



12-1973

The Effect of the Degree of Cationic Charge on the Binding Strength of a Cationic Starch-Kaolin Clay Coating

Hugh K. Myers

Follow this and additional works at: https://scholarworks.wmich.edu/masters_theses

 Part of the Chemistry Commons

Recommended Citation

Myers, Hugh K., "The Effect of the Degree of Cationic Charge on the Binding Strength of a Cationic Starch-Kaolin Clay Coating" (1973). *Master's Theses*. 2672.

https://scholarworks.wmich.edu/masters_theses/2672

This Masters Thesis-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Master's Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



THE EFFECT OF THE DEGREE
OF CATIONIC CHARGE
ON THE BINDING STRENGTH OF
A CATIONIC STARCH-KAOLIN CLAY COATING

by

Hugh K. Myers

A Thesis
Submitted to the Faculty
of The Graduate College
in partial fulfillment
of the
Degree of Master of Sciences

Western Michigan University
Kalamazoo, Michigan
December 1973

ACKNOWLEDGEMENTS

The author expresses his gratitude to Dr. Stephen I. Kukolich for his individual encouragement, guidance, and constructive criticism. Additional credit should be given to Dr. Dale Williams of the Institute of Paper Chemistry, Donald Johnson and Kenneth Moser of A.E. Staley Company, Douglas Thorton, National Starch and Chemical Company, and Appleton Papers for their support and guidance.

Hugh K. Myers

INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.
5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms

300 North Zeeb Road
Ann Arbor, Michigan 48106

MASTERS THESIS

M-5246

MYERS, Hugh Kirby

THE EFFECT OF THE DEGREE OF CATIONIC CHARGE
ON THE BINDING STRENGTH OF A CATIONIC STARCH-
KAOLIN CLAY COATING.

Western Michigan University, M.S., 1973
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

TABLE OF CONTENTS

CHAPTER		PAGE
I	INTRODUCTION.	1
II	REVIEW OF LITERATURE.	2
III	PRESENTATION OF THE PROBLEM	7
IV	EXPERIMENTAL PROCEDURES, MATERIALS, AND EQUIPMENT.	9
	Cationic Starch.	9
	Clay	9
	Water.	9
	Mass Transport Analyzer.	10
	Zero Point of Charge Technique	11
	Sample Preparation	12
	Coating.	12
	Binding Strength Testing	12
	Basestock.	12
V	PRESENTATION OF DATA.	14
	Cationic Starch.	14
	Zero Point of Charge Titration Data.	15
	Kaolin Clay	18
	Coating Color.	18
	Color Condition.	19
	Coated Paper	19
VI	DATA SUMMARY.	23
VII	EXPERIMENTAL RESULTS AND DISCUSSION	24

TABLE OF CONTENTS (Continued)

CHAPTER		PAGE
VIII	SUMMARY AND CONCLUSIONS.	29
IX	LITERATURE CITED	30
X	APPENDIX	32

INTRODUCTION

Coating colors are composed of colloidal materials which exhibit a large surface area per unit of mass. This condition generates electrokinetic effects which determine numerous important properties of coating colors including dispersion, viscosity, retention and possibly adhesion.

The object of this project was to determine the effect of electrokinetics on adhesion following drying of a clay-cationic starch coating on paper. In accomplishing such a goal, measurement techniques had to be evaluated and possibly adjusted to handle the materials of the study. Problems associated with coating colors were solids, viscosity, and specific gravity. All of these factors presented a definite problem in electrokinetic measurement.

The scope of this project included the following: (1) a literature review of electrokinetic and adhesion theory, and (2) electrokinetic measurements of both cationic starch and kaolin clay, (3) pilot coating of the coating colors, (4) adhesion testing of the coated paper.

REVIEW OF LITERATURE

It has long been known that a solid surface in contact with a polar liquid usually behaves as if the surface carried an electrical charge. Reuss (1) observed in 1808 that a migration of water occurred when an electric current was passed through a porous diaphragm of wet clay. This property was termed electroosmosis. Further work in the field was done in 1861 by Quinke (2) who studied electroosmotic flow in single capillaries. He discovered the phenomenon of streaming potential, the converse of electroosmosis. Quinke promoted the hypothesis that there were electrically charged layers of opposite sign at the solid liquid boundary.

This theory was later advanced in 1879 by Helmholtz (3) in his discussion of the electrical double layer. He showed mathematically that electroosmosis flow was proportional to charge separation in the double layer. This charge separation corresponded to the potential drop across the layer of charge contained in the moving liquid. The potential drop was termed electrokinetic potential.

Electrokinetic potential is important in the area of coating colors because the material is colloidal and exhibits a large surface area per unit of mass. This large surface area makes electrical double layer effects significant.

The concept of the double layer was further developed by Gouy-Chapman (4). In his discussion, the charged solid surface is surrounded by an ionic atmosphere in which the liquid potential is equal to the zeta potential at the solids surface and decreased exponentially

with increasing distance from the surface.

Stern modified the theory to include an inner region of absorbed ions (5). Across this layer of charge, there is a linear change of liquid potential ϕ . At the outer boundary of the fixed layer is the surface of shear; at this point the liquid potential is equal to the zeta potential. With increasing distance from this point ϕ falls off exponentially as in a conventional Gouy-Chapman diffuse layer.

The Stern model is the basis of the present electrokinetic potential concept. It tends to explain more currently observed phenomena than the earlier theories.

Electrokinetic potentials can be measured by several means as described in the following Table I (6).

Table I. Procedures for Measuring Electrokinetic Potentials

<u>Name of Procedure</u>	<u>Property Measured</u>	<u>Mobile Phase</u>	<u>Example</u>
Electrophoresis	Particle mobility	Particles	Microelectrophoresis Moving boundary Mass transfer
Sedimentation potential	Voltage	Particles	Sedimentation potential
Streaming current (potential)	Current (potential)	Liquid	Streaming current (potential)
Electroosmosis	Pressure velocity	None Liquid	Electroosmosis

Of the above mentioned procedures, only the mass transfer technique lends itself to the measurement of coating colors. Sedimentation

potential could not be used because the particles sediment too slowly. Streaming potential and electroosmosis would be impractical since coating colors and their components are not easily formed into plugs.

The mass transfer process is a form of electrophoresis. Micro-electrophoresis has been used for many years in the study of colloidal and particulate systems. In this technique, particles are observed as they migrate in an electric field. The speed of the particles is measured under a known potential gradient. The approximate zeta potential can then be calculated from the equation

$$\zeta = \frac{4\pi\eta V}{HD}$$

where V is the velocity, H is the potential gradient, D is the dielectric constant and η is the viscosity.

In the case of the mass transfer cell, instead of measuring the velocity of the particles under a given potential, we measure the mass of the particles transferred per unit time. From these measurements we can calculate the electrophoretic mobility with the following equation:

$$V_e = \Delta W \lambda / t i \phi (1 - \phi) (\rho_s - \rho_w)$$

V_e = electrophoretic velocity cm/sec/volt/cm

ΔW = weight gain of cell

λ = specific conductance ohm⁻¹ cm⁻¹

t = time seconds

i = current amps

ϕ = volume fraction dispersed phase

ρ_s = specific gravity of particles g/ml

ρ_w = specific gravity of the suspending fluid g/ml

The electrophoretic mass transfer cell was developed by Sennet (6) for work on coating colors. It has been demonstrated (7,8) that mobility measurements using this technique are independent of current and time.

In the Sennett and Oliver (6) technique a relatively concentrated suspension is placed in a cell consisting of two compartments with an orifice between them. The cell is so constructed that one portion may be removed for weighing. After suspension in this part is weighed prior to an experiment, the cell is assembled and an electric current passed through it so that particles exhibiting electrophoretic mobility will pass through the orifice. At the completion of an experiment, the cell is dismantled and reweighed and the mass of material that has passed through the orifice is calculated. From this, it is easy to derive the electrophoretic mobility. Long and Ross (7) modified the apparatus by rotating the cell to prevent sedimentation and in this form it is commercially available. (Micromeritics Instrument Corporation). See figure 1, page 10.

Micromeritics' standard mass transport cell was made of a polymethylmethacrylate material that is capable of adsorbing 0.7% of its weight in water (9). Akers and Riley (10) made two small modifications in the cell which facilitate accurate weighing in spite of the water adsorbing characteristics of the cell.

Sennett (6) used the cell to measure the electrokinetic properties of a kaolin clay-anionic starch coating color. The cell was well suited to the job because it tolerated relatively high solids systems with appreciable sedimentation velocities. Sennett discovered that anionic starch increased the negative zeta potential of the pigment.

Further work was suggested at the end of the report but none was done.

The previous mentioned techniques of electrokinetic measurements are all direct measurements characterized by sophisticated apparatus and rigorous procedure. There exist, however, different indirect techniques which are much simpler and require only basic hardware. Dorchak, Maxim, and Kuist (11) devised an electrokinetic method based on turbidimetric measurements. The method was correlated with cationic corn starches. These workers discovered that at the pH of zero zeta potential, the starch sol exhibits a transmission minimum.

The method is based on the principle that in the electrical double layer, a reversible transfer of hydrogen and hydroxyl ions takes place. The net surface charge density for this system is expressed by

$$G_s = F(Z_+ \Gamma_+ + Z_- \Gamma_-)$$

where

G_s = net surface charge density

F = Faraday constant

$Z_+ Z_-$ = valence including sign

$\Gamma_+ \Gamma_-$ = adsorption density of the potential determining ions
at the zero point of charge $G_s = 0$.

The workers compared pH of zero point of charge determined with a zeta meter and that determined by transmission minimum for fourteen different starches and obtained a correlation coefficient of 0.98. They theorized that the presence of charged ionic groups in a swollen granule creates osmotic forces which swell the granule. The ionic groups create a region of high ionic strength. At the zero point of charge, the ionic or swelling forces are therefore at a minimum and the granule assumes maximum density or minimum transmission.

PRESENTATION OF THE PROBLEM

Review of the literature showed that no systematic study exists that describes the electrokinetic characteristics of a cationic starch-kaolin clay coating color. Sennett studied anionic starch-kaolin clay. As a step toward a more fundamental understanding of the mechanism of cationic starch-clay adhesion, it is proposed to examine the relationship between the degree of charge on cationic starch and the starch's binding strength in a kaolin clay-cationic starch coating.

In a study such as this, it is important to exercise control over extraneous variables. The literature review revealed the dependence of zeta potential on substrate, drying rate, extraneous ions and the nature of the starch molecule. In an attempt to control these variables, the cationic starch used in the study was synthesized using the same basic starch molecule, varying only the concentration of cationic material on the molecule. In addition, all water used in the study was distilled and deionized to eliminate any extraneous ions which would complicate the system.

The factors of greatest concern for this study are the electrokinetic potential or mobility of the various cationic starches and clay, and the binding strength of resultant coating color. The following hypotheses regarding the above mentioned factors are proposed for testing in this study:

1. There is a definite relationship between the degree of cationic substitution on a starch molecule and its electrophoretic mobility in a water dispersion.

2. The degree of cationic substitution on a starch molecule should influence its binding strength in a kaolin clay coating.

It is the broad goal of this study to add to the fundamental knowledge of cationic starch-clay adhesion.

EXPERIMENTAL PROCEDURES, MATERIALS, AND EQUIPMENT

Experimental Approach

1. Five cationic starches were gelatinized and measured for electrokinetic properties. Kaolin clay was also measured for electrokinetic properties.
2. Five coating colors were prepared from the starches and clay of (1.) and measured for viscosity and electrokinetic properties.
3. The five coating colors from (2.) were coated on a pilot coater.
4. The coated sheets were checked for binding strength.

Cationic Starch

The cationic starch used in the program was provided by A.E. Staley Company and consisted of cationic variations on an acid hydrolyzed corn starch. Five starches were provided which varied the degree of cationic quaternary amine substitution of the basic starch molecule.

Clay

The clay used was a No. 2 grade kaolin provided by the Engelhard Minerals and Chemicals Corporation. The clay carries the commercial name, HT.

This clay was selected because of its widespread use and average

particle size. It is predispersed and has a .8 μ average particle size.

Water

Water used for the study was entirely deionized and then distilled for maximum purity. Deionization was accomplished by running through a Barnstead mixed bed cartridge.

Mass Transport Analyzer

Electrophoretic mobilities were run on a Micromeritic Instrument Corporation electrophoretic mass transport analyzer. The instrument discussed in the literature is schematically illustrated in Figure 1.

There was a lack of success in measuring cationic starch on the mass transport analyzer. The writer's technique was checked using clay on the instrument and data agreed with published values. See Table IV, page 17. The problem with cationic starch was verified by Mr. Douglas Thorton of National Starch and Chemical Corporation (12). His experience was identical in that there was not enough mass per unit volume of starch transferred to the negative terminal to measure with any degree of precision. His recommendation was the zero point of charge technique described in the literature review. Failure data can be found in the appendix.

The zero point of titration was tried quite successfully showing an excellent correlation with the supplier degree of substitution data. The method is straightforward and is accomplished with equipment any laboratory should have access to.

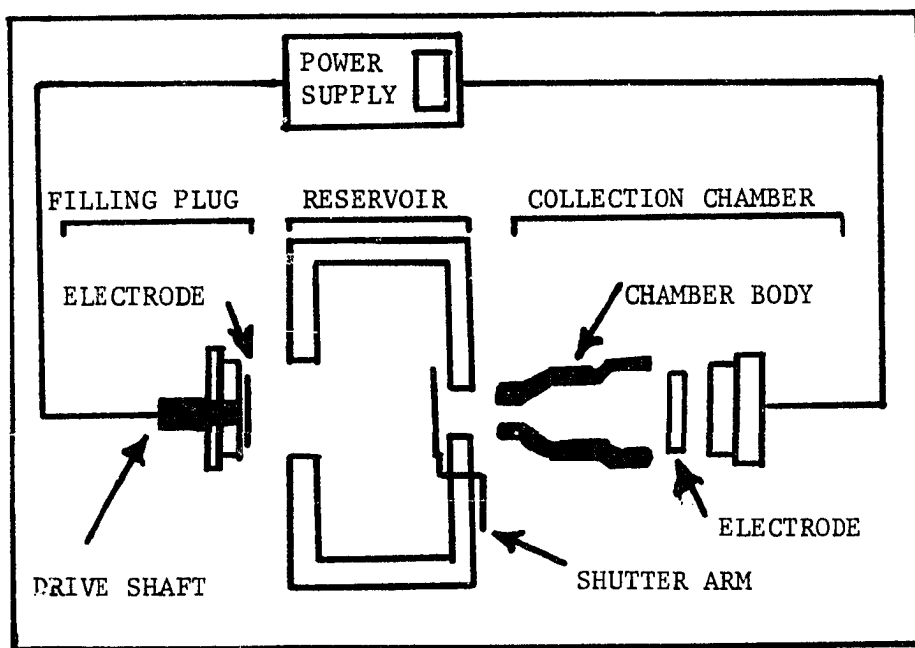


FIGURE 1 SCHEMATIC DIAGRAM OF THE MASS
TRANSPORT ANALYZER

Zero Point of Charge Technique

Electrophoretic mobilities of cationic starch were indirectly determined by the zero point of charge technique discussed in the literature review. The technique utilized a Bausch and Lomb Spectronic 20 colorimeter set at 550m , an accurate pH meter (Corning Model 7) and a 50 ml buret.

A sample of starch sol (0.1% solids) was checked for initial pH and transmission. Titrant 0.025N sodium hydroxide was added and a pH and transmission measurement was taken after each addition, until the end point of the titration (the transmission minimum) was achieved. The point of zero zeta potential correspond to the minimum transmission.

Sample Preparation

The coating materials were prepared for testing and coating with the following conditions:

1. Starches were cooked at 10% oven dry solids for 20 minutes in a stainless steel double boiler @ 95°C until gelatinization was complete. Water was then added to bring the sample back to 10% moisture.
2. Clay-starch coating colors were dispersed for 5 minutes at high speed in a Waring blender.

Coating

Clay-cationic starch coating colors were applied on a Keegan laboratory pilot coater. Application was performed in the rod coating mode using a No. 12 wire wound rod and applicator roll against the web direction. Speed was 6 feet/minute with 220°F high velocity forced air drying. Coat weight was manually controlled at 4 lb./3,300 ft.².

Binding Strength Testing

Binding strength evaluations were carried out with an IGT printability tester under TAPPI atmospheric conditions using a D-7 polyisobutene ink. Results are reported in VVP (velocity-viscosity product) units at the first significant continuous coating pick. Fiber pick occurred at higher velocities than the coating pick.

Basestock

Basestock was a bleached kraft, hardwood-softwood coating base

30.5 lb./3,300 ft.². The basestock was moderately alkaline sized and was provided by Northwest Paper Company.

PRESENTATION OF RESULTS

Cationic Starch

Table II - Supplier data

<u>Code Number</u>	<u>% Moisture</u>	<u>% N Dry Basis</u>	<u>% N* (Corrected)</u>	<u>Degree of Substitution</u>
0	11.0	0.05	----	0
1	9.5	0.11	0.06	.007
2	9.8	0.17	0.12	.014
3	10.5	0.22	0.17	.020
4	10.5	0.27	0.22	.026
5	10.5	0.34	0.30	.035

Table III - Research data

<u>Code Number</u>	<u>pH</u>	<u>Brookfield Viscosity 60 rpm 25°C</u>	<u>Viscosity @ 5% Solids</u>
1	7.0	3,000 cps	60 cps
2	7.4	2,200	71
3	7.4	640	37
4	7.6	350	24
5	7.7	155	15

* Corrected of the protein in starting starch, code 0

Table III - Zero Point of Charge Titration Data

Titrant - 0.25N NaOH

Starch Solids - 0.1%

B. and L. Spectronic 20 550m μ

	<u>ml NaOH</u>	<u>pH</u>	<u>% Transmission</u>
Starch No. 1	0.00	5.90	54.5
	1.00	8.40	52.0
	2.00	8.90	51.0
	3.00	9.10	51.0
	4.00	9.30	50.5 Z.P.C.
	5.00	9.45	51.0
	6.00	9.65	51.0
Starch No. 2	5.00	9.20	55.0
	10.00	9.50	54.0
	12.00	9.60	53.0 Z.P.C.
	14.00	9.70	53.0
	16.00	9.80	54.0
	20.00	10.00	54.0
	30.00	10.20	55.5
Starch No. 3	10.00	9.60	60.0
	20.00	10.10	58.0
	25.00	10.15	57.5 Z.P.C.
	30.00	10.20	58.0
	35.00	10.25	59.0

Titration Data (Continued)

	<u>ml NaOH</u>	<u>pH</u>	<u>% Transmission</u>
Starch No. 4	20.00	10.00	61.0
	25.00	10.15	60.0
	30.00	10.30	60.0
	35.00	10.35	59.8
	40.00	10.40	59.5 Z.P.C.
	50.00	10.60	60.0
Starch No. 5	25.00	10.20	79.0
	50.00	10.55	77.0
	55.00	10.60	77.0
	60.00	10.65	76.0
	70.00	10.70	76.0 Z.P.C.
	100.00	10.90	80.0

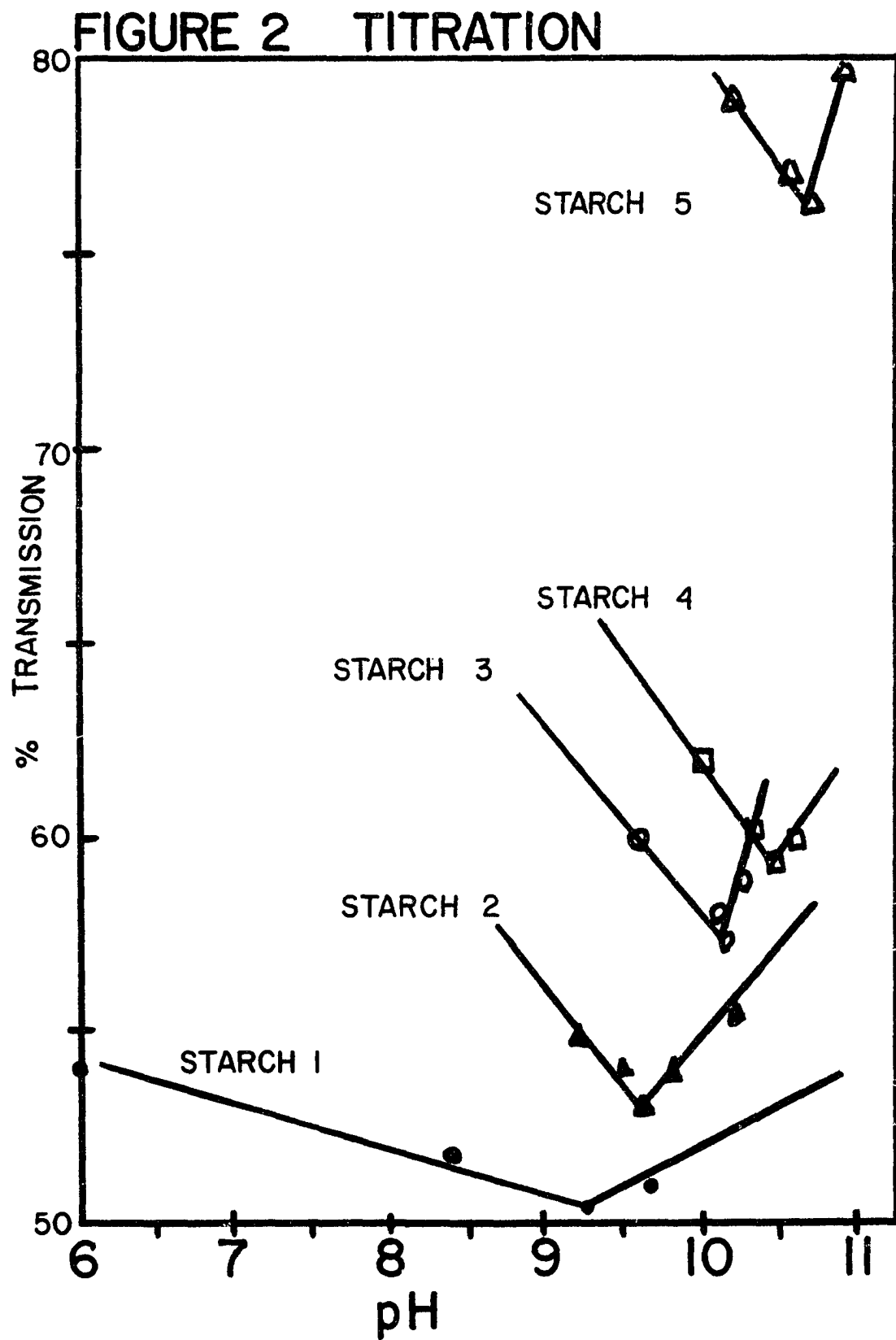


Table IV - Kaolin Clay

Mass Transport Analyzer Data
20% Solids No. 2 Kaolin Clay

<u>Trial</u>	<u>λ Specific Conductance *</u>	<u>\dot{z}_{ma}</u>	<u>W/g</u>	<u>Time Sec.</u>	<u>V_e **</u>
1	7.55×10^{-4}	2.0	.0928	600	4.71
2	7.55×10^{-4}	2.0	.1005	600	4.85
3	7.66×10^{-4}	2.0	.0903	600	4.69
4	9.78×10^{-4}	2.0	.0748	600	4.85
5	9.78×10^{-4}	2.0	.0742	600	4.81
Sennet, Oliver, Morris (6) data similar clay					
a	7.29×10^{-4}	4.81	.2329	600	4.64
b	7.55×10^{-4}	4.82	.2238	600	4.56

*ohm⁻¹ cm⁻¹

**cm sec⁻¹/volt cm⁻¹

Table V - Coating Color

<u>Formulation</u>	<u>Wet g</u>	<u>Dry g</u>	
Clay	230	156.5	
Cat. Starch	194	19.4	
Water	<u>466</u>	<u>---</u>	% Solids
Total	890g	175.9g	19.7

% binder on pigment - 12.4

Table VI - Color Condition

<u>Sample No.</u>	<u>pH</u>	<u>Brookfield Viscosity</u>	60 rpm	81°F
1	7.1	250	cps	
2	7.0	325		
3	7.1	275		
4	7.0	185		
5	7.1	190		

Table VII - Coated Paper

IGT Binding Strength
D-7 Ink 73°F

<u>Sample</u>	<u>IGT VVP</u>
1	0
2	6.0
3	27.6
4	34.4
5	36.6

FIGURE 3

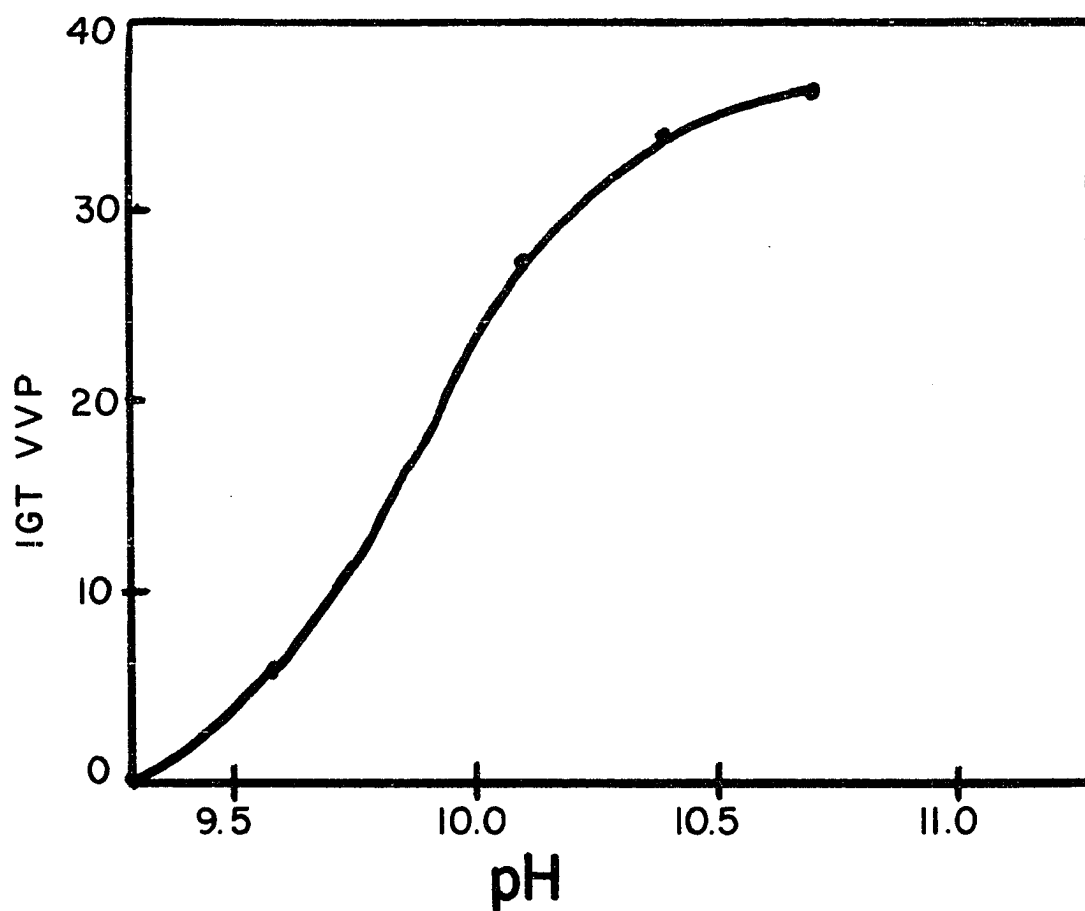
BINDING STRENGTH VS.
ISOELECTRIC POINT

FIGURE 4

BINDING STRENGTH VS.
DEGREE OF SUBSTITUTION

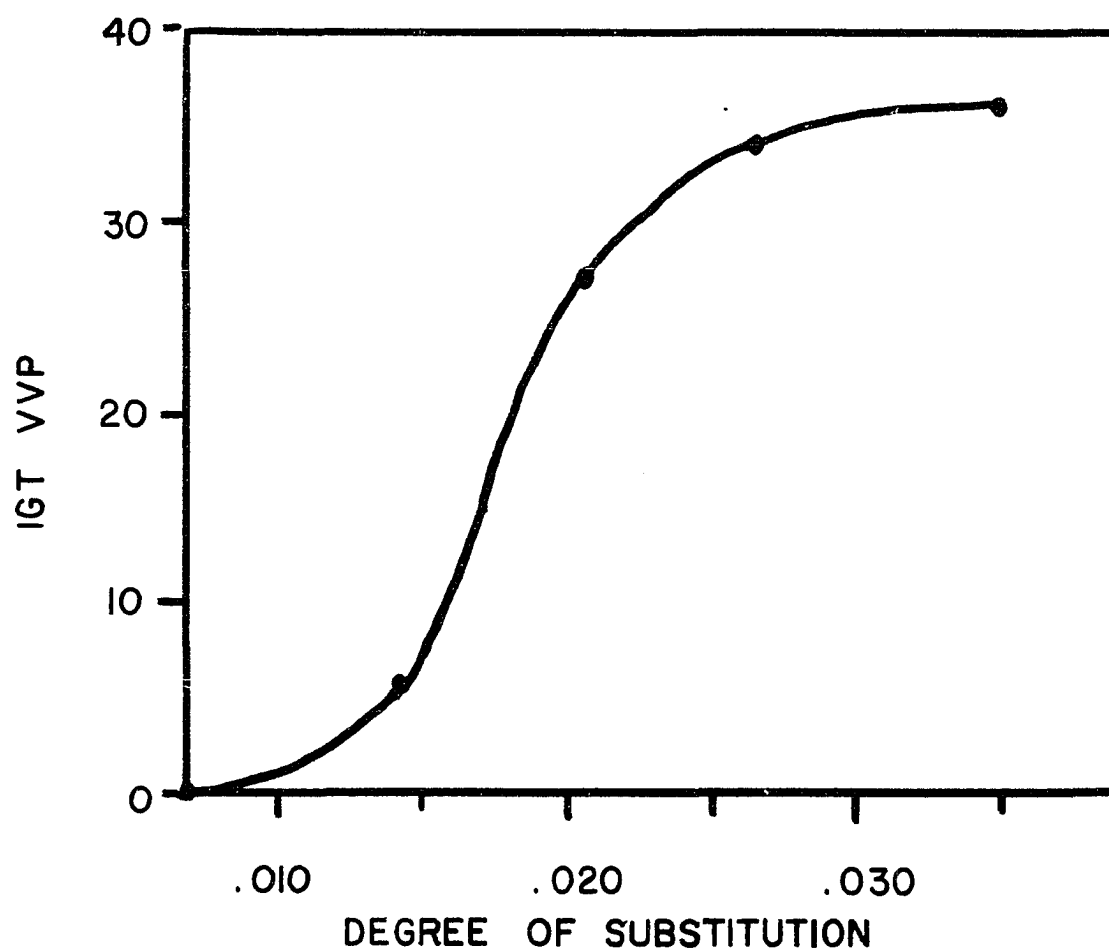
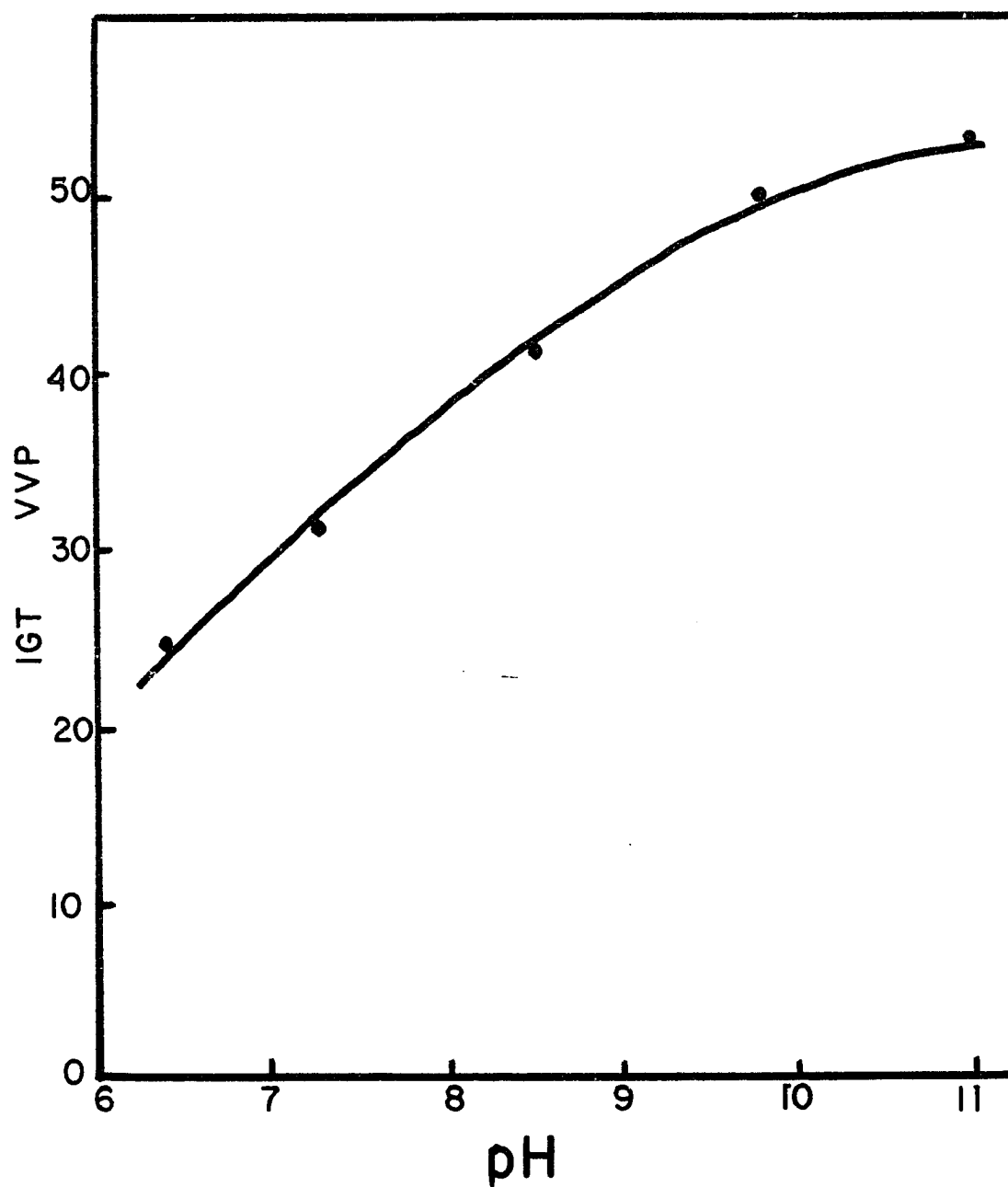


FIGURE 5

BINDING STRENGTH VS. pH
for starch coating no. 3



DATA SUMMARY

Table VIII

<u>Starch Sample No.</u>	<u>pH of Z.P.C.</u>	<u>Degree of Cation Substitution</u>	<u>IGT VVP</u>
1	9.3	.007	0.0
2	9.6	.014	6.0
3	10.1	.020	27.6
4	10.4	.026	34.4
5	10.7	.035	36.6

EXPERIMENTAL RESULTS AND DISCUSSION

Initial viscosity measurements on the cationic starches indicated that the increased charge on the starch molecule had a side effect of reducing the starch viscosity. The viscosity of the mixed coating was more uniform than the starting starch. This resulted in uniform coat weights over the range of coating colors with the same coating conditions (4.0 lbs./3,300 ft.²).

Uniform coat weights and basestock should insure that the variation in binding strength observed in Figure 3 was due to differences in the binder—namely cationic charge. This relationship of binding strength to zero point of charge was very similar to the relationship between the binding strength and of degree of cationic substitution shown in Figure 4. This gave validity to the zero point of charge data. The results indicated that the cationic charge on the starch molecule was increasing the binding strength of the starch on the clay.

The binding strength data would only be valid if the coating were done in a uniform manner. Rod coating on a draw-down block would not insure this kind of uniform coating.

A Keegan coater was selected because of material quantity considerations, plus the need for reproducible drying. Binding strength testing would only be meaningful on sheets dried in a consistent manner. The binding results represent the binding strength of the

coating, not the basestock since all pick measurements were coating pick and not fiber failure.

One might argue that the differences in coating pick were due to a variance in adhesive migration and not to the cationic material. In an attempt to disprove this theory, scanning electron micrographs were taken at 3, 5, and 10,000 times magnification. These pictures are shown in Figure 6.

FIGURE 6

10,000X



1

2

FIGURE 6

10,000X



3

4

5

The shots reveal no visible differences in surface binder in any of the five samples.

The mechanism of increased adhesion observed in this study is quite complex. Kline (13) deduced that cationic starches are more readily adsorbed on kaolin clay than oxidized starch. This would suggest that the starch with the higher cationic charge was more completely adsorbed on the clay particles and developed a greater bonding area and resultant binding strength.

Another possible theory is that of Skinner and co-workers (14) and Deryaguin and co-workers (15) who theorized that electrostatic attraction between charged layers caused an adhesive force.

Voyutskii (16), however, disputed this theory and posed arguments which limit its validity.

A, perhaps, more valid theory would be the effect of cationic charge on secondary valence forces, namely hydrogen bonds. Janes (17) discusses the importance of the hydrogen bond in the adhesion of starch-cellulose. The bond is electrostatic in nature; and, therefore, should be influenced by the electrostatic effect of the cationic starch.

McLaren and co-workers (18-20) found that adhesion was proportional to polar group concentration between cellulose and high polymer adhesives. Perhaps polar group concentration in his study is equivalent to the degree of cationic charge in the study at hand.

Figure 5 shows what happened when one of the coating colors was altered by the addition of sodium hydroxide to change the zeta potential of the system. This data further substantiates the claim that the bonding strength of a cationic starch coating color is very much related to its

zeta potential. This relationship tells us we must optimize the zeta potential of the coating color to get maximum binding strength.

SUMMARY AND CONCLUSIONS

Both direct and indirect electrokinetic measurements were made on kaolin clay and a range of cationic starches. The direct method was performed on the mass transport analyzer which functioned quite well for kaolin clay, but was not usable for cationic starch or the mixed coating color. The indirect method, zero point of charge technique, was used for cationic starch and functioned very efficiently.

Results for kaolin clay agreed with literature values and results for cationic starch correlated with related supplier data. These values were then correlated with I.G.T. binding strength on paper coated with color made from kaolin clay and the range of starches. The results are summarized below:

1. Mass transport analysis does not lend itself to the measurement of cationic starch or related coating color.
2. The zero point of charge technique was an excellent method for the electrokinetic measurement of cationic corn starch.
3. Binding strength correlated very well with a). pH of the zero point of charge of the starch, b). degree of cationic substitution of the starch.

LITERATURE CITED

1. Reuss, F.F., Mem. Soc. Imperiale Natural, Moscou 2:327(1809).
2. Quinke, G., Pogg. Ann. 113:513(1861).
3. Helmholtz, H., Wied. Ann. 7:337(1879).
4. Van Wazer, J.R., and Besmertnuk, E., J. Phys. Colloid Chem. 54:89(1950).
5. Stern, O., Elektrochem. 30:508(1924).
6. Sennett, P., Olivier, J.P., and Morris, H.H., Tappi 52, No. 6:1154 (June 1969).
7. Long, R.P., and Ross, S., J. Colloid Sci. 20:438(1965).
8. Olivier, J.P., and Sennett, P., Clays and Clay Minerals. Proceedings of the Fifteenth Conference, New York, Pergamon, 1962. 345 p.
9. Akers, R.J., American Laboratory 6:41-53(June 1972).
10. Akers, R.J., and Riley, R.W., unpublished results.
11. Dorchak, T.P., Maxim, L.D., and Kuist, C.H., paper presented American Chemical Society (April 1967).
12. Thorton, Douglas, personal communication, 1973.
13. Kline, J.E., Tappi 55, No. 4:556-62(April 1972).
14. Skinner, S.M., Savage, R.L., and Rutzler, J.E., J. Appl. Phys. 24:438.
15. Deryaguin, B.V., Krotova, N.A., Karassev, V.V., Kirillova, Y.M., and Aleinikova, I.N. In Proc. Second International Congress of Surface Activity. Vol. III. London, Butlerworths, 1957. 417 p.
16. Voyutskii, S.S., Autohesion and Adhesion of High Polymers. New York, Interscience, 1963. 272 p.
17. Janes, R.L., A Study of Adhesion in the Cellulose-Starch-Cellulose System, Doctor's Dissertation. Appleton, Wisconsin, Institute of Paper Chemistry, 1968, 200 p.

18. Hofrichter, C.H., Jr., and McLaren, A.D., Ind. Eng. Chem. 40, No. 2:329-31(1948).
19. McLaren, A.D., J. Polymer Sci. 3, No. 5:652-62(1948); 4:63(1949).
20. McLaren, A.D., Li, T.T., Rager, R., and Mark, H., J. Polymer Sci. 7, No. 3:463(1951).

APPENDIX

Additional test data compiled by Zafar Chaudhri at Western Michigan University using the starches described on page 9 of this paper were listed below. The work utilized a streaming current detector.

<u>STARCH NO</u>	<u>% TRANSMISSION</u>	<u>pH</u>	<u>S.C.D. READING</u>	<u>pH of Z.P.C. (writer)</u>
1	66	6.65	+12	9.3
2	62	6.50	+22	9.6
3	45	6.42	+30	10.1
4	47	6.33	+30	10.4
5	63	6.58	+32	10.7

After titration with NaOH the following was obtained:

1	69	11.49	-18.0	----
2	62	11.57	-13.5	----
3	58	11.62	-16.0	----
4	34	10.72	- 2.0	----
5	50	10.70	0.0	----

These results verify the writer's findings in that the S.C.D. readings correlate very well with pH of Z.P.C. data as well as the degree of substitution data from the starch supplier. The data also verifies the transmission zeta potential property described in the literature. Note that on starch No. 5, the pH of Z.P.C. determined by the writer 10.7 matches the pH of zero streaming current 10.7.

Additional data were also included to verify the cationic starch. Below is listed mass transport failure data for the cationic starches of this study.

<u>SAMPLE NO.</u>	<u> </u>	<u> </u>	<u> </u>	<u>TIME SEC.</u>	<u> </u>
5-1	4.80×10^{-4}	2.0	.0355	300	---
5-2	4.80×10^{-4}	2.0	.0200	300	---
5-3	4.80×10^{-4}	2.0	.0057	300	---

The above data cannot be tabulated because a minimum of 0.3g must be measured for a valid calculation. It appears the specific gravity of the particle measured must be significantly greater than the suspending medium to use this technique.