Polyelectrolyte interactions with papermaking fibers: the mechanism of surface-charge decay

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ABSTRACT: The time dependence of surface charge was investigated for six polymers and three pulps. The observed charge decay for the various polymers can be explained by a three-step process: (a) adsorption of polymer segments onto fiber surfaces, (b) reconformation of polymer into a flat configuration, and (c) diffusion of polymer into fiber pores. High-molecular-weight polymers undergo the greatest reconformation and thus suffer the greatest charge decay. At the other extreme, low-molecular-weight polymers (<10,000) are adsorbed in a very flat conformation and immediately begin to diffuse into the fiber pores. The results demonstrate the importance of selecting polymer addition points as close to the point of desired effect as possible.

KEYWORDS: Adsorption, characteristics, diffusion, electric charge, fibers, molecular structure, molecular weight, polyelectrolytes, polymers, pulps, surface properties.

The time of contact between polymer additives and papermaking fibers is an important process variable. Time has a significant impact on zeta potential, polymer adsorption, and retention. The dynamics of wet-end chemistry in a papermaking system have received only a limited amount of study. Effective management of the paper machine's wet-end chemistry requires a better understanding of the dynamic behavior of charge.

The main objective of our research was to determine the correlation between furnish properties and the dynamic behavior of charge. We focused specifically on the influence of polymer molecular weight, charge density, and main-chain structure on charge-decay behavior. We also studied the effects of pulp carboxyl content, slurry agitation rate, polymer dosage level, pH, and refining on charge decay. Finally, we also investigated the relationship between polymer adsorption rates and zeta potential.

In this report, we describe the effects of polymer characteristics and pH on the charge-decay behavior of three pulps. The effects of the other variables will be presented in a future report.

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Effect of time on electrokinetic charge

The papermaking process is a dynamic system. The electrokinetic charge of the system can be unstable when polymers added to the system do not have enough time to reach equilibrium with fiber surfaces. Thus, contact time between polymer and fiber is one of the most important factors to be recognized and understood when monitoring the zeta potential of a system.

Addition of a cationic polymer generally results in a positive increase in zeta potential within seconds. However, the highly positive charge decays rapidly. The polymer is believed to interact first with easily accessible surfaces, spreading to less accessible regions by diffusion *(1)*. Such diffusion has been postulated to cause a decay in charge, thus affecting the efficiency of the adsorbed polymers.

Several previous studies have reported the time dependence of charge. In one experiment, Strazdins *(2)* illustrated how electrophoretic mobility decayed from +1.2 $m^2/V{\cdot}s$ to −1.5 $m^2/V{\cdot}s$ within 600 s on a bleached softwood/hardwood pulp. Strazdins also

found that the rate of charge decay was highly dependent on polymer size, cellulose accessibility, and rate of shear. In another investigation, Strazdins *(3)* treated mixed European waste fibers with two different sizes of polyamine polymer. He found that (a) the smaller polymer decayed more rapidly than the larger polymer, (b) zeta potential decreased from highly positive values to zero within a 2-min interval, and (c) charge decay accelerated when pH was increased.

Davison *(4)* also studied the effect of polymer size on charge-decay behavior. He used two polyethyleneimines (PEI) of different molecular weight with a southern softwood bleached kraft pulp at a pH of 4 and a 0.2% PEI addition level. After 5 min of contact, he found similar zeta potentials. After prolonged exposure times, however, the two furnishes had completely different zeta potentials. The higher-molecular-weight polymer maintained a strongly positive zeta potential throughout a 24-h span, while the low-molecular-weight polymer decayed in charge.

Lindström *et al. (5)* showed that maximum flocculation occurs immediately after mixing polymer with pulp. Over time, the furnish charge became more electronegative, and retention decreased. They stated that charge decay was due to the adsorption of polymer onto the coarse fibers and desorption from fines *(5, 6)*. They also indicated that adsorption onto the fines was faster than onto the long fiber chains. In one experiment, they added enough polyacrylamide (PAM) to a bleached sulfite pulp to make the mixture positively charged and measured the effect of time on zeta potential and turbidity for 30 min. The furnish's electrophoretic mobility decayed from about +2 $m^2/V \cdot s$ to zero within the 30-min time span. A simultaneous increase in relative turbidity from 0.2 to 1.0 signified a decrease in retention.

Lindström *et al. (5)* also studied the effect of sequential polymer additions. Three dosages of 1% PAM were added at 20-min intervals. Each polymer addition increased the zeta potential and decreased the turbidity. However, again, the charge decreased and the turbidity increased over time. Further, the later additions of polymer became increasingly less efficient at decreasing the turbidity.

Strazdins *(7)* studied the effect of stock-agitation time on charge decay. He treated three different levels of refined, bleached sulfite pulp with PEI and agitated the mixtures for 1 min, 5 min, and 10 min. The cationic demand increased with increasing agitation time. Strazdins estimated that a 30-min stock agitation time was required for a stable surface potential.

In another study, Strazdins *(8)* measured charge decay in slurries at 0.3% and 0.6% consistency at slow and fast agitation rates. The greater shear and frictional resistance (0.6% consistency at a fast agitation rate) caused the greatest decay in charge.

Penniman *(9)* added different amounts of cationic PAM to a fines fraction of 1% and then combined it with long fibers. He showed that unless an excess of polymer was added, charge equilibrium of the fines and fibers could take up to an hour. He also stated that fines equilibrate much more quickly than the furnish as a whole.

Strazdins *(7)* supported this hypothesis in an experiment using PAM resin on an unbleached kraft pulp. Within 20 min, the charge of fines decayed only slightly in comparison with the charge of the furnish, which decayed to a strongly negative zeta potential. Strazdins believed that the large aqueous phase that buffered the fines, along with their large surface area, allowed for a high uptake of polymer, thus decreasing redistribution of the adsorbed polymer and causing only a slight decay in charge.

These previous studies relied on the use of manual instruments that were limited in terms of the amount of charge data that could be collected and the ease with which short-term measurements could be made. The major impetus for our study was the opportunity to use an on-line streaming-potential sensor capable of determining the charge-decay dynamics of the long-fiber portion of the furnish.

I. Pulp properties[a]

Pulp	Carboxyl (COOH) content, meq/100g	Freeness, mL CSF	Fines content, %
Bleached SW[b]	1.3	760	2.5
CTMP[c]	16.0	750	4.2
Eucalyptus	12.5	630	2.5

[a]Average of two determinations
[b]Unbeaten bleached softwood
[c]Chemithermomechanical pulp

Experimental

Experimental design

The experimental program was divided into two parts.

Part I was carried out to determine the basic characteristics of the three pulps and six polymers used in the study. **Table I** lists the properties (carboxyl content, freeness, fines content) of the three fines-free pulps. **Table II** lists the properties of the six polymers. The charge density of each polymer was determined by colloid titration.

Part II was performed to investigate the effect of cationic polymer type, pulp type, and pH on charge-decay rates. The tested variables included two levels of pH, three pulps, and six polymers, as illustrated in **Fig. 1.**

Instrumental methods

We used three common methods to measure the charge in a papermaking furnish. These procedures covered all aspects of charge, including dissolved charge, fiber surface charge, and fines surface charge.

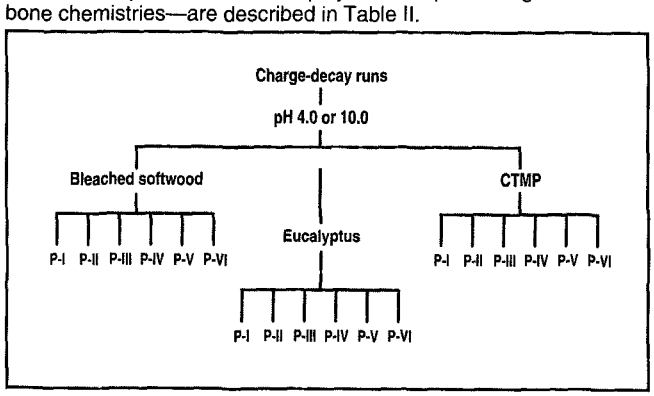
Microelectrophoresis. Microelectrophoresis is the most commonly used and simplest method of measuring zeta potential in the paper industry. We

II. Polymer properties

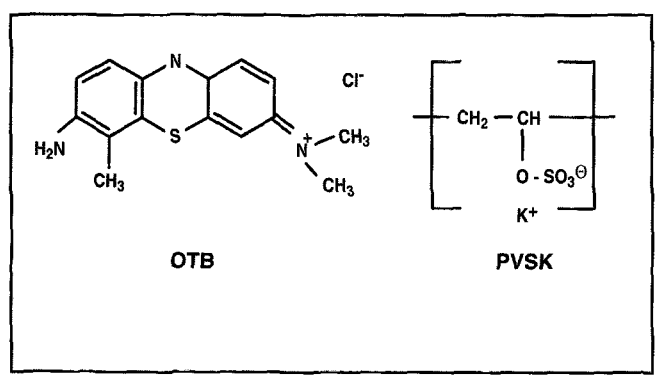
Polymer No.	Main chain	Molecular weight, g/mole	Charge density		Charge per unit mass of monomer	Charges per chain[a]	Total charges added
			Relative	meq/g			
P-I	Polyamine[b]	10,000	High	6.81	1 per 101 g	99	1.1×10^{21}
P-II	Polyamine	250,000	High	6.81	1 per 101 g	2,475	1.1×10^{21}
P-III	Poly-DADMAC[c]	100,000	Medium	5.49	1 per 126 g	794	8.7×10^{20}
P-IV	Poly-DADMAC	300,000	Medium	6.37	1 per 126 g	2,381	8.7×10^{20}
P-V	PAM[d]	6,000,000	Low	...	1 per 215 g[e]	27,907	5.1×10^{20}
P-VI	PAM	12,000,000	Low	...	1 per 215 g[e]	55,814	5.1×10^{20}

[a]Calculated by dividing molecular weight by the charge per unit mass of monomer
[b]Poly(2-hydroxypropyl-1, 1-N-dimethylammonium chloride)
[c]Polydiallyl dimethyl ammonium chloride
[d]Cationic polyacrylamide
[e]Calculated assuming that 50% of the monomer units have charge functionality

1. Charge decay was investigated for six polymers on three pulps at two levels of pH. The six tested polymers—representing three backbone chemistries—are described in Table II.



2. Structures of o-toluidine blue and PVSK



used it to determine the charge on the fines in the system.

Streaming potential. Streaming potential is commonly used to measure the charge of the whole furnish. We used streaming potential to measure the charge on the fibers in the system, independent of the fines fraction.

Colloid titration. Colloid titration *(10)* is another method of charge measurement. It differs from the previous techniques in that it measures the total charge. The total charge includes both the charges on the surfaces of particles and the charge in solution. We used colloid titration to track the adsorption rate of cationic polymer onto fiber surfaces and to determine the charge densities of the polymers studied.

Samples were filtered through a 150-mL fritted-glass filtering funnel to remove the suspended particles in solution. In the case of charge-density determination, a known amount of diluted polymer was used. In all cases, a known amount of dye was added to the sample, and then their mixture was titrated with an anionic polymer. The dye used was o-toluidine blue (OTB), and the anionic polymer was polyvinyl sulfate potassium salt (PVSK). Their structures are given in **Fig. 2.**

Once the anionic PVSK neutralized all of the dissolved cationic material, it reacted with the dye, turning the solution from blue to pink. Subtracting the amount of PVSK required to titrate the dye from the amount required to titrate the polymer, we were able to calculate either the cationic polymer's charge density or the unadsorbed cationic polymer remaining in solution.

The following equation was used to calculate the polymer's charge density in units of milliequivalents per milliliter or milliequivalents per gram *(10)*.

$$\text{charge density} = [(A-B)C]/D$$

where

A = amount of PVSK required to titrate sample, mL

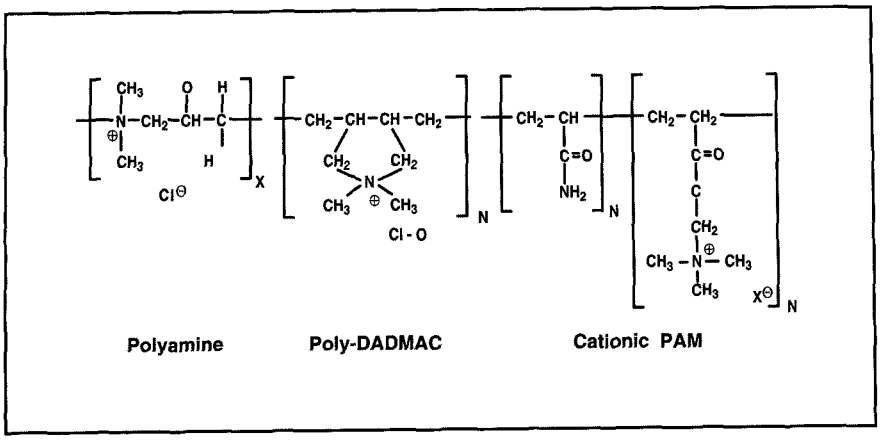
B = amount of PVSK required to titrate dye, mL

C = normality of PVSK = 0.001 meq/mL

D = sample size, mL or g.

The charge-density results were used, in turn, to determine adsorption data. The following equation was used to calculate the amount of cationic charge

3. Main-chain structures of the three polymer types



III. Minimum amount of polymer detectable in solution

Polymer	Detection limit, g
P-I	1.42×10^{-5}
P-II	1.42×10^{-5}
P-III	2.84×10^{-5}
P-IV	2.84×10^{-5}
P-V	...
P-VI	...

(meq) remaining in a filtrate sample from the 16-L fiber furnish.

$$\text{cationic charge} = [(A-B)\,xC\,x1000\ \text{mL/L}\ x16\text{L}]/D$$

where D, the sample size, is in units of milliliters.

The resulting charge value was then converted into weight (g) using polymer charge densities.

$$\text{cationic polymer in filtrate} = \text{charge in filtrate/charge density}$$

This, in turn, allowed calculation of retention values when the total amount of polymer added was known.

Materials

Pulp. Three different pulps (Table I) were chosen for this research based on their differences in carboxyl content. Bleached softwood was chosen because of its cleanliness and relatively low carboxyl content. CTMP pulp was selected because of its high content of both carboxyl and sulfonic acid groups. Eucalyptus fibers were chosen because they had carboxyl contents intermediate to the other two pulps.

Each pulp slurry was mixed thoroughly in a Valley beater and the freeness measured. Fines were removed from each pulp using a sidehill screen. After fines separation, we determined the carboxyl content (TAPPI T 237 om-88) and fines content (TAPPI T 261 cm-90) for each pulp.

Pulp type had little influence on the electrokinetic behavior of the tested polymers. Consequently, the results presented in this report are the average of the responses obtained with the three pulps.

Polymers. Six cationic polymers (Table II) were used in the experiment. The polymers were selected based on their differences in molecular weight, charge density, and main-chain chemistry. The polymer structures are given in **Fig. 3**. Polymer charge densities were determined by colloid titration.

No charge-density results were determined for the high-molecular-weight (HMW), low-charge-density (LCD), polymers P-V and P-VI. While determining charge density for the other four polymers, we discovered that they had different lowest detection limits. An inverse correlation was found to exist between charge density and the minimum amount of polymer detectable using colloid titration. As charge density decreased, the level of detection also decreased. **Table III** shows the minimum amount of polymer, in grams, that needed to be present in the solution for it to be detected using colloid titration. The relationship between charge density and minimum amount of polymer detectable is shown in **Fig. 4**.

Operating conditions and equipment

Each of the fines-free pulps was prepared at 0.5% consistency with deionized water. The conductivity was adjusted to approximately 500 µS/cm using sodium chloride. The two pH levels (4.0, 10.0) were adjusted using sodium hydroxide and hydrochloric acid.

The charge of the fiber slurry before polymer addition was recorded for 10 min at the beginning of each experiment. Pulp was circulated at a rate of 37 L/min. (The pump was adjusted to 17 L/min and 53 L/min for the agitation experiments.) Streaming-potential measurements were made approximately every minute. Microelectrophoresis measurements (average of three readings) were recorded approximately every 10 min.

A dosage of 5 lb/ton of selected polymer was added to 16 L of fiber furnish at 0.5% consistency and at the desired pH. Charge response was monitored for approximately 90 min at pH 10 and 120 min at pH 4. Each run maintained a constant conductivity and pH. Selected runs were duplicated.

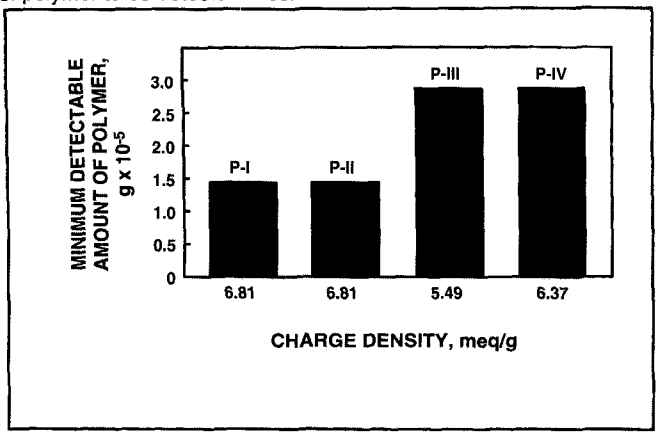
Figure 5 is a schematic diagram of the flow loop and instrumentation.

Results and discussion

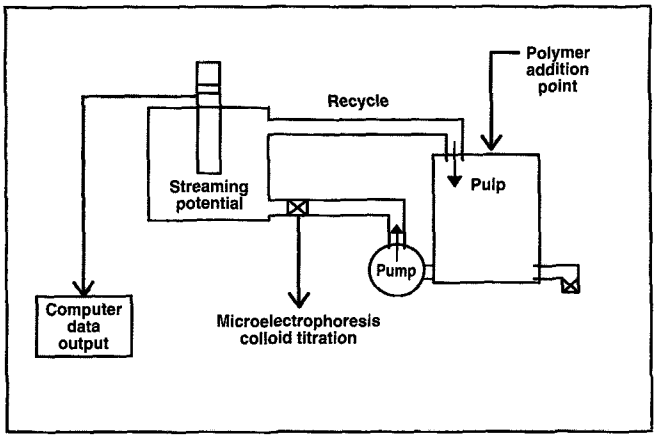
Effect of polymer dosage on charge decay and sorption

The effect of polymer dosage rate was investigated using low-molecular-weight (LMW), high-charge-density (HCD) polymer P-II at addition levels

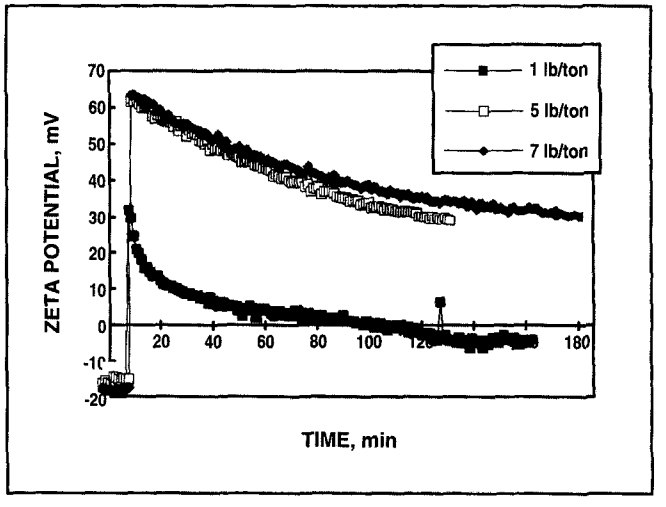
4. Relationship between polymer charge density and minimum amount of polymer detectable. A higher charge density permits smaller amounts of polymer to be detected in solution.



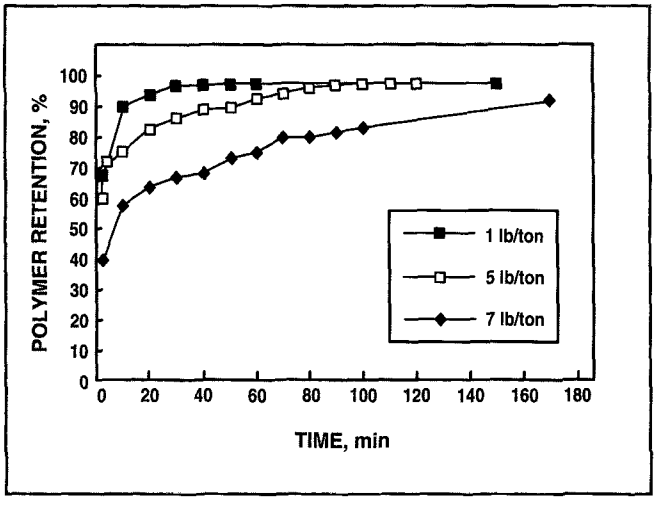
5. Flow loop and instrumentation



6. Rate of charge decay at three levels of polymer dosage (P-II, pH 4, charge measured by streaming potential, polymer response averaged over all three pulps)



7. Percent polymer retention over time at three levels of polymer dosage (P-II, pH 4)



of 1 lb/ton, 5 lb/ton, and 7 lb/ton on a bleached softwood furnish. The system was run at pH 4, and the results were measured by both streaming potential and colloid titration.

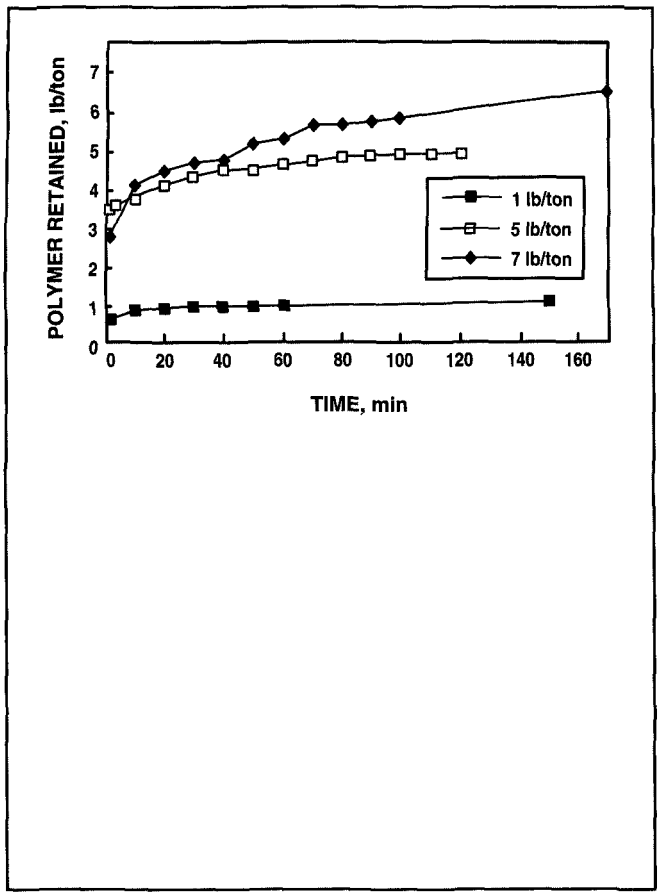
Figure 6 shows charge decay as measured by streaming potential. **Figure 7** shows polymer adsorption over time in terms of percent polymer retention. Finally, **Fig. 8** shows the actual pounds of polymer retained with time.

As seen in Fig. 6, the largest dosage of P-II produced the highest initial zeta potential, while the smallest dosage produced the lowest initial charge. It is apparent that an increase in dosage increases the electrokinetic charge response, since more positive charge is added.

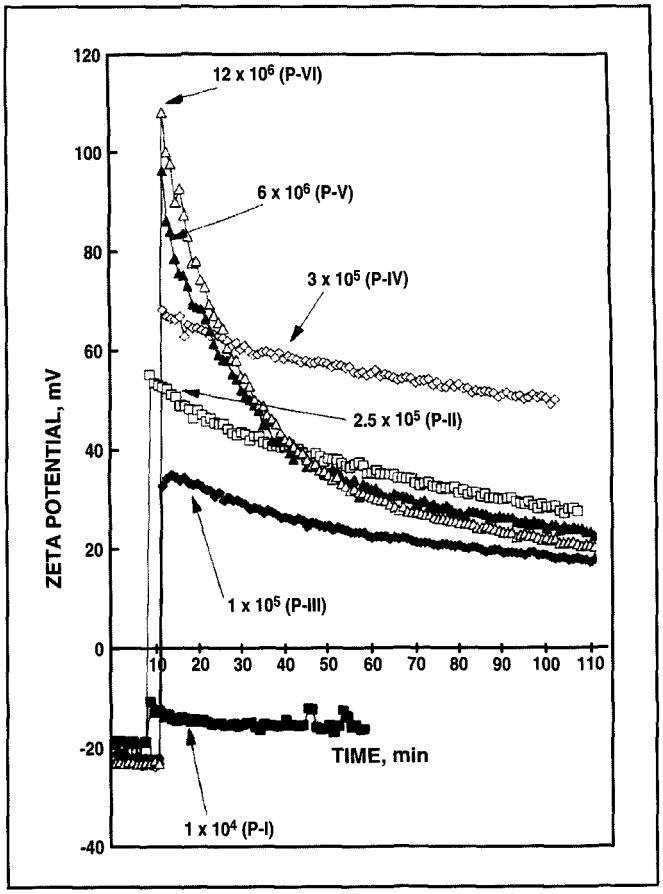
The charge response for the addition levels of 5 lb/ton and 7 lb/ton was initially similar and then began to diverge over time (Fig. 6). The same effect was found in the adsorption data (Fig. 8), confirming a correlation between the two procedures. The fact that charge decay occurs even as polymer continues to be adsorbed from solution is clear evidence that the declining charge is not the result of polymer desorption from the fiber surface.

Even though the final zeta potential readings are different, all three addition levels reach approximately the same ultimate retention percentage (Fig. 7). The higher dosage required more time to reach this adsorption level. The difference in zeta potential readings among the dosage levels is probably due to the fact that, at the lower dosage, the entire polymer dose rapidly diffuses into the fibers, and there is no more polymer available for further adsorption. In such a case, the surface charge decays toward zero mV. At higher addition levels, polymer continues to adsorb on fiber surfaces, replenishing the surface charge. The result is an overall higher zeta potential.

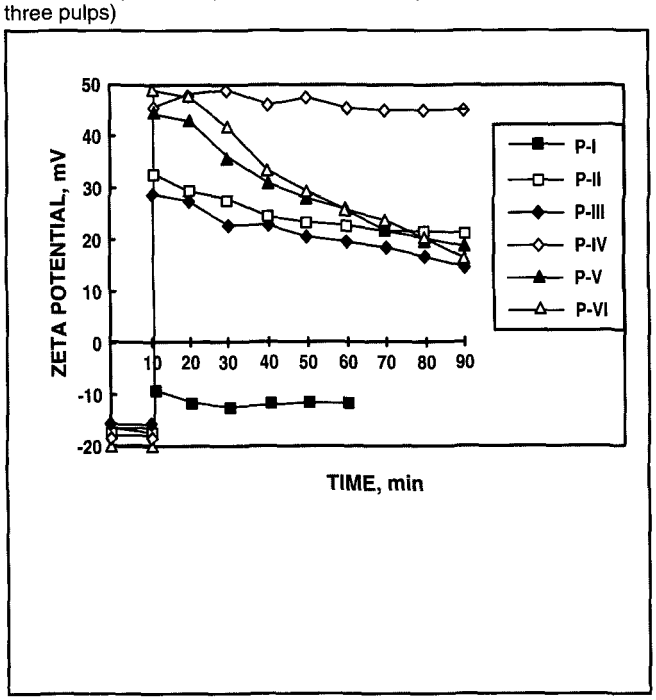
8. Weight of polymer retained over time at three levels of polymer dosage (P-II, pH 4)



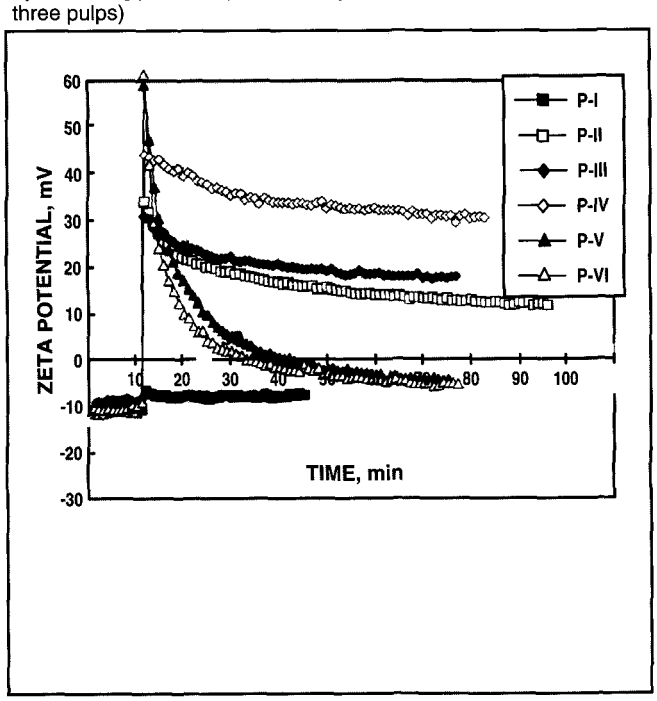
9. Rate of charge decay for six polymers at pH 4.0 as measured by streaming potential (5 lb/ton, polymer response averaged over all three pulps)



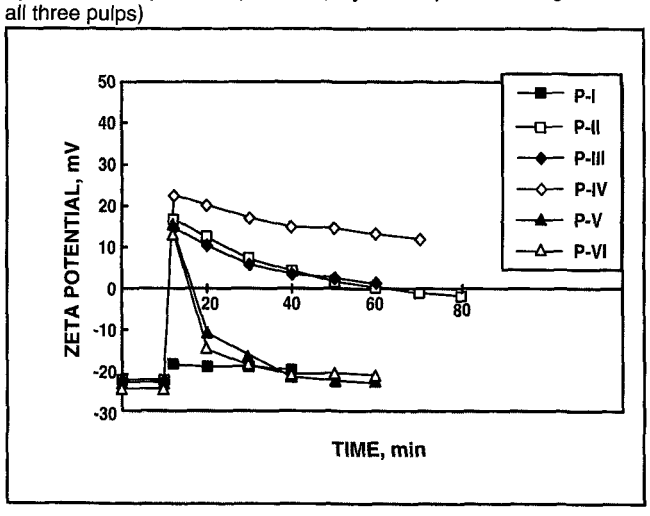
10. Rate of charge decay for six polymers at pH 4.0 as measured by microelectrophoresis (5 lb/ton, polymer response averaged over all three pulps)



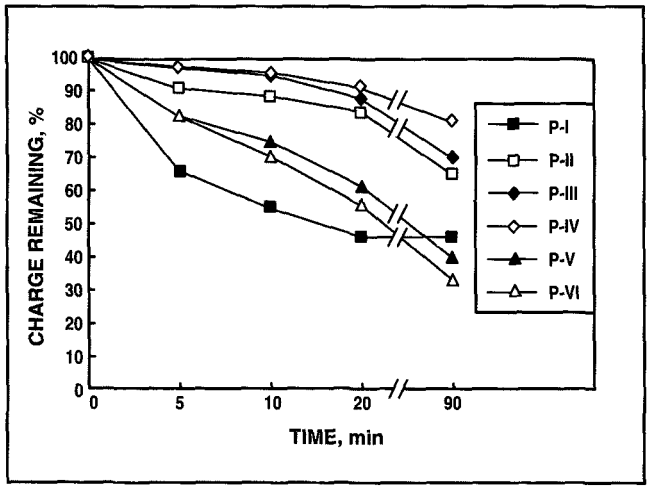
11. Rate of charge decay for six polymers at pH 10.0 as measured by streaming potential (5 lb/ton, polymer response averaged over all three pulps)



12. Rate of charge decay for six polymers at pH 10.0 as measured by microelectrophoresis (5 lb/ton, polymer response averaged over all three pulps)



13. Charge decay for six polymers at pH 4.0 (5 lb/ton, charge measured by streaming potential, polymer response averaged over all three pulps)



Effect of polymer on initial charge response

Polymer type played a significant role in determining the charge magnitude when polymer was first added to the pulp suspension. **Figure 9** shows the average responses of the six polymers at pH 4. (Polymer abbreviations are defined in Table II.) The data were collected using the streaming-potential method. The base charge of the furnish—before addition of polymer—is established during the first 10 min. As seen in Fig. 9, base charge showed little variation from run to run.

After approximately 10 min, we added polymer at a dosage of 5 lb/ton and monitored the charge response. The initial responses for zeta potential in Fig. 9 show that the molecular weight of the polymer plays a significant role. The highest-molecular-weight polymer, P-VI, produced, on average, the most dramatic increase in charge upon addition. In contrast, the lowest-molecular-weight polymer, P-I, displayed the lowest zeta potential response. Figure 9 shows the strong dependence of initial charge on molecular weight, with the magnitude of initial charge decreasing with decreasing molecular weight. This response seems to be independent of charge density and main-chain chemistry.

The high initial-charge magnitude of the HMW–LCD polymers, P-V and P-VI, can be explained by comparing the total charges present per chain for each of the six polymers. The number of charges per chain is calculated from the charge per unit weight of monomer and the molecular weight of the polymer (Table II). The two high-molecular-weight polymers are PAMs with approximately 50% of their monomer units having charge functionality. The low-molecular-weight polymers are polyamines and poly-DADMACs, each carrying a charge on every monomer unit. This information was used to calculate the "charges per chain" in Table II.

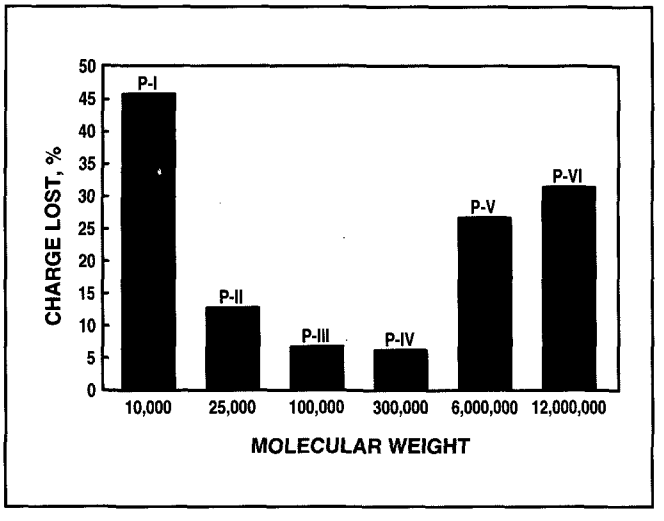
These calculations show that the PAM polymers carry 23 times as much charge per chain as the poly-DADMAC polymers, explaining the PAM's large initial increase in zeta potential. In other words, more than 20 poly-DADMAC chains must be adsorbed to get the same charge as a single chain of PAM.

Later, under the heading "Proposed mechanism," the polymer adsorption rate is seen to be a strong function of molecular weight. Thus, of the various polymers examined in this project, the high-molecular-weight PAMs also should have the highest adsorption rate. Coupling this fact with their high charge per chain provides a possible explanation for the very high initial zeta potential observed with these polymers.

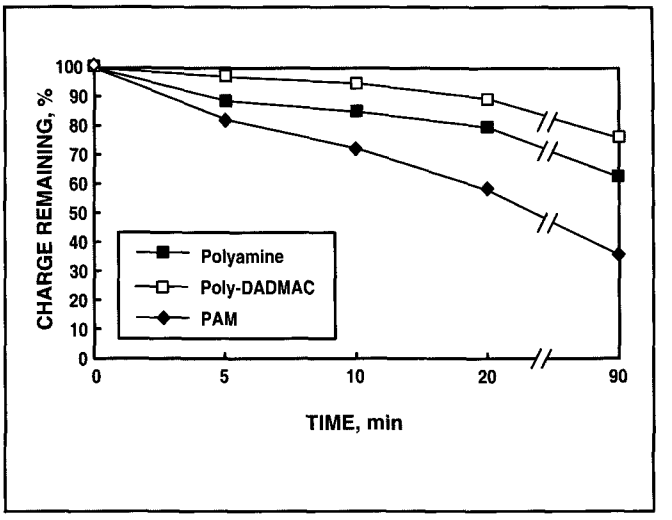
We also measured charge decay for the six polymers using microelectrophoresis. The results in **Fig. 10**, at the same pH, show the same trends as those observed in Fig. 9, which is based on streaming-potential data. The overall lower magnitude of charge found when using microelectrophoresis could be related to the fact that microelectrophoresis involved a manual measurement. Time was lost in preparing the sample, so the first few minutes of charge response could not be measured. This would explain the different response found between the two measurements with the high-molecular-weight polymers, which decayed so rapidly. Despite these differences, the correlation between molecular weight and initial magnitude of zeta potential is clearly apparent in the microelectrophoresis data.

Figure 11 shows the zeta potential as measured by streaming potential at pH 10. The initial charge at pH 10 corresponds to the results obtained at pH 4. The higher-molecular-weight polymers exhibited the highest initial zeta potential, while the lower-molecular-weight polymers showed the smallest response. The lower overall initial magnitude of zeta potential at pH 10, compared with that at pH 4, can be

14. Charge decay after 10 min for six polymers at pH 4.0 (5 lb/ton, charge measured by streaming potential, polymer response averaged over all three pulps)



15. Charge decay for three polymers at pH 4.0 (5 lb/ton, charge measured by streaming potential, polymer response averaged over all three pulps and for both polymers within each main-chain classification)



attributed to the ionization of fiber carboxyl groups. As the pH is increased and carboxyl groups on the fiber ionize, more negative sites are created for the polymer to react with, giving a lower initial zeta potential when polymer is added. Similar results were found using microelectrophoresis at pH 10, as seen in **Fig. 12.** The slightly different initial response can again be attributed to time loss during sample preparation and the extremely fast decay of the high-molecular-weight polymers.

In summary, the magnitude of the initial charge is strongly dependent on the polymer's molecular weight, with initial charge increasing with molecular weight. This relationship is independent of pH and charge-determination method. We postulate that this effect can be attributed to two factors:

1. The greater number of charges per polymer chain for high-molecular-weight polymers
2. The rapid adsorption of high-molecular-weight polymers on fiber surfaces.

Effect of polymer on charge decay

The polymer type also significantly affects the rate of charge decay. Figures 9–12 show the average charge responses over time after adding polymer at a dosage of 5 lb/ton.

At pH 4. The effect of polymer type on the rate of charge decay at pH 4 is shown in **Fig. 13.** The average decay rates were measured by streaming potential at 5 min, 10 min, 20 min, and 90 min after polymer addition.

Decay rates were analyzed by calculating the percent of initial charge remaining after each time interval. For example, the high-molecular-weight polymer P-VI exhibited an average initial charge increase of 134 mV. After 5 min, the charge had decayed to 110 mV, or 82% of the initial charge. This procedure was used to calculate the percent charge remaining for each polymer at both pH levels.

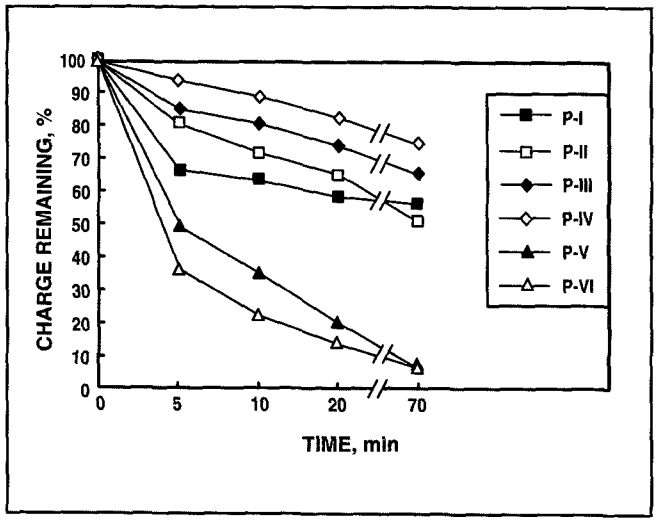
The significant difference in decay rates among the six polymers at pH 4 can be seen in **Fig. 14**, which shows the amount of charge lost 10 min after polymer addition. Three different charge-decay behaviors are evident. The lowest-molecular-weight polymer (P-I) decayed the most rapidly. The two HMW–LCD polymers (P-V, P-VI) exhibited similar behavior and decayed at an intermediate rate. Finally, the medium-molecular-weight polymers (P-II, P-III, P-IV) all decayed at a much lower rate.

Figure 15 illustrates the dependence of charge decay on polymer main-chain structure. In general, the poly-DADMAC polymers, P-III and P-IV, decayed more slowly than the polyamines, P-I and P-II. This may be attributed to the higher charge density found with the polyamines. The HMW–LCD PAMs, P-V and P-VI, reacted differently from the other polymers in that they brought a very high initial charge to the fiber that decayed rapidly.

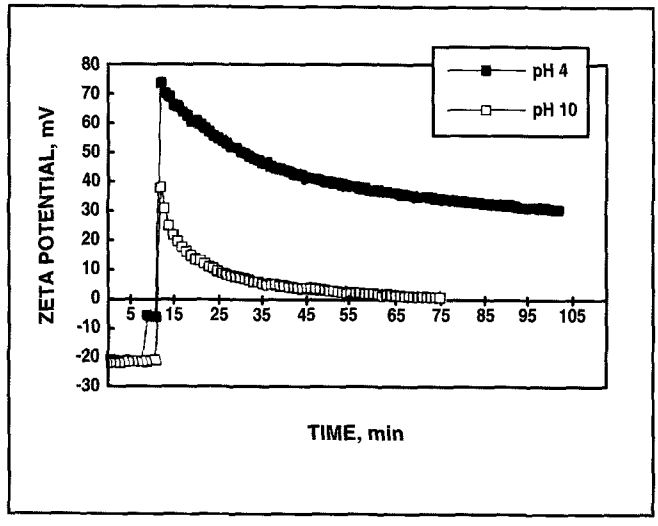
At pH 10. The effect of polymer type on the rate of charge decay at pH 10 is shown in **Fig. 16.** Zeta potential was monitored for a shorter period at pH 10 because of its swifter decay. Decay rates were compared at 5 min, 10 min, 20 min, and 70 min after polymer addition. Similar trends were found to exist at pH 10 as at pH 4 (Fig. 13).

Again, three different decay behaviors exist, but they are not as evident as those at pH 4. However, the dependence on molecular weight is still obvious, as evidenced by the behavior of the HMW–LCD polymers (P-V, P-VI) and the lower-molecular-weight polyamines (P-I, P-II) and poly-DADMACs (P-III, P-IV). The polyamines, with their greater charge density, once again were found to de-

16. Charge decay for three polymers at pH 10.0 (5 lb/ton, charge measured by streaming potential, polymer response averaged over all three pulps and for the two polymers within each main-chain classification)



17. Rate of charge decay at two levels of pH (5 lb/ton, charge measured by streaming potential, polymer response averaged over all pulps and polymers)



cay faster than the poly-DADMACs. However, the high-molecular-weight polymers decayed at a significantly more rapid rate than occurred at pH 4. This can be attributed to the stronger interactions occurring with the more highly charged fiber surface at pH 10, resulting in a more rapid polymer reconformation process.

Effect of pH on charge decay

System pH strongly affects charge phenomena. **Figure 17** illustrates the average difference in charge response at pH 4 and pH 10. **Figure 18** expresses charge decay in terms of the average percent charge remaining over time.

Increasing the pH leads to (a) ionization of the carboxyl groups on the fiber surface and (b) fiber swelling. Both phenomena help explain the lower surface charge at pH 10, compared with surface charge at pH 4 (Fig. 17). An increase in negative surface charge at high pH implies a greater consumption of polymer and thus a lower zeta potential at an equivalent polymer dose. An increase in fiber swelling implies greater surface area and thus greater accessibility for polymer redistribution.

Proposed mechanism

The data suggest that surface-charge decay is a three-step process that varies slightly for polymers of different molecular weights. The three step-process is illustrated in **Fig. 19**.

HMW–LCD polymers

Wågberg *et al. (11)* postulated that high-molecular-weight polymers initially adsorb in a coiled conformation with only a few segments attached to fiber surfaces. While studying a cationic PAM with a molecular mass of 4,000,000 g/mole, they found that 50% of equilibrium adsorption was achieved within 10 s after 0.75% polymer addition. After 2 min, 70% of the polymer was adsorbed. Lindström *(12)* concluded that with high-molecular-weight polymers, the loops and chains protruding away from the fiber surface into the surrounding water cause the shear plane, where the zeta potential is determined, to be displaced outward from the surface.

Earlier, we calculated that the high-molecular-weight cationic PAMs used in this study carry a very large number of charges per average chain. This fact, coupled with (a) the highly rapid adsorption behavior attributed to these polymers and (b) their extended shear plane, all serve to place a large number of positive charges some distance away from the fiber surface. During the time that this situation exists, the effective "surface charge" is very high and highly cationic. Hence, the measured zeta potential would be expected to be very high, as observed.

Wågberg *et al. (11)* suggested that, with time, the extended, adsorbed polymer loops and trains reconform to a flatter configuration onto the fiber surface. Lindström *(12)* supported this proposal by stating that, over time, more polymer–fiber contacts occur and the loops become less extended.

Reconformation of the polymer chains onto the fiber surface would be expected to result in a "collapse" of the cationically charged layer and a decrease in the observed zeta potential as the cationic groups on the reconforming polymer chains react with the anionic fiber surface carboxylate groups (i.e., charge decay would be observed). This is exactly what occurred.

Increasing the pH from 4.0 to 10.0 increases the degree of ionization of fiber surface carboxyl groups from approximately 45% to 100%. At pH 10, therefore, the surface carboxylate groups would more effectively neutralize polymer cationic groups under

all circumstances. Hence, it would be expected that the initial zeta potential at pH 10 would be lower than at pH 4.0 and that charge decay would be faster. Both phenomena were observed.

Wågberg *et al. (11)* and Lindström *(12)* both postulated that polymer penetration into a porous substrate is possible. Winter *et al. (13)* agree that after initial adsorption, polymer can continue to diffuse into the fiber pores as long as there is an electrostatic driving force. This would explain the long-term, gradual decay of surface charge after completion of polymer reconformation onto the fiber surface.

The slurry pumping rate (i.e., degree of agitation) had a small, positive effect on the initial charge-decay rate of high-molecular-weight PAMs. We believe that this phenomenon was the result of enhanced reconformation at the higher agitation rates, since increased mixing would be expected to drive the loops and trains down onto the fiber surface more rapidly, hastening the rate of charge decay. Lindström *(12)* reported similar findings and postulated that an increase in agitation would cause the adsorbed polymers to curl back and reconform onto the particle surface more rapidly than under less turbulent conditions.

Once the polymer is adsorbed on the fiber surface in a flat conformation, agitation would not be expected to affect the rate of diffusion into fiber pores. This was apparently the case, since we observed similar "final" charge-decay rates at all three agitation levels (17 L/min, 37 L/min, and 53 L/min).

LMW–HCD polymers

Wågberg *et al. (11)* found that when using a 3,6-ionene polymer with a molecular weight of 5900 g/mole, 80% adsorption was obtained almost immediately. After 3 min, no further adsorption was detected. They found that the quaternary ammonium ions of low-molecular-weight polymers achieve a 1:1 stoichiometric proportion with the fiber carboxyl groups. This electrostatic interaction is believed to be the driving force for polymer adsorption *(11–13)*.

The polymer's high charge density also promotes a fast adsorption of polymer onto the fiber in a flat configuration *(11–13)*. The polymer's accessibility to both internal and external carboxyl groups enhances this cation-exchange mechanism. These effects are seen in the data, as the initial zeta potential never reaches zero mV. In general, extremely low-molecular-weight polymers are capable of adsorbing rapidly onto the fiber surface and then diffusing into fiber pores almost immediately, with no need for a reconformational mechanism.

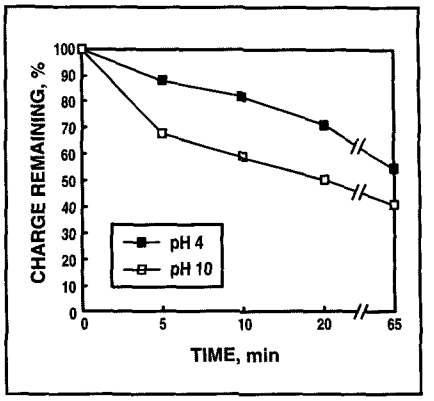
This behavior was observed with polyamine polymer P-I, which was not able to reverse the sign of the surface charge. Figures 9 and 12 illustrate this point. Evidently, the polymer's very low molecular weight of 10,000 leads to rapid diffusion into fiber pores.

Winter *et al. (13)* studied the adsorption behavior of a dimethyl diallyl ammonium chloride (DMDAAC) polymer with a molecular mass of 150,000 g/mole. They found adsorption to be lower than with the 3,6-ionene polymer, and the resulting equilibrium adsorption was not stoichiometrically proportional to the charge on the fiber. They speculated that the fiber carboxyl groups were not as accessible because of the polymer's larger size. This theory explains the higher initial charge found with the medium-sized polymers (100,000–300,000 g/mole), which could not be as readily adsorbed (and neutralized) on the fiber surface as a polymer with a molecular mass of 10,000 g/mole.

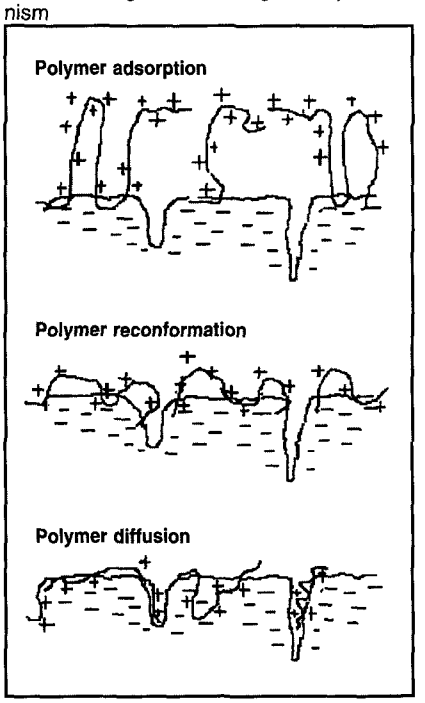
The initial charge-decay results also suggest that some reconformation of the polymer onto the surface occurred, but not nearly to the extent found with the high-molecular-weight polymers. Once a flatter configuration was achieved, which occurred much more quickly than with the higher molecular weights, diffusion into the porous fiber began, as evidenced by the gradual decay with time.

Slurry agitation had no influence on the initial charge of the medium-molecular-weight polymers. This was expected, since the driving force for adsorption is dominated more by electrostatic interactions when using lower-molecular-weight polymers than is the case with high-molecular-weight polymers *(11, 12)*. However, agitation increased the charge-decay rate, supporting the theory that some polymer reconformation occurs with medium-sized polymers. The rate of

18. Charge decay at two levels of pH (5 lb/ton, charge measured by streaming potential, polymer response averaged over all pulps and polymers)



19. Three stages of the charge-decay mechanism



diffusion, on the other hand, was not affected by agitation, as evidenced by the similar decay rates found near equilibrium.

Finally, Wågberg *et al. (11)* believed that adsorption of LMW–HCD polymers occurs by electrostatic mechanisms and is not driven by the amount of polymer added. This was also found to be the case over the addition ranges studied in this work.

Practical implications

Our results clearly show the influence of time on polymer–fiber interactions. Cationic additives lose their charging ability and efficiency with time as they reconform to the surface and begin diffusion into the porous fiber. Thus for greatest efficiency, polymers should be added immediately before the point where the charge needs to be modified.

Other studies highlight the importance of paper machine dynamics. Lindström *(5)* found that maximum flocculation occurred immediately after polymer mixing, with retention decreasing and turbidity increasing over time.

While turbulence is required to achieve good polymer distribution in a furnish, it also can accelerate the polymer-reconformation process and decrease the bridging capability of high-molecular-weight polymers. The importance of promoting bridging is evidenced by the recent interest in dual cationic-polymer systems.

Espy *(14)* found that when wet-strength resin-treated pulps were held too long before sheet formation, wet-strength responses suffered. He also found that migration of the resin molecules into the fiber decreased the effectiveness of fiber-to-fiber bonding. In addition, both Lindström *(5)* and Davison *(4)* found a decrease in wet-strength development with time in the laboratory. The same detrimental effects are expected to occur with dry-strength development.

Conclusions

Charge decay can be defined as a three-step process:

1. Polymer adsorption onto the fiber surface
2. Polymer reconformation into a flatter configuration on the fiber surface
3. Polymer diffusion into fiber pores.

This process was first proposed by Wågberg, Lindström, and coworkers *(11, 13)*.

The process of charge decay is highly dependent on polymer molecular weight. The reconformation step is strongly influenced by molecular weight, with the highest-molecular-weight polymers undergoing the greatest reconformation and charge decay. Polymers of very low molecular weight (<10,000), on the other hand, are initially adsorbed in a flat conformation and immediately begin to diffuse into fiber pores without undergoing the reconformation step.

Time has a profoundly adverse effect on electrokinetic charge. If polymers are to be used to their greatest efficiency, they must be added immediately before the point where charge modification is desired. ■

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