

# The Preparation of Monodisperse Latexes with Well-Characterized Surfaces\*

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## I. INTRODUCTION

For many years The Dow Chemical Company has prepared and distributed monodisperse polystyrene latexes as a scientific service. These latexes have found a wide variety of applications: (1) the calibration of various measuring instruments and techniques, e. g., electron microscopes,

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\* This work was begun during the year one of us (JWV) spent at the van't Hoff Laboratory of the University of Utrecht and was continued in The Plastics Laboratory of The Dow Chemical Company.

light-scattering instruments, optical microscopes, ultracentrifuges, aerosol counting instruments such as the Goetz Aerosol Spectrometer, electronic particle counting instruments such as the Coulter Counter, and small-angle X-ray diffraction apparatus; (2) medical diagnostic tests for rheumatoid arthritis, leptospirosis, disseminated lupus erythematosus, tuberculosis, C-reactive protein, histoplasmosis, trichinosis, and human pregnancy; (3) the counting of virus particles; (4) the determination of the pore size of filters and biological membranes, e. g., the exit channels of the human eye; (5) studies of the reticulo-endothelial system; (6) stimulation of antibody production; (7) purification of antibodies; (8) investigations of the mechanism and kinetics of emulsion polymerization; (9) analysis of flagellate locomotion mechanisms; and (10) model systems in colloidal studies. Despite their obvious utility, these latexes have been used in only a few colloidal investigations. One reason for this is that, although their distributions of particle sizes are very narrow, little is known about the characteristics of their surfaces. Recently we have begun to characterize these latex surfaces with regard to the number and acid strength of their negative groups, in order to enhance the use of the latexes in colloidal investigations.

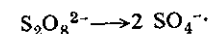
The preparation and characterization of these monodisperse latexes is described in the following sections: (1) latex preparation; (2) desorption of emulsifier; (3) purification of the ion exchange resins; (4) determination of the surface charge density; (5) properties of the ion exchanged latexes, e. g., stability, adsorption of emulsifier, viscosity, interference colors, conductance, and sedimentation.

## II. LATEX PREPARATION

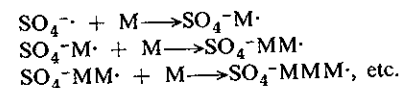
The latexes were prepared by the emulsion polymerization of styrene. There are four essential ingredients in such a polymerization: styrene monomer, water, emulsifier, and a free radical initiator. Thus, emulsion polymerization is free radical polymerization, with the conventional reactions of initiation, propagation, termination, and chain transfer superimposed on the colloidal emulsion system. The styrene is emulsified in water to form droplets as small as about  $1\mu$  in diameter. This emulsion is heated to decompose the free radical initiator, and the free radicals thus formed initiate the polymerization, which continues until the supply of monomer or radicals is exhausted. At this point, the latex consists of a sub-microscopic dispersion of polymer spheres, about tenfold smaller in diameter than the original emulsion droplets.

The classical Harkins (1) and Smith-Ewart (2) theories for the mechanism of emulsion polymerization postulate that the principal locus of polymerization initiation is the monomer-swollen micelles. According to this mechanism, the emulsifier is initially in three loci: adsorbed at the water/droplet interface; dissolved in the aqueous phase; and aggregated into micelles. Most of the emulsifier is in the micelles. The monomer is also in three loci: in the emulsion droplets; dissolved in the aqueous phase; and solubilized in the micelles. Most of the monomer is in the droplets. Free radicals are initiated in the aqueous phase and enter the monomer-swollen micelles to initiate polymerization. Once in the micelle, the radical continues to grow by the addition of monomer molecules until another radical enters and causes termination. Thus the monomer-swollen micelle is transformed into a monomer-swollen polymer particle of much greater size. As monomer is consumed in the polymerization, more diffuses from the droplets through the aqueous phase to the site of polymerization. This particle initiation process proceeds until all of the micelles have disappeared, either by capturing radicals and becoming polymer particles, or by disbanding to give up their emulsifier to neighboring micelles which have captured radicals. The disappearance of the micelles separates the particle initiation stage from the particle growth stage, in which a constant number of polymer particles continue to grow until the supply of monomer or radicals is exhausted. A more detailed discussion of these particle initiation and growth stages is beyond the scope of this paper; however, for the purposes of our discussion, let us assume that the reaction has proceeded to the particle growth stage; i. e., a constant number of particles are growing continuously, fed by monomer diffusing from the reservoir droplets and by radicals diffusing from the aqueous phase.

The latexes used in this investigation were prepared with various anionic emulsifiers (described later) and persulfate ion initiator. The decomposition of this initiator is considered to proceed as follows:



These sulfate ion radicals have little or no tendency to migrate to, or penetrate, the oil/water interface; however, there is a small concentration of solute monomer in the aqueous phase with which they may react.



As these reactions proceed, the number of monomer units incorporated

into the oligomeric ion radical increases until the hydrophobic chain length becomes sufficiently long to confer surface-active properties, e. g., when the number reaches 4,5, or 6. Oligomeric radicals of this composition would have a strong tendency to migrate to an oil/water interface and adsorb there with the radical end oriented toward the hydrophobic phase. Thus polymerization in the latex particle would be initiated at the particle surface, and the radical would grow into and through the monomer-swollen particle by propagation. This growth would continue until another such oligomeric ion radical enters the particle and eventually meets the polymeric radical already growing there to cause termination by combination or

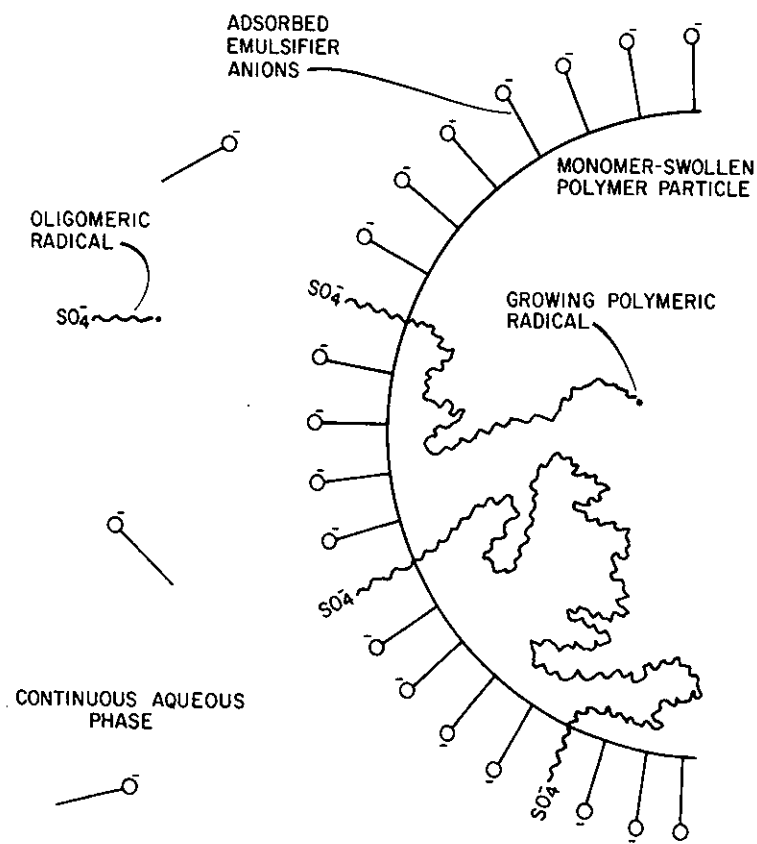


Fig. 1. Schematic representation of initiation of emulsion polymerization.

disproportionation. This reaction mechanism is shown schematically in Fig. 1.

Therefore, according to this mechanism, we should find two sulfate end groups on the particle surface for each polystyrene molecule formed assuming that: (1) the sulfate ion radical does not undergo a transfer reaction to introduce a different end group into the polymer molecule; (2) none of the sulfate end groups are buried within the particle; (3) termination within the particle occurs by combination rather than by disproportionation; and (4) transfer reactions with monomer and emulsifier can be neglected.

Thus the aqueous phase of the latex may contain emulsifier, residual initiator and its decomposition products, and buffer. The latex particle surface may contain both physically adsorbed emulsifier molecules and chemically bound emulsifier groups (i. e., the sulfate end groups as well as other groups formed in side reactions, such as carboxyls). If the emulsifier and inorganic salts were removed from the aqueous phase and particle surface, the result would be a system of monodisperse particles stabilized only by chemically bound emulsifier groups. If the number of these chemically bound groups were determined, the result would form an ideal model for colloidal studies, i. e., monodisperse spheres with a constant and known surface charge density.

### III. DESORPTION OF EMULSIFIER

Other reasons for removing the emulsifier and the inorganic salts from the aqueous phase and particle surface of the latex are: (1) to characterize the surface in terms of the number and acid strength of the chemically bound groups; (2) to prepare clean surfaces for studies of emulsifier adsorption; and (3) to prepare clean surfaces for the easy attachment of protein molecules for physiological studies.

In the past conductometric titration has been used to determine the surface charge density of acidified silver iodide sols (3). This technique measures only the total number of negative groups; i. e., in our latex systems it cannot distinguish between the sulfate end groups of the polymer molecules and the adsorbed emulsifier anions, except on the basis of acid strength. Moreover, the physically adsorbed emulsifier may desorb during the course of an experiment and thus change the surface charge. Therefore, we tried to remove this emulsifier as completely as possible, relying upon the sulfate end groups to stabilize the particles.

Dialysis is a method frequently used to remove emulsifiers and inorganic salts from colloidal sols. We dialyzed several latexes extensively, not only to remove these materials, but also in the hope that the  $\text{Na}^+$  and  $\text{K}^+$  cations of the sulfate end groups would be exchanged for  $\text{H}^+$  ions, so that the number of these end groups could be determined by conductometric titration with base. About 100 ml of latex in a cleaned and rinsed cellophane dialysis bag was suspended in a 4-liter beaker of distilled water; the beakers were stirred in most cases, and the distilled water was changed at least 25 times during the 3–4 week dialysis; the dialyses were carried out in a cold room to inhibit bacterial growth. This dialysis was considered extensive, if not exhaustive. We intended to titrate these samples shortly after dialysis; however, in error, the dialyzed samples were stored in *soft glass* bottles. Within a short time, their viscosities decreased considerably, presumably because of ions dissolved from the glass. Rather than repeat the time-consuming dialysis, we tried to remove the contaminating ions by ion exchange; this would also ensure the complete exchange of the  $\text{Na}^+$  and  $\text{K}^+$  cations of the sulfate end groups for  $\text{H}^+$  ions. The ion exchange resins used were the 20–50 mesh Dowex 50W-X8 sulfonic acid and Dowex 1-X8 benzyltrimethylammonium resins. These were conditioned separately by four or five successive exchanges between hydrochloric acid and sodium or potassium hydroxides, with copious rinsing between each exchange. The purpose of this conditioning was to remove soluble materials, presumably low molecular weight polyelectrolytes, which had been found to be leached from ion exchange resins (4). The color of the resins was improved significantly by this conditioning. The ion exchanges were carried out in small columns, either successively in a column of Dowex 50W followed by a column of Dowex 1, or in a single column of mixed resin.

We soon found that a succession of ion exchange cycles was required to reduce the surface charge to a reproducible value. From this we concluded that the dialysis had removed only part of the emulsifier and that the remaining emulsifier was removed with some difficulty by ion exchange. Later, however, we found that extensively dialyzed samples sometimes displayed a *very low* surface charge, seemingly indicating that the dialysis removed the emulsifier much more effectively than ion exchange. These low titration values, however, were the result of incomplete exchange of the  $\text{Na}^+$  and  $\text{K}^+$  cations for  $\text{H}^+$  ions; atomic absorption measurements showed that these cations were still present in the dialyzed latexes, whereas in the ion exchanged samples, the exchange for protons was complete. Moreover, ion exchange of the dialyzed samples gave the same (higher) surface charge as did the original latex after ion exchange.

Other workers have also found that dialysis was not effective in completely removing emulsifiers from latexes. Brodnyan and Kelley (5) found that  $^{14}\text{C}$ -tagged sodium lauryl sulfate solutions in dialysis bags equilibrated with the surrounding medium in less than 24 hr, but that only 9.5 and 22% of the same emulsifier was removed from two polystyrene latexes under the same conditions. Edelhauser (6) found that the rate of dialysis of sodium lauryl sulfate was high initially, but soon dropped off without reaching an equilibrium [several earlier similar examples are also cited in Ref. (6)]. Force et al. (7) found with a styrene/butadiene copolymer latex stabilized with Dresinate 214 that only about 50% of the emulsifier was removed upon dialysis for 160 days. On the other hand, however, Ottewill and Shaw (8) found from measurements of the electrophoretic mobility and from dialysis experiments using  $^{14}\text{C}$ -tagged emulsifiers, that the emulsifiers were completely removed by dialysis, or at least that a constant surface charge was attained.

#### IV. CONDITIONING AND PURITY OF THE ION EXCHANGE RESINS

Other workers have reported results which discouraged the use of ion exchange resins in colloidal studies. Schenkel and Kitchener (4) found that deionized water contained a weakly basic polyelectrolyte and warned against its use in experiments with *small* surface areas, e. g., glass capillaries. Ottewill (9) found, in some cases, that the charge of colloidal sols was reversed upon treatment with ion exchange resins. Therefore, in view of these experiences, it was of utmost importance to condition the ion exchange resins so as to completely remove any soluble polyelectrolytes. The resins selected for this rigorous conditioning were the 20–50 mesh Dowex 50W-X4 and Dowex 1-X4 resins. The lower degree of cross-linking (4%) was used instead of the usual 8% to facilitate the pickup of soluble polyelectrolytes and emulsifier anions.

After considerable work, the following procedure was developed for conditioning the resins. Separately the resins were washed with 85° water and methanol until no more colored material was removed. They were then eluted consecutively with a threefold excess of 3 *N* sodium hydroxide, hot water, methanol, cold water, a threefold excess of 3 *N* hydrochloric acid, hot water, methanol, and cold water. This cycle was repeated four times. The last cycle was completed by the slow elution of the Dowex 50W with a fivefold excess of 3 *N* hydrochloric acid to convert it to the  $\text{H}^+$  form and likewise of the Dowex 1 with a fivefold excess of 3 *N* sodium

hydroxide to convert it to the OH<sup>-</sup> form. The Dowex 1 was stored in the Cl<sup>-</sup> form and converted to the OH<sup>-</sup> form only shortly before use. The resins were rinsed copiously with double distilled water and mixed under stirring. Before use they were washed under agitation and decanted or filtered.

The color of Dowex 50W was improved considerably by this conditioning; the red color which remained after rinsing with 85° water and methanol was removed in the first two base/acid cycles. The light straw color of the Dowex 1 was improved only slightly by the conditioning. The conditioned Dowex 50W resin was odorless in both the H<sup>+</sup> and Na<sup>+</sup> forms, as was the Dowex 1 in the Cl<sup>-</sup> form; however, the Dowex 1 in the OH<sup>-</sup> form gave off an odor of amines upon standing, so this resin was stored in the Cl<sup>-</sup> form.

The purity of the resins was controlled by measurements of the conductance, surface tension, ultraviolet absorption (224 mμ), and the acid or base required for neutralization of the water in which the resin was agitated for 2 hr. The conductance of the wash water from the separate resins was 1–2 μmho, from the mixed resins 0.2–0.3 μmho. In our experience, values of 0.2–0.3 μmho are excellent, lower values being below the sensitivity of our conductivity bridge [however, Akelroyd and Kressman(10) measured values for pure water as low as 0.066 μmho, as compared with the theoretical value of 0.055 μmho]. No polyelectrolytes were detected by other methods in samples with conductances in the 0.2–0.3–μmho range. The surface tension (DuNouy ring method) of the wash water from the separate resins was 70–72 dyn/cm, from the mixed resins 71–73 dyn/cm. The polyelectrolytes leached from the resins do not lower the surface tension appreciably, and, therefore, this method does not give a sensitive measure of their presence.

Boyd and Bunzl (11) found that the polyelectrolytes leached from Dowex ion exchange resins displayed a strong ultraviolet absorption at 224 mμ. We found an appreciable absorption at this wavelength in the wash water from the separate resins before conditioning. Table 1 gives typical results of this analysis at various stages of the resin purification. Repeated washing completely removed the polyelectrolyte from the Dowex 1. It was much more difficult to remove from the Dowex 50W, however; a small amount was found in the wash water from the Dowex 50W after conditioning. The mixed resins, however, showed only a negligible absorption, even without conditioning; apparently the polyelectrolyte released by one resin is picked up readily by the other.

The wash water from the resins was also titrated conductometrically with 0.01 N sodium hydroxide or hydrochloric acid to determine the acid

TABLE 1  
Quality of Ion Exchange Resins<sup>a</sup>

	% Transmission, 224 mμ	Acid or Base, eq/100 ml
Dowex 50W, as received	0.09	$7.8 \times 10^{-5}$
Dowex 50W, washed with water	30.8	—
Dowex 50W, purified	15.6	$1.1 \times 10^{-5}$
Dowex 50W, purified, washed with water	86.2	$1.1 \times 10^{-6}$
Dowex 1, as received	66.3	—
Dowex 1, washed with water	98.8	—
Dowex 1, washed with methanol	~100	$<0.1 \times 10^{-6}$
Mixed resin	~100	$0.28 \times 10^{-6}$
Mixed resin, washed with water	~100	$<0.1 \times 10^{-6}$

<sup>a</sup> Ultraviolet absorption and titration values of deionized water treated with the indicated resin.

or base content. Blank titrations were carried out on distilled water or on distilled water boiled out and titrated under nitrogen. By this method acid or base can be detected in concentrations of less than  $10^{-6}$  N. The results of this analysis shown in Table 1 confirm those of the ultraviolet absorption. Repeated washing of the Dowex 1 reduced the base content of the wash water to a very low value; the slope of the conductometric titration curve showed that the material leached was a weak base. The Dowex 50W was much more difficult to purify—a small concentration of a strong acid was leached even from the purified resin. The wash water from the mixed resins, however, contained no strong acid within the limits of detection; also, no base was detected. Thus, both the titration method and the ultraviolet absorption at 224 mμ are sensitive measures of the purity of the conditioned resins.

The purity which can be achieved routinely using the foregoing conditioning technique is shown by a typical analysis of the wash water in which the mixed resin was agitated for 2 hr: 72 dyn/cm surface tension; 0.2 μmho specific conductance; 100% transmission (within the limits of error) at 224 mμ; and  $<0.1$  μeq/100 ml of acid (limits of detection). Thus, in a 2.5% solids sample of Latex A-2, which by titration showed a surface charge of  $5 \times 10^{-5}$  eq/100 ml, the contamination from the mixed resin would amount at most to about  $10^{-7}$  eq of acid, or about 0.2% of the total charge. Thus the ion exchange resins can be purified to such an extent that they can at least be used in experiments of large surface area without introducing an appreciable amount of contamination.

The ion exchange technique finally developed consisted of mixing 300–500 ml latex with a fivefold excess (estimated from the emulsifier and electrolyte content) of mixed resin under agitation for 2 hr, filtering through a sintered-glass Büchner funnel to remove the resin beads, and titrating. This process was repeated until a constant value was obtained for the surface charge. Earlier batch experiments used only a twofold excess of resin and a 3-hr contact time; this proved less efficient than the foregoing procedure. Our first ion exchanges were carried out in columns, either a single column of mixed resin or separate columns of Dowex 50W and Dowex 1, rather than in batch; both variations proved less efficient than the batch technique.

#### V. DETERMINATION OF THE SURFACE CHARGE DENSITY

After ion exchange the latex particles are stabilized only by the sulfate end groups of the polymer chains, all of which are in the  $H^+$  form. Thus their number can be determined by titration with base. Generally we followed these titrations conductometrically. In the first experiments, small increments of 0.1 *N* sodium hydroxide were added with a microsyringe to the latex under nitrogen, and the resistance was measured after each addition by balancing the conductivity bridge; a dip-type cell was used and the resistance was measured at 1000 Hz. Later the conductometric titrations were carried out with dip-type cells, adding 0.01 *N* sodium hydroxide continuously with a constant rate burette. In some titrations, the resistance was measured at various intervals while the sodium hydroxide was being added continuously; the resistance was measured at 1000 Hz using a General Radio model 1650A conductivity bridge. In others, the voltage drop across a 10- $\Omega$  resistor in series with the cell and in parallel with a 6-V transformer was recorded continuously. All titrations were carried out at  $25.0 \pm 0.1^\circ C$ .

Figure 2 shows a conductometric titration curve for an ion exchanged sample of Latex A-2, the variation of specific conductance with added sodium hydroxide. Both the descending and ascending legs are linear, and their extrapolation to intersection at 3.38 ml gives the equivalence point. The rounded minimum is due principally to the slow attainment of equilibrium near the equivalence point. This shape of curve is typical of what we found in the titration of strong acid surface groups with a strong base. The descending leg is linear because the strong acid surface groups have an equal preference for  $Na^+$  and  $H^+$  counterions; however, because of the limited mobility of these counterions in the double layer, its slope

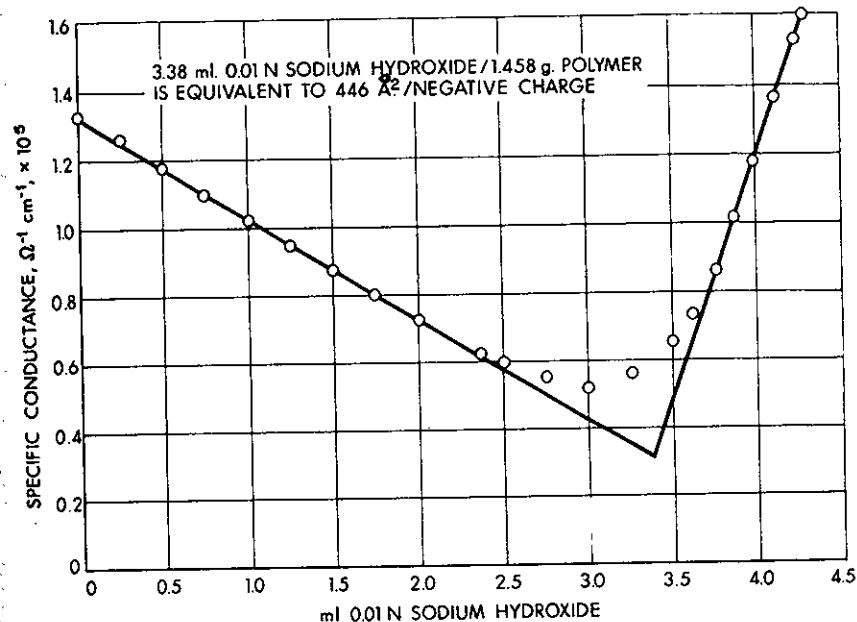


Fig. 2. Conductometric titration of ion exchanged Latex A-2 with sodium hydroxide.

is much smaller than for a strong acid in solution. Beyond the equivalence point, the specific conductance increases linearly with sodium hydroxide added in excess. An equivalence point of 3.38 ml 0.01 *N* sodium hydroxide for 1.458 g latex polymer corresponds to a surface charge of  $3.60 \mu C/cm^2$  (Note: We shall define the "surface charge" or "surface charge density" as the total charge measured by titration; this is distinguished from the "effective charge" or diffuse charge, which takes into account any undissociated negative groups and any counterions residing in the Stern layer; thus the effective charge is the product of the surface charge and the "apparent degree of dissociation"  $\alpha$ ; we shall see later that the effective charge is much smaller than the surface charge.)

Figure 3 shows a conductometric titration curve of the same sample of Latex A-2 with barium hydroxide. Only the ascending leg is linear; the descending leg is curved initially, but eventually becomes linear, so that extrapolation to intersection at 1.84 ml gives the equivalence point. The descending leg is curved because the innermost  $H^+$  ions in the double layer, i. e., those that contribute least to the conductivity of the latex, are

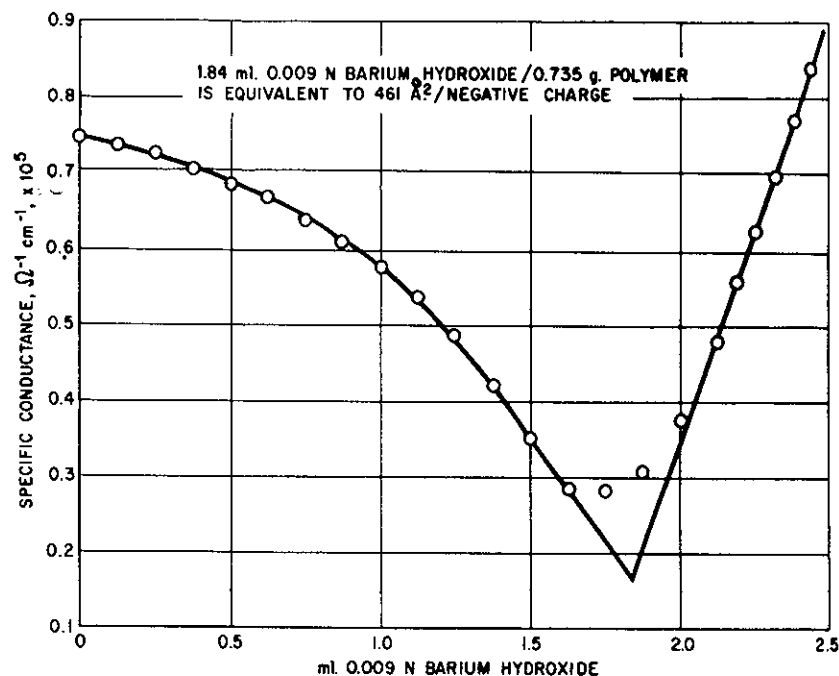


Fig. 3. Conductometric titration of ion exchanged Latex A-2 with barium hydroxide.

replaced first by the  $\text{Ba}^{2+}$  ions, and only later are the outermost, faster-moving  $\text{H}^+$  ions exchanged. Since the mobilities of the  $\text{Ba}^{2+}$  and  $\text{H}^+$  ions are markedly different, the initial addition of  $\text{Ba}^{2+}$  ions gives only a slight decrease in the conductivity, but further additions give an increasing decrement in the conductivity until the descending leg becomes linear. An equivalence point of 1.84 ml 0.009 *N* barium hydroxide for 0.735 g latex polymer corresponds to a surface charge of  $3.47 \mu\text{C}/\text{cm}^2$ , which is in good agreement with the value obtained with sodium hydroxide.

These results for the conductometric titration of ion exchanged Latex A-2 with sodium and barium hydroxides are similar to those obtained earlier (3) for acidified silver iodide sols.

The reproducibility of this analysis is shown by the 3.60 and  $3.47 \mu\text{C}/\text{cm}^2$  values obtained for the same sample of Latex A-2 by titration with sodium and barium hydroxides, respectively. This is confirmed by the 3.58 and  $3.61 \mu\text{C}/\text{cm}^2$  values obtained in duplicate titrations carried out

on the same day and the  $3.60$  and  $3.50 \mu\text{C}/\text{cm}^2$  values from duplicate titrations carried out 14 days apart. Although the close agreement of these values demonstrates the reproducibility of the titrations, the average value of  $3.56 \mu\text{C}/\text{cm}^2$  does not accurately represent the surface charge of Latex A-2. This sample was ion exchanged at an early stage of this work, before the conditioning technique was fully developed. Later experiments with Latex A-2 using mixed resins purified according to our best technique gave a slightly smaller value for the surface charge; the average of 20 determinations was  $3.3 \pm 0.1 \mu\text{C}/\text{cm}^2$ . The reproducibility of the ion exchange and conductometric titration is also shown by the results for Latex A-3. Early experiments using the column technique of ion exchange gave a value of  $1.97 \mu\text{C}/\text{cm}^2$  for the surface charge. Later experiments with another sample of the same latex using the batch technique of ion exchange and the rigorously purified resins gave a value of  $2.02 \mu\text{C}/\text{cm}^2$ . Although the final values were in good agreement, it took several passes through the ion exchange columns to achieve the same surface charge obtained after one batch treatment. Thus these results demonstrate the reproducibility not only of the conductometric titration, but also of the ion exchange technique.

Table 2 shows the variation of the surface charge of Latex A-2 with the number of ion exchange cycles. This series of experiments used the earlier batch procedure of ion exchange, i. e., a twofold excess of resin and a 3-hr contact time (thus necessitating more ion exchange cycles to achieve a constant surface charge than if the newer procedure were used). The surface charge reached a constant value of  $3.3 \mu\text{C}/\text{cm}^2$  after three ion exchange cycles; however, it reached a minimum value of  $2.86 \mu\text{C}/\text{cm}^2$  after the first cycle and then increased to the constant value. It is tempting to take this minimum value as the surface charge of Latex A-2 and attrib-

TABLE 2  
Variation of Surface Charge of  
Latex A-2 with the Number of Ion Exchange Cycles

Weight of latex, g	Weight of wet resin, g <sup>a</sup>	Contact time, hr	Surface charge, $\mu\text{C}/\text{cm}^2$	Surface area/negative charge, $\text{\AA}^2$
Original	—	—	10.7	150-160
180	100	16	2.86	563
500	50	3	3.11	517
500	50	3	3.28	490
500	50	4.5	3.30	487
500	50	16	3.23	498

<sup>a</sup> About 50% water.

ute the increase in charge upon further ion exchange to contamination by polyelectrolytes leached from the resins. In fact, however, this minimum results from the incomplete exchange of  $\text{Na}^+$  and  $\text{K}^+$  ions for  $\text{H}^+$  ions. This is shown by the constancy of the surface charge at a higher value of  $3.3 \mu\text{C}/\text{cm}^2$ , whereas additional ion exchange cycles should add to the contamination and thus gradually increase the surface charge. This incompleteness of the ion exchange is also confirmed by experiments with emulsifier solutions, in which the same phenomenon was observed in the absence of the latex particle surfaces.

In these experiments, the specific conductance of a given volume of emulsifier solution in contact with 15 g mixed resin (0.125 meq) was measured as a function of time. The amount of emulsifier was varied from 0.125 to  $10^{-4}$  meq, to give ratios of meq ion exchange capacity per meq emulsifier ranging from 1 to 900. For ratios in the range 10–900, the specific conductance decreased sharply to a constant value equivalent to that of pure water within about 1 hr. For the ratio of 3.2, however, the specific conductance increased twofold within about 15 min, then decreased to a constant value after 8 hr; the increase was attributed to the incomplete exchange of  $\text{Na}^+$  ions for  $\text{H}^+$  ions, since titration of the 24-hr sample with 0.01 *N* sodium hydroxide showed that 44% of the initial  $3.7 \times 10^{-2}$  meq emulsifier had been removed and that 84% of that remaining was in the  $\text{Na}^+$  form and only 16% in the  $\text{H}^+$  form. Similarly, for the ratio of 1.0, 37% of the emulsifier had been removed in 24 hr and 44% of that remaining was in the  $\text{Na}^+$  form. Thus the completeness of the ion exchange is limited by the exchange of  $\text{H}^+$  for  $\text{Na}^+$  ions, as well as by that of  $\text{OH}^-$  ions for emulsifier anions, independent of whether the emulsifier is in solution or absorbed on the latex particle surface.

Table 2 shows that the surface charge of Latex A-2 reached a constant value of  $3.3 \mu\text{C}/\text{cm}^2$  after three ion exchange cycles. That this value represents the number of bound negative groups remaining after complete desorption of the emulsifier was shown by several additional experiments. A sample of this rigorously ion exchanged latex was dialyzed in a cellophane bag for 5 days at  $45^\circ\text{C}$  with at least 20 changes of water; titration of this sample gave a value of  $3.4 \mu\text{C}/\text{cm}^2$  for the surface charge, indicating that dialysis after ion exchange did not remove any additional surface groups. Another sample of rigorously ion exchanged latex was subjected to four more ion exchange cycles, for a total contact time of 40 hr; the final surface charge of this sample was also  $3.4 \mu\text{C}/\text{cm}^2$ , indicating that additional ion exchange cycles neither increased the surface charge by contamination nor decreased it by removing more negative groups. In other

experiments, five different emulsifiers (Sipon WD, Aerosol MA, Aerosol OT, potassium oleate, and Dresinate 214) were added to samples of ion exchanged latex in such concentrations as to exceed the critical micelle concentration in the aqueous phase; these samples were then ion exchanged to remove this added emulsifier; the conductometric titration of the ion exchanged samples showed, in all five cases, that the added emulsifier was removed completely after two ion exchange cycles, and the average of the final surface charges was  $3.4 \mu\text{C}/\text{cm}^2$ . Thus the emulsifier is desorbed completely by the ion exchange without introducing enough ionic contaminants to significantly affect the particle charge.

Dialysis was compared with ion exchange by dialyzing samples of Latex A-2 at 25 and  $45^\circ\text{C}$  and then measuring the surface charge density by conductometric titration and the concentration of  $\text{Na}^+$  and  $\text{K}^+$  ions by atomic absorption. The results are shown in Table 3. The surface charge measured by conductometric titration was  $3.4 \mu\text{C}/\text{cm}^2$  for the ion exchanged sample, which is in good agreement with other determinations of this latex. The values for both dialyzed samples, however, were considerably smaller. This might have been construed as evidence for the more complete removal of emulsifier anions by dialysis were it not for the fact that these dialyzed samples also contained a much greater concentration of  $\text{Na}^+$  and  $\text{K}^+$  ions than the ion exchanged sample. The conductometric titration measures only the number of  $\text{H}^+$  ions; any anion which has a  $\text{Na}^+$  or  $\text{K}^+$  counterion will go undetected by this technique. Therefore, the total concentration of anions (i. e., the bound negative groups plus the remaining emulsifier and inorganic anions) is the sum of the concentrations of the  $\text{H}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  ions; this is shown in the last column of Table 3 as the total surface charge. These values are significantly greater for the dialyzed samples than for the ion exchanged sample. Moreover, the total concentration of  $\text{Na}^+$  and  $\text{K}^+$  ions in the ion exchanged sample is negligible compared to the concentration of  $\text{H}^+$  ions, but in the dialyzed samples

TABLE 3  
Comparison of Dialysis with Ion Exchange for Latex A-2

Treatment	Surface charge by conductometric titration		Total concentration of $\text{Na}^+$ and $\text{K}^+$ ions, eq/g polymer	Total surface charge, $\mu\text{C}/\text{cm}^2$
	$\mu\text{C}/\text{cm}^2$	eq/g polymer		
Ion exchanged	3.4	$2.1 \times 10^{-5}$	$< 0.1 \times 10^{-5}$	3.4
Dialyzed at $25^\circ$	2.1	$1.3 \times 10^{-5}$	$\sim 2.0 \times 10^{-5}$	$\sim 5.3$
Dialyzed at $45^\circ$	1.7	$1.0 \times 10^{-5}$	$\sim 3.0 \times 10^{-5}$	$\sim 5.5$



it is so much greater that, if neglected, it can lead to a serious error in determination of the surface charge. Thus dialysis is less effective than ion exchange, both in removing emulsifier and inorganic anions and in exchanging  $H^+$  ions for the  $Na^+$  and  $K^+$  ions.

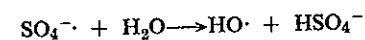
Table 4 summarizes the results for 10 latexes ion exchanged to constant surface charge. In several cases, the surface charge was constant after only one ion exchange cycle; however, Latex A-1, which had the smallest particle diameter and was prepared with a high concentration of emulsifier, required at least three cycles. The latexes prepared with potassium oleate were first ion exchanged with a mixed resin in the  $Na^+/OH^-$  form to keep the emulsifier completely dissociated; the  $Na^+$  ions were then exchanged for  $H^+$  ions in the subsequent cycles. These ten latexes, prepared with four different emulsifiers, represent a particle diameter range of 250–4470 Å. The particle diameters are the number average diameters determined by electron microscopy (12). The values of the surface charge were determined by conductometric titration. The area per charge was calculated using the values for the average particle volume and surface area determined by electron microscopy. The number of charges per molecule was calculated using the average particle volume determined by electron microscopy and the number average molecular weight of the polymer determined by osmometry. The values of the surface charge ranged from 0.5

TABLE 4  
Residual Charge of Polystyrene Latexes after Ion Exchange<sup>a</sup>

Latex	Particle diameter, Å	Surface charge, $\mu C/cm^2$	Surface area/charge, Å <sup>2</sup>	Negative charges/polymer molecule
A-1	250	0.5	3100	—
A-2	880	3.3	500	0.99
A-3	2340	2.0	800	0.87
B-1	1580	4.2	390	1.26
B-2	2480	5.7	280	1.02
C-1	2540	5.4	300	0.95
D-1	1090	1.6	1000	0.95
D-2	1870	1.8	910	0.90
D-3	2850	4.9	330	1.03
D-4	4470	8.1	200	0.93

<sup>a</sup> A series: Aerosol MA bis-1,3-dimethylbutyl ester of sulfosuccinic acid, sodium salt, American Cyanamid Company. B series: Sapon WD sodium lauryl sulfate, American Alcolac Corporation. C series: Aerosol OT di-2-ethylhexyl ester of sulfosuccinic acid, sodium salt, American Cyanamid Company. D series: potassium oleate.

to  $8.1 \mu C/cm^2$  and generally increased with increasing particle diameter. This increase with particle diameter is to be expected if all the polymer end groups are on the surface of the particles, because the number average molecular weights were in the relatively narrow range of 45,000–100,000 and the surface/volume ratio decreases with increasing particle diameter. The values of the number of charges per polymer molecule were all close to unity (the average was 0.99 charges per molecule). This is only about half of the value of two charges per molecule expected from the hypothesis advanced earlier. This lower-than-expected value might result if some sulfate end groups were buried within the particle and, hence, remained undetected by the conductometric titration. To investigate this, samples of polymer were recovered from the ion exchanged latexes and analyzed for sulfur content by X-ray fluorescence. The number of charges per molecule was 1.5 for Latexes A-2 and D-3 and 1.0–1.6 for most other latexes, values that are somewhat greater than those determined by conductometric titration. These values in the range of 1.0–1.6 charges per molecule are in good agreement with the value of 1.2 sulfate end groups per molecule, determined by Kolthoff et al. (13) using a radioactive tracer technique, for polystyrene prepared with the Mutual Recipe at  $80^\circ C$ . Thus the sulfate end groups comprise only 50–80% of the total number of end groups, the remainder being nonionic groups; most of the sulfate end groups are on the surface of the particles, with only a small proportion buried within the particle. One possible explanation for the discrepancy between the experimental and expected values of the number of charges per molecule is that termination occurs by disproportionation rather than by combination; however, there is considerable evidence from other studies (14) that combination is the predominant mechanism. Another (and more likely) explanation stems from the production of hydroxyl radicals according to the following reaction suggested by Kolthoff and Miller (15).



These hydroxyl radicals would presumably initiate polymerization in a manner similar to that of the sulfate ion radicals, and the nonionic hydroxyl end groups thus incorporated into the polymer chains would not be detected by the foregoing analyses.

## VI. PROPERTIES OF THE ION EXCHANGED LATEXES

The latexes were ion exchanged at low concentrations, usually 5% or

less, depending upon the particle diameter. After 15–30 min of contact with the ion exchange resin, the viscosity of the latexes increased twofold or more, the conductance decreased greatly, and, in some samples, interference colors became apparent. These changes are indications of the reduction of the electrolyte concentration to a low level and the resulting expansion of the double layer. These ion exchanged latexes, which are composed of monodisperse spherical particles of known and constant surface charge, are ideal models for colloidal studies. This section describes a number of preliminary studies of: (1) stability; (2) adsorption; (3) viscosity; (4) interference colors; (5) conductance; and (6) sedimentation.

#### A. Stability

These emulsifier- and electrolyte-free latexes form excellent models to test the theory of colloid stability (16). Quantitative data is not yet available; however, most of the latexes listed in Table 4 were stable after ion exchange. For example, Latex A-2 (880 Å diameter;  $3.3 \mu\text{C}/\text{cm}^2$  surface charge) showed no coagulation during ultracentrifugation at 14,300 rpm, either in the electrolyte-free latex, or in the presence of 100 mM potassium nitrate or 2.5 mM barium nitrate. The critical coagulation concentrations for sodium chloride, calcium chloride, aluminum chloride (pH 3), and aluminum chloride (pH 7) were 180, 18.5, 0.37, and 0.15 mM, respectively (the values for sodium chloride and calcium chloride were independent of pH). Latex A-1 (250 Å;  $0.5 \mu\text{C}/\text{cm}^2$ ), however, flocculated at least partially during ion exchange and completely upon titration with sodium hydroxide, presumably because of its combination of small particle diameter and low surface charge. Also, Latexes D-1 (1090 Å;  $1.6 \mu\text{C}/\text{cm}^2$ ) and D-2 (1870 Å;  $1.8 \mu\text{C}/\text{cm}^2$ ) flocculated slowly upon standing after titration (excess of  $10^{-4} M$  sodium hydroxide), presumably because of their low surface charge. Most of the other latexes, however, were stable enough to be used as model colloids. Their stability in the  $\text{H}^+$  form, as well as the shape of the conductometric titration curves, indicates that the negative groups stabilizing the particles are strong acid groups, most probably the sulfate end groups of the polymer molecules.

#### B. Adsorption

The titration of latexes with emulsifier solutions was proposed by Maron, et al. (17) as a method to determine the surface area of latex particles, provided the molecular area of the emulsifier is known. An ion exchanged sample of Latex A-2 titrated conductometrically with sodium lauryl sulfate

gave a saturation adsorption of  $2.04 \times 10^{-4}$  moles/g polymer. Using 50 Å<sup>2</sup> for the molecular area, as suggested by Cockbain (18), Sawyer and Rehfeld (19), and our measurements of adsorption at the octane/water interface (20), we obtained  $61.6 \text{ m}^2/\text{g}$  for the latex surface area, which is in good agreement with the electron microscope value of  $64.7 \text{ m}^2/\text{g}$ . In principle, the complete adsorption isotherm of an emulsifier on the latex particles can be determined, just as in the emulsifier titration, by adding increments of emulsifier and measuring the surface tension; the equilibrium concentration can then be calculated, and the adsorption determined from the material balance. For sodium lauryl sulfate in Latex A-2, the DuNouy ring method gave a saturation adsorption of  $2.25 \times 10^{-4}$  moles/g polymer, or a surface area of  $67.5 \text{ m}^2/\text{g}$ , which is in reasonable agreement with the above values. However, more accurate surface tension measurements, now in progress, are needed to characterize the complete adsorption isotherm.

#### C. Viscosity

The viscosity of the small particle size latexes increased greatly during the ion exchange because of the removal of electrolyte; e. g., the ion exchange of Latex A-2 was limited to solids concentrations of 5% or less because at higher concentrations the latex became gelled. The addition of electrolyte, however, decreased the viscosity, so that emulsifier-free latexes of higher solids contents can be prepared by evaporation. The viscosity of the original and the ion exchanged Latex A-2 was measured at small values of the volume fraction of polymer  $\varphi$ . The viscosity behavior of the original latex was Newtonian at values of  $\varphi$  below 0.15. The ion exchanged latex, however, displayed non-Newtonian behavior at values of  $\varphi$  as small as 0.0047 (0.5% solids). The addition of small concentrations of electrolyte, e. g.,  $10^{-3} M$  potassium nitrate, was sufficient to restore the Newtonian flow.

A detailed analysis of the viscosity of the electrolyte- and emulsifier-free latexes at low electrolyte concentration is possible only if the electrokinetic parameters of the latex are known. These have not yet been determined, but the results can be discussed in terms of the *effective* volume fraction of polymer  $\varphi_f$ . Table 5 shows the variation of the reduced specific viscosity  $(\eta - \eta_0)/\eta_0\varphi$  with  $\varphi$ . These values are much greater than the limiting value of 2.5 for the reduced specific viscosity.

It is of interest to determine whether this large electroviscous effect observed in ion exchanged Latex A-2 is a primary effect (i. e., due to distortion of the electric field around the particle by the flow) or a secondary effect (i. e., due to double layer interaction). Booth's treatment of the

TABLE 5  
Reduced Specific Viscosity for  
Emulsifier- and Electrolyte-Free Latex A-2

$\varphi$ , %	Reduced specific viscosity
3.07	143
1.90	91
0.95	76
0.47	65
0.09	29

primary electroviscous effect (21), when applied to our results, accounts for only 1–5% of the observed increase in viscosity, depending upon the value selected for the zeta potential. Therefore, the secondary effect is the predominant one, as is also expected from the non-Newtonian viscosity behavior (see Ref. 22).

Our data were analyzed by the method of Saunders (23), who rewrote Mooney's equation (24) in the form

$$\varphi/\log \eta_r = (2.303/k_0 f) - (2.303 z/k_0)\varphi$$

in which  $\eta_r$  is the relative viscosity,  $z$  is the so-called selfcrowding factor,  $f$  is the ratio  $\varphi_f/\varphi$ , and  $k_0$  has the value 2.5. The values of  $\varphi/\log \eta_r$  varied linearly with  $\varphi$ , so that  $f$ , and hence  $\varphi_f$ , could be determined from the intercept. The effective volume fraction corresponds to an *effective particle radius* that is indicative of the double layer interaction. The calculated values of this effective particle radius are 458 Å for the original Latex A-2, 474 Å for the ion exchanged latex in 0.01 M potassium nitrate, and 1250 Å for the ion exchanged latex in water. The first two values are in good agreement with the sum of the electron microscope radius and the thickness of the double layer, 470 Å. The effective particle radius of 1250 Å for the ion exchanged latex in water is the same as that indicated by the interference colors of the latex (see following section). Thus the viscosity measurements show that the double layer expanded greatly when the electrolyte was removed by ion exchange, but decreased in thickness to the original value when electrolyte was added back to the ion exchanged latex.

#### D. Interference Colors

Dried films of certain monodisperse polystyrene latexes display brilliant, iridescent colors. These colors have been attributed to the diffraction of

visible light by latex particle crystallites (25,26). When dried at room temperature, polystyrene latexes form opaque, white, friable, discontinuous films. Figure 4 is an electron micrograph of a surface replica of a polystyrene latex film, showing the monodisperse spheres packed in a uniform hexagonal array without appreciable coalescence. If the distance between the particle centers (or, in this case, the particle diameter, since the spheres are in contact with one another) is within a certain range, the crystallite diffracts visible light and the interference colors are observed. These color combinations are specific for the latex particle diameter, as described in Table 6.

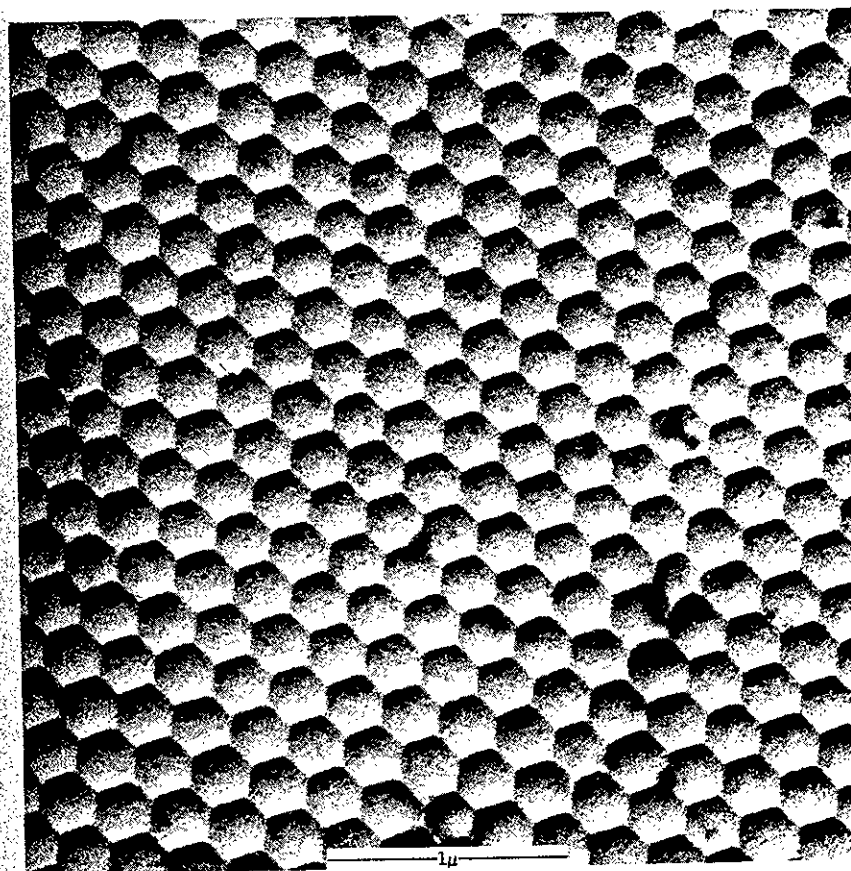


Fig. 4. Electron photomicrograph of a dried film of Latex A-3 (direct silicon monoxide replica shadowed with chromium metal).

TABLE 6  
Interference Colors of Dried Polystyrene Latex Films

Approximate particle diameter range, Å	Color combinations <sup>a</sup>
Less than 1700	No colors
1700-2200	Yellow-violet
2200-2700	Pink-green
2700-2900	Turquoise-gold
2900-3100	Red-olive green <sup>b</sup>
About 3500 and greater	Rainbow colors <sup>c</sup>

<sup>a</sup> Which color is observed depends upon the angle of observation.

<sup>b</sup> The olive green is seen only infrequently.

<sup>c</sup> The rainbow colors are usually weak in intensity.

These interference colors are occasionally seen in the latex, on the wall of the sample bottle, or floating on the latex surface. Presumably, in these cases, the colors arise from the diffraction of light by "liquid crystals," i.e., aggregates of latex particles packed in orderly arrays. In some cases, the color combinations observed in the latex are the same as those observed in the dried film of the same latex, but in other cases, the color combinations are different. This is not unexpected because the distance between the particle centers may be greater in the liquid crystal than in the dried film; in the latex state, the mutual approach of neighboring particles is hindered by the double-layer repulsion, so that particles aggregated in orderly arrays may not be in intimate contact with one another; however, the forces involved in drying tend to force the particles into close-packed arrays, despite the double-layer repulsion (27); thus the difference in the distance between the particle centers could be great enough to give a different color combination, since some of the ranges shown in Table 6 are narrow.

The ion exchange not only desorbs the emulsifier from the particle surface, but also removes the electrolyte from the aqueous phase. This decrease in electrolyte concentration increases the thickness of the double layer, so that neighboring particles interact with one another at greater distances. For example, the original Latex A-2 (880 Å diameter) displayed no interference colors, either in the latex or in the dried film. No colors were expected because of the small particle diameter. After two ion exchange cycles, however, the yellow-violet combination was observed in the latex, indicating that the distance between the particle centers was at least 1700 Å. After several additional ion exchange cycles, the pink-

green combination was observed in the latex, indicating that this distance had increased to at least 2200 Å. This sample also contained 10-300 μ blue and green liquid crystals, not only on the wall of the container and surface of the latex, but throughout the body of the sample. Figure 5 is a photomicrograph showing several of these liquid crystals. These disappeared when the sample was shaken or heated to 35-40°C, only to reappear again upon standing at room temperature. Such structures observed here in samples containing only 1-2% polymer are similar to those observed earlier



Fig. 5. Optical photomicrograph of liquid crystals in Latex A-2.

by Luck and Wesslau (26), but in samples of much higher solids contents. Another sample of Latex A-2 subjected to five ion exchange cycles showed different color combinations upon dilution, the yellow-violet combination observed at 3.24% polymer changing to violet-green at 2.00% and pink-green at 1.00 and 0.50%, indicating that the distance between particle centers increased upon dilution.

In another example, the original Latex A-4 (1760 Å diameter) displayed the yellow-violet combination, both in the dried film and in the latex. After the latex was dialyzed extensively, the pink-green combination was observed, indicating that the distance between particle centers was 400-900 Å greater than the particle diameter. After only one ion exchange cycle, the rainbow colors were observed, indicating that this 400-900 Å distance had increased to at least 1200 Å.

The ion exchange of some latexes not only produced different interference colors but also changed the sedimentation pattern of the particles. Monodisperse polystyrene latex particles, particularly the larger sizes, tend to settle out upon standing because of the density of the polymer (1.05 g/cc). The approximate times for virtually complete settling of the particles, leaving a clear supernatant layer, are 1-3, 3-6, and 6-12 months for particle diameters of 10,000, 8000, and 5000 Å, respectively; particles 3500 Å or smaller in diameter show no settling upon standing for several years. For example, particles of Latex A-3 (2340 Å diameter) showed no settling upon standing for many months; this sample also showed the pink-green color combination expected for its particle diameter, both in the latex and in the dried film. After extensive dialysis, the turquoise-gold combination was observed in the latex, indicating that the distance between the particle centers was now 2700-2900 Å. After one ion exchange cycle, the turquoise-gold combination changed to a rainbow of colors, indicating that this distance had increased to at least 3500 Å. After several more ion exchange cycles, the rainbow colors were still observed but with increased brilliance and with various colors of the spectrum emphasized. Within 1-2 weeks, the particles of this sample settled into a packed layer, leaving a thin, clear supernatant layer; this packed layer showed brilliant interference colors. When the sample was shaken, the packed layer of particles redispersed, only to reform again upon standing. Thus the ion exchange not only increased the distance between the particle centers in the latex state, but also increased the rate of compacting of these particles into packed arrays.

In summary the ion exchange treatment reduces the electrolyte concentration of the latex to such a level that the double layer is expanded

greatly and the distance between the particle centers in the ordered arrays is considerably greater than one particle diameter. One possible explanation for the formation of these ordered arrays in the latex state is flocculation in the secondary minimum; the combination of the electrostatic repulsive forces and the van der Waals attractive forces is such that there exists a minimum in the potential energy-distance curve (i. e., the net force is attraction) at a given distance from the particle surface, bounded by distances at which the net force is repulsion. This concept has been proposed on theoretical grounds by Verwey and Overbeek (16), and it has been used by Schenkel and Kitchener (28) to explain the results they obtained with styrene/divinylbenzene copolymer spheres of 9 μ diameter. According to this concept, the latex particles would be forced closer to one another until the distance separating them corresponds to this minimum; they would then remain at this distance, moving neither closer nor further apart, until the structure is disrupted. The narrow particle size distribution of our latexes would favor the formation of ordered arrays by this mechanism, and our observations that the liquid crystals are easily disrupted and easily reformed is consistent with the shallowness of the minimum usually found by theoretical calculations. However, preliminary calculations show that at distances of 1000-1500 Å the van der Waals energies of attraction are insignificant compared to the repulsive energies, which are in the order of 5 *kT*. These attractive energies are significant for the large particle size spheres used by Schenkel and Kitchener, but are very small for our submicroscopic size latex particles. The most probable explanation is that the particles are crowded together into these ordered arrays by the expansion of their double layers, yet are held apart by the repulsive forces between them. For example, the 2500 Å distance between the particle centers in the ordered arrays found in ion exchanged Latex A-2 corresponds to a 23-fold increase in the effective particle volume. Thus the particles of an ion exchanged sample of Latex A-2 containing 2% solids may be as crowded as those in the original latex would be if it contained 46% solids. This 2500 Å distance is only a measure of the distance separating the particles in the ordered arrays—their double layers may interact at even greater distances. These ordered arrays offer the most economical packing arrangement of the crowded particles; moreover, their structure could be disrupted easily by agitation or heating, yet they would be expected to reform readily if the sample were left disturbed.

#### E. Conductance

In most colloidal properties, e.g., stability, viscosity, or sedimentation,

it is the potential of the outer Helmholtz layer  $\psi_s$  (or the diffuse double-layer potential) that is more important than the surface potential  $\psi_0$ . The values of  $\psi_0$  are calculated from the surface charge, i.e., the total charge measured by conductometric titration. The values of  $\psi_s$  are calculated from the "effective charge" or diffuse charge, which takes into account undissociated negative groups and counterions in the Stern layer and which is represented by the surface charge multiplied by the "apparent degree of dissociation"  $\alpha$ . If the values of  $\alpha$  can be determined, then the values of  $\psi_s$  can be calculated and compared with such direct experimental measures of the zeta potential as the electrophoretic mobility.

To obtain accurate measurements of  $\alpha$ , the specific conductance of the ion exchanged latexes was measured at different concentrations in a Washburn-type cell at  $25 \pm 0.01^\circ\text{C}$ . It was assumed that the electrolyte concentration of the ion exchanged latexes was zero and that the conductance was due mainly to the counterions, the contribution of the charged particles to the conductance being 10% or less. Therefore,  $\alpha$  is defined as the ratio of the measured conductance to the conductance expected from the known number of  $\text{H}^+$  ions (from the conductometric titration). The measured conductances were corrected for the conductance of pure water and the expected conductances for the presence of the charged particles. Table 7 shows the values of  $\alpha$  determined in this manner for six latexes. These values range from 0.05 to 0.39 and generally decrease with increasing surface charge, indicating that the greater the surface charge, the more tightly are the counterions held in the double layer.

TABLE 7  
"Apparent Degree of Dissociation"  $\alpha$  of the Surface Groups

Latex	Surface charge, $\mu\text{C}/\text{cm}^2$	$\alpha$
A-2	3.3	0.21
A-3	2.0	0.39
B-1	4.2	0.10
B-2	5.7	0.054
D-1	1.5	0.35
D-4	8.1	0.05

#### F. Sedimentation

Latex A-2 was sedimented in the ultracentrifuge to determine the influence of the double layer on the sedimentation rate. The latex polymer concentration was 0.08%. The effects of the double layer on the sedi-

TABLE 8  
The Particle Diameter of Latex A-2 as Determined by Ultracentrifugation

Latex treatment, medium	Particle diameter, $\text{\AA}$
Ion exchanged, in water	756
Ion exchanged, in electrolyte	790
Ion exchanged, in 0.1% Aerosol MA	822
Original latex, in 0.1% Aerosol MA	854
(Electron microscope)	(880)

mentation rate of these 880  $\text{\AA}$  diameter particles were found to be small, but the reproducibility of the measurements was very good. Table 8 shows the values obtained for various samples of this latex. The values of the ion exchanged latex diluted in electrolyte ( $10^{-4}$  to  $10^{-1}$  M potassium nitrate) were all in the range  $790 \pm 8 \text{\AA}$ . Those of the ion exchanged latex diluted in water were in the range  $756 \pm 15 \text{\AA}$ . The values of three different samples of the original latex diluted in emulsifier solution were 854, 856, and 854  $\text{\AA}$ .

To interpret these data, let us assume that the 790  $\text{\AA}$  value measured for the ion exchanged latex diluted in electrolyte represents the actual diameter of the polystyrene particles, since the thickness of the double layer is minimized in this medium. This value is 90  $\text{\AA}$  (or about 10%) smaller than the electron-microscope value of 880  $\text{\AA}$ . This discrepancy is probably significant in view of the 80  $\text{\AA}$  standard deviation of the electron-microscope average. This 790  $\text{\AA}$  value, however, is in good agreement with the light scattering values of 800  $\text{\AA}$  (29) and 760  $\text{\AA}$  (30) and the small-angle X-ray scattering value of 780  $\text{\AA}$  (31). Therefore, if we make this assumption, the 822  $\text{\AA}$  value for the ion exchanged latex diluted in emulsifier solution gives the reasonable value of 16  $\text{\AA}$  for the thickness of the emulsifier layer. If this represents a monolayer of emulsifier, then the 854  $\text{\AA}$  diameter of the original latex diluted in emulsifier solution is just 32  $\text{\AA}$  larger, suggesting that this sample was stabilized with a bimolecular layer of emulsifier.

On the other hand, the value of 756  $\text{\AA}$  for the ion exchanged latex diluted in water should show the effect of the expanded double layer on the sedimentation rate. Taking the value of  $\alpha = 0.21$  determined by conductance measurements for this latex, let us assume that 79% of the counterions are in the Stern layer and 21% in the diffuse double layer. Using the potentials calculated from the tables of Loeb et al. (32), this gives at an electrolyte concentration of  $2.6 \times 10^{-6}$  M, -190 mV for the Stern potential, and 0.23 for  $\kappa\alpha$ , where  $\kappa$  is the reciprocal thickness of the double

layer and  $a$  is the particle radius. Substituting these values in Booth's equation (33) for the change in sedimentation rate due to the double-layer effect, we obtain a sedimentation diameter of 760 Å, which is in excellent agreement with the measured value of 756 Å.

To confirm these effects unequivocally, the foregoing experiments should be rerun using latexes of smaller particle diameter, e.g., 200-600 Å. These experiments now in progress should show clearly the double layer and primary electroviscous effects.

Finally, let us return to the excellent work of Ottewill and Shaw (34). These investigators prepared monodisperse polystyrene latexes of various particle diameters and studied their colloidal properties. Their latexes were purified by extensive dialysis. They found convincing evidence for the presence of bound carboxyl groups in the polystyrene by the variation of the electrophoretic mobility with pH, the infrared spectra of the recovered polymer, and the potentiometric titration of the recovered polymer. These carboxyl groups generally were found in all their latexes, whether prepared with persulfate ion or some other initiator such as hydrogen peroxide. The presence of two different types of negative groups bound to the particle surface complicates the colloidal behavior of the particles and makes their use as model colloids less unequivocal. Therefore, it is of interest to determine if our latexes used in this study also contained carboxyl groups. Thus far we have found no evidence for the presence of carboxyl groups in the ion exchanged samples used in this study from infrared spectra or the conductometric titration. In some samples, however, carboxyl groups have been introduced into the polymer by oxidation; in these cases, they were readily detectable by the conductometric titration. The experiments defining the conditions under which the carboxyl groups are formed are now in progress, but at this point, the presence or absence of these groups must be attributed speculatively to differences in the method of latex preparation.

## VII. SUMMARY

Monodisperse polystyrene latexes prepared with persulfate ion initiator can be ion exchanged to remove the adsorbed emulsifier and solute electrolyte. Rigorous purification of the ion exchange resin is necessary to avoid contamination by leached polyelectrolytes. These ion exchanged latexes are stabilized by a certain number of strong acid groups which cannot be removed by ion exchange, presumably the sulfate end groups of the polymer molecules. The number and acid strength of these groups can be

determined by conductometric titration. The result is a dispersion of monodisperse particles with a constant and known surface charge density. These are ideal models for colloidal studies. Preliminary results of experiments using them for this purpose are reported and suggestions are made for their further use.

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