

# Use of the HLB System in Selecting Emulsifiers for Emulsion Polymerization

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## I. INTRODUCTION

The mechanism of emulsion polymerization has been elucidated by several investigators.<sup>1-3</sup> However, the systematic selection of a suitable surface-active agent for the polymerization of a specific monomer has received little consideration in spite of the major importance of the emulsifier's effect on the properties of the polymer emulsion. In the past, the selection of an emulsifier has often been a trial-and-error process involving the screening of tens or hundreds of surface-active agents. This paper attempts to show how emulsion stability and other polymer emulsion properties can often be correlated with a certain property of the emulsion known as the "HLB value." The present investigation is limited to the homopolymerization of styrene and vinyl acetate.

The HLB system of emulsifier classification has been described in several publications.<sup>4-6</sup> Briefly, the HLB value indicates the "hydrophilic-lipophilic balance" of a particular emulsifier. Most of the commonly encountered nonionic and anionic surface-active agents lie in an HLB range from one to twenty. An HLB value of one indicates oil solubility, while an HLB value of twenty indicates a high degree of water solubility. Some of the methods for determining the HLB of an emulsifier involve computations based on chemical structure,<sup>4</sup> solubility studies,<sup>6</sup> and cloud point determinations.<sup>6</sup> Although the HLB value was formerly regarded as a semiempirical property, Ross<sup>7</sup> has recently demonstrated that the HLB value can be correlated with a fundamental physical property of the system oil-water-emulsifier, namely, the spreading coefficient of the internal phase liquid on the surface of a 1% solution of the emulsifier in the external phase.

There have been some prior attempts to develop a systematic scheme of classification for surfactants employed in emulsion polymerization. Helin<sup>8</sup> computed a "solubility index" for a wide variety of chemical types of emulsifiers and attempted to correlate this index with emulsifier performance in

the polymerization of butadiene/styrene copolymer. A plot of conversion rate versus solubility index was drawn for each chemical type, and for each chemical type there was a particular solubility index corresponding to a maximum conversion rate. Helin found that latex stability was apparently unrelated to solubility index.

Budewitz<sup>9</sup> disclosed the use of a numerical value referred to as the "Hydrophilic Number" or simply as the HN. He related the HN to the HLB by the following simple equation:

$$HN = 5(HLB)$$

He then defined an optimum HN range of 65 to 75 for the emulsifier in the polymerization of vinyl acetate, which would correspond to an HLB range of 13 to 15.

In using the HLB system to solve a given emulsification problem, the usual procedure is to plot the property of particular interest against the HLB. It is often found that the curve for each chemical type will pass through a maximum at a given HLB value, thus indicating the proper HLB for obtaining the optimum performance with respect to the property being investigated. In the present work, useful information was obtained by plotting the emulsion stability, particle size, emulsion viscosity, and conversion rate against the HLB. In plotting typical property versus HLB curves, the maximum may be shifted slightly as the chemical type of surfactant is altered.

## II. STYRENE POLYMERIZATION

### A. Experimental Procedure

Each polymerization run was made in a four-necked, one-liter flask fitted with a reflux condenser, variable speed stirrer, nitrogen inlet and outlet, thermometer, and dropping funnel. The reaction flask was immersed in a constant temperature bath adjusted to  $50 \pm 1^\circ\text{C}$ . The nitrogen used was Seaford grade, obtained from Air Reduction Com-

pany. The styrene was the monomer grade of Shell Chemical Company, and contained 10 to 15 ppm of *tert*-butyl catechol as a polymerization inhibitor. The inhibitor was first removed by the following procedure.

One liter of styrene was washed in a two-liter separatory funnel with three 300-ml. portions of 5% aqueous sodium hydroxide solution. The styrene was then washed with three 300-ml. portions of distilled water, and dried over 250 g. of calcium chloride for 4 hr. The calcium chloride was filtered out, and the styrene was stored in a well stoppered bottle in a cool place.

The formulation shown in Table I was used to obtain all data, except in some instances where the amount of emulsifier was changed to determine the effect of emulsifier concentration.

In making a polymerization run, the emulsifier

TABLE I

Ingredient	Wt., g.
Styrene	200.00
Distilled water	300.00
Potassium persulfate	0.75
Sodium bisulfite	0.30
Emulsifier	20.00

and persulfate were first dissolved in distilled water. While the solution was stirred, the flow of nitrogen through the reaction vessel was started to purge the system of any oxygen. After bringing the contents of the flask up to 50°C. the styrene was allowed to run in at a moderate rate (200 g. in 15 min.). Samples were removed from the flask at half-hour intervals, and the per cent conversion of styrene to polystyrene was determined by measuring the per cent solids present. After plotting per cent conversion versus time, the rate of con-

version was determined from the straight-line portion of the curve. After a short induction period the polymerization proceeded at a rapid rate until 80 to 90% conversion had been reached, and then slowed down as the remainder of the styrene was polymerized. After polymerization was complete, the emulsions were cooled to room temperature and stored.

## B. Experimental Results

A number of runs were made using a blend of an anionic emulsifier and a nonionic emulsifier. In this series the anionic material was an alkyl aryl sulfonate (G-3300), while the nonionic ingredient was a polyoxyethylene oleyl ether (G-3920). By using selected ratios of G-3300/G-3920, the HLB was varied over a range from 11.7 to 15.3. The general composition of each type of formula-

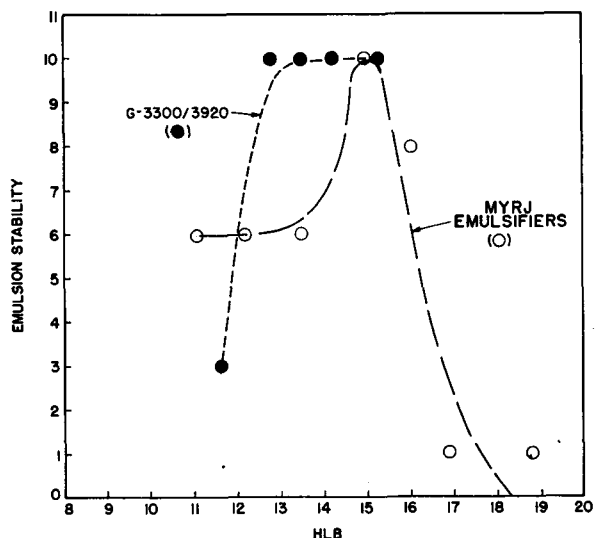


Fig. 1. Emulsion stability vs. emulsifier HLB in polystyrene emulsions.

TABLE II  
Styrene Emulsion Polymerization Formulas

	A	G	H	I	J	K	L	M	O
Styrene, g.	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00	200.00
Water, g.	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00	300.00
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , g.	0.50	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
NaHSO <sub>3</sub> , g.	0.20	0.30	0.30	0.30	0.30	0.30	0.30	0.30	—
Emulsifier, g.	5.00	10.00	12.50	15.00	17.50	20.00	22.50	25.00	10.00
Styrene, %	39.55	39.14	38.95	38.75	38.54	38.39	38.20	38.04	39.17
Water, %	59.33	58.70	58.42	58.14	57.90	57.57	57.30	57.01	58.78
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , %	0.09	0.14	0.16	0.16	0.15	0.14	0.15	0.15	0.10
NaHSO <sub>3</sub> , %	0.04	0.06	0.06	0.06	0.06	0.06	0.05	0.05	—
Emulsifier, %	0.99	1.96	2.41	2.89	3.35	3.84	4.30	4.75	1.95

TABLE III  
Polystyrene (40% Solids) Emulsion Polymerization Runs

Run	Emulsifier	HLB	Formula	Total conversion, %	Conversion rate, %/hr.	Emulsion stability <sup>a</sup>	Emulsion viscosity, cpoise	Particle size, (microns)	Emulsifier, %
52	G-3300/G-3920, 100/0	11.7	K	41.8	7.0	3	7	0.09	3.84
48	G-3300/G-3920, 70/30	12.8	K	96.9	59.0	10	172	0.06	3.84
49	G-3300/G-3920, 50/50	13.5	K	98.8	62.0	10	375	0.06	3.84
50	G-3300/G-3920, 30/70	14.2	K	97.4	58.0	10	174	0.06	3.84
51	G-3300/G-3920, 0/100	15.3	K	95.7	59.6	10	18	0.09	3.84
101	G-3300/G-3920, 100/0	11.7	O	96.2	22.0	10	24	0.13	1.95
102	G-3300/G-3920, 70/30	12.8	O	94.9	51.0	10	55	0.10	1.95
88	G-3300/G-3920, 50/50	13.5	O	94.9	60.0	10	125	0.08	1.95
103	G-3300/G-3920, 30/70	14.2	O	74.0	45.0	4	38	0.10	1.95
105	G-3300/G-3920, 0/100	15.3	O	16.9	5.0	4	—	0.10	1.95
88	G-3300/G-3920, 50/50	13.5	O	94.9	60.0	10	125	0.08	1.95
73	G-3300/G-3920, 50/50	13.5	H	93.4	89.0	10	30	0.08	2.41
70	G-3300/G-3920, 50/50	13.5	I	94.4	89.2	10	43	0.07	2.89
74	G-3300/G-3920, 50/50	13.5	J	96.1	88.7	10	125	0.07	3.45
69	G-3300/G-3920, 50/50	13.5	K	98.8	92.0	10	225	0.06	3.84
79	G-3300/G-3920, 50/50	13.5	L	98.0	88.1	10	832	0.05	4.30
80	G-3300/G-3920, 50/50	13.5	M	100.0	91.9	10	7000	0.05	4.75
199A <sup>a</sup>	G-3300/G-3920, 50/50	13.5	O	90.3	58.0	10	120	0.093	1.95
199B <sup>a</sup>	G-3300/G-3920, 50/50	13.5	O	99.3	—	10	46	0.092	1.95

<sup>a</sup> See Table IV.

<sup>b</sup> 199A and 199B were parts of the same run; Part A was at 50°C. for 2 hr.; Part B was then made at 90°C. for 2 hr.

tion is presented in Table II. All ratios of G-3300/G-3920 evaluated are summarized in Table III.

The first and most important requirement for an emulsifier is the production of a stable emulsion. Figure 1 presents a plot of emulsion stability versus HLB of the G-3300/G-3920 blend. Emulsion stability was rated from 0 to 10 on an arbitrary scale, with 10 corresponding to excellent stability. The complete explanation of the emulsion stability scale is given in Table IV. Examination of Figure

1 shows that emulsions of excellent stability were obtained in an HLB range from 13 to 15 by the use of the G-3300/G-3920 blend. The emulsion

TABLE IV  
Emulsion Stability Rating

Rating	Definition
0	Lumps formed within 1/2 hr. after start of polymerization
1	Lumps formed within 1 hr. after start of polymerization
2	Lumps formed within 2 hr. after start of polymerization
3	Excessive prefloc formation
4	Prefloc formation
5	Very little prefloc formation
6	Stable for less than 1 day
7	Stable for 1 day
8	Stable for 3 days
9	Stable for 1 week
10	Stable for more than 1 week

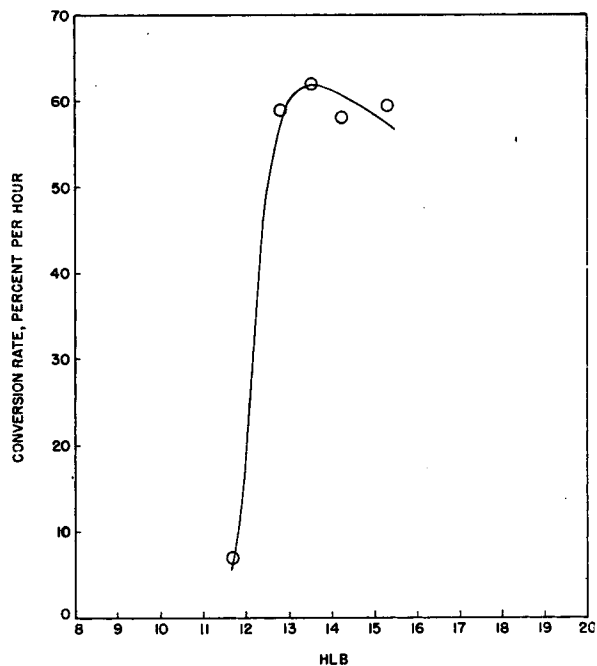


Fig. 2. Conversion rate vs. emulsifier HLB in styrene polymerization at 50°C. using 3.84% of G-3300/G-3920 blend.

from Run No. 49 (Table III) was placed in a centrifuge and subjected to 30,000  $g$  for 3 hr., but no sedimentation resulted.

A practice sometimes followed in the manufacture of polystyrene emulsions is to increase the tempera-

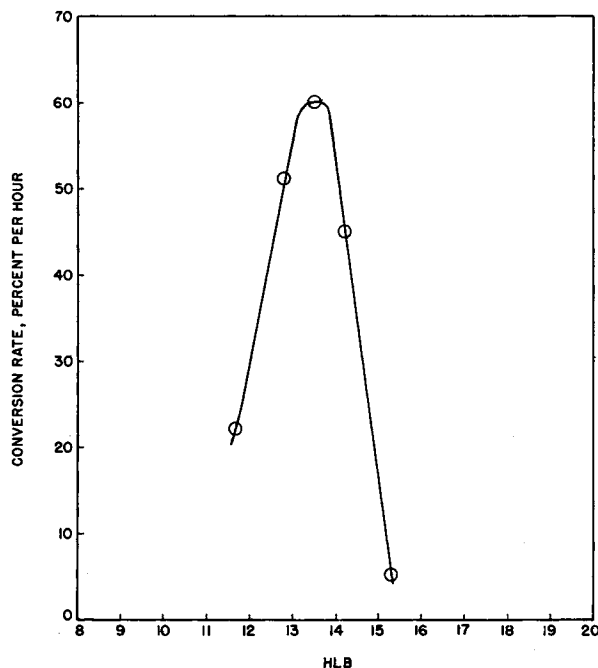


Fig. 3. Conversion rate vs. emulsifier HLB in styrene polymerization at 50°C. using 1.96% of G-3300/G-3920 blend.

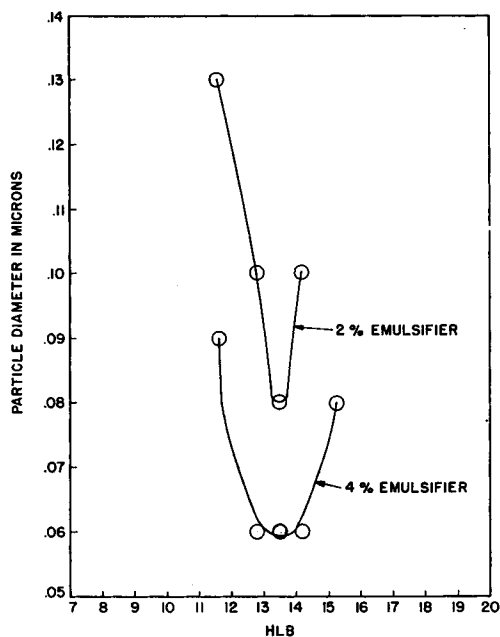


Fig. 4. Particle diameter vs. emulsifier HLB in styrene polymerization at 50°C. using G-3300/G-3920 blend.

ture of the polymerization at the end of the run to 90°C. in order to aid in the polymerization of the last traces of styrene monomer. One difficulty encountered in this technique is that many emulsifiers will not maintain a stable emulsion when the temperature is increased to this level. A run was made (No. 199) using a 1.95% concentration of the 50/50 blend of G-3300/G-3920. After 2 hr. the temperature was increased from 50°C. to 90°C. and held there for an additional 2 hr. A sample was taken before and after the temperature increase. The results in Table III show that the emulsion stability was not adversely affected by the higher temperature. Plots of conversion rate versus HLB for the G-3300/G-3920 combinations are presented in Figures 2 and 3. The curves indicate that the maximum rate was obtained when the HLB was 13.5. This maximum occurred at the same HLB regardless of whether 2% or 4% emulsifier was used.

Figure 4 presents a plot of emulsion particle diameter versus HLB. The average particle size for each emulsion was determined from turbidity measurements on diluted emulsions of known concentration. The method was standardized by the determination of the particle size of a few of the emulsions by light scattering. The technique used was an adaption of a method developed by Billmeyer.<sup>10</sup> Examination of Figure 4 shows that the minimum particle size occurred at an HLB of 13.5, which is the same HLB that gave a maximum in the conversion rate curve (Fig. 3). This inverse relationship between particle size and polymerization rate would be expected on theoretical grounds, as indicated by the following equation of Smith and Ewart:<sup>11</sup>

$$R_p = k_p(N/2)[M] \quad (1)$$

where  $R_p$  is the rate of polymerization per cubic centimeter of water,  $k_p$  is the rate constant for the propagation step of the polymerization reaction,  $N$  is the number of particles in a cubic centimeter of the aqueous phase, and  $[M]$  represents the monomer concentration in the polymer particles. Since  $[M]$  and  $k_p$  will remain essentially constant,  $R_p$  should depend principally upon the number of particles present. As the particle size becomes smaller,  $N$  becomes larger, causing  $R_p$  to increase.

When the viscosity of the emulsion is plotted against HLB, the curves shown in Figure 5 result. This graph shows that the viscosity goes through a maximum as the HLB increases, and the peak occurs at an HLB of 13.5 for 2 and 4% emulsifier. The maximum viscosity thus occurs at the HLB

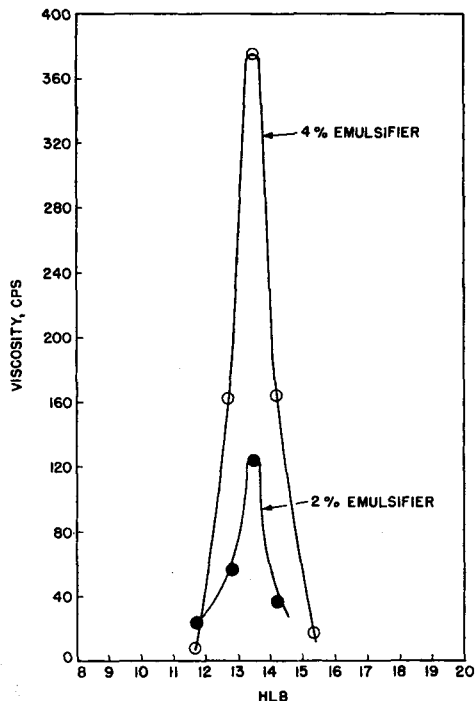


Fig. 5. Viscosity vs. HLB in styrene polymerization at 50°C. using G-3300/G-3920 blend.

corresponding to the minimum particle size (see Fig. 4).

The effects of emulsifier concentration are illustrated by Figures 6, 7, and 8. These studies were made at the optimum HLB of 13.5 (50/50 blend of G-3300/G-3920). The conversion rate versus emulsifier concentration curve (Fig. 6) shows no increase in rate above an emulsifier concentration of

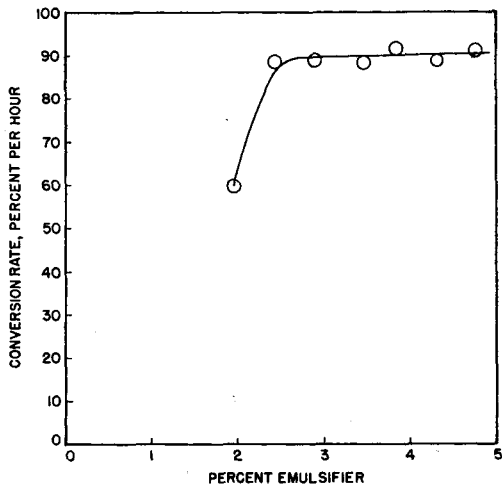


Fig. 6. Conversion rate vs. emulsifier concentration in styrene polymerization at 50°C. using G-3300/G-3920 at 50/50 ratio

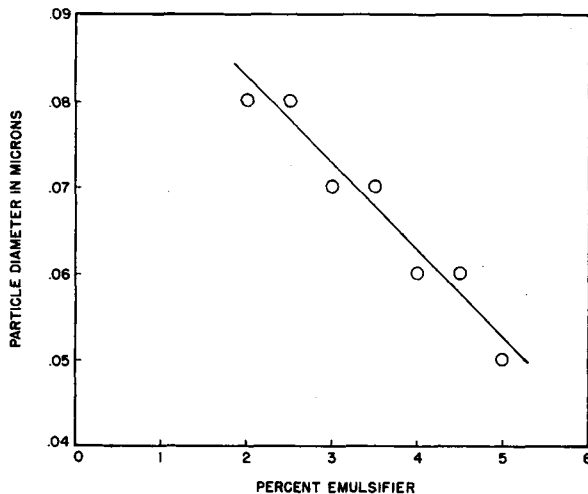


Fig. 7. Effect of emulsifier concentration on particle size in styrene polymerization at 50°C. using G-3300/G-3920 at 50/50 ratio.

about 2.5%. The particle size versus emulsifier concentration curve (Fig. 7) shows a definite decrease in particle size as the per cent emulsifier increases. The viscosity curve (Fig. 8) shows a rapid increase in emulsion viscosity as the emulsifier concentration increases.

Another extensive series of runs was carried out with the use of the Myrj emulsifiers. (Myrj, Brij, Tween, Renex, and Span are registered trade-

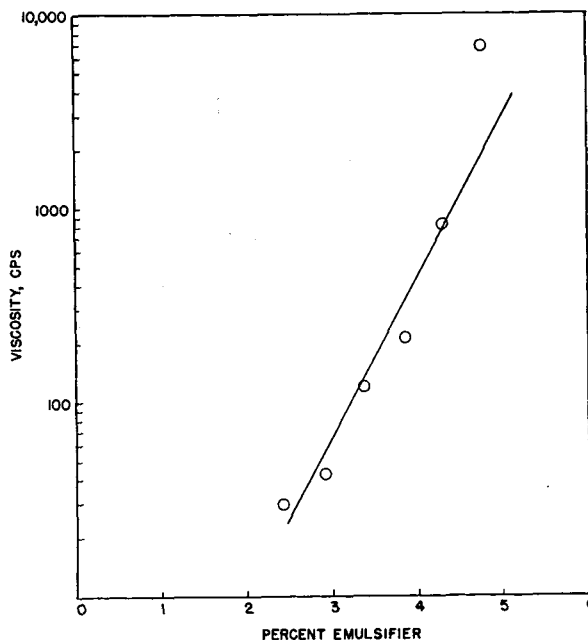


Fig. 8. Effect of emulsifier concentration on viscosity in styrene polymerization at 50°C. using G-3300/G-3920 at 50/50 ratio.

TABLE V  
Polystyrene (40% Solids) Emulsions Using Myrj Emulsifiers

Run	Emulsifier	HLB	Formula	Total conversion, %	Conversion rate, %/hr.	Emulsion stability <sup>a</sup>	Emulsion viscosity, cpoises	Emulsifier, %
54	G-2145	11.1	K	8.7	1.5	6	—	3.84
55	G-2155	12.2	K	17.7	3.2	6	—	3.84
56	G-2145/G-2149, 40/60	13.5	K	33.0	6.0	6	—	3.84
53	G-2149	15.0	K	96.3	46.2	10	10.0	3.84
64	G-2151	16.0	K	99.0	78.0	8	—	3.84
57	G-2152	16.9	K	—	—	1	—	3.84
58	G-2159	18.8	K	—	—	1	—	3.84
30	G-2145/G-2152, 33/67	15.0	A	38.4	9.0	2	—	0.99
31	G-2145/G-2152, 33/67	15.0	G	54.6	9.1	5	—	1.96
32	G-2145/G-2152, 33/67	15.0	I	95.3	15.9	5	11.0	2.89
84	G-2145/G-2152, 33/67	15.0	J	—	—	2	—	3.35
38	G-2145/G-2152, 33/67	15.0	K	99.3	30.0	10	—	3.84
85	G-2145/G-2152, 33/67	15.0	L	—	—	1	—	4.30
86	G-2145/G-2152, 33/67	15.0	M	—	—	1	—	4.75

<sup>a</sup> See Table IV.

marks of Atlas Powder Company.) The Myrj materials are polyoxyethylene stearates, with the HLB value dependent on the length of the polyoxyethylene chain. Figure 9 presents a plot of conversion rate versus HLB for the Myrj emulsifiers. In preparing Figure 9, the Myrj blends

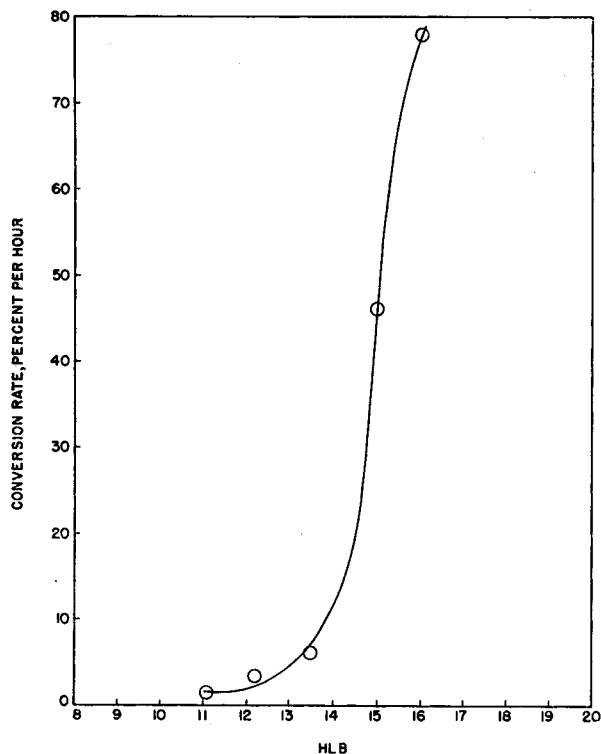


Fig. 9. Rate vs. HLB for styrene polymerization at 50°C. using Myrj emulsifiers.

listed in Table V were used. An emulsion of good stability and high conversion rate was obtained at an HLB of 15. Emulsions which coagulated during the polymerization run were obtained above an HLB of 16 and below an HLB of 13.5. A plot of emulsion stability versus the HLB of the Myrj emulsifiers is presented in Figure 1. Hence the optimum HLB range for the Myrj materials is from 14.5 to 15.5.

Table V summarizes the emulsion properties obtained using the Myrj emulsifiers. By employing 3.84% emulsifier of HLB 15.0 a conversion rate of 30%/hr. was obtained, total conversion was

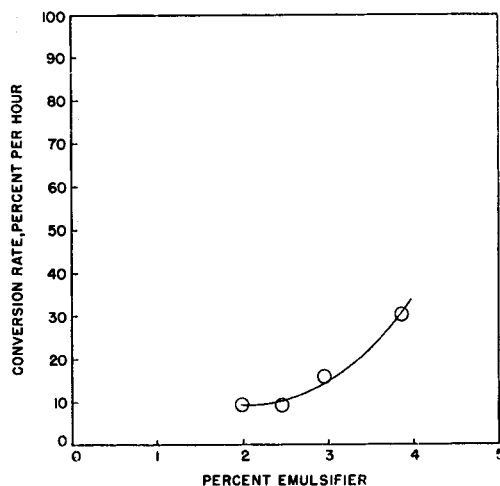


Fig. 10. Effect of emulsifier concentration on rate in styrene polymerization at 50°C. with Myrj 45/Myrj 52 at 33/67 ratio.

TABLE VI  
Polystyrene (40% Solids) Emulsions Using Miscellaneous Emulsifiers

Run	Emulsifier	HLB	Formula	Total conversion, %	Conversion rate, %/hr.	Emulsion stability <sup>a</sup>	Emulsion viscosity, cpoise	Particle size, microns	Emulsifier, %
111	G-3300/Renex 678, 60/40	13.0	O	90.6	47.0	9	29	0.09	1.95
112	G-3300/Renex 678, 45/55	13.5	O	91.9	43.0	9	32	0.10	1.95
113	G-3300/Renex 678, 30/70	14.0	O	91.7	56.0	8	30	0.10	1.95
115	G-3300/Brij 35, 70/30	13.4	O	81.5	43.0	10	41	0.09	1.95
116	G-3300/Tween 20, 70/30	13.2	O	85.4	47.0	10	42	0.08	1.95
119	G-3300/Renex 650, 50/50	15.0	O	85.3	22.0	5	10	0.14	1.95
127	G-2162	16.0	K	92.9	19.0	10	10	0.18	3.84
137	Renex 31	15.4	K	52.4	7.0	10	13	1.15	3.84
150	G-3300/G-2162, 55/45	13.5	O	94.7	60.0	10	160	0.09	1.95
209	G-263 (cationic)	30	(b)	95.8	100.0	10	6000	0.07	3.84
210	G-263 (cationic)	30	O	87.2	72.0	5	16	0.07	1.95

<sup>a</sup> See Table IV.

<sup>b</sup> Formula contained 200 parts styrene, 263 parts water, 0.5 parts potassium persulfate, and 57 parts G-263.

99.3%, and emulsion stability rating was 10 (Run No. 38). Figure 10 demonstrates that an increase in Myrj concentration produces an increase in conversion rate.

On the basis of the above work a number of emulsifiers of various chemical types falling within an HLB range of 13 to 16 were evaluated. Table VI presents the properties of the emulsions obtained. The chemical nature of the various emulsifier types is given in Table XIII. Adequate conversion rates and emulsions of excellent stability were obtained with G-3300/Brij 35, G-3300/Tween 20, G-2162 alone, Renex 31 alone, and G-3300/G-2162. A cationic-type emulsifier, G-263, was evaluated in Run 209. This emulsifier produced a stable emulsion which had a particle diameter of 0.07 microns.

### C. Discussion

In the present work, emulsion stability and conversion rate were chosen as criteria of emulsifier performance because satisfactory performance in these respects is the minimum requirement for an acceptable emulsifier. If the rate of conversion is too low, the polymerization equipment will be tied up too long and the cost of the product will increase. If the emulsion is so unstable that it coagulates during polymerization, the basic benefits of handling the product in emulsion form are lost.

The preceding data demonstrate that, for most types of emulsifiers evaluated, satisfactory conversion rates coupled with good emulsion stabilities are obtained in an HLB range of 13 to 16. Figure 1, together with the data in Table VI clearly shows that the emulsions with the best stability are made

using emulsifiers within the 13 to 16 HLB range. This finding means that the HLB system can be used as a guide by the polymer chemist in the selection of an emulsifier for styrene polymerization.

It should be noted that G-263 (Table II, Run No. 209) produces stable polystyrene emulsions, although it has an HLB of about 30. Furthermore, water-soluble sulfonates of quite high HLB are used commercially in the emulsion polymerization of styrene. These facts diminish but do not eliminate the usefulness of the 13-16 HLB range rule for guiding the selection of emulsifiers. On the basis of the work to date, it appears that the 13 to 16 HLB rule applies to nonionics alone and to non-ionic/anionic combinations. The employment of an emulsifier selection system of even limited applicability is an improvement over the trial and error method in wide use at present.

The above data also offer clues on how to control emulsion properties such as viscosity and particle size. The desired particle diameter, for example, increases as one goes from floor wax (0.03 to 0.1 microns) to latex paints (0.1 to 1.0 microns) to adhesives (1.0 to 5.0 microns). One way to decrease particle size is to increase the concentration of the G-3300/G-3920 emulsifier (see Fig. 7). Another way to modify particle size is to change the G-3300/G-3920 ratio (see Fig. 4 and Table III). The particle size is also strongly dependent on the chemical type of emulsifier used as shown in Table VI, when the particle diameter ranges from 0.07 for G-263 to 1.15 for Renex 31.

The viscosity of the resulting emulsion can be greatly increased by slightly increasing the con-

centration of the G-3300/G-3920 emulsifier blend (Fig. 8). By changing the G-3300/G-3920 ratio, and thereby changing the HLB, the viscosity can be varied from 18 to 375 cpoise (Table III). The chemical composition of the emulsifier is also important in controlling viscosity, as shown by a viscosity of 10 cpoise obtained with G-2162 versus 6000 cpoise obtained with G-263 (Table III).

### III. VINYL ACETATE POLYMERIZATION

#### A. Experimental Procedure

The apparatus used for the polymerization of vinyl acetate was the same as that used for styrene, except that the temperature of the bath was adjusted to  $70 \pm 1^\circ\text{C}$ .

The formulation shown in Table VII was generally used, except in some instances where the

TABLE VII

Ingredient	Wt., g.
Vinyl acetate	275.00
Distilled water	211.50
Potassium persulfate	0.50
Cellosize WP-09 <sup>a</sup>	2.50
Emulsifier	10.00

<sup>a</sup> Hydroxyethyl cellulose (Union Carbide).

amount of emulsifier was changed to determine the effect of emulsifier concentration.

The purpose of the protective colloid (hydroxyethyl cellulose) was to prevent agglomeration of the polymer particles.

The vinyl acetate monomer was obtained from the Air Reduction Company and was their Aircro

"H" grade. This grade contains 14 to 17 ppm of hydroquinone as an inhibitor. Before use, the inhibitor was removed by vacuum distillation at  $30^\circ\text{C}$ . and 140 mm. pressure.

The procedure for a polymerization run was to dissolve the emulsifier, protective colloid, and persulfate in the distilled water. While the solution was stirred, the nitrogen purging was started to remove oxygen from the system. An initial addition of 12.5 g. of vinyl acetate was made to this aqueous system. The mixture was then allowed to heat up to  $70^\circ\text{C}$ . while stirring, by which time polymerization had begun. The remaining vinyl acetate was added gradually. For the recipe shown in Table VII, this required about 2.5 hr. This method of monomer addition made it impossible to determine conversion rate, but the total per cent conversion was recorded for each run. After monomer addition was completed, the contents were agitated for another half hour at  $70^\circ\text{C}$ ., then cooled.

#### B. Experimental Results

The first type of surfactant to be evaluated in vinyl acetate polymerization was an anionic/nonionic blend consisting of a combination of G-3300/G-3920 at various ratios. The formulations used are presented in Table VIII. The results listed in Table IX indicate that stable emulsions were obtained with G-3300/G-3920 when the HLB fell within the 15.0 to 15.3 range. The particle diameter was approximately 2 microns for both 2% and 4% emulsifier. When particle diameter was greater than 1.3 microns, it was determined by diluting the emulsion, drying on a glass

TABLE VIII  
Vinyl Acetate Polymerization Formulas

	A	I	J	K	L	M
Vinyl acetate, g.	250.00	275.00	275.00	275.00	275.00	275.00
Water, g.	200.00	211.50	201.50	211.50	204.50	199.00
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , g.	0.15	1.00	1.00	1.00	1.00	1.00
Emulsifier, g.	10.00	10.00	20.00	10.00	17.00	25.00
WP-09, g. <sup>a</sup>	—	2.50	2.50	—	—	—
Elvanol, g. <sup>b</sup>	—	—	—	2.50	2.50	—
Vinyl acetate, %	54.35	55.00	55.00	55.00	55.00	55.00
Water, %	43.45	42.30	40.30	42.30	40.80	39.80
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , %	0.03	0.20	0.20	0.20	0.20	0.20
Emulsifier, %	2.17	2.00	4.00	2.00	3.50	5.00
WP-09, % <sup>a</sup>	—	0.50	0.50	—	—	—
Elvanol, % <sup>b</sup>	—	—	—	0.50	0.50	—

<sup>a</sup> Cellosize WP-09 is hydroxyethyl cellulose (Union Carbide).

<sup>b</sup> Elvanol 51-02/50-42 80/20 is polyvinyl alcohol (Du Pont).



TABLE IX  
 Polyvinyl Acetate (55% Solids) Emulsion Polymerization

Run	Emulsifier	HLB	Formula	Total conversion, %	Emulsion stability <sup>a</sup>	Viscosity, cpoise	pH	Particle size, microns	Emulsifier, %
218	G-3300/G-3920, 100/0	11.7	I	—	0	—	—	—	2.00
219	G-3300/G-3920, 70/30	12.8	I	—	0	—	—	—	2.00
220	G-3300/G-3920, 50/50	13.5	I	—	1	—	—	—	2.00
221	G-3300/G-3920, 30/70	14.2	I	—	2	—	—	—	2.00
222	G-3300/G-3920, 0/100	15.3	I	100.0	10	150	2.20	1.6	2.00
259	G-3300/G-3920, 50/50	13.5	J	—	2	—	—	—	4.00
260	G-3300/G-3920, 30/70	14.2	J	—	2	—	—	—	4.00
267	G-3300/G-3920, 10/90	15.0	J	90.8	10	144	2.40	2.0	4.00
261	G-3300/G-3920, 0/100	15.3	J	63.1	10	85	4.10	2.4	4.00
166	G-3300/G-3920, 100/0	11.7	A	89.0	2	—	—	—	2.17
165	G-3300/G-3920, 70/30	12.8	A	85.9	2	—	—	—	2.17
164	G-3300/G-3920, 50/50	13.5	A	63.1	2	—	—	—	2.17
163	G-3300/G-3920, 20/80	14.6	A	70.0	2	—	—	—	2.17
162	G-3300/G-3920, 10/90	15.0	A	80.8	10	44.0	2.65	0.23	2.17
157	G-3300/G-3920, 10/90	15.0	A	83.6	10	55.0	—	0.24	2.17
156	G-3300/G-3920, 10/90	15.0	A	85.3	10	69.0	2.45	0.24	2.17
161	G-3300/G-3920, 0/100	15.3	A	43.9	2	—	—	—	2.17
271	G-3300/G-3920, 0/100	15.3	L	88.2	10	63.0	2.60	1.0	2.00
275	G-3300/G-3920, 0/100	15.3	K	—	3	—	—	—	3.50
279	G-3300/G-3920, 0/100	15.3	M	72.1	10	7175	2.50	10.0	5.00
196	G-2145/G-2152, 100/0	11.1	I	—	0	—	—	19.0	2.00
197	G-2145/G-2152, 80/20	12.3	I	—	3	—	—	1.4	2.00
198	G-2145/G-2152, 60/40	13.4	I	—	3	—	—	—	2.00
200	G-2145/G-2152, 40/60	14.6	I	87.6	8	40	1.85	1.0	2.00
201	G-2145/G-2152, 20/80	15.7	I	99.5	8	45	1.80	1.0	2.00
202	G-2145/G-2152, 0/100	16.9	I	100.0	10	36	1.80	1.5	2.00
229	G-2153	17.9	I	—	8	—	—	—	2.00
238	G-2159	18.8	I	—	0	—	—	—	2.00
268	G-2145/G-2152, 0/100	16.9	J	96.3	10	126	1.80	1.0	4.00
212	Span 20/Tween 20, 80/20	10.2	I	—	0	—	—	—	2.00
213	Span 20/Tween 20, 60/40	11.8	I	—	0	—	—	—	2.00
214	Span 20/Tween 20, 50/50	12.7	I	—	1	—	—	—	2.00
215	Span 20/Tween 20, 40/60	13.5	I	98.3	8	33	1.90	2.4	2.00
216	Span 20/Tween 20, 20/80	15.1	I	93.7	10	26	1.70	1.8	2.00
217	Span 20/Tween 20, 0/100	16.7	I	97.3	10	39	1.80	1.6	2.00
266	Span 20/Tween 20, 40/60	13.5	J	99.5	10	143	1.90	1.0	4.00
265	Span 20/Tween 20, 20/80	15.1	J	97.7	10	88	1.90	1.6	4.00
264	Span 20/Tween 20, 0/100	16.7	J	98.2	10	76	1.90	4.8	4.00

<sup>a</sup> See Table IV.

slide, and examining with a microscope fitted with a micrometer eyepiece. The emulsion stability curve (Fig. 11) illustrates that, as the HLB increased to 15.3, more stable emulsions were obtained. Formula I was used for all runs shown in Figure 11.

Another type of surfactant investigated was a blend of Span 20/Tween 20. The bottom portion of Table IX lists the properties of emulsions made

with this blend. Figure 11 shows the effect of the HLB of the Span 20/Tween 20 combinations on emulsion stability. Stable emulsions were obtained when the HLB fell between 15.0 and 16.7. Figure 12 shows the effect of HLB on particle size, and indicates that particle size decreases as HLB increases.

A study was made of the effect of Myrj poly-

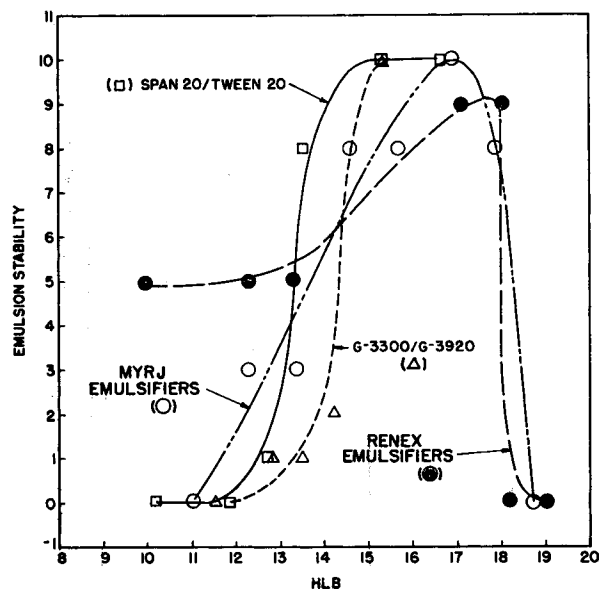


Fig. 11. Emulsion stability vs. emulsifier HLB in the polymerization of vinyl acetate at 70°C.

oxyethylene stearate type emulsifiers over a range of HLB from 11.1 to 18.8. The results are presented in Table IX. Figure 11 demonstrates that the emulsion stability rating goes through a peak as the HLB increases. The most stable emulsion was obtained at an HLB of 16.9, and the range for good emulsions was from 15 to 18. Figure 12 shows the effect of HLB on particle size for several Myrj emulsifier blends. In this case the particle size goes through a minimum at an HLB of 15.

An investigation was made of Renex polyoxy-

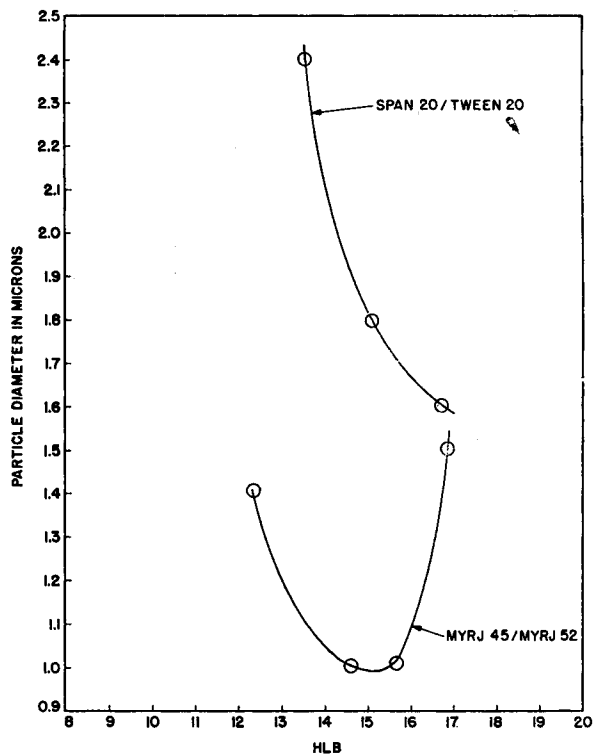


Fig. 12. Effect of HLB on particle size in the polymerization of vinyl acetate at 70°C.

ethylene alkyl aryl ether types covering an HLB range from 10.0 to 19.0. The properties of the resulting emulsions are given in Table X. Figure 11 again shows a peak in the emulsion stability versus HLB curves. The peak stability occurs at an HLB of 17.5, approximately. The particle

TABLE X  
Polyvinyl Acetate (55% Solids) Polymerization Using Renex Emulsifiers

Run	Emulsifier	HLB	Formula	Total conversion, %	Emulsion stability <sup>a</sup>	Viscosity, cpoise	pH	Particle size, microns	Emulsifier, %
190	Renex 648	10.0	I	97.1	5	110	—	10.0	2.00
191	Renex 688	12.3	I	99.5	5	140	—	5.0	2.00
189	Renex 690	13.3	I	100.0	5	150	—	2.5	2.00
192	Renex 678	15.0	I	99.4	7	180	—	1.5	2.00
193	Renex 649	16.0	I	98.4	8	80	—	1.2	2.00
194	Renex 650	17.1	I	100.0	9	300	1.85	0.34	2.00
195	<sup>b</sup>	18.0	I	100.0	9	720	1.95	0.35	2.00
227	<sup>b</sup>	18.2	I	—	2	—	—	—	2.00
228	<sup>b</sup>	19.0	I	—	2	—	—	—	2.00
255	Renex 690	13.3	J	98.0	10	73	2.45	5.0	4.00
256	Renex 678	15.0	J	97.9	9	116	2.40	8.4	4.00
257	Renex 649	16.0	J	—	3	—	—	—	4.00
258	Renex 650	17.1	J	98.7	10	754	2.10	1.0	4.00

<sup>a</sup> See Table IV.

<sup>b</sup> Experimental product similar to Renex 650.

TABLE XI  
Polyvinyl Acetate (55%) Using Various Emulsifiers

Run	Emulsifier	HLB	Formula	Total conversion, %	Emulsion stability <sup>a</sup>	Viscosity, cpoise	pH	Particle size, microns
240	G-7596H	14.3	I	99.6	10	30	—	2.0
245	G-8916P	14.6	I	41.3	10	170	3.4	1.0
232	Tween 60	14.9	I	—	3	—	—	—
241	G-7596J	14.9	I	96.2	4	30	—	—
235	Tween 80	15.0	I	91.5	10	97	2.15	—
192	Renex 678	15.0	I	99.4	7	180	—	—
222	G-3920	15.3	I	100.0	10	150	2.2	1.6
246	G-8916T	15.4	I	44.5	10	90	3.6	1.0
249	Renex 31	15.4	I	94.5	7	52	2.1	8.0
237	G-2079	15.5	I	—	3	—	—	—
243	Tween 40	15.6	I	96.8	7	57	2.2	1.8
236	G-2162	16.0	I	—	3	—	—	—
193	Renex 649	16.0	I	98.4	8	80	—	1.2
250	Myrj 51	16.5	I	92.8	8	64	2.1	1.0
244	G-9046T	16.7	I	97.3	7	63	2.1	8.0
230	Tween 20	16.7	I	—	5	—	—	—
234	Brij 35	16.9	I	99.0	10	52	—	5.0
194	Renex 650	17.1	I	100.0	10	80	—	1.2
202	Myrj 52	17.2	I	100.0	10	36	1.8	1.5
253	G-1295	17.5	I	—	1	—	—	—
229	Myrj 53	17.9	I	—	7	—	—	—

<sup>a</sup> See Table IV.

diameter versus HLB curve (Fig. 13) shows a rapid decrease in particle size as HLB increases.

After studying Figure 11, a list of emulsifiers which fell in the HLB range from 14 to 18 was selected for evaluation. The results of these evaluations are shown in Table XI. All emulsifiers listed in the table were employed at a concentration of 2.0%. Five of them gave very good results:

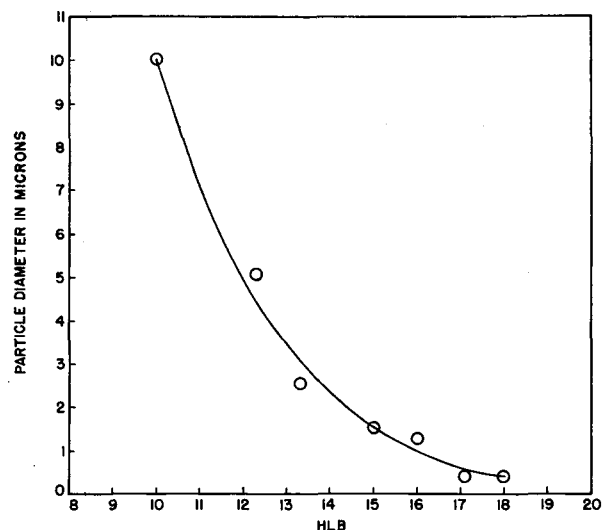


Fig. 13. Effect of HLB on particle size in vinyl acetate polymerization at 70°C. using Renex emulsifiers.

G-3920, Myrj 52, Renex 650, Brij 35, and Tween 20. The data also indicated that the emulsifiers which gave fair to good results fell within the HLB range of 14.5 to 17.5.

A further series of runs was made to determine the effect of using polyvinyl alcohol as the protective colloid instead of hydroxyethyl cellulose, and to study the effect of leaving out the protective colloid altogether. Table X shows that G-3920 or Renex 650 gives stable emulsions in combination with either hydroxyethyl cellulose or polyvinyl alcohol, or when used with no protective colloid.

A 10/90 blend of G-3300/G-3920 gave an emulsion of very fine particle size (0.24 microns) which was stable for more than six months at room temperature. The properties for this emulsion are listed in Table IX under Runs 156, 157, and 162. A film drawn with this emulsion and dried at room temperature for 48 hr. was found to be transparent and not subject to water spotting. Hence reduced water sensitivity is one advantage of leaving out the protective colloid.

### C. Discussion

Examination of Figure 11 and the corresponding tables indicates that the most stable polyvinyl acetate emulsions were obtained in an HLB range

TABLE XII  
 Effect of Protective Colloid on Emulsion Stability

Run	Emulsifier	Emulsi- fier, %	Protective colloid	Formula	Emulsion stability <sup>a</sup>	Total conversion, %	Viscosity, cP
222	G-3920	2	Hydroxyethyl cellulose	I	10	95.5	150
261	G-3920	4	Hydroxyethyl cellulose	J	10	63.1	85
275	G-3920	2	Polyvinyl alcohol	K	3	—	—
271	G-3920	4	Polyvinyl alcohol	L	10	88.2	63
279	G-3920	5	None	M	10	72.1	7175
194	Renex 650	2	Hydroxyethyl cellulose	I	10	100.0	300
258	Renex 650	4	Hydroxyethyl cellulose	J	10	98.7	754
276	Renex 650	2	Polyvinyl alcohol	K	10	97.3	664
272	Renex 650	4	Polyvinyl alcohol	L	10	98.8	1009
280	Renex 650	5	None	M	10	90.7	124
202	Myrj 52	2	Hydroxyethyl cellulose	I	10	100.0	36
268	Myrj 52	4	Hydroxyethyl cellulose	J	10	96.3	126
277	Myrj 52	2	Polyvinyl alcohol	K	10	87.9	259
273	Myrj 52	4	Polyvinyl alcohol	L	2	—	—
281	Myrj 52	5	None	M	2	—	—
234	Brij 35	2	Hydroxyethyl cellulose	I	10	99.0	52
263	Brij 35	4	Hydroxyethyl cellulose	J	7	78.7	—
278	Brij 35	2	Polyvinyl alcohol	K	10	95.4	258
274	Brij 35	4	Polyvinyl alcohol	L	3	—	—
282	Brij 35	5	None	M	0	—	—

from 14.5 to 17.5. This is a slightly higher range than that found for styrene (13 to 16). Since a higher HLB range corresponds to greater water solubility, this shift may be related to the higher water solubility of vinyl acetate (2.5/100 ml. H<sub>2</sub>O) compared to that of styrene (0.0125 g./100 ml. H<sub>2</sub>O).

The data presented in Figures 12 and 13, and in Tables IX through XII are also useful in selecting polymerization conditions to control emulsion properties. Particle size is often strongly dependent on the HLB of the emulsifier, as shown in Figures 12 and 13. Figure 12 also demonstrates that the Span 20/Tween 20 blend gives generally larger particle sizes than the Myrj 45/Myrj 52 combination.

Table XII gives some indication of an interaction of emulsifier and protective colloid in their effect on emulsion stability. When Myrj 52 or Brij 35 is used as the emulsifier, an increase in polyvinyl alcohol concentration from 2% to 4% actually decreases the emulsion stability. This is not the case when G-3920 or Renex 650 is used. An increase in hydroxyethyl cellulose concentration from 2% to 4% concentration may have an adverse effect on total conversion, as shown in Runs 261 and 263 (Table XII).

With vinyl acetate it is not easy to perceive

 TABLE XIII  
 Composition of Surfactants Evaluated

Surfactant	Composition
G-3300	Alkyl aryl sulfonate
G-3920	Polyoxyethylene oleyl ether
Myrj emulsifiers	Polyoxyethylene stearate
Brij emulsifiers	Polyoxyethylene lauryl ether
Tween 20	Polyoxyethylene sorbitan monolaurate
G-2162	Polyoxyethylene oxypropylene stearate
G-263	Cetyl ethyl morpholinium ethosulfate (35% aqueous solution)
Span 20	Sorbitan monolaurate
Renex 648 to 697	Polyoxyethylene alkyl aryl ethers
Renex 31	Polyoxyethylene ether alcohol
G-7596H	Polyoxyethylene sorbitan monolaurate
G-8916P	Polyoxyethylene sorbitan esters of mixed acids
Tween 40	Polyoxyethylene sorbitan monopalmitate
Tween 60	Polyoxyethylene sorbitan monostearate
G-7596J	Polyoxyethylene sorbitan monolaurate
Tween 80	Polyoxyethylene sorbitan monooleate
G-8916T	Polyoxyethylene sorbitan esters of mixed acids
G-2079	Polyoxyethylene palmitate
G-9046T	Polyoxyethylene mannitan monolaurate
G-1295	Polyoxyethylene fatty glyceride

clear-cut relationships between emulsifier properties and viscosity of the resulting emulsion, as it was in

the case of styrene. Examination of Table X, however, shows that viscosity tends to increase for Renex emulsifiers as the HLB increases. Doubling the concentration of the Renex 650 results in a great increase in viscosity, and also gives a more stable emulsion. A change in the HLB of the Span 20/Tween 20 blend has no significant effect on emulsion viscosity (Table IX). Table IX shows that the use of 5% G-3920 leads to a very high viscosity (7175 cpoise). The lack of a clear-cut relationship between emulsion viscosity and emulsifier properties may have resulted from the obscuring effect of the protective colloid which was used in most runs.

No attempt was made in the present work to regulate the pH of the emulsions. However, the pH fell within a rather narrow range from 1.7 to 3.4, and hence the pH fluctuations from run to run are probably not wide enough to invalidate the comparisons made above. The optimum pH range for polyvinyl acetate emulsion stability is said to be 4.5 to 5.5.<sup>12</sup>

#### IV. GENERAL CONCLUSIONS

On the basis of all the data discussed above, the following general conclusions can be drawn about the application of the HLB system to the emulsion polymerization of vinyl monomers.

1. In the emulsion polymerization of styrene, plots of emulsion stability versus HLB value for various chemical types of emulsifiers exhibited broad peaks at HLB values of 14 and 15, approximately.

2. In vinyl acetate polymerization, similar plots of emulsion stability versus HLB showed broad maxima at HLB values of 16, 17, and 17.5.

3. Other properties of polymer emulsions, such as particle size and emulsion viscosity, were found to be strongly dependent upon the HLB of the emulsifier, and could hence be controlled to some extent by the proper choice of emulsifier HLB.

4. For both styrene and vinyl acetate the most generally satisfactory emulsion properties have been obtained in the present work by the use of an anionic/nonionic blend (G-3300/G-3920).

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#### Synopsis

In the present work a wide variety of nonionic emulsifiers and anionic/nonionic blends of emulsifiers were evaluated in the emulsion polymerization of vinyl acetate and styrene. It was found that the emulsion stability and other polymer emulsion properties are often dependent upon a certain property of the emulsifier known as the HLB value. It has been shown elsewhere that the HLB value can be correlated with a fundamental physical property of the system oil-water-emulsifier, namely, the spreading coefficient of the internal phase liquid on the surface of a 1% solution of the emulsifier in the external phase. In the emulsion polymerization of styrene, good emulsion stability coupled with adequate conversion rate was obtained in an emulsifier HLB range of 13 to 16. For certain emulsifier blends it was found that emulsion viscosity and emulsion particle size were strongly dependent on the HLB of the emulsifier. Similar comments apply to vinyl acetate polymerization, except that the most stable emulsions were obtained with emulsifiers in an HLB range from 14.5 to 17.5. These observations on preferred HLB ranges apply only to nonionic emulsifiers and anionic/nonionic emulsifier blends, which were the emulsifier types screened in the present investigation. For both styrene and vinyl acetate the most generally satisfactory emulsion properties were obtained in the present work by the use of an anionic/nonionic emulsifier blend (G-3300/G-3920).

#### Résumé

Dans ce travail, on a estimé la valeur d'une grande variété d'émulsifiants non-ioniques et des mélanges d'émulsifiants anioniques non-ioniques dans la polymérisation en émulsion de l'acétate de vinyle et de styrène. On a trouvé que la stabilité de l'émulsion et les autres propriétés de l'émulsion polymérique dépendent souvent d'une certaine propriété de l'émulsifiant connue comme la "valeur HLB." On a montré ailleurs que la valeur HLB peut être mise en corrélation avec une propriété physique fondamentale du système huile-eau-émulsifiant, à savoir, le coefficient de dispersion de la phase liquide interne sur la surface d'une solution à 1% de l'émulsifiant dans la phase externe. Dans la polymérisation en émulsion du styrène on a obtenu une bonne stabilité de l'émulsion de même qu'une vitesse de conversion adéquate, dans un ordre d'émulsifiant HLB de 13 à 16. On a trouvé que pour certains mélanges d'émulsifiants, la viscosité de l'émulsion et la dimension de la particule de l'émulsion

dépendent étroitement de l'HLB de l'émulsifiant. Des commentaires semblables s'appliquent à la polymérisation de l'acétate de vinyle excepté que les émulsions les plus stables sont obtenues avec des émulsifiants dans un ordre HLB de 14,5 à 17,5. Ces observations sur des ordres HLB préférentiels s'appliquent uniquement à des émulsifiants non-ioniques et à des mélanges d'émulsifiants anioniques/non-ioniques, qui étaient les types d'émulsifiants employés dans ces recherches présentes. Dans le présent travail aussi bien pour le styrène que pour l'acétate de vinyle, on a obtenu les propriétés émulsionnantes les plus satisfaisantes en utilisant un mélange d'émulsifiant anionique/non-ionique (G-3300/G-3920).

### Zusammenfassung

In der vorliegenden Arbeit wird eine grosse Vielfalt von nichtionischen Emulgatoren und von Gemischen von anionischen und nichtionischen Emulgatoren bei der Emulsionspolymerisation von Vinylacetat und Styrol erprobt. Es wurde gefunden, dass die Stabilität der Emulsion und andere Eigenschaften der Polymeremulsion oft von einer bestimmten, als "HLB-Wert" bekannten Eigenschaft des Emulgators abhängen. Es wurde an anderer Stelle gezeigt, dass der "HLB"-Wert zu einer grundlegenden physikalischen

Eigenschaft des Systems Öl-Wasser-Emulgator in Beziehung gebracht werden kann, nämlich zum Spreitungskoeffizienten der inneren Flüssigkeitsphase auf der Oberfläche einer 1% Lösung des Emulgators in der äusseren Phase. Bei der Emulsionspolymerisation von Styrol wurde gute Emulsionsstabilität, gekoppelt mit einer brauchbaren Polymerisationsgeschwindigkeit in einem HLB-Bereich der Emulgatoren von 13 bis 16 erhalten. Bei bestimmten Emulgatormischungen wurde gefunden, dass die Viskosität der Emulsion und die Partikelgrösse stark vom HLB des Emulgators abhängt. Ähnliches gilt für die Vinylacetatpolymerisation, mit der Ausnahme, dass die stabilsten Emulsionen mit Emulgatoren in einem HLB-Bereich von 14,5 bis 17,5 erhalten wurden. Diese Beobachtungen über bevorzugte HLB-Bereiche gelten nur für nicht-ionische Emulgatoren und für Mischungen von anionischen und nicht-ionischen Emulgatoren; diese Emulgatortypen wurden in der vorliegenden Untersuchung erprobt. Sowohl für Styrol als auch für Vinylacetat wurden dabei die in allgemeiner Hinsicht am befriedigendsten Eigenschaften bei Verwendung eines Gemisches anionischer und nichtionischer Emulgatoren erhalten.

Received July 28, 1960