

## Carboxyl-Stabilized Emulsion Polymers

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### Synopsis

An emulsion polymerization process is reported for the production of high-solids, surfactant-free styrene/butadiene latices. With this procedure latices require no surfactants, for stabilization is built into the emulsion particles by means of copolymerized acid monomers. This "pH variable" method is a two-step, batch-on-batch polymerization. In the first step, all the ingredients are present in the reaction mixture; however, only enough styrene and butadiene is added to reach a low solids content. This step, carried out at low pH, produces a carboxylated seed latex. On raising the pH of this low-solids emulsion, the copolymerized carboxyl groups ionize, and the now highly charged latex particles provide an expedient locus for the generation of stable, high-solids latices. Neutralizing the carboxyl groups of the seed latex before adding the remaining monomers induces the highly hydrophilic carboxyl anions to remain on the surface of the latex particle, nearer to the aqueous environment of the surrounding media. Hence, the maximum stabilization capacity of the acid monomers is utilized. The process was evaluated to ascertain the effects of the following variables: the particle size and solids content of the first step, the nature of the base used to raise the pH, the pH of the dispersion prior to the second step, and the effect of the acid monomer on the latex stability.

### INTRODUCTION

A number of papers and patents have been written describing the beneficial properties derived from producing hydrophobic emulsion polymers containing hydrophilic, chemically bound stabilizers in place of the physically adsorbed soaps and surfactants classically used in emulsion polymerization.<sup>1,2</sup> Results show that particle charge derived from copolymerized monomer is more effective against mechanical shear coagulation than is adsorbed charge because of differences in the ability of charges to move about the surface of the particle.<sup>3-6</sup> Among the advantages gained by the use of chemically bound stabilizers are: (1) higher mechanical stability per quantity of stabilizer; (2) better water resistance in paper, textile, and paint applications; (3) increased aging resistance; and (4) no surfactant migration in films.

The above advantages can be obtained by preparing soap-free latices stabilized by carboxylic monomers, such as acrylic, methacrylic, and itaconic acids. These water-soluble monomers have been shown to induce particle formation in surfactant-free emulsion polymerizations.<sup>7</sup> At high pH, these copolymerized acids are very effective in promoting the colloidal stability of emulsion polymers. However, in practice, it is often difficult

to place these carboxyl monomers on the surface of the latex particle and thereby fully utilize their stabilizing capacity. If the carboxyl monomer is buried inside the latex particle or if it homopolymerizes in the aqueous phase, its stabilization capacity may be virtually destroyed. Whether an acid monomer eventually resides inside a particle, on the particle surface, or in the aqueous phase is dependent on a combination of its reactivity and its solubility distribution between water, monomer, and polymer.<sup>7-11</sup> This paper describes a new polymerization procedure which induces carboxylic monomer to be efficiently placed on the surface of latex particle where it can most effectively stabilize the emulsion polymer.

## EXPERIMENTAL

### Materials

ARCO/Polymers' polymer grade styrene and ARCO's butadiene containing 12 and 100 ppm of *t*-butylcatechol, respectively, were used in all polymerizations. The persulfate used was Baker reagent grade. Distilled water was used in all polymerizations.

### Procedures

The polymerizations were performed in quart bottles in a rotary bottle polymerizer. All ingredients were weighed accurately to 0.1 g on a top-loading balance accurate to 0.01 g.

Photomicrographs were taken with a Philips EM-75B electron microscope calibrated with a carbon replica grading having 54,864 lines per inch. Particle sizes determined by light transmission were carried out following the method of Maron et al.<sup>12</sup>

Surface tension measurements were carried out at ambient temperature with a du Nouy tensiometer. No ring correction factors were applied.

## RESULTS AND DISCUSSION

### The Preparation of High-Solids, Surfactant-Free Latices

The polymerization method discussed in this paper is a two-step, batch-on-batch process. Typical examples of formulations used to prepare styrene/butadiene latices carboxylated with acrylic and itaconic acids are shown in Table I. In the first step, all the ingredients are present in the reaction mixture; however, only enough styrene and butadiene are present to have the reaction proceed to approximately 25% solids. This step, carried out at low pH, produces a highly carboxylated seed latex. On raising the pH of this low-solids emulsion, the carboxyl groups ionize and the now highly charged latex particles provide a convenient locus for promoting the production of stable, high-solids latices. Neutralizing the carboxyl groups after the first step induces the highly hydrophilic carboxyl anions to remain on the surface of the latex particle, nearer to the aqueous environ-

TABLE I  
Surfactant-Free Formulations Prepared by the pH Variable Process<sup>a</sup>

	Step 1		Step 2	
	Low-pH step	High-pH step	Low-pH step	High-pH step
Styrene, g	32	28	32	28
Butadiene, g	22	18	22	18
Acrylic acid, g	4	—	—	—
Itaconic acid, g	—	—	4.0	—
Potassium persulfate, g	0.30	0.10	0.30	0.10
pH	2.5	9.5	2.5	9.5

<sup>a</sup> Polymerization temperature 70°C. Low pH step run to approximately 25% solids second step run to 40% solids.

ment of the surrounding medium. The low-pH step presents an optimum medium for carboxyl monomer copolymerization (un-ionized carboxyl groups), whereas the high-pH step furnishes a medium for maximum carboxyl-charge stabilization (ionized carboxyl groups). With this procedure, the preparation of latices requires no anionic or nonionic surfactants, for particle formation and stabilization are provided by the carboxylic acid monomer.

### Important Factors in the pH Variable Process

#### *Particle Size and Solids Content of Carboxylated Seed*

Initial polymerization studies demonstrated an important relationship between the size of the particle formed in step 1 of the pH Variable Process and the success achieved in carrying out step 2. Particle size analysis of the formulation shown in Table II is described in Figure 1. The data indicate that step 1 produces the bulk of particle initiation, whereas step 2 is predominately a particle growth step. At a particular acid level, the growth a carboxylated particle will be able to sustain in step 2 without coagulating will depend on the particle size established in the low-pH step. Also of importance is the solids content of step 1 at any particular acid level. At 1% to 3% carboxylic monomer content (based on monomer in

TABLE II  
Surfactant-Free Formulation for Particle Size Analysis<sup>a</sup>

	Low-pH step	High-pH step
Styrene, g	18	26
Butadiene, g	12	17
Itaconic acid, g	1.5	—
Potassium persulfate, g	0.30	0.10
pH	2.5	9.5

<sup>a</sup> Polymerization temperature 70°C. First step run to approximately 20% solids; second step run to 40% solids.

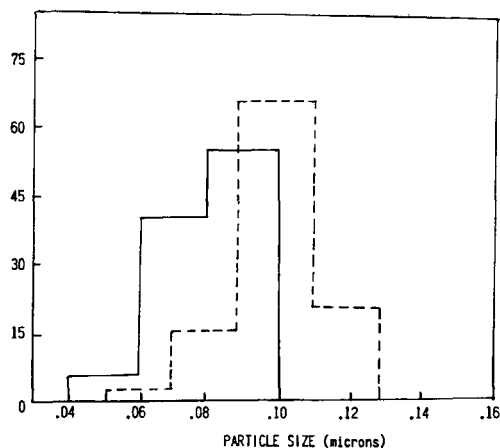


Fig. 1. Particle size distribution of carboxylated latex described in Table II. Solid line represents distribution after step 1; dashed line represents distribution after step 2.

steps 1 and 2), a solids level of 20–25% has been found to be satisfactory for step 1. The production of a higher solids content in this lower-stability, low-pH step results in curd formation. Coagulation begins to take place in step 1 when the particle becomes too large to be stabilized by the un-ionized carboxyl groups. If the seed particle is too small, coagulation may take place in step 2 due to the explosive increase in surface area during the growth step. This increase in surface area separates the neutralized carboxyl groups to such an extent that they can no longer effectively stabilize the growing particles.

#### *Effect of Latex Particle Counterion*

To ascertain the effect of neutralizing bases on polymerization, separate samples of the seed latex shown in Table III were neutralized before step 2 to a pH of 8 with ammonia, potassium hydroxide, morpholine, and 2-methyl-2-amino-1-propanol (AMP). The latex neutralized with ammonia went to high solids with 1% curd formation, that employing KOH contained 8% curd, whereas the latices containing AMP and morpholine co-

TABLE III  
Carboxylated Seed Latex Used to Evaluate Polymerization Variables of  
pH Variable Process. Materials and Evaluation

Styrene	60 g
Butadiene	40 g
Acrylic acid	0.50 g
Itaconic acid	2.00 g
Potassium persulfate	0.20 g
Solids	25.0%
Surface tension	52 dynes/cm
pH	2.6

agulated within 1 hr. Apparently small, highly solvated cations provide more stability for they do not negate the negative charge of the carboxylate anions on the surface of the emulsion particle as effectively as large, less solvated cations. The ammonium ion is known to be a highly solvated moiety due to the multiple hydrogen bonding sites of its acidic hydrogens.<sup>13-15</sup> This experiment suggests that ammonium salts of anionic surfactants will more effectively stabilize dispersed particles than their corresponding potassium salts.

#### *Effect of pH in Step 2*

The pH to which the seed latex was adjusted at the beginning of step 2 was found to be an important variable governing curd formation and resulting particle size. When the mixed-acid seed latex shown in Table III was run in step 2 at pH values of 5.0, 7.0, 8.5, 9.0, 9.5, and 10.0, the results displayed in Table IV were obtained. Surprisingly, minimum curd formation and smaller particle sizes were produced at the lower pH values (except at pH 5.0). Since no new particles should be formed in step 2, these results suggest that particle agglomeration increases with pH and eventually leads to a coagulated product. This hypothesis seems to contradict the fact that the final latex acquires increased mechanical stability as the pH is raised to higher values. For instance, the latex produced at pH 7.0 did not become mechanically stable (20 min at high speed on a Hamilton Beach mixer with no curd formation) until its pH was raised to 9.0. Presumably, at this point, sufficient carboxyl groups are ionized to promote stabilization. The production of water-soluble polymer formed by the homopolymerization of acrylic acid or the copolymerization of acrylic acid and itaconic acid in the highly carboxylated first step could account for this agglomeration at high pH. This water-soluble polymer could expand on ionizing in step 2 at higher pH's and promote flocculation and agglomeration through a particle-bridging mechanism.<sup>16</sup> This phenomenon is dependent on the type and amount of carboxyl monomer present since no agglomeration was evident in the particle size analysis of the formulation shown in Table II. Agglomeration would produce a more heterodisperse system than that found in the particle distribution shown in Figure 1. Since the recipe of Table II con-

TABLE IV  
Evaluation of Varied pH Runs\*

pH of Step 2	Curd formation, %	Particle size, Å <sup>b</sup>
5.0	coagulated	—
7.0	1.0	1540
8.5	1.0	1686
9.0	6.0	1800
9.5	15.0	1836
10.0	coagulated	—

\* pH adjusted with aqueous ammonia.

<sup>b</sup> Light transmission method.

tains only itaconic acid, which has little tendency to homopolymerize, the production of water-soluble polymer would be minimized. The stability of the growing particles in step 2 appears to be governed by two factors: the particle charge which increases stability as the pH is raised and the extent of particle agglomeration by water-soluble polymer which decreases stability as the media becomes more alkaline.

### Location of Bound Carboxyl Groups

Recently, considerable interest has been generated on the location of bound acid monomers in carboxylated emulsion polymers.<sup>7-9</sup> Since the latices described in this paper derive almost all of their stability from copolymerized acid monomer, the position of the carboxyl functionality on or in the latex particle is a most important factor. For example, an acid monomer which polymerizes and becomes buried inside a latex particle will provide no stability to the dispersion. Conversely, a high concentration of surface carboxyls will enhance stability. Indeed, the fundamental advantage of the two-step, pH-variable process is its capacity to direct carboxyl groups to the surface of the particle at low pH and maintain them at the particle surface at high pH. The production of high-solids, mechanically stable latices without surfactant and containing only small amounts of acid monomer is evidence that this attempt to place acid functionalities on the particle surface has been successful.

Previous work employing acid-base titrations of typical low-pH seed latex preparations has demonstrated the increased affinity of acrylic acid compared to methacrylic acid to accumulate at the particle-water interface or in the aqueous phase.<sup>7</sup> The data of Tables V and VI describe the increase in stability of high-solids latices containing acrylic acid versus methacrylic acid as a result of this phenomenon. Evaluation in Table VI of the two latices described in Table V containing acrylic and methacrylic acid illustrates the important role played by surface carboxyls in promoting mechanical stability. As Table VI indicates, acrylic acid is far more efficient than methacrylic acid in promoting mechanical stability. An important factor in the burial of methacrylic acid inside the latex particle as compared to acrylic acid is its higher monomer solubility. Under equiva-

TABLE V  
High-Solids, Surfactant-Free Latices Carboxylated with Acrylic and Methacrylic Acids<sup>a</sup>

	Step 1	Step 2
Styrene, g	18.5	18.5
Butadiene, g	12.5	12.5
Acrylic acid, g	1.50	—
Methacrylic acid, g	—	1.50
Potassium persulfate, g	0.25	0.25

<sup>a</sup> Temperature 70°C. Low-pH step run to approximately 20% solids. The pH was then adjusted to 7.5 and enough styrene and butadiene added to reach 40% solids. An additional 0.1 part of persulfate was added on step 2.

TABLE VI  
Evaluation of Latices Carboxylated with  
Acrylic and Methacrylic Acids as Described in Table V

	Sample containing acrylic acid	Sample containing methacrylic acid
Solids, %	48.7	48.6
Surface tension, dynes/cm	59	69
Mechanical stability at pH 7.5 <sup>a</sup>	pass	instant failure
Mechanical stability at pH 10.0	pass	failed in 2 min

<sup>a</sup> Latex run in Hamilton Beach Mixer for 20 min at high speed and filtered through 100-mesh screen.

lent conditions, the distribution ratio of methacrylic acid between styrene and water is 1.94 as compared to 0.175 for acrylic acid.<sup>17</sup> This ability to place functional monomers at the particle core and/or the particle-water interface is invaluable in designing emulsion polymers to meet the wide range of industrial applications to which they are applied.

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