

Cationic Latex Interaction with Pulp Fibers. I. Deposition of Styrene-Butadiene Latex Having Quaternized Amino Groups

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Synopsis

Four experimental latexes of different styrene-butadiene ratios stabilized with quaternized amino groups were employed in deposition studies on unbeaten kraft pulp fibers. The attraction between the oppositely charged latex and fibers facilitates a ready latex deposition in the pH region between the points of zero charge of the latex and of the fibers. The rate of deposition appears to be controlled by latex diffusion and convection up to the fiber surface. The distribution of latex particles deposited on the fiber surface is related to the butadiene content and the latex stability. Polystyrene latex is the most stable and covers the fibers uniformly as individual particles. With increased butadiene content, the coagulation region of the latex is more extended and the tendency to deposit as aggregates is promoted.

Wet-end addition of latex is the most convenient way of introducing polymer into paper, but because most conventional latexes are anionic they do not deposit on negative pulp fibers without some kind of deposition aid. The potential advantage of using cationic latex is in the natural attraction between oppositely charged latex particles and fibers. It has been shown¹ that latex stabilized with built-in tertiary amino groups not only readily deposits on fibers, but offers an opportunity to regulate the latex distribution on fibers by controlling the pH and salt concentration. A uniform coverage of fibers by individual particles of film-forming latex was found to be most effective for paper reinforcement. However, the latex with tertiary amino groups has certain shortcomings, because the uniform latex deposition is achieved only at very low pH and above neutral pH the latex does not deposit due to the reversal of its charge.

In the present study, latex stabilized with built-in quaternized amino groups was employed. Such latex is expected to be less sensitive to pH and the range over which it deposits should be extended. The stability and deposition characteristics of four experimental latexes with different styrene-butadiene ratio were examined.

EXPERIMENTAL

Materials

Pulp Fibers. Bleached, unbeaten kraft fibers, washed three times with distilled water in order to remove fines, were used.

Latex. Four experimental cationic latexes of different softness (styrene-butadiene ratio) were prepared in the absence of emulsifier by a procedure described elsewhere.¹ The cationic charge was supplied by 1% 2-(diethyl amino) ethyl methacrylate quaternized by dimethylsulfate and added to the reaction

mixture. It was believed to copolymerize with styrene and butadiene to provide a built-in surface charge characteristic of quaternary amino groups. The integral nature of the stabilization avoids any difficulties with destabilization during dilution or other effects associated with the desorption or distribution of stabilizers.

Polymerization was carried out at 60°C for 8 hr using H_2O_2 and $\text{Fe}(\text{NO}_3)_3$ as initiator. The latex was subjected to flash evaporation to remove the unreacted monomer, followed by dialysis for 1 week. The latexes were reasonably monodisperse, with particle size between 120 and 160 nm as estimated from electron microscopy. The ratio of styrene-butadiene of the final product was determined by the consumption of bromine by the olefinic double bonds in the styrene-butadiene molecule.²

Methods

Electrophoretic Mobility. A Rank Bros Mark II Electrophoresis Apparatus (Cambridge) with a flat rectangular cell fitted with platinum-coated electrodes was employed. The latex mobilities were determined in both distilled water and in the presence of the required NaCl concentrations as a function of pH. The mobility of fines derived from the fibers were determined as a function of pH and assumed to be representative of the fibers.

Stability of Latex. To establish the boundaries of the stability region, a latex suspension (200 ppm) was adjusted to a desired pH by HCl or NaOH and light transmittance was measured at timed intervals. A change in transmittance within 60 min was used as the basis for assessing the loss of stability.

Rate of Latex Deposition. An appropriate amount of latex diluted in 100 ml distilled water and adjusted to the required pH by means of HCl or NaOH was added to a pH-adjusted fiber suspension (1 g in 400 ml) under slow (90 rpm) paddle stirring. The amount of latex deposited on fibers was determined from the change in latex concentration by means of turbidity measurement. For this a 5-ml sample was withdrawn by a pipet fitted with a filter made from glass fibers in order to prevent fibers from entering the pipet. The samples were taken at time intervals starting 1 min after latex addition. The calibration—latex concentration versus log transmittance—curves were identical over the whole range of pH outside the coagulation region. When coagulation was suspected, the sample was subjected to ultrasonic treatment for 1 min to ensure redispersion.

Latex Distribution on Fibers. Scanning-electron microscopy was employed for this observation. A sample of the fibers was washed in distilled water and brominated in order to prevent coalescence upon drying of the film-forming polystyrene-butadiene (PSB) latex particles.³ Bromination was not required in the case of nonfilm-forming polystyrene (PS) latex.

RESULTS AND DISCUSSION

The general properties of the four latexes employed in this study are in Table I.

It has been shown¹ that the deposition of a cationic latex with built-in tertiary amino groups on pulp fibers is affected by the latex stability. Latex deposited under conditions promoting its stability tends to cover the fibers as individual

TABLE I
 Latex Characteristics

Styrene-butadiene ratio	100/0	71/29	63/37	55/45
Particle radius (nm)	80	80	70	60
Specific surface (m ² /g)	38	38	43	50
Point of zero charge (pH)	9.5	9.5	9.5	9.8
Glass transition temp (°C) ^a	100	16	0	-14

^a From L. A. Wood, *J. Polym. Sci.*, **28**, 319 (1958).

particles, whereas unstable latex deposits in the form of aggregates. Since the stability of a colloidal system depends on the repulsion between particles due to their surface electric charge, the electrophoretic mobility determination provides an indication of the behavior to be expected. In general, the relationship between the mobility and the stability of hydrophobic sols is based on the DLVO theory of colloid stability,⁴ which considers two main interactions between particles as a function of their separation distance (1) the energy of attraction due to London-van der Waals forces and (2) the energy of repulsion due to their electric double layer. The total potential energy of interaction resulting from the superposition of both energies determines the stability. With high repulsion, the potential energy curve has a maximum and the system is stable. Coagulation takes place when the attraction between particles predominates at all distances, as in the case of insufficient or opposite surface potentials.

Figure 1 shows the mobilities of the four latexes determined in distilled water as a function of pH. Up to pH 8, all the latexes maintain a positive charge of such a magnitude that a stable suspension would be expected according to the DLVO theory. In the vicinity of pH 9.5, a zero mobility is reached; consequently, the suspension should destabilize. At still higher pH, a reversal of charge takes place, and a stable suspension should again result.

The relation between mobility and stability as a function of pH is observed

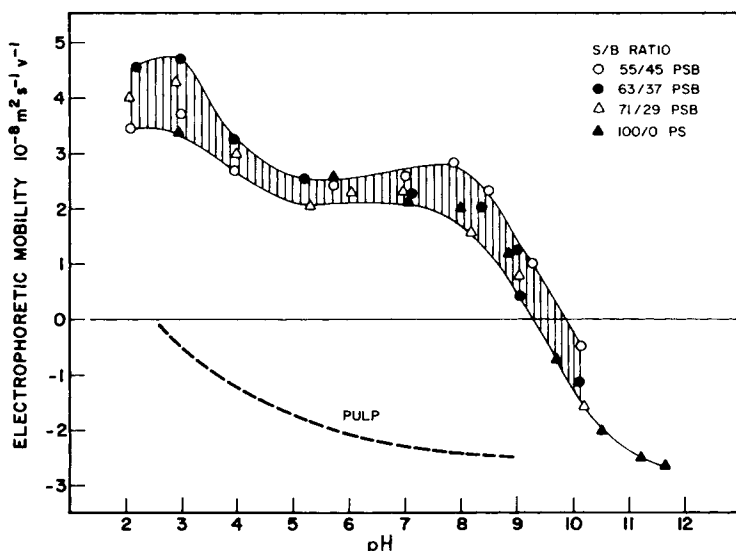


Fig. 1. Electrophoretic mobilities as a function of pH determined in the absence of salt: ○, 55/45 PSB; ●, 63/77 PSB; △, 71/29 PSB; ▲, 100/0 PS.

in the case of polystyrene latex PS 100/0. The zero mobility in the absence of salt is reached around pH 9.5, which compares reasonably well with the established stability up to pH 10. While the behavior of polystyrene latex follows the theoretical assumptions reasonably well, the copolymer styrene-butadiene latexes shows a considerable departure. The mobility versus pH is similar to polystyrene latex, but the coagulation of the 55/45 latex takes place at pH as low as 7.

No explanation of the greater ease of coagulation of the soft latex is available since the two main interactions, attractive and repulsive, are apparently similar for both latexes. In the theory of colloid stability, it is generally the surface potential that determines the repulsive energy. It is customary to use zeta potential calculated from mobilities for arriving at the surface potential, and these are similar for the two latexes. The second factor contributing to the total potential energy is the interparticle attraction, which is represented by a Hamaker constant. In a study of styrene-acrylonitrile copolymer latex stability,⁵ it was shown that with increasing acrylonitrile content the latex stability decreases, while the electrokinetic potential was independent of the latex chemical composition. The explanation was found in the increasing Hamaker constant and the higher cohesive energy density as the fraction of acrylonitrile increased. In our case, this argument is difficult to advance since the cohesive energy densities of both styrene and butadiene are similar. Also, the Hamaker constant was found to be similar for both styrene and styrene-butadiene polymers, although the data of various authors obtained by different methods vary considerably: $0.1\text{--}11.0 \times 10^{-20}$ J for polystyrene and $0.2\text{--}2.6 \times 10^{-20}$ J for styrene-butadiene copolymer.⁶ It is speculated that the deformability of the styrene-butadiene latex particles might be responsible for the differences in stability. The larger contact area of deformable particles upon their collision could result in a stronger interparticle adhesion and a more extended region of coagulation.

Latex Deposition on Pulp Fibers

Assuming that the theoretical treatment of mutual coagulation (heterocoagulation)⁷⁻⁹ and particularly the interaction of spherical colloidal particles with planar surfaces^{10,11} can be considered applicable, the following behavior of a fiber-latex system would be expected. As long as the two components are oppositely charged, the latex deposition should be controlled only by latex diffusion and convection up to the fiber surface. When the charge of one component is reversed, and both then have like charge, the mutual repulsion prevents the latex deposition if the potentials are sufficiently high. At zero charge, or at a low potential of one component, the colloidal particles should still attract each other. This means that deposition might take place when either latex or fiber are uncharged, but perhaps to a lesser extent.

A theory of the kinetics of the mutual coagulation of unlike colloidal particles^{9,14} is graphically depicted in Figure 2. In the upper part, the zeta potential behavior of the two components as a function of pH is shown schematically. In the lower part, the rates of coagulation, expressed as a stability ratio W , for the individual components are indicated by the solid lines. The overall stability ratio of a dispersion containing two kinds of particles (1 and 2) is composed of three separate stability ratios: W_{11} , W_{22} , and W_{12} . According to the theory, the overall stability ratio will remain almost constant over the pH range between the points of zero charge of the two components and similar in magnitude to that

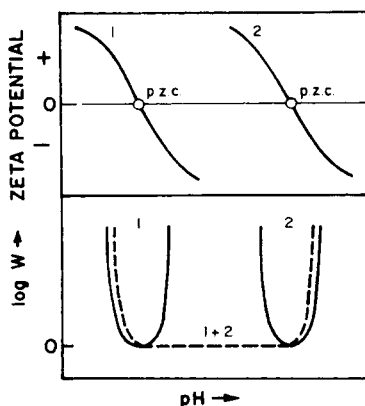


Fig. 2. Schematic representation of the variation of the zeta potential of two separate colloids as a function of pH (upper) and the predicted coagulation behavior expressed as log stability ratio W for the separate colloids (solid line) and the mixed system (dashed line).¹⁴

of dispersions of the separate components at their parts of zero charge. The predicted curve for heterocoagulation has the general form of the dashed line. The theoretical treatment is restricted to spherical particles of similar size and composition with the double-layer thickness less than the particle radius ($\kappa a > 1$) and a surface potential less than 50–60 mV. Our system is not suitable for a quantitative experimental verification of the theory because it does not fulfill these requirements, except for the potential, and because of its complicated hydrodynamics. However, if the some mixing conditions are maintained, the results should provide a basis for a qualitative comparison.

Our interest centers on the rate and extent of latex deposition under various conditions. By analogy with established practice in coagulation studies, the ratio of the maximum initial rate of deposition to the initial rate of deposition under the specified conditions will be referred to as the stability ratio W .

The rates of deposition for all four latexes are similar to the PS latex 100/0 shown in Figure 3. At four levels of latex addition (10, 20, 50, and 100 mg/1 g fiber) at pH 6, a full deposition is achieved. It is believed that the initial slopes of the plots of latex deposited versus the square root of time are linear and indicate that the process is probably diffusion controlled.

Figure 4 shows the effect of pH on the rate of deposition of PS latex added in

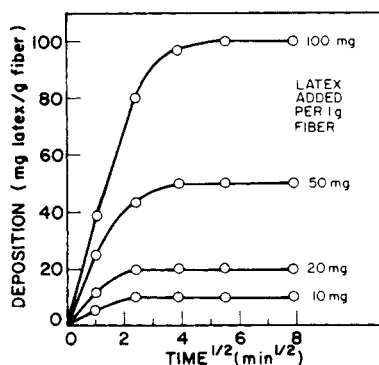


Fig. 3. Rate of deposition at pH 6 of PS 100/0 latex at four levels of latex addition. Similar behavior observed for all employed latexes.

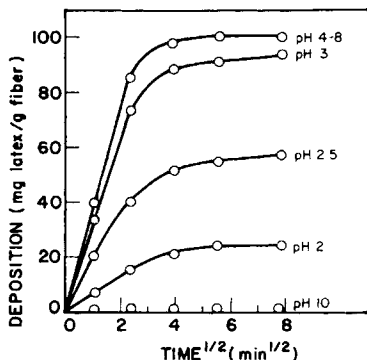


Fig. 4. Rate of deposition at different pH for PS 100/0 latex added in the amount of 100 mg/1 g fiber. Similar behavior observed with PSB latexes, except that no deposition takes place at pH 8.

an amount of 100 mg/1 g fiber. Similar curves were obtained with the other three PSB latexes with the exception of pH 8. Whereas the PS deposited fully at pH 8 and did not deposit at pH 10, the PSB did not deposit at pH 8.

The behavior of PS latex correlates well with mobility versus pH dependence shown in Figure 1. At pH 10 the PS latex has become negatively charged, and a repulsion between latex and fibers prevents its deposition. That the PSB latex does not deposit at pH 8 indicates a reversal of charge has already taken place at this lower pH. A probable explanation for the different behavior of PS and PSB is sought in the presence of fibers, more specifically, in the presence of water-soluble anionic substances—polyuronic acids and low-molecular-weight hemicelluloses—that are probably leached out of the fibers. An illustration of the effect of “water solubles” is shown in Table II, where the latex mobilities in distilled water and in a filtrate from fibers are compared. At pH 3, both PS and PSB remain positively charged in the filtrate, although considerably below the value in distilled water. At pH 9, a reversal of charge is observed in the case of PSB.

A similar observation was reported for an anatase-fines system.¹² The anatase alone was positively charged up to pH 6–7; yet in the presence of fines from bleached sulfate fibers, it had already acquired a negative potential at pH 3.

The ratio of the maximum initial rate of deposition to the initial rate of deposition at a given pH is expressed in Figure 5 as a stability ratio W versus pH. The vertical dashed lines represent the point of zero charge for pulp at pH 2.5 and for latex at pH 9.5 in water (Fig. 1). The lack of data in the region between pH 8 and 10 prevents the construction of the full curve, yet a qualitatively good agreement with the theoretical prediction (Fig. 2) is apparent. The rather

TABLE II
Latex Mobilities in Water and in Filtrate from Fibers

Latex	Medium	Mobility ($10^{-8} \text{ m}^2 \text{ sec}^{-1} \text{ V}^{-1}$)	
		pH 3	pH 9
PS 100/0	Water	+3.4	+1.0
	Filtrate	+0.6	+1.0
PSB 55/45	Water	+3.6	+1.5
	Filtrate	+0.5	-0.8

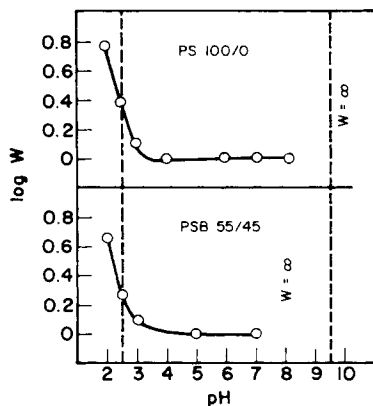


Fig. 5. Stability ratio, W , expressed as the ratio of maximum initial rate of deposition (regardless of pH) to the initial rate of deposition at the indicated pH. The vertical dashed lines represent the point of zero charge of pulp at pH 2.5 and of latex at pH 9.5. Lack of data at higher pH prevents construction of the full curve. $W = \infty$ indicates no deposition of PSB 55/45 at pH 8 and PS 100/0 at pH 10.

constant value between pH 4 and pH 8 in the case of PS indicates that the deposition is controlled by mass transfer, i.e., diffusion of latex to the fiber surface. At pH 2.5—the point of zero charge of fibers—the rate of deposition is considerably less and decreases further at pH 2. At this pH the fibers might already be positively charged, as has been found in the case of cotton.¹³

Besides the total amount of latex and its rate of deposition, the distribution of latex on fibers is of interest. It has been shown for PSB latex with built-in tertiary amino groups that the mechanical properties of a sheet formed from latex-treated fibers are considerably dependent on its distribution.² Other properties, such as water repellancy, dimensional stability, porosity, opacity, etc., might be also significantly affected by the way latex deposits on fibers. Figure 6 shows the distribution of PS 100/0 latex deposited at pH 6; the latex is in the form of individual particles, and, depending on its amount, it may encapsulate the fiber completely. The uniform deposition was found to be essentially the same over the whole range of pH 2–8 for PS 100/0 latex. A similar situation was found in case of PSB 71/29 latex, with the exception of pH 8, where this and other PSB latexes do not deposit. Figure 7 shows the distribution of PSB 63/37 latex deposited at pH 6. A uniform coverage is observed at pH 3, whereas a tendency to deposit in the form of aggregates is apparent at pH 6. The softest latex, PSB 55/45, shown in Figure 8 deposits over the whole range of pH 2–7 predominantly as aggregates. It is rather obvious that the difference in the mode of deposition and the response to pH can be identified with the chemical composition of the latex, i.e., the ratio of styrene to butadiene. The chemical composition was also found to affect considerably the latex stability, which decreases with increasing butadiene content.

The reason for the variation in deposition is therefore sought in the stability of the particular latex. Needless to say, the stability in the presence of fibers has to be considered since this might differ considerably from the stability determined in the absence of fibers. The stability then reflects the effect of both the polymer composition and the sensitivity toward the water-soluble anionic substances originating with the fibers.

The uniform deposition of PS 100/0 latex over the whole range of pH 2–8 gives

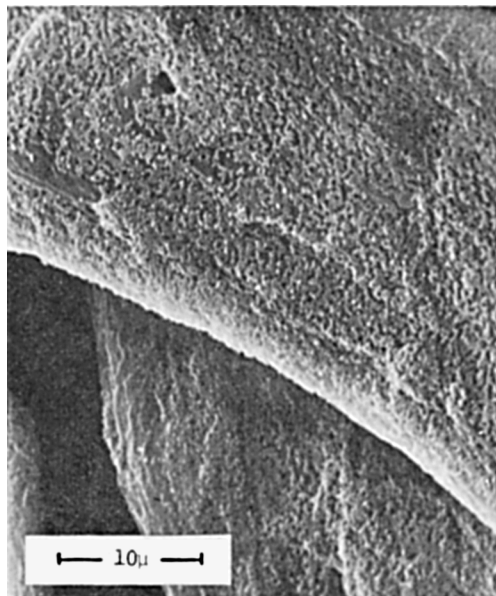


Fig. 6. Distribution of PS 100/0 latex deposited at pH 6. The uniform coverage of fibers by individual particles was observed over the whole range of pH 2-8.



Fig. 7. Distribution of PSB 63/37 latex deposited at pH 6. A tendency to deposit as aggregates is apparent. At pH 3 the fibers are covered uniformly with individual particles.

evidence of its stability in this region. The behavior of PSB 71/29 latex is similar, except at pH 8, where a reversal of charge prevents its deposition. PSB 63/37 latex is stable at low pH, but at pH 6 its deposition as aggregates indicates partial destabilization. It is understood that the aggregation might take place only in the vicinity of the fiber surface, where the latex particles concentrate as a result of the attraction between fiber and latex. This would explain why the aggregate deposition is not always accompanied by latex coagulation in the bulk. That



Fig. 8. Distribution of PSB 54/45 latex deposited at pH 6. The coverage of fibers predominantly in the form of aggregates is observed over the whole range of pH 2-7.

the softest latex, PSB 55/45, tends to deposit as aggregates regardless of pH is taken as an indication of the ease of destabilization.

CONCLUSIONS

1. Cationic latexes stabilized by built-in quaternized amino groups are positively charged in distilled water up to pH 9.5, and the electrophoretic mobility versus pH dependence is similar regardless of styrene-butadiene ratio.
2. The latex stability as a function of pH differs considerably with butadiene content, the coagulation region of the soft latex being more extended than that of hard polystyrene latex.
3. The presence of soluble matter originating from the fibers may affect the latex electrophoretic mobility and consequently its deposition.
4. Cationic latexes of different styrene-butadiene polymer ratios readily deposit on pulp fibers, and the rate of deposition is apparently diffusion controlled.
5. In conformity with the theory of heterocoagulation, the deposition takes place in the pH region between the zero mobility of fibers and the zero mobility of latex. Beyond the pH of latex charge reversal, no deposition is observed.
6. The distribution of latex on the fiber surface depends on the latex stability; a stable cationic latex deposits as individual particles; a decreased stability promotes the tendency to deposit as aggregates.

References

1. B. Alinec, M. Inoue, and A. A. Robertson, *J. Appl. Polym. Sci.*, **20**, 2209 (1976).
2. A. Homola, Ph.D. thesis, McGill University, Montreal, 1974.
3. E. B. Bradford and J. W. Vanderhoff, *J. Colloid Sci.*, **14**, 543 (1959).
4. See for example, H. R. Kruyt, Ed., *Colloid Science*, Vol. 1, Elsevier, 1952, Chap. 6.
5. H. Ono, F. Sato, E. Jidai, and K. Shihayama, *Colloid Polym. Sci.*, **253**, 538 (1975).

6. J. Visser, *Adv. Colloid Interface Sci.*, **3**, 331 (1972).
7. B. V. Derjaguin, *Discuss. Faraday Soc.*, **18**, 85 (1954).
8. O. F. Devereux and P. L. de Bruyn, *Interaction of Plane-Parallel Double Layers*, MIT Press, Cambridge, Mass., 1963.
9. R. Hogg, T. W. Healy, and D. W. Fuerstenau, *Trans. Faraday Soc.*, **62**, 1638 (1966).
10. M. Hull and J. A. Kitchener, *Trans. Faraday Soc.*, **65**, 3093 (1969).
11. G. E. Clint, J. H. Clint, J. M. Corkill, and T. Walker, *J. Colloid Interface Sci.*, **44**, 121 (1973).
12. M. J. and Jaycock and J. L. Pearson, *Sven. Papperstidn.*, **78**, 289 (1975).
13. G. L. Madan and S. K. Shrivastava, *Colloid Polymer Sci.*, **253**, 969 (1975).
14. T. W. Healy, G. R. Wiese, D. E. Yates, and B. W. Kavanagh, *J. Colloid Interface Sci.* **42**, 647 (1973).

Received March 4, 1977

Revised December 15, 1977