			2.15
23	0	0	-2	0	0.22	0.21	0.24	0.34		0.33		0.41			0.57
24	0	0	0	2	0.78	0.97	1.15	1.45		1.44		1.58			1.79
25	0	0	0	-2	0.29	0.39	0.44	0.76		0.82		1.04			1.51

TABLE V
Particle Size Distributions After Variable
Agglomerating Times and Treatments

Particle size, A.	Weight-%								
	0000	2000	−2000	0200	0–200	0020	00–20	0002	000–2
After 3 hr.									
<600	14.9	12.1	17.4	13.0	16.3	11.3	15.8	12.9	15.8
600–800	18.8	20.8	20.1	21.0	21.4	19.4	23.3	20.5	21.1
800–1000	42.9	26.1	50.6	35.8	42.9	20.0	52.7	34.5	44.3
1000–2000	4.8	6.0	3.4	6.7	5.0	6.4	3.2	4.8	5.6
2000–4000	8.2	11.5	2.0	7.8	6.6	7.9	2.7	6.0	7.3
>4000	10.4	23.6	6.6	15.6	7.8	35.1	2.3	21.2	5.9
After 24 hr.									
<575				9.2	11.2	9.7	19.4	12.0	11.6
<600	14.6	13.4	14.8						
600–725	.			16.4	16.4	15.5	13.3	16.1	16.7
725–800	19.7	16.8	21.4						
800–940				25.0	36.5	21.9	46.3	33.2	41.3
940–1000	26.1	15.4	48.1						
1000–1800				4.0	5.4	5.2	12.6	3.4	6.0
1800–2000	1.3	9.4	1.8						
2000–3600				7.4	7.8	5.8	2.7	7.0	10.4
3600–4000	12.7	10.9	5.2						
>3600				37.5	22.8	41.9	5.8	28.4	14.0
>4000	25.7	34.2	8.8						
After 118 hr.									
<575	10.8	12.1	16.2	10.8	10.6	14.6	14.8	11.1	9.9
575–725	16.7	14.	15.2	12.3	13.6	10.4	16.5	11.9	14.1
725–940	21.2	16.7	48.1	23.4	23.0	19.0	50.3	32.1	29.0
940–1800	3.6	8.4	2.4	4.2	8.0	4.6	4.8	6.5	5.0
1800–3600	7.9	12.7	3.0	7.3	1.2	8.9	5.4	8.4	11.4
3600–9500	33.5	29.8	15.1	31.2	38.6	33.7	7.4	21.1	28.3
>9500	6.3	6.3	None	10.9	5.0	8.8	0.7	9.0	2.6

It is quite apparent in both Tables IV and V that agglomeration has occurred in these samples and that both the rate and extent of the agglomeration depend upon the controlled variations made. Plots of reciprocal numbers of particles against time for two of the samples (5 and 15) are presented in Figure 6. Here it is seen that although sample 5, which has the slower rate appears to show a linear relation sample 15, having the faster rate shows definite curvilinearity. The curves as drawn are plots of the curvilinear regression equations derived from the observed results. The equations have the form

$$1/n = (1/n_0) + aT - bT^2 \qquad (2)$$

The negative coefficient for the second-order time term shows that these systems become more stable as the process proceeds and indeed reach a stable state at finite times. Statistical tests of the second-order terms prove them to be statistically significant beyond the 99% confidence limits.
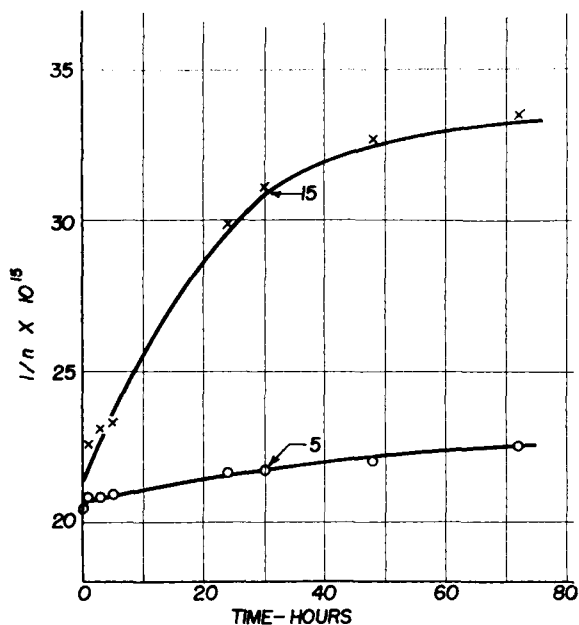
Fig. 6. Change of reciprocal number with time.

The regression equations for all the samples tested are given in Table VI. It was observed here, as was also the experience of van den Tempel[10] with oil emulsions and Gillepsie[11] with methyl cellulose as a latex creaming (aggregation) agent, that appreciable and variable agglomeration had occurred prior to the actual beginning of the tests. This is apparent in these equations, since the $1/n_0$ terms are not constant within a group run at the same initial solids content. To compensate, at least partially, for this adventitious effect, these equations were calculated with the use of the initial $1/n_0$ value of the unagglomerated latex; otherwise samples which actually had very fast initial rates would show abnormally low rates with abnormally high $1/n_0$ values.

The limiting values of $1/n$, that is the equilibria states, were determined by setting the first derivative, with respect to time, of the regression equations equal to zero and solving for the time (T_E). The $1/n_E$ values were then obtained by solving the regression equation at T_E.

Variation of Rates of Agglomeration. The initial agglomeration rates are the coefficients of the linear time terms. The effects of each of the controlled variables on the observed variations in these rates were determined by statistical analyses. The analysis of variance of these rates is summarized in Table VII. Here it is seen that the regression accounts for a highly significant amount of the variation, reaching beyond a 99% confidence level. Furthermore, it is seen that the level of PVM present and the latex solids have statistically significant effects on this rate. Increases in either of these factors give increased rates.

TABLE VI
Reciprocal Number of Particles Per Unit Volume
As Function of Time

		$1/n_0 \times 10^{17}$	$T \times 10^{21}$	$T^2 \times 10^{27}$	Equilibria $1/n \times 10^{17}$	
					Per unit volume	Per unit weight
1	$1/n =$	58.2	+0.11	−0.16	60.6	21.3
2	=	58.9	+0.29	−0.54	64.4	22.5
3	=	58.5	+0.07	+0.02	66.3	23.3
4	=	59.0	+0.36	−0.30	69.7	24.5
5	=	46.0	+0.26	−0.41	50.2	22.5
6	=	46.8	+0.72	−1.28	57.0	25.5
7	=	46.6	+0.43	−0.58	54.4	24.2
8	=	47.2	+0.86	−0.84	69.0	30.9
9	=	48.2	+0.55	−0.11	58.6	25.8
10	=	47.7	+1.58	−2.87	69.5	30.7
11	=	48.0	+0.97	−1.37	65.2	28.5
12	=	49.1	+2.02	−4.44	72.0	32.0
13	=	48.9	+1.49	−2.09	75.3	32.9
14	=	50.8	+2.10	−5.27	71.7	31.6
15	=	49.2	+2.68	−6.30	77.7	33.9
16	=	52.6	+1.84	−4.63	70.8	31.3
17	=	55.8	+2.20	−3.76	88.6	35.5
18	=	64.4	+1.99	−3.60	91.6	36.7
19	=	52.8	+0.68	−0.95	65.1	26.0
20	=	58.5	+2.30	−4.09	90.7	36.3
21	=	55.3	+2.13	−3.37	89.1	35.5
22	=	58.3	+1.13	−2.07	73.7	35.6
23	=	69.9	+0.44	−0.55	78.7	23.7
24	=	60.8	+1.53	−2.61	83.1	33.5
25	=	54.0	+1.10	−1.41	75.6	30.2

TABLE VII
Regression Analysis of Initial Agglomeration Rates[a]

Source of variation	Sums of squares	dF	Mean sums of squares	F
Due to regression	13.8013	14	0.9858	6.500**
About regression (error)	1.5165	10	0.1517	
Total	15.3178	25−1		

[a] Regression equation (coded):

$$a \times 10^{21} = 1.621 + 0.283\overset{*}{X_1} + 0.056X_2 + 0.191\overset{+}{X_3} + 0.133X_4 + 0.074X_1X_2$$

$$+0.036X_1X_3 - 0.091X_1X_4 + 0.101X_2X_3 - 0.074X_2X_4 + 0.002X_3X_4$$

$$- 0.022X_1{}^2 + 0.150\overset{+}{X_2{}^2} - 0.207\overset{*}{X_3{}^2} - 0.049X_4{}^2$$

Here + denotes significant beyond 90% confidence limit, * denotes significant beyond 95% confidence limit, ** denotes significant beyond 99% confidence limit.
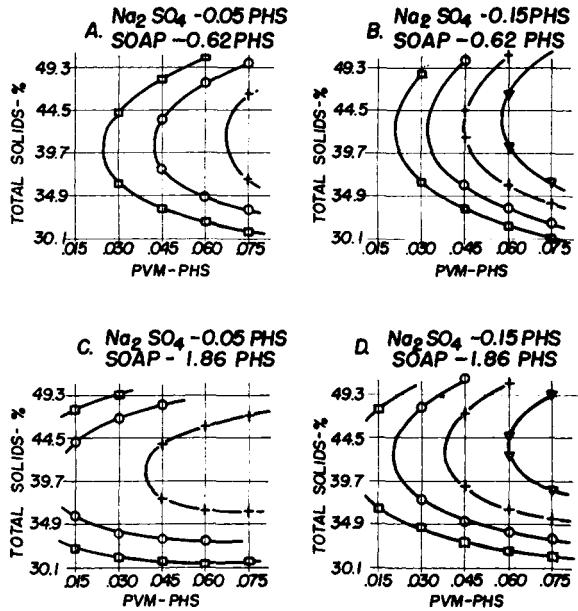
Fig. 7. Agglomeration rate as function of agglomerants: ($\square$) 1.0×10^{-21} cm.^{3}/sec.; ($\bigcirc$) 1.4×10^{-21} cm.^{3}/sec.; ($+$) 1.8×10^{-21} cm.^{3}/sec.; (∇) 2.2×10^{-21} cm.^{3}/sec.

These effects are presented graphically in Figure 7, where the total regression equation is plotted. The lines on this graph are contours connecting combinations of the controlled variables that give the same rates of agglomeration. The positive effect of increase in PVM is clear under any of the combinations presented. However, the amount of this effect is modified by the level of the other factors. For example, in Figure 7A, where the electrolyte and soap levels are low, the rate varies from 1.0 to 1.8 units, while at the higher levels of electrolyte and soap (Fig. 7D) the rates vary over the range of 1–2.2 units for comparable changes in PVM. It is also quite clear that increases in soap, and also in electrolyte, give increased agglomeration rates.

The soap effect is somewhat surprising in that *a priori* considerations would lead to the opposite conclusion. That is, it would normally be expected that increased soap would give increased coverage of the particle surfaces with consequent increased stability and therefore slower agglomeration. Possibly the effect of the soap as an electrolyte predominates over its effect as a surface active stabilizing agent.

The total solids content has a maximum effect at any given level of PVM and any combination of electrolyte and soap, and the maximum may shift to slightly higher solids at higher soap and electrolyte levels.

Equilibrium States. The analysis of variance of the calculated limits of the agglomerations, on a weight basis, is given in Table VIII. Here it is seen that the regression accounts for a very highly significant amount of

TABLE VIII
Regression Analysis of Equilibrium States of Agglomeration
(Weight Basis)[a]

Source of variation	Sums of squares	dF	Mean sums of squares	F
Due to regression	544.0485	14	38.8606	4.789**
About regression	81.1539	10	8.1154	
Total	625.2024			

[a] Regression equation (coded):

$$(1/n)_E = 32.801 + 1.8631\overset{*}{X_1} - 0.139X_2 + 1.418\overset{+}{X_3} + 0.469X_4 - 0.052X_1X_2$$
$$-0.089X_1X_3 - 0.463X_1X_4 + 0.456X_2X_3 - 0.403X_2X_4 - 0.071X_3X_4$$
$$-0.500X_1{}^2 + 0.430X_2{}^2 - 1.133\overset{+}{X_3}{}^2 - 0.453X_4{}^2$$

Here + denotes significant beyond 90% confidence limits, * denotes significant beyond 95% confidence limits, ** denotes significant beyond 99% confidence limits.

the variation in this response. It is also shown that the equilibrium states are controlled by the amount of PVM and the solids level at which the agglomeration is conducted. Since these are reciprocal numbers, increases indicate decreases in number of particles and therefore increased agglomeration. Increases in either PVM or solids content gives increased agglomeration. However, since the total solids second-order term is negative, the effect of increases in this factor is reduced with each increment of increase.
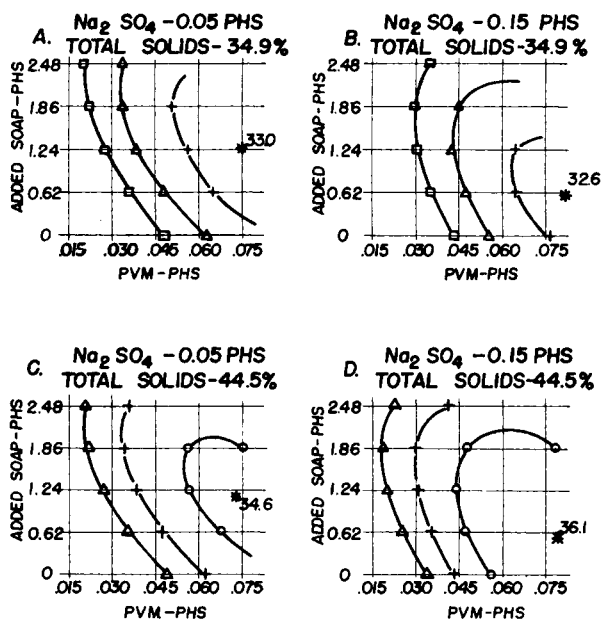

Fig. 8. Equilibrium states of agglomeration: (□) 28.0 × 10⁻¹⁷ g./part; (△) 30.0 × 10⁻¹⁷ g./part; (+) 32.0 × 10⁻¹⁷ g./part; (O) 34.0 × 10⁻¹⁷ g./part.

This regression equation is presented graphically in Figure 8. Here it may be seen that increases in the PVM under any combination of the other ingredients give increased agglomeration, although as the soap is increased the effect is lessened. It is also evident that, as the soap content is increased, the actual extent of agglomeration is increased up to a level of soap beyond which the extent is reduced by increased soap.

Comparison With Smoluchowski Theory. It is apparent that the PVM agglomeration as conducted does not follow the Smoluchowski kinetics in that the relationship found between the reciprocal number and time is not linear. Furthermore, as was seen in Table VI, the initial agglomeration rates varied over the range $(0.07-2.68) \times 10^{-21}$ cm.^{3}/sec., which shows these systems to be between 0.07 and 2.68×10^{10} times slower than the Smoluchowski fast coagulation rate of 10^{-11} cm.^{3}/sec. for unagitated systems. Furthermore, since the present systems were all subjected to continuous agitation, their relative stabilities are even greater than the above comparisons indicate.

IV. SUMMARY AND CONCLUSIONS

Although additional work is needed to completely define the PVM mechanism some definite conclusions can be drawn at this time.

(1) A bridging by the PVM such as that found by La Mer, Smellie, and Lee[2] for polymeric flocculants is consistent with the experimental evidence. Indeed PVM satisfies all four of the criteria (adsorbable on colloidal particle surface, polymeric, water-soluble, and effective at low concentrations) set forth by these authors for an effective flocculating agent. The results presented show that both the rate and extent of agglomeration increase with increases in PVM levels under any of the conditions tested. However, the relative magnitude of the PVM effect is modified by the levels of the other factors studied.

(2) The observed electrolyte effect, i.e., increases in electrolyte give increased effect of PVM, can be attributed to the electrostatic stabilization of the latex particles. Increases in electrolyte (increased ionic strength of the aqueous phase) reduce the thickness of the ionic double layer.[9] This reduction in ionic double layer reduces the length of polymer necessary to bridge between two particles. This then could make the PVM more effective in that additional lengths of the molecule would be available for adsorption. This same effect could be part of the explanation for increased rates of agglomeration, with increased solids content, in that as the latex solids content is increased the electrolyte present in the aqueous phase is also increased, giving higher ionic strength.

(3) The total solids effect, whereby the rate is increased as solids is increased, is also a function of increased collision due to increased concentration of polymer particles.

(4) The soap effect on the agglomeration rates at the levels tested is that which could be expected as a result of increasing the ionic strength of the

aqueous phase and consequent reduction in thickness of the ionic double layer.

(5) The soap level also controls the final equilibrium state because, as the surface area of the polymer particles decreases to the point at which they can be fully saturated with soap, the preferred adsorption of the soap prevents PVM adsorption.

(6) The observed decrease in rate after the total solids content reaches a given level is not completely understood at this time.   However, the increased ionic strength of the aqueous phase may in some way (e.g., by dehydration) decrease the molecular dimensions or even salt out the PVM and thus reduce its effectiveness.   This point is under further investigation.

The fate of the PVM is also being studied experimentally to be sure that the self-limiting feature of the process is merely due to the soap saturation of the polymer surfaces and not partially to occlusion (or solution) of the PVM in the particles it bridges and the consequent unavailability of PVM for further bridging.   It is expected that these features will be subjects of further communications.

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Résumé

Des petites particules (environ 700 A.) de Latex-SBR peuvent être agglomérées (par assemblage ou par coalescence) pour former des particules de dimensions importantes et de distribution hétérogène comme le requiert les suspensions de Latex a forte concentration.   Cette agglomération est favorisée par des matériaux d'un poids moléculaire élevé tel que l'éther de méthyle-polyvinyle (PVM).   On a examiné le mécanisme de

cette agglomération.   On a étudié l'effet de la variation contrôlée des quantités de PVM, d'électrolyte, de savon et du contenu solide du Latex en utilisant des expériences projetées de manière statistique.   Le phénomène d'agglomération diffère de la cinétique de Smoluchowski parce qu'il peut être décrit par la relation: $(1/n) = (1/n_0) + at - bt^2$ où n représente le nombre de particules, t le temps et où a et b sont 2 constantes.   Les vitesses d'agglomération sont environ 10^{11} à 10^{12} plus lentes que ne le prévoirait une vitesse rapide de coagulation suivant la théorie de Smoluchowski.   Lorsqu'on augmente la quantité de PVM, de savon et de latex solide, on augmente la vitesse d'agglomération.   Les agglomérations se limitent d'elles-mêmes et atteignent un équilibre qui augmente avec l'élévation de la concentration en PVM et diminue avec l'addition de savon.   On dérive des équations de régression qui relient les effets des variables contrôlable sur la vitesse d'agglomération et sur les états d'équilibre; on représente également ces équations graphiquement.   La distribution du volume des particules du Latex obtenu est reliée a celle que l'on pouvait déduire d'une théorie sur les collisions.

Zusammenfassung

Kleine Teilchen (ca. 700 A.) in einem SBR-Latex können zu höherer Grösse und heterogener Verteilung agglomerieren (Aggregierung und Koaleszenz), wie es für einen flüssigen Latex mit hohem Festkörpergehalt notwendig ist.   Die Agglomerierung wird durch hochmolekulare Stoffe wie Polyvinylmethyläther (PVM) begünstigt.   Der Mechanismus der Agglomerierung wurde untersucht.   Der Einfluss der Änderung der Menge von PVM, Elektrolyt, Seife und Feststoffgehalt des Latex wurde in statistisch ausgelegten Versuchen bestimmt.   Die Agglomerierung wich von dem kinetischen Verhalten nach Smoluchowski ab und konnte am besten durch die Beziehung: $(1/n = (1/n_0) + at - bt^2$ wiedergegeben werden, wo n = Teilchenzahl, t = Dauer und a und b Konstante sind.   Die Agglomerierungsgeschwindigkeit war etwa 10^{11} bis 10^{12} mal kleiner als die theoretische Geschwindigkeit einer raschen Koagulation nach Smoluchowski.   Eine Erhöhung von PVM, Seife und Latexfestkörper lieferte eine grössere Agglomerierungsgeschwindigkeit.   Die Agglomerierung kam von selbst zum Stillstand und das erreichte Gleichgewicht lag bei Zunahme von PVM höher, bei Zunahme an Seife niedriger.   Regressionsgleichungen für die Beziehungen zwischen dem Einfluss der untersuchten Variablen auf die Agglomerierungsgeschwindigkeit und den Gleichgewichtszuständen werden abgeleitet und graphisch dargestellt.   Die Partikelgrössenverteilung im Endlatex stand mit der nach der Stosstheorie zu erwartenden in erkennbarer Korrelation.