Emulsion Polymerization of Ethylene.   III.   Factors Affecting the Stability of Polyethylene Latexes

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Synopsis

A semiquantitative method for assessing the amount of visible solid matter in poly-ethylene latexes is described. As judged by this method and by the presence of particles larger than 50 μ, the stability of the latexes was related to (1) the type and concentration of post-emulsifier added to the latex, (2) the average size of the polymer particles, and (3) the concentration of solids. Generally, the appearance was better when the latexes had a low (30%) concentration of solids, a large (800 A.) average particle diameter, and enough post-emulsifier to cover most of the polymer surface. Specific samples, however, having a high (36%) concentration of solids and a small (300 A.) average particle diameter also showed good storage stability. According to tests on selected latexes, good resistance to coagulation by mechanical shear was obtained only if the surface of the polymer was completely covered with emulsifier. When polyethoxylated alkylphenols were used as post-emulsifiers, an inverse relation appeared to exist between latex stability and average number of ethylene oxide units per emulsifier molecule. Moreover, the addition of each ethylene oxide group increased the apparent area of the emulsifier molecule by about 4 A.^{2}

INTRODUCTION

Polymer latexes obtained by emulsion polymerization are thermo-dynamically unstable; hence their stability during storage is an important property, especially if they are to be used in products such as latex-based paints and polishes where the time between formulation and use could be about one year. In such latexes, the particle number and diameter, the type and amount of polymer, and—if the polymer surface is not entirely covered by the original emulsifier—the type and concentration of the second emulsifier (post-emulsifier) added to complete the coverage are critical factors affecting the stability of the latexes. Because these latexes seek a more stable state through the reduction of polymer surface, a tendency for agglomeration of particles is present, and the gradual advance of this process causes the formation of undesirably large particles with concurrent changes in the physical properties of the latex. The large particles may accumulate as a precipitate or cream, or the latex may develop a milky or chalky cast. Although these changes are subject to quantitative evaluation by gravimetric and light-scattering techniques, the relation

between measured values and desirable appearance is not well established; so commercial acceptance of a latex often depends on a subjective evaluation by an experienced formulator.

Actually, subjective methods of evaluation are widely used, but very few are reported in satisfactory detail owing to the difficulty in describing how the factors can be judged by odor, sight, sound, taste, or touch. ASTM method D 1791-60T, for example, describes an accelerated aging test for dry-bright polishes, which are basically mixtures of polymer latexes and wax emulsions. If the polish is unstable to an extent that it changes in appearance during the test, the changed sample is described as "slightly viscous," "viscous," "gelled," "creamed," or showing a "phase separation of liquid or solid." Definition of these terms is, to a great extent, left to whoever makes the test. In a "go, no-go" test such as this, the sample either changes or it doesn't, so recognition that a change has occurred is sufficient. When the degree of change is to be related to compositional differences among the samples, however, the descriptive terms must acquire a quantitative aspect.

This paper presents a system that was used to judge changes in the appearance of polyethylene latexes stored at ambient conditions. The subjective data, which are based solely on the separation of solid material from the latexes, were complemented with gravimetric determinations of the amount of solid material too large to pass through a 50-μ screen. In addition, the stability of a few latexes to mechanical shear was also measured.

EXPERIMENTAL AND RESULTS

Latex Description

The polyethylene latexes were prepared in an 18-gal. autoclave as described by Helin et al.[1] The latexes and the recipes and conditions used to make them are described in Table I, where parts are given per 100 parts of

TABLE I

	Run no. 94	Run no. 95	Run no. 135
Water, parts	90.5	84.5	85
tert-Butyl alcohol, parts	9.5	15.5	15
Polyethoxylated (9.5) nonylphenol, parts	—	—	3
Myristic acid, parts	2.90	1.09	—
Potassium hydroxide, part	0.71	0.27	—
Potassium phosphate, part	0.42	0.42	—
Potassium persulfate, part	0.16	0.16	0.3
Pressure, psig	3000	3000	3000
Temperature, °C.	80	80	80
Solids in latex, %	25.4	26.4	19.0
Surface tension, dynes/cm.	69.2	69.8	36.3
Avg. particle diameter, A	300	800	—

aqueous phase (water or water and *tert*-butyl alcohol). The latexes were concentrated to about 36% solids in a rotating flask evaporator at 70°C. under a reduced pressure controlled to keep the latex from foaming into the condensate receiver. The respective average particle diameters of latexes 94 and 95 were 300 and 800 A., as measured by a modification[2] of Maron's method.[3] Latexes such as these, which have a high surface tension because they contain less emulsifier than needed to cover the polymer surface, are often described as "unsaturated."

Sample Preparation

The experiment was arranged to show latex stability at average particle diameters of 300 and 800 A., at solids concentrations of 30 and 36%, and at two concentrations of six post-emulsifiers. (The experiment started with nine post-emulsifiers; the polyethoxylated (30) octylphenol was dropped because all samples to which it was added gelled, and two are not reported here owing to incomplete chemical identification.) Only one of the six post-emulsifiers was added to each sample, and the amounts used nominally covered either 50 or 100% of the polymer surface that was not already covered by the primary, or recipe, emulsifier.

The 56 samples described in Table II consist of two groups, the principal one containing 48 samples representing a 6×2^3 factorial arrangement[4] of six post-emulsifiers with the eight combinations of particle size, solids content, and post-emulsifier concentration. The remaining eight samples are controls prepared in duplicate for each of the four combinations of solids content and particle size.

In order to post-stabilize the latexes from runs 94 and 95, the capacity of the latexes to adsorb each emulsifier was determined by tensiometric titrations at room temperature on a Du Nouy tensiometer. The inflection points were based on the intersection of extrapolated linear segments of the plot of surface tension versus volume of emulsifier solution. Titrations made with the anionic emulsifiers exhibited a sharp break; so little or no extrapolation was needed to fix the point of intersection. But titrations with the polyethoxylated alkylphenols showed a gradual break; hence these inflection points underestimated by about 10–20% the amount of emulsifier needed to reach the critical micelle concentration (CMC) as determined from plots of surface tension versus the logarithm of volume of added emulsifier solution. Table III gives the amounts of each post-emulsifier required to complete the coverage of at least 90% of the total polymer surface in each latex.

The ingredients for each sample—300 ml. of base latex, emulsifier, and water—were added to quart bottles and warmed to 50°C. with frequent shaking. (The potassium soaps were made *in situ* by first adding to the latex the required potassium hydroxide dissolved in 20 ml. of water.) The mixed sample was filtered through $^1/_{16}$-in. felt, divided into four equal parts, and stored in capped 4-oz. bottles. The filtration generally removed less than 5 g. of wet solids (none appeared on filtering the controls); so no

TABLE II

Effect of Various Factors on the Stability of Polyethylene Latexes

	Solids %	Post-emulsifier, % of uncovered surface	Average particle diameter, A.	Rating, for various emulsifier types						
				Nonyl phenol, n = 9.5	Octyl phenol, n = 9.5	Octyl phenol, n = 16	Sodium lauryl sulfate	Potassium myristate	Potassium stearate	None[a]
Solids >50 μ (after 10 days), % × 1000	30	50	300	26	51	38	10	19	39	48
Solids >50 μ (after 60 days), % × 1000				154	66	103	63	90	203	92
Time between first and second determinations, days										
Visual score (after 10 days)[b]				48	54	52	52	51	52	54
Visual score (after 60 days)[b]				7	10	9	9	8	11	9
Solids >50 μ (after 10 days), % × 1000	30	50	800	9	12	8	10	12	15	10
Solids >50 μ (after 60 days), % × 1000				1	7	17	9	35	153	7
Time between first and second determinations, days				50	64	71	92	158	401[c]	120
Visual score (after 10 days)[b]				50	54	54	52	50	49	51
Visual score (after 60 days)[b]				9	8	9	9	9	7	7
Solids >50 μ (after 10 days), % × 1000	30	100	300	9	10	12	9	12	9	10
Solids >50 μ (after 60 days), % × 1000				43	17	55	7	8	2	34
Time between first and second determinations, days				66	115	136	56	99	31	115
Visual score (after 10 days)[b]				52	55	52	55	48	51	47
Visual score (after 60 days)[b]				7	11	11	11	6	6	11

This is a rotated (landscape) data table. Reconstructed below with the 7 sample columns and the five recipe blocks. Each block is identified by its three recipe parameters.

Block parameters (30, 100, 800)

Measurement	S1	S2	S3	S4	S5	S6	S7
Solids >50 μ (after 10 days), % × 1000	15	20	67	21	13	4	19
Solids >50 μ (after 60 days), % × 1000	65	207	266c	36	59	70	82
Time between first and second determinations, days	48	48	52	51	56	51	52
Visual score (after 10 days)[b]	8	7	7	4	5	7	4
Visual score (after 60 days)[b]	8	6	6	8	7	7	7

Block parameters (36, 50, 300)

Measurement	S1	S2	S3	S4	S5	S6	S7
Solids >50 μ (after 10 days), % × 1000	8	184	10	53	54	264	41
Solids >50 μ (after 60 days), % × 1000	212	415	87	123	411	302c	225
Time between first and second determinations, days	48	51	55	54	56	49	52
Visual score (after 10 days)[b]	9	11	9	11	8	7	8
Visual score (after 60 days)[b]	8	16	9	10	15	10	8

Block parameters (36, 50, 800)

Measurement	S1	S2	S3	S4	S5	S6	S7
Solids >50 μ (after 10 days), % × 1000	7	21	34	47	76	51	8
Solids >50 μ (after 60 days), % × 1000	76	119	88	87	104	112	86
Time between first and second determinations, days	51	51	52	51	54	51	49
Visual score (after 10 days)[b]	7	10	7	6	7	7	6
Visual score (after 60 days)[b]	10	11	9	9	11	8	8

Block parameters (36, 100, 300)

Measurement	S1	S2	S3	S4	S5	S6	S7
Solids >50 μ (after 10 days), % × 1000	1	62	49	33	30	114	17
Solids >50 μ (after 60 days), % × 1000	142	145	141	87	229	158	128
Time between first and second determinations, days	54	48	52	51	49	49	52
Visual score (after 10 days)[b]	9	7	6	15	6	5	6
Visual score (after 60 days)[b]	9	12	9	10	6	11	9

Block parameters (36, 100, 800)

Measurement	S1	S2	S3	S4	S5	S6	S7
Solids >50 μ (after 10 days), % × 1000	20	13	19	19	38	25	12
Solids >50 μ (after 60 days), % × 1000	65	73	124	53	64	166	77
Time between first and second determinations, days	51	52	51	52	54	50	54
Visual score (after 10 days)[b]	7	4	3	8	4	3	7
Visual score (after 60 days)[b]	10	6	8	7	8	6	8

[a] These are the control samples to which no post-emulsifier was added; so the samples appear in duplicate.

[b] See Table IV.

[c] Missing from original data. The reported values are those that minimize the sum of squares for the values of log $[(\Delta\%/\text{days})10^3]$.

TABLE III
Amount of Various Emulsifiers Used to Post-Stabilize Two Polyethylene Latexes

Post-emulsifier	Amount of added emulsifier, g./l. of latex[a]	
	Latex 94	Latex 95
Potassium myristate	63.7	30.6
Potassium stearate	78.6	44.9
Sodium lauryl sulfate	99.3	39.9
Polyethoxylated (9.5) nonylphenol	80.7	37.5
Polyethoxylated (9.5) octylphenol	70.2	37.2
Polyethoxylated (16) octylphenol	56.5	32.2

[a] This amount of emulsifier, which corresponds to the amount needed to cover a nominal 100% of the uncovered surface, and the amount of emulsifier used to prepare the latex, together cover more than 90% of the polymer surface.

correction was made to the solids concentration of the latex to compensate for the material lost.

Sample Evaluation

The samples were evaluated twice; once about 10 days after their preparation and again after a lapse of about 50 days.   The first step in the evaluation consisted of visually rating each sample according to the amount of separated matter appearing in the latex by the method outlined in Table IV. The undisturbed sample was first examined for cream, flakes, and visible sediment.   If no sediment was visible, the bottle was slowly inverted to expose any at the bottom of the latex.   The latex was then shaken to disperse the solids and rated for granules and wall film.   The visual score is the sum of the ratings for the five separate categories of solids.   In the last step of the evaluation, the latex was washed with distilled water through a 50-μ screen to determine the amount of material too large to pass through. These two sets of data, as well as the number of days between the determinations of solids, are given in Table II.

Data Analysis

The average effects of various factors on latex stability are given in Table V, along with the associated experimental error, the least significant difference (LSD) between averages of 8 observations, and a listing of the statistical importance of the two-factor interactions.[4]   The number of observations averaged to obtain each entry varies from 8 for the controls and post-emulsifiers to 24 for comparisons 6, 7, and 8.   The comparisons are made as indicated by taking the difference between appropriate averages.   Differences that are significantly large are marked with a symbol showing the probability against their arising merely from experimental error.   Although no numerical values are assigned to the interactions, the

TABLE IV

System for Describing the Appearance of Solids in a Latex

(The Visual Score for a Sample Is the Sum of the Ratings)

Form taken by the solids	Rating				
	0	1	2	3	4
Cream[a]	None	Not continuous	Continuous, $<1/16$ in. thick	Continuous, $<1/8$ in. thick	Continuous, $>1/8$ in. thick
Flakes[b]	None	On $<10\%$ of surface	On $<50\%$ of surface	On $>50\%$ of surface	—
Sediment[c]	None	—	Visible if bottle is inverted	—	Visible if bottle is not inverted
Granules[d]	None	Light	Moderate	Heavy	—
Wall film[e]	None	—	Some	—	Much

[a] A ring (collar) or layer of solids on the latex surface.

[b] Flat, well-defined particles on the latex surface.

[c] Any matter that settles to the bottom of the latex.

[d] Sandy or grainy specks appearing in a film of latex draining from the wall of the bottle.

[e] Any matter on the bottle wall undislodged by shaking the latex twice.

TABLE VA

Average Effects of Various Factors on the Stability of Polyethylene Latexes[a]

Factor	Average solids >50 μ, %			Average Change per Day × 10^5 [b]	Average visual scores		
	After 10 days	After 60 days	Change in solids		After 10 days	After 60 days	Change
Controls	0.018	0.111	0.093	151	8.1	9.5	1.4
Post-emulsifiers							
A. Polyethoxylated (9.5) nonylphenol	0.021	0.108	0.087	145	6.4	8.1	1.7
B. Polyethoxylated (9.5) octylphenol	0.067	0.132	0.065	105	6.6	9.4	2.8
C. Polyethoxylated (16) octylphenol	0.040	0.147	0.107	133	7.1	9.8	2.7
D. Sodium lauryl sulfate	0.025	0.075	0.050	91	9.3	9.3	0.0
E. Potassium myristate	0.030	0.132	0.102	184	6.5	8.9	2.4
F. Potassium stearate	0.062	0.187	0.125	203	7.9	10.1	2.2
Comparisons							
1. A and B	0.044	0.120	0.076	83	6.5	8.8	2.3
C	0.040	0.147	0.107	133	7.1	9.8	2.7
Difference	0.004	-0.027	-0.031	-50	-0.6	-1.0	-0.4
2. A	0.021	0.108	0.087	145	6.4	8.1	1.7
B	0.067	0.132	0.065	105	6.6	9.4	2.8
Difference	-0.043*	-0.024	0.022	40	-0.2	-1.3	-1.1
3. D	0.025	0.075	0.050	91	9.3	9.3	0.0
E and F	0.046	0.159	0.113	193	7.2	9.5	2.3
Difference	-0.021	-0.084	-0.063	-102**	2.1*	-0.2	-2.3*

4. E	0.030	0.132	0.102	184	6.5	8.9	2.4
F	0.062	0.187	0.125	203	7.9	10.1	2.2
Difference	-0.032‡	-0.055	-0.023	-19	-1.4‡	-1.2	0.2
5. A, B, and C	0.043	0.129	0.086	128	6.7	9.1	.42
D, E, and F	0.039	0.131	0.092	159	7.9	9.4	1.5
Difference	0.004	-0.002	-0.006	-32	-1.2†	-0.3	0.9
6. 100% Emulsifier	0.028	0.144	0.116	121	5.9	8.1	2.2
50% Emulsifier	0.048	0.308	0.260	155	8.2	10.5	2.3
Difference	-0.020*	-0.164	-0.144	-34†	-2.3***	2.4***	-0.1
7. 36% Solids	0.050	0.353	0.303	169	7.1	9.8	2.7
30% Solids	0.027	0.099	0.072	111	7.0	8.8	1.8
Difference	0.023*	0.254	0.231†	58**	0.1	1.0	0.9
8. 800 A diameter	0.028	0.101	0.073	118	6.4	8.2	1.8
300 A diameter	0.048	0.351	0.303	161	7.7	10.4	2.7
Difference	-0.020*	-0.250	-0.230†	43*	-1.3**	-2.2***	-0.9
Experimental error[c]	0.034	0.637	0.641	84	1.6	2.2	2.3
Least significant difference (LSD)[d]	0.035	0.650	0.654	85	1.6	2.2	2.4

[a] The level of statistical significance of the differences and the interactions is indicated thus: † = 80%; ‡ = 90%; * = 95%; ** = 99%; *** = 99.9%.

[b] The analysis of variance was made on logarithms of this expression.

[c] Based on the unlisted interactions from the complete experiment that included eight emulsifiers, two of which were excluded here on grounds of unknown composition.

[d] For differences between averages of eight observations.

TABLE VB
Statistical Importance of Two-Factor Interactions[a]

Two-factor interactions	Average solids >50 μ, %			Average change/day $\times 10^5$	Average visual scores		
	After 10 days	After 60 days	Change in solids		After 10 days	After 60 days	Change
Emulsifier concn. × solids concn.	—	—	—	—	—	—	—
Emulsifier concn. × diameter	—	—	—	—	—	—	—
Solids concn. × diameter	**	‡	†	***	*	*	—
Emulsifier type × emulsifier concn.	—	—	—	—	†	—	—
Emulsifier type × solids concn.	—	—	†	‡	—	—	—
Emulsifier type × diameter	—	—	†	†	†	—	†

[a] The level of statistical significance of the differences and the interactions is indicated thus: † = 80%; ‡ = 90%; * = 95%; ** = 99%; *** = 99.9%.

same marking scheme is used to indicate their importance. The experimental error, which is derived from the pooled sum of squares for the three- and four-factor interactions, is given in the units of the observation.

The results from the group of 48 experiments can be summarized as follows: (1) latexes looked better when the polymer surface was saturated with emulsifier than when not; (2) growth of solids >50 μ and deterioration of appearance were less in latexes having an average particle diameter of 800 A. than in those of 300 A., (3) the rate of growth of solids >50 μ was higher in latexes containing 36% solids than in those containing 30%; (4) no emulsifier or combination of emulsifiers was consistently outstanding; and (5) the combination of 36% solids and a 300 A. average particle diameter contributed most to poor appearance and growth of solids >50 μ. This last conclusion is not apparent, however, until the interaction between particle diameter and solids concentration is examined in the two-way breakdown given in Table VI, which is constructed by taking the average of the four groups of 12 latexes that have in common the indicated combinations of particle size and solids content.

The fact that the controls often contained less material exceeding 50 μ in size than did the post-stabilized samples is misleading without reference to the observation that the method by which the latexes were post-stabilized actually caused some coagulum to form (cf. sample preparation). The step causing the coagulum was the addition of the concentrated post-emulsifier directly to the concentrated latex. Although the formation of visible coagulum can be avoided by adding a dilute solution of emulsifier, the latex must then be concentrated to restore it to a high concentration of solids. Comparisons made within the post-stabilized group, except for

those between emulsifiers, are probably not affected by the coagulum. But its formation does complicate comparing the controls with the post-stabilized samples.

The average differences between controls and individual post-stabilizers suggest, when compared with the LSD, that the 10-day appearance is better in latexes post-stabilized with a polyethoxylated (9.5) alkylphenol than in the controls and that the $>50-\mu$ solids after 10 days are higher in the samples containing polyethoxylated (9.5) octylphenol and potassium stearate. Because this is not a persistent pattern (it is not present 50 days later) and because none of the other variations exceed the LSD, there is little assurance that any one emulsifier is a more effective post-stabilizer than the others.

TABLE VI

Effect of Average Particle Diameter and Solids Concentration on the Latex Appearance and the Amount of Particles Exceeding 50 μ in Size

Concentration of Solids, %	Time of analysis and attribute determined	Average particle diameter	
		300 A.	800 A.
30	10-day visual rating	7.8	7.1
	60-day visual rating	9.8	8.5
	10-day % solids >50 μ	0.026	0.030
	60-day % solids >50 μ	0.099	0.130
36	10-day visual rating	8.2	6.0
	60-day visual rating	10.4	8.2
	10-day % solids >50 μ	0.076	0.036
	60-day % solids >50 μ	0.204	0.096

It is still possible, however, to state that post-stabilization does improve the appearance of the latexes. If the act of post-stabilization is assumed to have no effect, either good or bad, on the stability of the latexes, then the 12 average visual ratings on the post-stabilized latexes should fall with equal frequency above and below the average for the controls. Application of the chi-square (χ^2) test[4] to the departure of the observed frequency from the postulated frequency yields a value of 3.33. Because the probability is only 0.05–0.10 that a value this large can occur without cause other than chance, the conclusion that post-stabilization does improve the appearance of the latexes is reasonable. When applied to the $>50-\mu$ solids, the test gives a χ^2 value of 6.67 for the same group of 12 latexes. Inasmuch as a value this large can occur by chance with a probability of only 0.01, the conclusion that the controls contain less large material than do the post-stabilized latexes is also reasonable. These two conclusions are not contradictory, however, because the better appearance of the post-stabilized samples, despite their containing more large particles than the controls, shows that post-stabilization is really quite effective in maintaining the latex appearance.

Mechanical Stability

The resistance of three latexes to coagulation by a shearing force (mechanical stability) was determined by stirring them in a Waring Blendor. Latex 95, which had a surface tension of 69 dynes/cm., coagulated after about 10 sec. of stirring. When post-stabilized with potassium myristate and concentrated to 40% solids, however, the same latex could be stirred 50 min. without coagulating. A similar increase in stability was obtained in latex 95 by post-stabilizing with morpholinium oleate to a surface tension of 30.8 dynes/cm. About 500 ml. of latex 135, which was prepared with an emulsifier of polyethoxylated (9.5) nonylphenol and had a surface tension of 36.3 dynes/cm., was put in the blender and stirred. At 1-min. intervals, the blender was stopped and a sample was withdrawn. The latex coagulated after 5.7 min. of stirring. The surface tension was measured on each of the seven samples, including an initial and final sample, after 10 g. of the sample had been diluted with 20 g. of water. (The dilution was made because some of the samples were so viscous that the surface tension could not otherwise be measured.) The viscosity of each sample, excluding the coagulated final sample, was estimated by means of a Gardner bubble viscometer. These data, which are given in Table VII, show that the surface tension fell and the viscosity rose while the latex was stirred.

TABLE VII

Effect of Agitation on Surface Tension and Viscosity of Latex 135

Duration of agitation, min.	Surface tension, dynes/cm.[a]	Kinematic viscosity, stokes[b]
0	36.3	0.85–1.00
1	34.6	2.25–2.50
2	35.9	2.75–3.00
3	35.0	4.70–5.00
4	33.9	8.84
5	32.9	17.6–22.7
5.7[c]	33.4	—

[a] Determined with a ring tensiometer on 10 g. sample diluted with 20 g. of water.

[b] Gardner bubble viscometer.

[c] Sample coagulated.

DISCUSSION

Apparent Molecular Area

The apparent molecular areas of the polyethoxylated alkylphenols used in this study are given in Table VIII. The values were obtained by multiplying the ratio C_m/C_p by 34.1, where C_m is the moles of potassium myristate needed to bring a liter of latex to the CMC, C_p is the corresponding amount of another emulsifier determined from a plot of surface tension versus log volume of emulsifier solution, and 34.1 is the effective molecular

TABLE VIII

Effect of Ethylene Oxide Content on the Apparent Molecular Area of
Polyethoxylated Octylphenols

Average number of ethylene oxide units	Apparent molecular area, A.^{2}	
	Latex 94	Latex 95
9.5[a]	56	51
9.5	53	60
16	80	83
30	170	122
30	179	138
30	—	138
30	—	152

[a] Nonylphenol.

area (in square Angstroms) reported by Maron[3] for a molecule of myristate soap. Theoretically, this ratio should be formed from the moles of adsorbed emulsifiers, but, owing to the lack of information of the relative amounts of potassium myristate (the recipe soap) and post-emulsifier in solution at the inflection point, the appropriate corrections could not be made. Actually, the critical micelle concentrations for these emulsifiers,[3,6] lead to values of dissolved emulsifier that are less than 1 g./l. This is a small correction, and its effect on the ratio C_m/C_p is negligible, inasmuch as it applies to both terms.
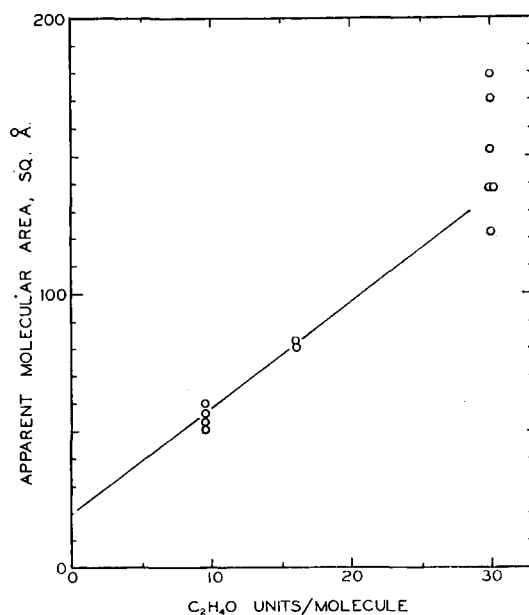

Fig. 1. Dependence of apparent molecular area of polyethoxylated alkylphenols on the number of units of ethylene oxide.

The apparent molecular areas for the polyethoxylated alkylphenols are plotted in Figure 1 against the number n of ethylene oxide units per molecule. If the intercept is taken as 20, the cross-sectional area of the alkyl chain,[6] the intercept and the average apparent areas at $n = 9.5$ and 16 appear to lie on a straight line having a slope of about 3.9 A.^{2}/unit of ethylene oxide. (This agrees well with the plot given by Orr and Breitman[5] for values of $n = 4$–30, which also has a slope of 3.9 A.^{2}/unit but an intercept of zero, implying that the alkylphenoxy part of the molecule has no apparent area.) Although the average of areas obtained at $n = 30$ lies above the straight line shown in Figure 1, the large variation among the individual values precludes deciding if the area per unit actually increases with chain length.

Latex Stability

The series of four emulsifiers wherein the number of ethylene oxide units varies is of special interest not only because of the change in apparent molecular area, but also because the latex stability appears to decrease as the number of units in the polyoxyethylene chain increases. Although the difference in stability between latexes containing 9.5 and 16 units was not statistically significant, the direction of change in 6 of the 7 entries for comparison 1 in Table V suggests that the stabler systems contain the smaller number of units. Coupling this, furthermore, with the observation that all samples made with polyethoxylated (30) octylphenol gelled, strongly suggests that the latex stability is an inverse function of the number of ethylene oxide groups.

In addition to the protective ability of the emulsifier, the stability of a latex also depends on the amount of polymer surface covered by adsorbed emulsifier. Latex 95 at 36% solids, for example, which had about 35% of the polymer surface covered with potassium myristate, coagulated after 10 sec. of high-shear stirring. When the latex was post-stabilized and concentrated to 40% solids, however, it did not coagulate even after 50 min. of stirring. Latex 135, which had about 90% of the polymer surface covered with polyethoxylated (9.5) nonylphenol, coagulated after 5.7 min. in the blender. The coagulation was gradual, moreover, as evidenced by the fall in surface tension and the rise in viscosity during stirring. The fall in surface tension is attributed to the increase in concentration of dissolved emulsifier brought about by the displacement of adsorbed emulsifier from the surface of coagulating particles.

Visible Solids

Usually, the amount of visible solids in these samples was not enough to disqualify them as latexes. But experience with polishes shows that visible solids in any form are related to poor shelf-stability and low gloss; hence formulators prefer to use latexes and emulsions that contain no large, visible particles. Basically, there are two kinds of particles—those that float and those that sink—and their formation depends to a large extent

on the kind of polymer and emulsifier present in the latex.   In polyethylene latexes, the light material can be attributed to clusters of destabilized polymer, which has a density less than that of water.   The sediment, however, appears to be associated with the emulsifier, as latexes containing sodium lauryl sulfate developed unusually large amounts of sediment and some of those containing only potassium myristate yielded a precipitate identified as the double salt of myristic acid and potassium myristate. Obviously, the five categories—collar, flakes, granules, sediment, and wall film—used to describe the two kinds of particles are not independent, e.g., floating material might be observed as flakes and granules as well as a collar.   Hence no analysis of the individual categories was made.   Moreover, no provision was made to accommodate samples that ceased to be latexes.   For example, a latex might be rated 18, the poorest score possible, yet it could still be usable, if not in paints and polishes, in treating paper and textiles;   another might, owing to the single defect of having a $1/2$-in. layer of sediment, receive a rating of 4 yet it would no longer be useful as a latex.

CONCLUSIONS

A semiquantitative method of subjectively evaluating the appearances of latexes yielded useful information on the effect of particle size, polymer concentration, and amount and type of post-emulsifiers on latex stability. Post-stabilization improved the storage stability of latexes, as judged by appearance, and greatly increased their resistance to coagulation by mechanical shear.

1. Helin, A. F., H. K. Stryker, and G. J. Mantell, *J. Appl. Polymer Sci.*, **9,** 1797 (1965).
2. Stryker, H. K., A. F. Helin, G. J. Mantell, *J. Appl. Polymer Sci.*, **9,** 1806 (1965).
3. Maron, S., M. E. Elder, and Z. N. Ulevitch, *J. Colloid Sci.*, **9,** 89 (1954).
4. Davies, O. L., *The Design and Analysis of Industrial Experiments*, 2nd Ed., Hafner, New York, 1956.
5. Orr, R. S., and L. Breitman, *Can. J. Chem.*, **38,** 668 (1960).
6. Schick, M. J., *J. Colloid Sci* , **17,** 801 (1962).

Résumé

Une méthode semi-quantitative pour attribuer la quantité de matériau solide visible dans des réseaux de polyéthylènes est décrite. Jugée par cette méthode et sur la base de la présence de particules plus larges que 50 μ, la stabilité des latex peut être reliée primo au type et concentration de postémulsifiants additionnés au latex, deuxièmement à la grandeur moyenne des particules de polymères et troisièmement la concentration en solide.   Généralement, l'aspect est meilleur lorsque les latex contiennent 1°/une faible concentration en solides (30%), 2°/un diamètre moyen de particules élevé (800 A.) et 3°/suffisamment de post-émulsifiants pour couvrir la plus grande partie de la surface polymérique.   Les échantillons spécifiques toutefois ayant une concentration de solide

élevée (jusqu'à 36%) et un diamètre de particules petits (300 A.) peuvent également présenter une stabilité bonne au stockage. En accord avec des essais sur des latex choisis, une bonne résistance à la coagulation par cisaillement mécanique a été obtenue uniquement si la surface du polymère est complétement recouverte par l'émulsifiant. Lorsque les alcoyle-phénols polyéthoxylés étaient utilisés comme post-émulsifiants, une relation inverse semble exister entre la stabilité du latex et le nombre moyen d'unités d'oxyde d'éthylène par molécule d'émulsifiant. Toutefois, l'addition de chaque groupe d'oxyde d'éthylène accroît la surface apparente de la molécule de l'émulsifiant d'environ 4 A.².

Zusammenfassung

Eine halbquantitative Methode zur Bestimmung der Menge an sichtbarem Festkörper in Polyäthylenlatices wird beschrieben. Nach dieser Methode und nach der Anwesenheit von Teilchen grösser als 50 μ zu schliessen, ist die Stabilität der Latices bestimmt durch (1) Typus und Konzentration des nachträglich dem Latex zugesetzten Emulgators, (2) die mittlere Grösse der Polymerpartikel und (3) den Festkörpergehalt. Im allgemeinen war die Erscheinung besser, wenn die Latices (1) einen niedrigen (30%) Festkörpergehalt, (2) einen grossen (800 A.) mittleren Teilchendurchmesser und (3) genug Nach-Emulgator zur Bedeckung des grössten Teils der Polymeroberfläche besassen. Spezifische Proben mit einem hohen (36%) Festkörpergehalt und einem kleinen (300 A.) mittleren Teilchendurchmesser zeigten jedoch ebenfalls eine gute Lagerungsfähigkeit. Nach an ausgewählten Latices ausgeführten Tests wurd eine gute Koagulationsbeständigkeit bei mechanischer Scherung nur dann erhalten, wenn die Oberfläche des Polymeren vollständig mit Emulgator bedeckt war. Bei Verwendung von polyäthoxylierten Alkylphenolen als Nach-Emulgator scheint eine umgekehrte Beziehung zwischen Latexstabilität und mittlerer Zahl von Äthylenoxydeinheiten pro Emulgatormolekül zu bestehen. Ausserdem erhöhte die Zufügung jeder Äthylenoxydgruppe den scheinbaren Flächenbedarf des Emulgatormoleküls um etwa 4 A.².