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SILANE TREATED
KAOLINS FOR
PAPER COATING

By
Jeffrey M. Brock

A Thesis submitted
in partial fulfillment of
the course requirements for
The Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
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ABSTRACT

Silanes have been used as coupling agents between inorganic reinforcements (such as clay) and polymer composites such as rubber and plastic for the past few years. The rubber industry uses silane-treated kaolin as reinforcements for SBR tires.

It is possible that silane-treated kaolin may provide desirable crosslinking properties in coatings used in the paper industry. This would provide strength to the coating and possibly maintain optical properties upon supercalendering. This study shows this may be possible from increased pick resistance with silane-treated kaolin coatings and a protein binder. These same coatings also yielded less ink absorption with silane-treated kaolins. Latex coatings with silane-treated kaolins yield better opacity but show no increase in pick resistance. Overall results of the study show possibilities for future work in using silane-treated kaolins for paper coating.

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INTRODUCTION

A coating is a thin layer of material intended to protect, decorate, or improve printing quality of a substrate. Coating of paper to improve surface properties and general sheet appearance has been a general practice in the paper industry for many years. In applying the coating to paper, a binder is needed. The binders generally used are starches, proteins, and latexes with an increasing trend toward latexes.

It is a well known fact that latex improves the strength, flexibility and printing ink hold-out of the coatings while opacity, brightness, and gloss decrease with increased latex usage. Therefore, it would be beneficial to have a binder that would adequately bind the coating to the sheet using lower binder levels, which would better maintain optical properties. This study proposes to do this by the use of silanes in combination with latex. It is believed that the silane may act as a coupling agent between the clay surface and the binder, thus reducing the level of binder needed.

LITERATURE REVIEW

BASIC PRINCIPLES OF ADHESION^{1,2}

As a starting point, it is advantageous to begin with a discussion of some principles of adhesive bonding. This will be followed by a more specific discussion of silanes used as coupling agents to reduce the amount of binder required.

All good adhesives must either be macromolecules or contain macromolecules, because only a macromolecular layer between two solid surfaces to be joined together will provide for the necessary tensile or shearing strength of the adhesive bond. In addition to strength, a good adhesive must be applicable within a short period. This means that the wetting of the two solid surfaces by the adhesive must be rapid. Therefore, the viscosity at the time of application must be low, while the final strength and toughness has to be great. In order to combine rapid wetting with firm holding, there must be a transition from fluid to solid taking place in a controlled fashion within a short time period. This requires a compromise between the rate phenomenon of wetting and the equilibrium phenomenon of bonding.

In principle, the transition from fluid to solid can be accomplished in the following ways:

- 1) The adhesive can be applied as a melt at elevated temperatures and can solidify upon cooling to a tough, rigid layer between the surfaces which have to be bonded.
- 2) The adhesive can be applied as a solution and can be solidified by evaporation or absorption of the solvent.

- 3) The adhesive can be a system capable of undergoing polymerization or crosslinking. It can be applied in a state of relatively low degree of polymerization (and hence low viscosity) and can then be cured into its final state of firm bonding.

Each of these possibilities has its advantages and disadvantages.

One particular way to effect fluid-solid transition may be used separately or combinations may be used. Silanes fall under that condition best described under the third method which will now be discussed.

Curing adhesives are applied at a low viscosity and at a low degree of polymerization and then cured into a firm-holding three-dimensional network of covalent bonds. In most cases, water is eliminated during the cure and must be either evaporated or removed by diffusion or wicking. The crosslinking reaction is often slow and in most cases requires elevated temperatures. This cannot be under complete control, so there is the danger of stress accumulations in the final bond. Many silanes used as "coupling agents" to bond kaolin to other composites generally yield less stress accumulation and fracture points.³ Because of the delicate nature of the crosslinking process, adhesives of this type are not very stable in the initial liquid state and frequently show a tendency for gelation or syneresis. This may often be true with solutions of silanes. On the other hand, the bonds established by adhesives of this type are very strong and resist the influence of high temperatures as well as the attack of solvents or chemical agents. Sometimes they have the tendency of a slow and gradual aftercure which eventually leads to the formation of cracks and later to a complete failure of the bond.

The two specific properties that make a macromolecule a good adhesive are: 1) rapid segment diffusion in solution, and 2) strong bonding in the solidified state.

The first property would depend primarily upon the degree of polymerization, the macromolecules being linear or branched, and the flexibility of the macromolecule. A low degree of polymerization will provide for rapid wet-out from its low viscosity but will not provide for the firm holding as will higher polymerization. Therefore, there is a trade-off which usually is a compromise of medium molecular weight. A small number of large branches would be desirable because they reduce viscosity in solution, also, the larger number of free chain ends increases the mobility of the individual segments and favors more rapid wet-out. If the branching is excessive, both the wetting and holding are adversely affected. Greater flexibility of the macromolecule will provide for rapid segment diffusion, although most linear polymers in dilute solution are adequate. It is interesting to note that $-O-Si-O-$ bonds are considered very flexible.

The second property for good adhesives, namely strong bonding, is dependent upon the presence of groups which develop molecular forces. These forces include dispersion (or London) forces, interaction of permanent dipoles, induction forces and hydrogen bonds. Of most importance to this study will be hydrogen bonds and dispersion forces to help in adhesion.

The requirements for a good adhesive can be seen as a compromise between internal mobility and intermolecular bonding capacity. If there are too many groups in a macromolecule there

is decreased flexibility; on the other hand, if there are not enough interacting groups, the bonding strength will be weak although the wetting characteristics will be superior.

SILICON

Basic to any discussion of silanes is that of silicon. Compounds of silicon, in the form of naturally occurring silicates, have been of service to man for thousands of years. Silicon has some advantages that are unmatched; there is an inexhaustible supply amounting to 28% of the earth, and the element is easily and inexpensively obtained from natural sources.⁴ The biggest reason for limited use of silicon is because free silicon does not occur in nature, nor do its organic compounds. Silicon has a natural association with oxygen and together these two elements constitute three-fourths of the world around us.⁴ It has only been through relatively recent "laboratory" chemistry that has produced information about the reactive and covalent compounds of silicon. This research has brought about the commercial preparation of organosilicon compounds, which are of primary consideration to this project.

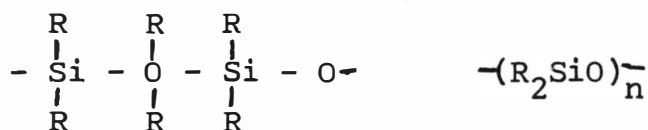
This report begins with a consideration of the chemical behavior of silicon. This provides an introduction to the chemistry of more complex substance and the background to help in an understanding of organosilicon compounds.

Elementary silicon shows no oxidation or corrosion at ordinary room temperatures and oxidizes very slowly below red heat. It is attacked more readily by halogens at 250°C or more.⁴

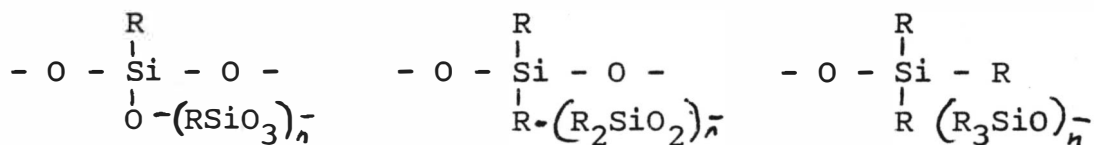
Silicon is usually tetravalent as might be expected, however, since it lies in the second short period on the periodic chart, its maximum covalency is not four but six. In this respect, it differs markedly from carbon. Silicon builds up with oxygen crystalline silicates with polymeric anions as stable end products, while carbon compounds are degraded by oxygen to gaseous carbon dioxide.

CHEMISTRY OF THE SILICONES

The term silicone or polyorganosiloxane will be used to describe organosilicon polymers containing Si-O-Si bonds with Si-O-Si being the siloxane unit. Siloxane being defined accordingly by Noll, as organosilicon polymers in which the silicon atoms are bound to each other through oxygen atoms. The silicon valences not taken up by oxygen are saturated by at least one organic group.⁵ The following being a simple linear polymer, when R is an organic group.



Silicones are an intermediate between organic and inorganic compounds, and in particular, between silicates and organic polymers. The silicon in polyorganosiloxanes can be combined with one, two, or three organic groups with the remaining valences being satisfied by oxygen. This yields three siloxane units of the polymers which are:



These siloxane units lie between the two extremes of R_4Si (a nonfunctional organosilicon compound) and the complex ion $(\text{SiO}_4)^{-4}$. One can readily see the dual nature of the polyorganosiloxanes as a link between silicate chemistry and organic chemistry.

The functionality of each siloxane unit is determined by the free valences on the oxygen atom. R_3SiO^- , $\text{R}_2\text{SiO}_2^{-2}$, and RSiO_3^{-3} are monofunctional, difunctional, and trifunctional respectively. One must also consider the tetrafunctional group SiO_4^{-4} because it is often used with the others in the synthesis of organosiloxane polymers.

A wide diversity of compounds is possible because different siloxane units can be combined with one another in the same molecule. This leads to molecules that are linear, cyclic, branched or spiral with varying properties. The siloxane units follow well established rules of macromolecular chemistry and combine functionally as follows: monofunctional units act as chain stoppers or regulators; difunctional units form linear chains or rings; and the tri and sometimes quadifunctional units serve as centers for crosslinking and, eventually, network formation.

Another parameter influencing the properties of the molecules is the nature of the functional group(s) on the silicon atoms.

SILANES

The present-day use of the word "silane" has been proposed by Stock, who called SiH_4 "silane", by analogy to CH_4 , methane.⁶ In addition, Stock coined terms such as "silanol" for H_3SiOH and "disiloxane" for $\text{H}_3\text{SiOSiH}_3$, which are now part of current usage.⁶

ORGANOFUNCTIONAL SILANES

Interest in recent years has been given to developing organofunctional silanes, beyond the traditional silanes with only alkyl, aryl, or arylalkyl groups attached to the silicon atom. Organofunctional silanes are molecules with unsaturated or functionally substituted hydrocarbon radicals. These functional groups vary in reactivity and impart interesting physical properties to the silanes. Scientific and technical research with organofunctional silanes has developed widespread use in industry, particularly as coupling agents.

COUPLING AGENTS^{7,8,9,10}

Silane coupling agents are bifunctional molecules with the ability to bond inorganic reinforcements and organic polymer matrices. This results in stronger composites and retention of properties after prolonged exposure to moisture. Chemically they have the functionality of an inorganic reactive group at one end and organic at the other. The commercially available silane coupling agents are organofunctional silanes represented by the general structure: $(\text{RO})_3\text{SiR}'\text{X}$ where X is a functional organic group attached by a carbon linkage; R' is usually $-(\text{CH}_2)_3-$, and

RO is a hydrolyzable group.¹¹ Typical hydrolyzable groups include alkoxy of 1 to 4 carbon atoms; alkoxyalkoxy containing up to about 6 carbon atoms; halogens such as chlorine, fluorine, and bromine; acyloxy of 2 to about 4 carbon atoms; phenoxy; and oxime. The preferred hydrolyzable groups are alkoxy, alkoxyalkoxy, and acyloxy.¹¹ The alkoxy group hydrolyzes in aqueous solution to form -Si(OH)_3 , a silanol group.

Kaolin has a rather unreactive silica sheet surface and as a result, has relatively weak crosslinking reactions with conventional elastomer polymers.¹² This is changed by modifying the kaolin with silanes or another appropriate adhesive.

The coupling mechanism is complex but fairly well understood. Ambifunctional (organofunctional) silanes are selected that form stable covalent bonds with the resin while presenting silanol functionality to the mineral surface. The silane portion of the molecule has a strong affinity for the silica sheet in kaolin and attaches readily to it while leaving a chemically bound organic functionality.¹² More specifically, the coupling agent is typically supplied to the surface of the inorganic oxide through the hydrolyzable or silanol groups, (--Si - OH) . Bonding through siloxy moieties (--Si - O -) is effected.¹¹ This is known as a silanol condensation (or step polymerization.) Figures 1 and 2 show clay platelets with two different organic groups attached to clay via a silanol condensation.

Silanol Condensations

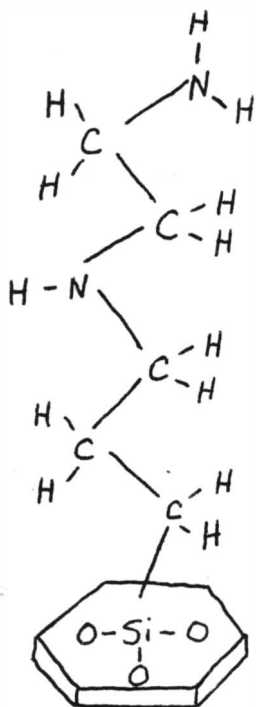


Fig. 1. Condensation of a diamino functional silane

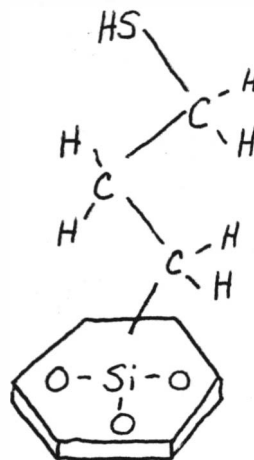


Fig. 2. Condensation of a mercapto functional silane

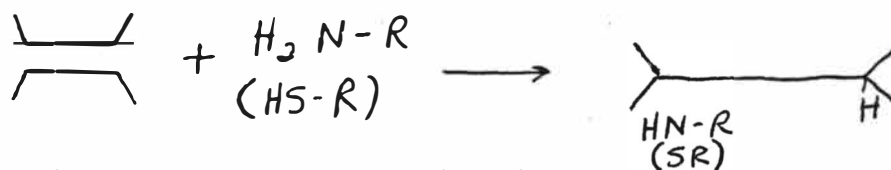
(It should be noted that although both amino and mercapto functional silanes are relatively hazardous and toxic materials, the modified clays have been found to be safe.)¹³

Silanols bond with hydrated oxide mineral surfaces under conditions that allow stress relaxation through a chemical equilibrium in the presence of water while maintaining overall adhesion.¹⁴ Once reacted, the organic groups are left unreacted but are permanently attached to the clay surface. Tests have shown that extraction techniques have not been able to remove these chemically bound groups, also long term storage tests have shown that they maintain their original activity.^{12, 13} The unreacted organic groups are then available for crosslinking to the polymer or binder, resulting in strong chemical bonds of pigment to polymer or binder. Typical commercial organic

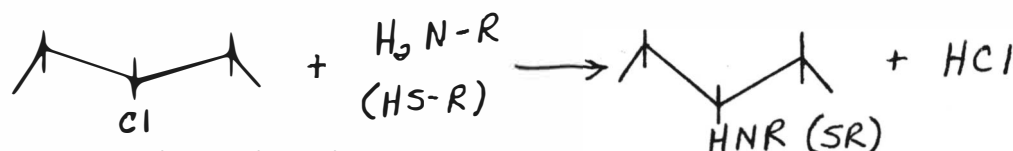
functional groups are vinyl, methacryloxy, primary amino, beta-aminoethylamino, glycidyl, epoxycyclohexyl, mercapto, polysulfide, ureido, and polyazamide.

The functional organic groups on the clay offer many possible reactions and from the following abbreviated list, it is apparent that the modified pigment may increase reactivity directly with elastomeric polymers and become an integral part of the polymer matrix.

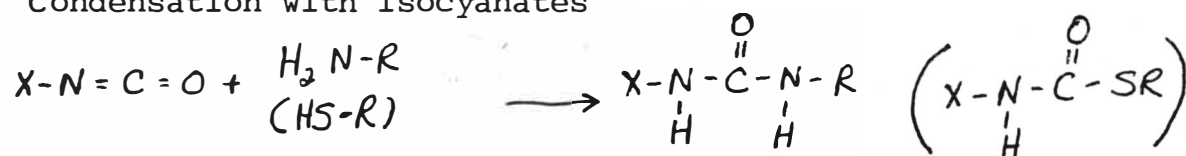
1. Addition to double bonds



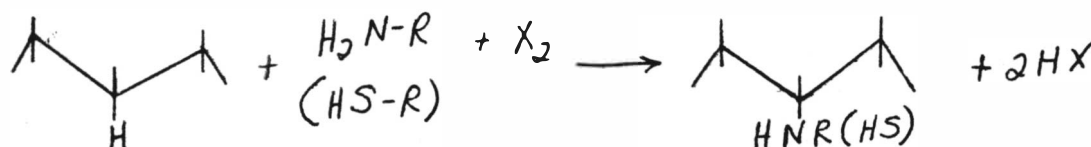
2. Displacement of Chloride ions



3. Condensation with isocyanates



4. Reaction with saturated polymers



As mentioned previously, attachment of the silane to the clay is a chemical bond and not merely a coating. As a rule, coupling agents enhance the chemical bonding between the medium and the inorganic surface to achieve improved adhesion. This could affect the strength properties of the composite of the plastic or resin associated with the inorganic oxide substrate or substrates. However, in only rare instances do coupling agents provide benefits

other than increased adhesion. One particular exception is the use of vinyl silanes on aluminum trihydrate to enhance their dispersion in polyester resin systems.¹⁵

DRY BLENDING OF FILLERS WITH SILANE

The most efficient use of silanes as coupling agents is by direct application to the inorganic surface. Neutral silanes may require an organic solvent as a catalyst for best utilization, however, solvent treatment of fillers is not general commercial practice because of added costs and the hazards involved with handling large volumes of organic solvents. The silanes may also be dry blended with the filler with high shear at room or elevated temperatures. One such method is described in a patent by T. A. Grillo.¹⁵ Some silanes disperse very readily over the filler, while others may require prolonged storage times and catalysts due to their slower hydrolysis reaction with the filler surface. It has been observed occasionally that old samples of treated filler, after standing in closed containers for six months, give lower viscosities in polymer mixes than freshly treated filler.¹⁷ If a silane is slow in diffusing throughout the filler, it may be diluted to about 10 times its weight in water or a medium alcohol before mixing with the filler. This may be rather effective but the treated filler must then be dried.

The effectiveness of the silane treatment on the filler may then be determined by the Daniel's Flow Point Test¹⁷ or as a reduction in viscosity of a polymer mix. This often correlates

well with performance of the filler as shown by increased flexural strength and chemical resistance in composites used in the plastics industry.

RHEOLOGY

There have not been any systematic and quantitative studies done on the rheology of silane treated fillers, but a general discussion may be presented.

Surface modification alters the rheology of the polymer by changing wet-out, dispersion of particles, viscosity, thixotrophy and flow during plastic fabrication. H. Burrell sought for a "pigment wetting parameter" and a "pigment dispersion parameter" as an aid in predicting pigment dispersion in inks and coating.¹⁸ He concluded that all pigments (and fillers) have water absorbed on their surfaces which affects each stage of the dispersion process. Adsorbed water acts as an adhesive to cement ultimate particles together. If the particles are separated by high shear, they reagglomerate in the absence of something to hold them apart. Once the agglomerate has been sheared, a polymer molecule can move in and stabilize the dispersion by entropic repulsion. The preferred dispersant is an organic molecule that is soluble in the solvent with functional groups that can bridge absorbed water on the pigment surface. They are active in the order amide > amine > phenol > hydroxyl > carboxyl > ester > ether > nitrite > phenyl. Therefore, a silane with the proper functionality may be chosen. Berger proposes that certain silanes may be used in what he describes as "dispersion promotes."¹⁵ He suggests that

"dispersion promotes" alter the surface characteristics of titanium dioxide so that the treated clay became more readily dispersed within the polymer matrix in which they are incorporated. This will also enhance the appearance of the resulting composite. The overall strength of the composite increased when the silane treated titanium dioxide was used to reinforce the composite. It is noted that these silanes differ from classical coupling agents (although there may be limited bonding) in that they have relatively low reactive organic groups.

SILANE-MODIFIED CLAYS IN THE RUBBER INDUSTRY ^{12,13,19}

The rubber industry has available to it silane modified kaolin pigments which offer high modulus and low hysteresis as well as offering low compression set and low viscosity which promotes high performance compounding. ¹² It is well known that elastomers are reinforced by fillers by means of a chemical crosslinking between the pigment surface and polymer molecules of the elastomer. While reinforcement of the elastomer is influenced greatly by particle size and dispersion of the pigment, the crosslinking of the pigment is determined by the chemical characteristics of the pigment surface. As discussed previously, the silane treated kaolin has the functionality needed for crosslinking of the pigment to polymeric binders.

The coupling mechanism produces some noticeable changes in the physical properties of compounded rubber using silane-modified clays. ¹³ The polymer movement is restricted due to increased pigment to polymer bonding. This results in an increased modulus.

Tensile strength is not affected because the rupture strength of polymer-polymer linkages remains unchanged. In addition, there are other tests used in the rubber industry which would indicate increased pigment to polymer bonding in using silane-modified kaolin over unmodified kaolin. Improved pigment to polymer bonding with modified kaolin has also been seen in photomicrographs of the rubber compounds which show a reduced number of vacuoles.¹³ Reducing the number of vacuoles, in essence, closes up the surface (i.e. fills in the holes and hills and valleys of the surface.) This could be of interest in the coated paper industry for an improved printing surface due to a smoother and stronger surface. It has been shown that silane treated kaolin and ground crystalline silica used in polyester composites have increased flexural strength due to the increased bonding between the filler and resin.³ As could be seen from photomicrographs, the surface was smoother and the fracture points occurred preferentially in the resin and the filler.

It should be noted that SBR rubber is often used with the silane modified kaolin. In addition, commercial glass-fiber tire cords are first treated with an aminofunctional silane and then a resorcinol-formaldehyde modified vinylpyridine copolymer latex (RFL latex) to obtain adequate adhesion to rubber for tire building.²⁰

STATEMENT OF PROBLEM

Based on the analysis of previous studies, it is proposed that silane-modified kaolin will improve the qualities of coated paper as seen in improvements in the properties of composites in the rubber and plastics industries. It is anticipated that there will be improved adhesion of pigment-to-pigment, pigment-to-adhesive, and coating composite to paper. It is possible that there may be improved rheology of the coating as well as a smoother sheet surface.

The above proposals yield an overall objective which is: use less binder in the coating and at the same time maintain or lessen the decrease in optical and printing properties. This may be possible with silanes known as coupling agents.

The experimentation to determine this overall objective will involve the following steps:

- 1) Determine the compatability of silane-modified clays with the coating formulation.
- 2) Make a basic determination of the rheology of the coating as compared to the unmodified clay.
- 3) Obtain a "usable" coated sheet by utilizing the Keegan coater.
- 4) Test the paper to determine how the desired properties for coated papers are affected by silane-modified clays as compared to the unmodified clay.

EXPERIMENTAL

INTRODUCTION

The experimentation will be based on the objective of the study which is to use less binder and maintain or lessen the decrease in optical and printing properties. It is proposed that silanes known as "coupling agents" will accomplish this by providing increased adhesion in the coating composite. Coatings will be made utilizing starch, protein, carboxylated latex, and PVAC latex to test the effect of four different silane treated clays against untreated clay. The functionality of the four Dow Corning silane coupling agents used in this study are as listed in Table I. Dow Corning dry blended these silanes with "Hydragloss" at high shear in a high intensity mixer. The clay was then dried at 80°C. The addition rate is 0.5% active silane based on clay.

EXPERIMENTAL DESIGN

Being an overview study, this project was designed to determine the interaction of the silane treated clays with starch, protein, carboxylated latex, and PVAC latex. Each of the treated clays was evaluated against the control which was untreated Hydragloss. Being interested in the differences between the various clays and not so much between the binder systems, a randomized complete block (RCB) design was established. This is shown in Table II along with the trade names.

This is the layout for the testing analysis as well as the experimental layout. In using a RCB design for this study, the

COUPLING AGENTS USED

<u>Exp Number</u>	<u>Silane</u>	<u>Functionality</u>	<u>Formula</u>
C1	Z-6040	Epoxy	$(\text{CH}_3\text{O})_3\text{-Si}(\text{CH}_2)_3\text{OCH}_2\text{CH}(\text{O})\text{CH}_2\text{-H}$ glycidoxypropyltrimethoxysilane
C2	Z-6020	Aminoalkyl	$(\text{CH}_3\text{O})_3\text{-Si}(\text{CH}_2)_3\text{NH-CH}_2\text{-NH}_2$ N-(2 aminoethyl)-3-aminopropyltrimethoxysilane
C3	Z-6030	Vinylbenzylamine	$(\text{CH}_3\text{O})_3\text{-Si}(\text{CH}_2)_3\text{-NH}(\text{CH}_2)_2\text{NHCH}_2\text{-C}_6\text{H}_5\text{-CH=CH}_2 \cdot \text{HCl}$ N-(N-Vinylbenzylamino) ethyl-γ-aminopropyltrimethoxy silane • HCl
C4	Z-6062	Mercapto	$(\text{CH}_3\text{O})_3\text{-Si}(\text{CH}_2)_3\text{-SH}$ mercaptopropyltrimethoxysilane

Table I

Table II EXPERIMENTAL DESIGN (RCB)

---binders---	---clays---				
	Control (Hydragloss; J. M. Huber)	C1 (Z-6040; Dow Corning)	C2 (Z-6020; Dow Corning)	C3 (Z-6030; Dow Corning)	C4 (Z-6062; Dow Corning)
Starch (Staco-M; Nat. Starch)					
Protein (Pro-cote 200; Ralston Purina)					
Carboxylated Latex (Dow 620; Dow Chem. Co.)					
PVAC Latex (Nat. Starch)					

binder systems are the blocks and the five different clays are the treatments. This design involved running the five different clays within a binder system at one time. The order in which the clays were run was randomized. In doing this, variations such as humidity, base stock, and conditions of the Keegan coater were kept to a minimum within a specific binder system. There was also a reduction of extraneous error, such as biasing, by randomizing the order in which the five clays were run. Finally, running the experimentation according to a preplanned design aided in statistically analyzing the data.

To provide for a more complete analysis, it was decided to replicate the design twice. This required each clay-binder-system to be run twice (i.e. 40 coatings overall). Replication provided for a better and more accurate "error" term in the analysis of variance table.

METHODS

Clay Dispersions

The first step to coating is to obtain good dispersions. Master batches of the five clays were dispersed in the Cowles dissolver. Standard procedure was used in which 2000g of clay was dispersed at 70% solids for 10 minutes. Water was first added to the beaker (857g) and then the clay was slowly added under shear. It was found with the silane treated clays that slightly more water had to be added in order to disperse all the clay. With the silane treated clays, 0.2% TSPP was used for the control. (Jim Kuhagan's rheological study²¹ showed 0.1% to be

closer to the optimum amount of TSPP for the silane-treated clays.) With the exception of C1, the silane-treated clays were pseudo-plastic. Water was added to these clays until an adequate dispersion was obtained. To each of the five clay dispersions 0.2% defoamer (Foammaster VF; Diamond Shamrock) and 0.5% calcium stearate (Nopcote C-104HS; Diamond Shamrock) was added. The dispersions were then adjusted to a pH of 9.5 with dilute NaOH. It should be noted that concentrated ammonia yielded pH shock. The final solids of the five clay dispersions (masterbatches) are listed in Table III.

Table III. Clay Dispersion Solids

<u>Clays</u>	<u>% Solids</u>
Control	67 %
C1	64 %
C2	55 %
C3	51.5%
C4	48 %

Coating Makedown

Once the masterbatches of clays are made, the coating makedown is a simple process of adding the appropriate binder to the clay dispersion. The binders added were starch (20%), protein (15%), Dow 620 (15%), and PVAC latex (15%). To achieve approximately the same solids for each coating, a visual determination was made by preparing a "usable" coating with one of the binders and the control.

The viscosity of the coating was determined by using the Brookfield viscometer with a #6 bob at 30 rpm and room temperature. The silane-treated clays were then prepared at the same

viscosity. The solids were then determined the following day after drying overnight in the oven. The breakdown for each of the binder systems is given in Table IV. (The numbers given are averages of the two replications as the two are similar.)

The binders for all coatings were mixed into the clay dispersion by use of a stirring rod. The latexes were added "as is." (i.e. Dow 620 @ 50% solids and PVAC latex @ 47% solids.) Starch (Stayco-M) was cooked at 20% solids for 30 minutes at 190°F. Protein (Pro-Cote 200) at 20% solids was soaked for 30 minutes. The temperature was then brought up to 135°F at which point 12% conc. ammonia was added. The protein was then cooked for 3 minutes at 140°F.

As mentioned previously, the five clays with a particular binder were all run at the same time. The procedure involved weighing out 50g (dry basis) of each of the five clays into a beaker. The beaker was then covered with tape to prevent the clay from skinning over. Then, in random order, the binder was added to a clay and the viscosity adjusted to the predetermined value by the method described previously. The coating was now ready for application to the paper.

Coating Application

Application of the coating to the base stock was accomplished by utilizing the 10" Keegan coater. For this project, the coater was used as a blade coater with the coating poured into the blade-paper nip and contained by wax end dams (see Fig. 3).

Table IV. Coating Makedown

Dow 620

<u>Clay</u>	<u>Latex</u>	<u>CMC</u>	<u>Viscosity</u>	<u>% Solids</u>
Control	15%	0.5%	29 (~10P)	49.0
C1	15%	none	28	58.5
C2	15%	none	30	49.5
C3	15%	none	29.5	48.5
C4	15%	none	31	45.5

PVAC Latex

<u>Clay</u>	<u>Latex</u>	<u>CMC</u>	<u>Viscosity</u>	<u>% Solids</u>
Control	15%	0.5%	30.5 (~10P)	49.5
C1	15%	none	29.5	59.0
C2	15%	0.15%*	16.5	48.0
C3	15%	0.14%*	16.5	49.0
C4	15%	0.11%*	18.0	44.5

*It was discovered that a 1% solution of CMC did not increase the viscosity of these silane-treated clay coatings and actually began to decrease viscosity.

Starch

<u>Clay</u>	<u>Starch</u>	<u>Viscosity</u>	<u>% Solids</u>
Control	20%	65 (~20P)	43.0
C1	20%	80	40.5
C2	20%	80	40.0
C3	20%	83	37.0
C4	20%	55	36.0

Protein*

<u>Clay</u>	<u>PVAC Latex</u>	<u>Protein</u>	<u>Viscosity</u>	<u>% Solids</u>
Control	10.5%	4.5%	51 (~17P)	44.5
C1	10.5%	4.5%	51	46.0
C2	10.5%	4.5%	47	42.0
C3	10.5%	4.5%	46	45.5
C4	10.5%	4.5%	57	41.5

*It was discovered that 15% protein (based on clay) yielded a very high viscosity coating. A coating within a usable viscosity range with protein would have been less than 30% solids. It was then decided to use a binder consisting of 70% PVAC latex and 30% protein and, henceforth, this 70-30 PVAC and protein combination will be called "protein."

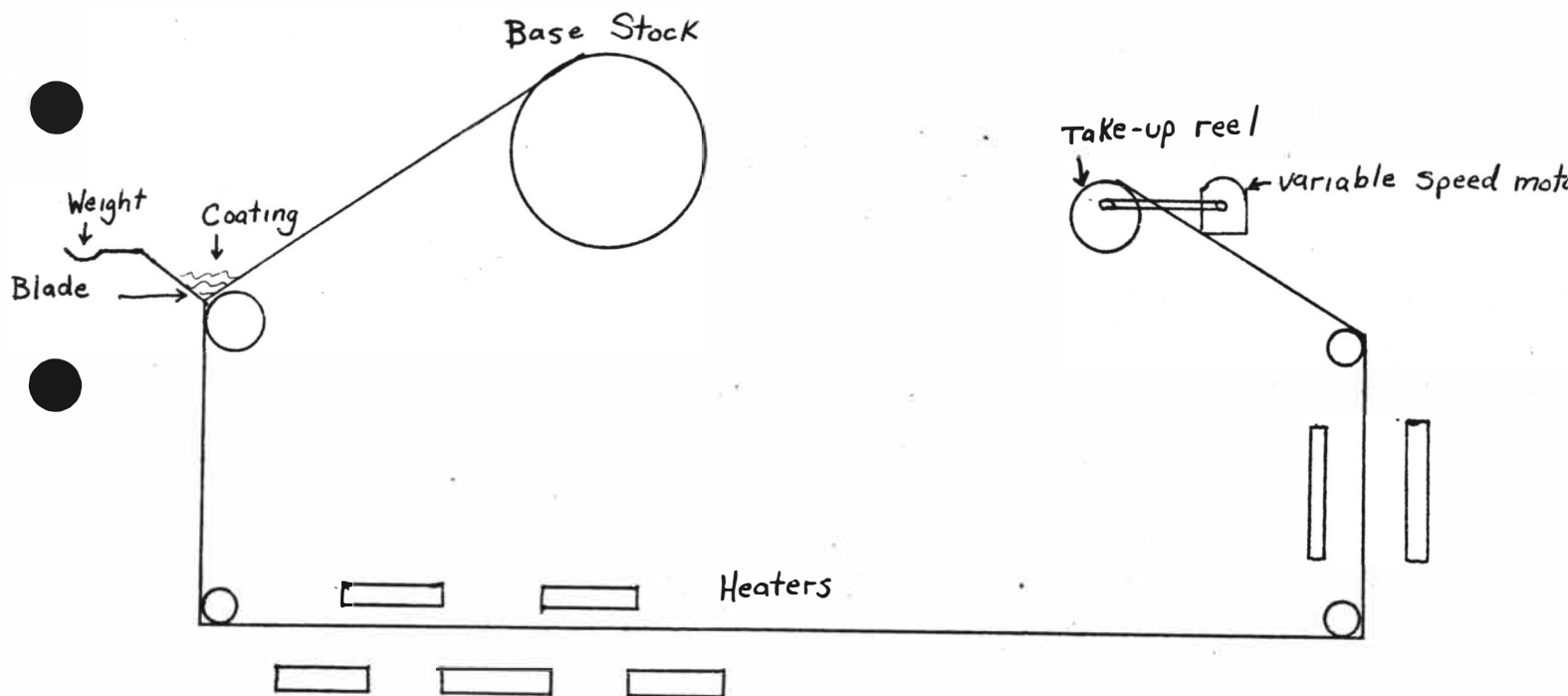


Fig. 3. Schematic of Keegan Coater

A coating was run on the coater and then another clay was selected--binder added--viscosity adjusted--and then run on the coater until all clays with a certain binder were run.

The targeted coat weights were 8 lbs. (12g/m^2) for the two latexes and 6 lbs. (9g/m^2) for starch and protein. (lbs. based on 25" X 38" X 500) The coat weight was varied on the Keegan coater by either changing the weight on the blade, the speed, or a combination of both. Two weights and three different speeds were run on each coating to obtain a spread of coat weights. Upon running the last coating with a certain binder, the coated paper was rolled up and stored in the constant humidity room.

Testing

The coated paper was cut into samples in which the coat weight was determined by difference between the coated paper and

the base stock. The weight of the base stock was determined at the start and finish of each coating, allowing for a more accurate determination of coat weight. Samples were selected for each coating that were closest to the targeted coat weight. In many cases, samples were selected for each coating in which a test value could be determined for the targeted coat weight. As an example, samples for the second run of C2 and starch were used that had coat weights of 5.1 lbs. and 7.6 lbs. A certain test could be run on both samples and then the value for the targeted 6 lbs. sheet could be obtained by extrapolation. The same samples were used for all tests. The tests performed are listed in Table 5.

Table V. Tests Performed

	Brightness	(Martin & Sweets)
	Caliper	
0 & 6 Nips	Gloss	(Hunter)
Supercalendering	Opacity	(BNL-2)
	Smoothness	(Sheffield)
	Porosity	(Sheffield)
6 Nips only	IGT Pick	
	K&N Ink	(Std. Ink after 2 min.)

The samples were tested both initially and after 6 nips of supercalendering. Additionally, gloss was measured at 4 and 6 nips to obtain gloss development curves.

PRESENTATION AND DISCUSSION OF RESULTS

ANALYSIS OF DATA

Basic to any discussion of results is the need to discuss how the numbers were obtained and the analysis of the numbers. The numbers for each test were obtained by taking 6-10 readings on each sample. (Usually ten readings were taken.) The only exception was IGT Pick in which two readings were taken per sample. An average was calculated for each coating using the 6-10 readings. Two samples were needed for each coating to obtain the test value at the targeted coat weight by extrapolation. This value was then recorded in the data table for one replication. The data tables contain forty values. (Twenty separate coatings --replicated twice.) The data for each test are presented in Appendix I.

The analysis of the data was accomplished by an analysis of variance (AOV). The AOV tables contain a complete breakdown. The least significant difference (LSD) value is included for comparison of each silane-treated clay against the control within a binder system. It should be noted that this LSD value can only be used when the F-test shows significance for either treatments (Trts), blocks (Blks), or block by treatment (Blk X Trt) interaction. If significance is not shown for Blk X Trt interaction, but shown for the Trts (clays), the LSD value is given for comparison of each clay. The F-test for blocks (binders) is not included, as by itself it is not important to this study. The AOV tables and LSD values are included in Appendix I along with the data tables.

The data from each test was then assembled onto a "master" data page. (see Table VI) These values are the average of the two replications. The only value missing is that of the Hercules size test for the base sheet--which was 0.6 sec. Using Table VI and the AOV tables (Appendix I) the results are discussed below.

RESULTS

The only results discussed here are those in which statistical difference was shown with the least significant difference (LSD) at $\alpha = .10$ (90% significance.) In which:

For comparison of clays within a binder:

$$LSD .10 = t_{.05}^{20} \sqrt{\frac{2MSE}{r}} = 1.725 \sqrt{MSE}$$

For comparison of clays with all binders:

$$LSD .10 = t_{.05}^{20} \sqrt{\frac{2MSE}{rb}} = 1.725 \sqrt{\frac{MSE}{4}}$$

Where: MSE = mean square error
r = replications
b = blocks

A discussion of results for this study is somewhat complicated. Therefore, it will be broken down into a discussion of each of the clays within a binder system. To aid in the discussion, "S. T. clays" will be used for silane-treated clays and "control" for untreated Hydragloss. Refer to Table VI for any values not included in the discussion.

(Pick resistance (IGT Pick) was of primary importance to this study. With the exception of the starch system coatings, the failure point in the coating had to be redefined. This was due to coatings having minute random pickouts from the beginning of the strip. A "gross" pickout or concentration of pickouts was then determined to be the point of coating failure. This was possibly due to binder migration and pigment agglomeration. Pigment agglomerates of 20 micron size were found in the dispersions by the grind gage test. Results reported in cm/sec.)

Table VI
EXPERIMENTAL DATA
(0 & 6 Nips Respectively)

Binder
System

	Clay	Brightness		Caliper		Gloss		Opacity		Smoothness		Porosity		Pick	K&N
620	Hydra	79.3	76.5	4.11	3.08	38.2	75.8	91.4	91.2	41.5	15.5	47.3	16.9	64	24.5
	C1	78.8	75.2	4.09	3.05	30.8	74.3	92.2	92.0	34.2	12.5	40.9	16.3	69	29.2
	C2	78.9	75.5	4.27	3.11	28.3	74.3	92.6	92.3	46.1	12.0	42.8	13.6	56	33.4
	C3	78.8	75.5	4.41	3.14	26.3	72.5	93.0	93.4	76.5	12.2	44.8	15.8	35	34.6
	C4	78.3	75.7	4.31	3.04	21.3	68.8	91.7	90.9	67.8	14.4	38.0	15.2	30	28.3
PVAC	Hydra	78.9	77.3	4.04	3.0	31.2	69.5	91.7	91.5	42.5	13.9	49.8	21.0	63	27.6
	C1	78.2	76.3	4.32	3.11	29.8	70.4	93.2	93.0	69.5	15.0	75.3	29.0	27	35.6
	C2	77.9	75.6	4.11	3.03	28.4	70.3	92.7	92.5	60.0	12.4	62.0	25.3	37	33.1
	C3	75.1	74.1	4.18	3.05	28.1	69.5	92.7	92.8	68.7	14.7	57.3	23.7	37	30.9
	C4	77.3	75.7	4.17	2.99	23.5	66.8	92.2	92.2	63.4	13.6	56.3	22.7	6	31.4
Protein	Hydra	79.4	76.9	4.02	3.16	24.4	69.0	92.4	91.7	47.4	15.8	61.3	25.3	24	31.3
	C1	77.6	75.3	3.93	3.06	21.0	61.6	92.1	91.1	58.8	17.4	68.9	28.5	51	27.9
	C2	78.4	75.7	4.02	3.04	20.8	67.4	92.9	91.5	62.6	17.8	65.5	19.2	39	30.5
	C3	78.1	75.4	3.94	3.05	19.4	60.4	92.1	91.5	57.6	17.8	73.3	29.2	38	29.3
	C4	78.2	76.4	3.96	3.04	13.9	52.6	92.0	90.8	68.4	16.3	64.8	21.9	64	26.0
Starch	Hydra	78.0	75.9	4.02	3.02	13.6	48.1	91.3	90.5	57.2	16.5	40.6	18.1	30	22.4
	C1	77.1	75.5	4.01	2.99	13.2	50.3	90.9	90.3	70.5	19.0	43.8	18.8	25	22.6
	C2	77.8	75.4	4.04	3.03	13.5	51.2	91.2	91.2	76.0	19.4	45.9	18.4	25	25.1
	C3	77.5	74.5	4.11	3.07	12.2	53.8	91.1	90.9	81.7	18.1	54.0	19.2	19	25.7
	C4	76.6	76.1	4.04	3.04	10.6	47.1	90.9	90.3	70.8	18.0	63.8	24.9	18	25.4
Base sheet		77.4	75.7	3.80	2.90	5.50	20.0	88.9	88.0	100	40	3.90	150	--	---

Carboxylated SB latex system

The statistically significant values for the SB latex system are given in Table VII.

Table VII Results of SB latex system

<u>Clay</u>	<u>Opacity</u>		<u>Gloss</u>		<u>K&N Ink***</u>	<u>IGT Pick</u>
	<u>0-Nips</u>	<u>6-Nips</u>	<u>0-Nips</u>	<u>6-Nips</u>	<u>6-Nips</u>	<u>6-Nips</u>
0**	91.4	91.2	38.2	75.8	24.5	64
C1	92.2	92.0*	30.2*	74.3	29.2*	69
C2	92.6*	92.3*	28.3*	74.3	33.4*	56
C3	93.0*	93.4*	26.3*	72.5	34.6*	35*
C4	91.7	90.9	21.3*	68.8*	28.3*	30*

*Indicates statistically significant difference.

**0 is used here and henceforth for the control clay.

***K&N Ink is reported as % loss of brightness.

The S.T. clays showed no improvement in pick resistance over the control with SB latex. C3 (vinylbenzlamino) and C4 (mercapto) actually had less pick resistance than the control.

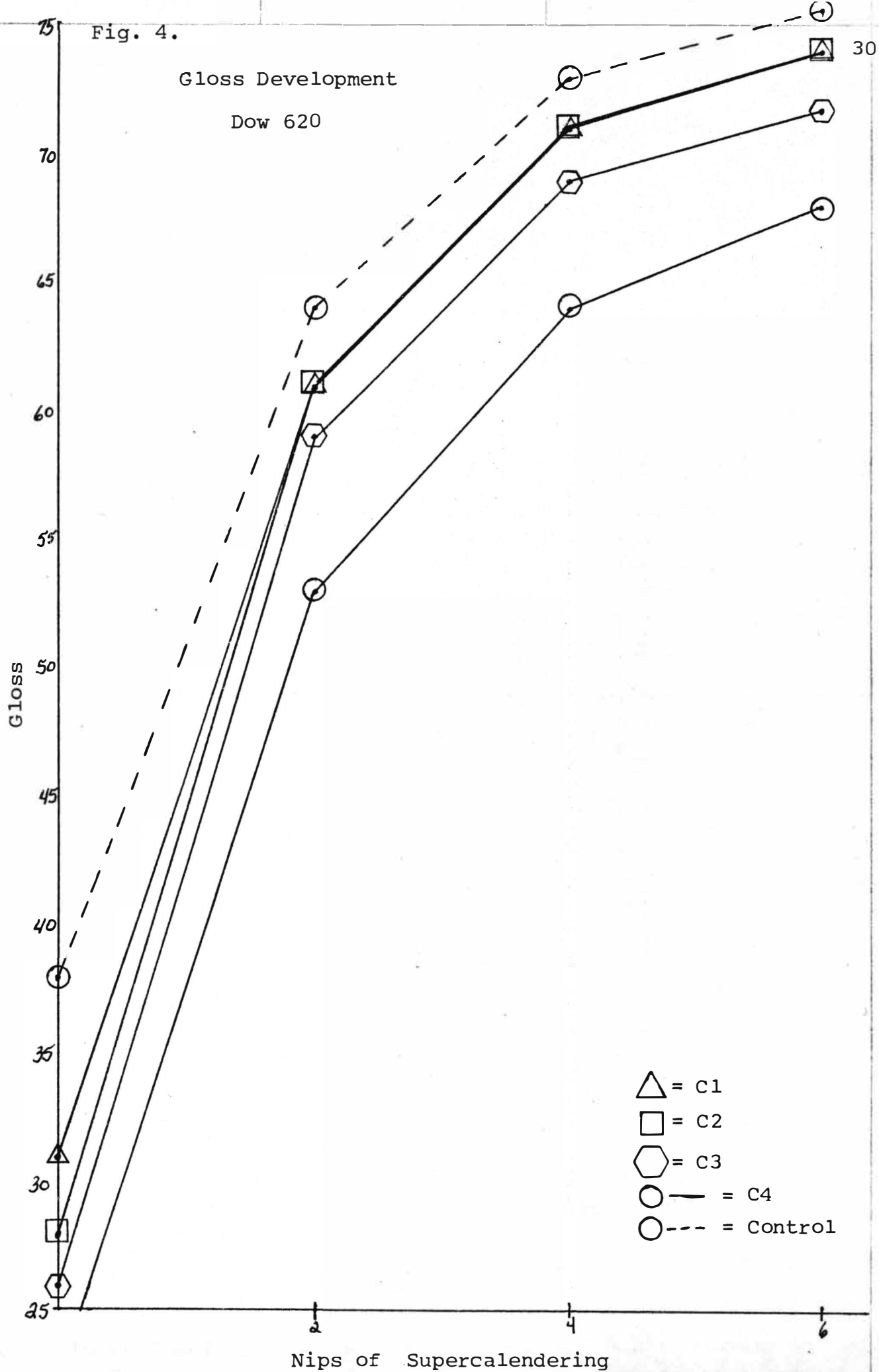
The opacity was initially greater with C2 (aminoalkyl) and C3 than the control. Upon supercalendering, the same result was seen along with C1 (epoxy) having higher opacity than the control. The K&N ink test showed the S.T. clays to have more ink absorption than the control. These observations suggest that the S.T. clay coatings have a more open structure with bigger pores than the control coating. This was contrary to what was expected. It is possible that the expected silane-to-binder coupling mechanism needed more time and/or higher temperatures than were used to obtain favorable results.

The gloss development curves for the SB latex system (Dow 620) are given in figure 4. The initial gloss was significantly lower

Fig. 4.

Gloss Development

Dow 620



with the S.T. clays than the control. Although, after six nips of supercalendering only C4 (mercapto) had lower gloss (Table VII.) The gloss development curves also show C4 having significantly lower gloss than the control at two and four nips. The curves also show C1, C2, and C3 to be essentially equal to the control after two nips of supercalendering. All the clays appear to be reaching a maximum value after six nips.

One other significant value was C2 (aminoalkyl) being smoother than the control upon supercalendering (Table VI). This was the only S.T. clay coating which yielded this result. All the other S.T. clay coatings were "equal" in smoothness to the control coating.

PVAC latex system

The statistically significant values for the PVAC latex system are given in Table VIII.

Table VIII Results of PVAC latex system

<u>Clay</u>	<u>Opacity</u>		<u>Smoothness</u>		<u>K&N Ink</u>	<u>IGT Pick</u>
	<u>0-Nips</u>	<u>6-Nips</u>	<u>0-Nips</u>	<u>6-Nips</u>	<u>6-Nips</u>	<u>6-Nips</u>
0	91.7	91.5	42.5	13.9	27.6	63
C1	93.2*	93.0*	69.5*	15.0	35.6*	27*
C2	92.7*	92.5*	60.0*	12.4	33.1*	37*
C3	92.7*	92.8*	68.7*	14.7	30.9*	37*
C4	92.2	92.2*	63.4*	13.6	31.4*	6*

*Indicates statistically significant difference.

The S.T. clays yielded less pick resistance than the control with PVAC latex. The S.T. clays also had greater ink absorption than the control. As with SB latex, this suggests a more open structure of the S.T. clay coatings over the control. It was

also possible that the ST clays may have had adverse reactions with the PVAC and formed agglomerates to yield less pick resistance.

The most favorable result with PVAC and ST clays was the increased opacity over the control. The smoothness was initially better with the control over the ST clays, but upon supercalendering the ST clays were "equal" in smoothness to the control.

The gloss development for PVAC curves are given in figure 5. C4 (mercapto) was shown to have significantly lower gloss initially and after two nips of supercalendering, but after four nips had the "same" gloss as the control. The other ST clays had essentially the same gloss development curves as the control.

Starch system

The statistically significant values for the starch system are given in table VIIII.

Table VIIII Results of Starch system

<u>Clay</u>	<u>Smoothness</u>		<u>Gloss</u>		<u>K&N Ink</u>
	<u>0-Nips</u>	<u>6-Nips</u>	<u>0-Nips</u>	<u>6-Nips</u>	<u>6-Nips</u>
0	57.2	16.5	13.6	48.1	22.4
C1	70.5*	19.0	13.2	50.3	22.6
C2	76.0*	19.4	13.5	51.2	25.1
C3	81.7*	18.1	12.2	53.8*	25.7*
C4	70.8*	18.0	10.6	47.1	25.4

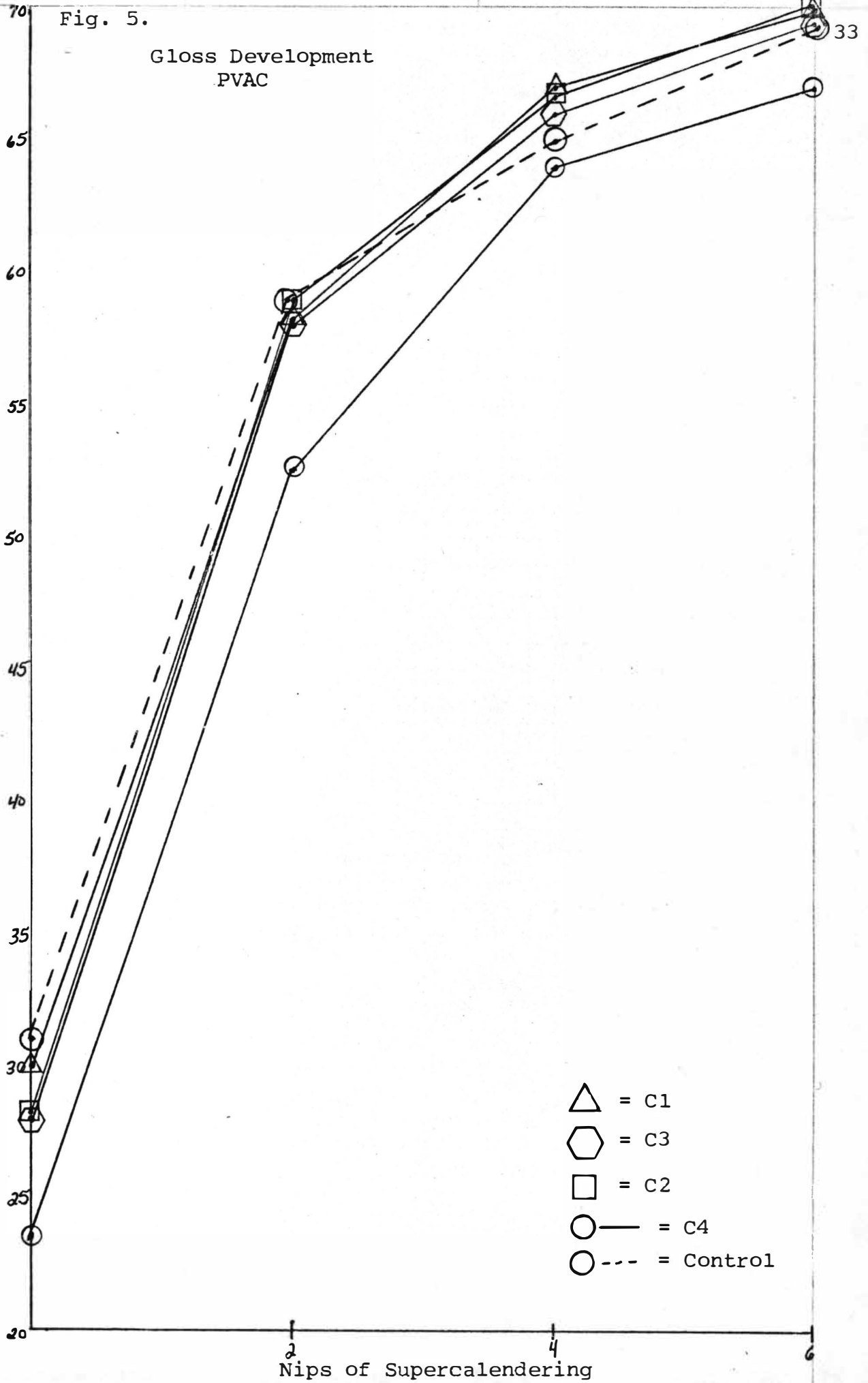
*Indicates statistically significant difference.

The most significant result in the starch system was the higher gloss of C3 (vinylbenzylamine) over the control. It should be noted that this was the only gloss value in the entire study in which a S.T. clay was higher than the control. The

Fig. 5.

Gloss Development
PVAC

Gloss



gloss development curves are given in figure 6. Up to four nips of supercalendering, all the S.T. clays are "equal" to Hydragloss. Between four and six nips C3 was seen to increase significantly over the control to yield a significantly higher gloss.

Also of significance, was that initially the control was smoother than the S.T. clays. After supercalendering, the S.T. clays have the same smoothness as the control (Table VIIII.) A second interesting observation with C3 and starch was that C3 has greater ink absorption than the control. (Table VIIII.) Another significant result with the starch system, was that C2 (aminoalkyl) had higher opacity than the control (Table VI.)

Protein--PVAC system

The statistically significant values for the Protein--PVAC system are given in Table X.

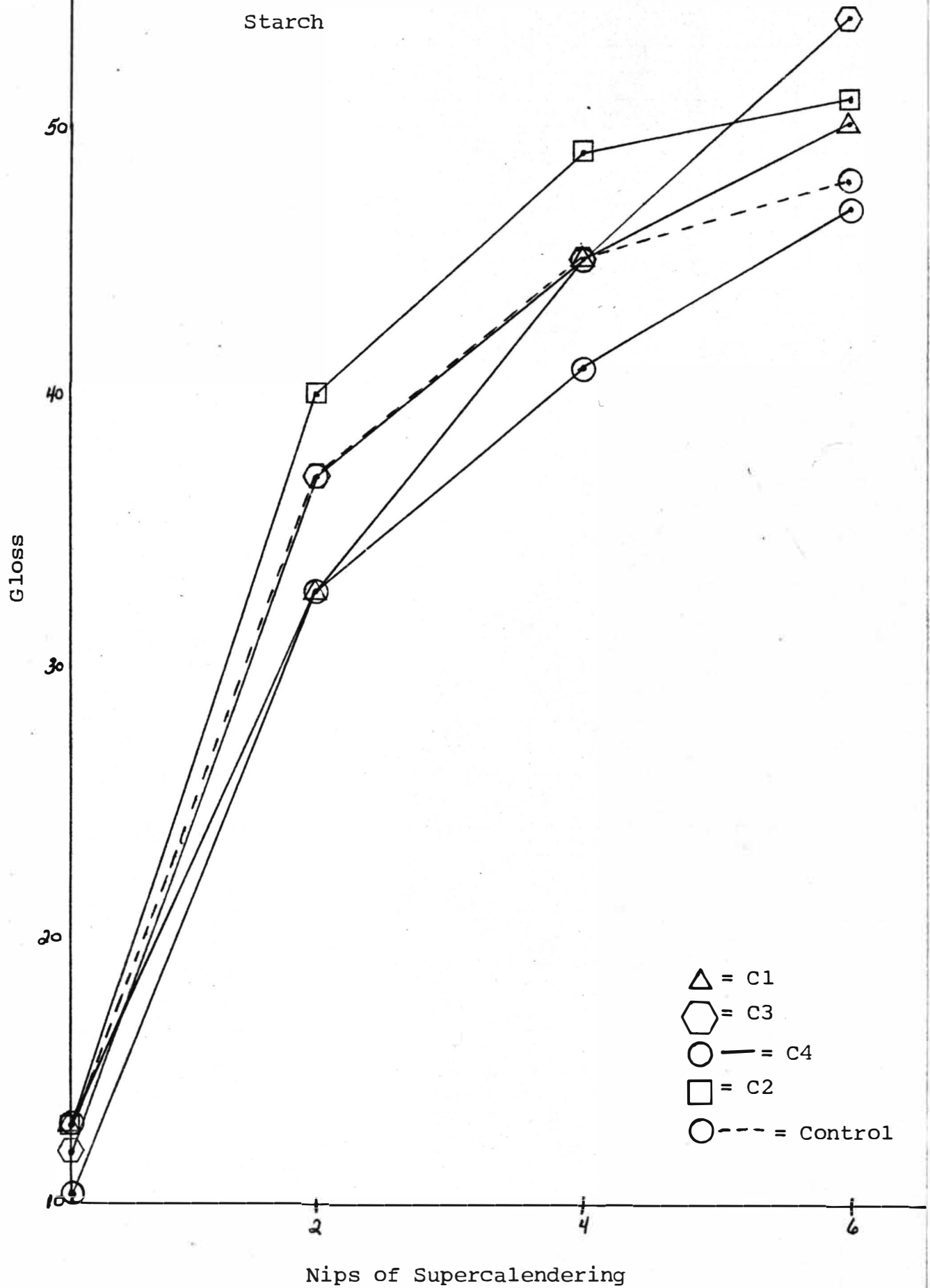
Table X. Results of Protein--PVAC system						
<u>Clay</u>	<u>Caliper</u>		<u>IGT Pick</u>	<u>K&N Ink</u>	<u>Gloss</u>	
	<u>Initially</u>	<u>6-Nips</u>	<u>6-Nips</u>	<u>6-Nips</u>	<u>0-Nips</u>	<u>6-Nips</u>
0	4.02	3.16	24	31.3	24.4	69.0
C1	3.93	3.06*	51*	27.9*	21.0	61.6*
C2	4.02	3.04*	39	30.5	20.8	67.4
C3	3.94	3.05*	38	29.3	19.4	60.4*
C4	3.96	3.04*	64*	26.0*	13.9*	52.6*

*Indicates significantly significant difference.

The most significant observations of the study were seen with the protein--PVAC system. As mentioned previously, 100% protein yielded high viscosity and, therefore, a binder of 70% PVAC and 30% protein was used for the coatings. Any difference between the protein--PVAC system and PVAC system can be attributed to the protein--ST clay interaction.

Gloss Development

Starch



As seen in Table X, pick resistance is greater for C1 (epoxy) and C4 (mercapto) than the control. The ink absorption for C1 and C4 was lower than the control. These two observations show a desirable interaction between the S.T. clays and protein which suggests increased crosslinking between the S.T. clay and protein.

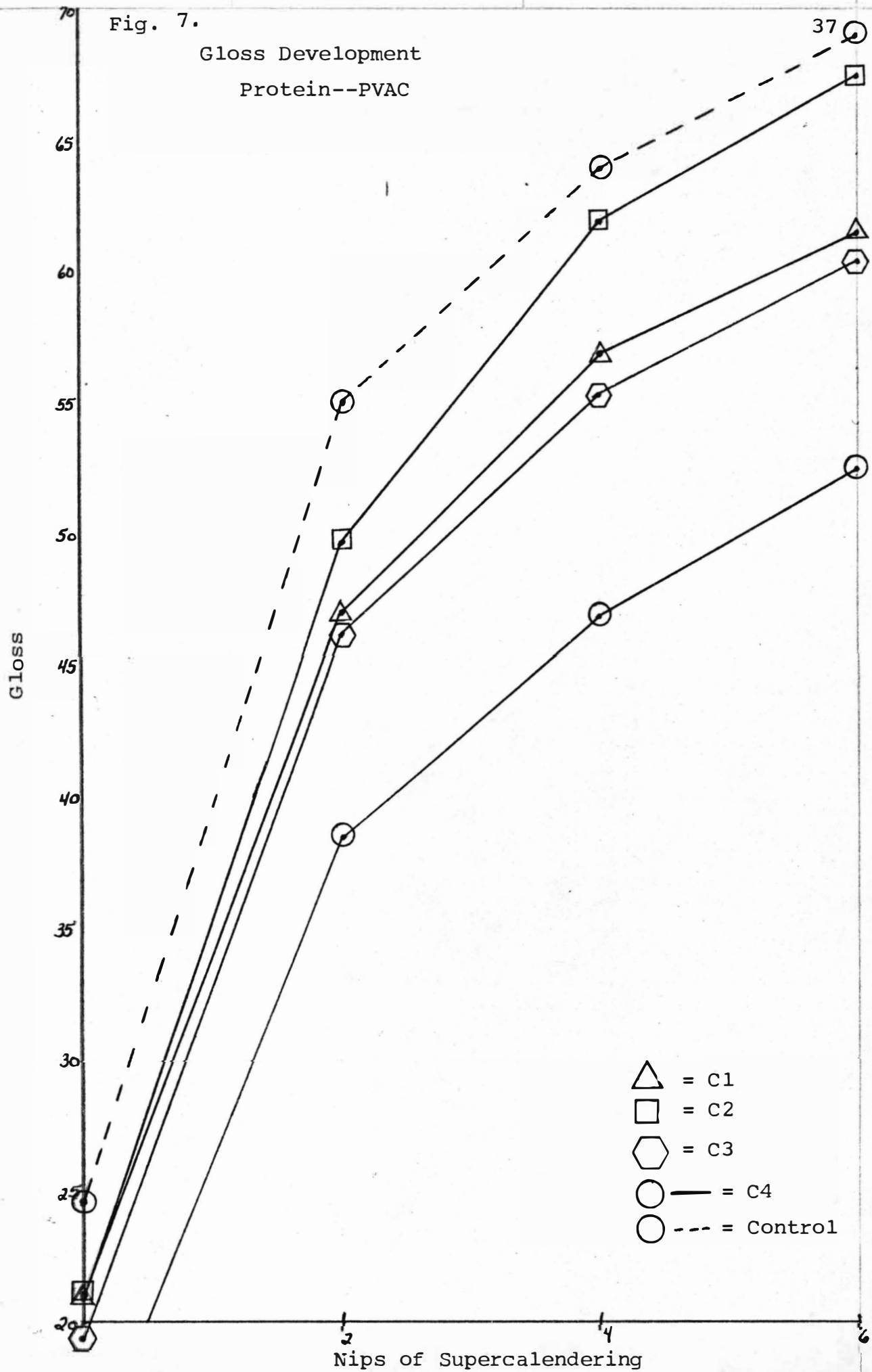
The caliper initially was the "same" for all the clays. After supercalendering, the S.T. clays all had lower caliper than the control. This suggests that the S.T. clay coating structure was more easily collapsed upon supercalendering. The increased pick resistance over the control then suggests that the S.T. coatings more readily hold onto the binder. This supports the possibility of increased crosslinking between the S.T. clay and protein.

The gloss development curves for the protein--PVAC system are given in figure 7. Initially, the gloss was lower for C4 (mercapto) than the control, with the other S.T. being "equal" to the control. After two nips of supercalendering, the only S.T. clay that had the same gloss as the control was C2 (aminoalkyl.) The other S.T. clays had lower gloss than the control. This may possibly have been due to the S.T. clay binding the protein more tightly while keeping the clay and PVAC on the surface to yield a higher gloss. If this were true, it would help substantiate the possibility of increased crosslinking between the S.T. clay and the protein.

The interaction between the S.T. clay and protein can more easily be seen by a direct comparison of the protein--PVAC system ("protein") and PVAC system as given in Table XI. From this

Fig. 7.

Gloss Development
Protein--PVAC



comparison, the increase in pick resistance and decrease in ink absorption of the S.T. clays over the control was seen to be quite significant.

Table XI. Comparison of "Protein and
PVAC systems after 6 nips of supercalendering

<u>Clay</u>	<u>Caliper</u>		<u>IGT Pick</u>		<u>K&N Ink</u>	
	<u>PVAC</u>	<u>Pro</u>	<u>PVAC</u>	<u>Pro</u>	<u>PVAC</u>	<u>Pro</u>
0	3.00	3.16	63	24	27.6	31.3
C1	3.11*	3.06*	27*	51*	35.6*	27.9*
C2	3.03	3.04*	37*	39	33.1*	30.5
C3	3.05	3.05*	37*	38	30.9*	29.3
C4	2.99	3.04*	6*	64*	31.4*	26.0*

*Indicates significantly significant difference

CONCLUSIONS

From the previous discussion of the experimental results, the following conclusions can be made concerning the role of the different silane-treated clays on coated paper properties after supercalendering. The comparisons are to untreated Hydragloss.

With Protein:

- 1) C1(epoxy) and C4(mercapto) had higher pick resistance.
- 2) C1(epoxy) and C4(mercapto) had lower ink absorption.
- 3) The silane-treated clays had lower caliper.
- 4) C1, C4, and C3(vinylbenzylamine) had lower gloss.

This suggests that crosslinking between the silane-treated clay and protein is probable. It is also probable that the surface collapses easier upon supercalendering with ST clays.

With Latexes (SB & PVAC):

- 5) The silane-treated clays had higher opacity.
- 6) The silane-treated clays had lower brightness.
- 7) The silane-treated clays had greater ink absorption.
- 8) The silane-treated clays had less pick resistance.
- 9) The silane-treated clays with PVAC had lower brightness.

This suggests a more open structure with larger pores than the control coating.

With Starch:

- 10) C3 had better gloss.
- 11) C3 had greater ink absorption.

It appears that it may be possible to obtain better pick resistance under the proper crosslinking conditions as seen with the protein system. The increased opacity with the latexes is also desirable. These conclusions suggest possibilities for future work with silane-treated clays. Their biggest drawback is cost and a slight loss in brightness.

FURTHER CONSIDERATIONS

Any future study of silane-treated clays should be done on a sized base sheet to prevent binder migration. The shearing time in the Cowles dissolver should be extended to insure proper clay dispersion before coating.

The author feels that now some basic relationships and rheology of the coatings are known. This allows for a more quantitative approach to the problem. For instance, time, temp, and pH dependent relationships could be studied in order to attempt to increase the amount of coupling between the silane-treated clay and binder. Finally, the author feels that it may be possible to modify the silanes to fit specific requirements in much the same way modern starches and latexes have been modified.

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APPENDIX I
Brightness (0-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	79.9	78.7	78.9	78.1	78.3
	78.6	78.8	78.8	79.5	78.3
PVAC	79.0	77.7	79.0	77.3	78.6
	78.8	78.7	76.8	72.8	76.0
Starch	78.0	76.9	77.5	77.0	75.5
	78.0	77.2	78.0	78.0	77.0
Protein	78.7	77.6	78.5	78.1	78.3
	80.1	77.6	78.2	78.1	78.0

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	60.6637			
Blks (Binder)	3	14.0367			*
TRTS (Clay)	4	11.4325	2.8581	2.57	2.87
Blk X TRT	12	12.9696	1.0808	0.9	2.28
Error	20	22.2250	1.1113		

LSD .10 = 1.82
(for comparison between clays)

Brightness (6-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	76.6	75.4	75.4	75.6	75.7
	76.3	75.0	75.5	75.3	75.6
PVAC	77.3	76.4	75.4	71.9	75.3
	77.2	76.1	75.8	76.3	76.0
Starch	75.3	75.5	74.9	73.2	76.2
	76.5	75.4	75.8	75.7	75.9
Protein	76.6	75.3	75.8	75.2	76.4
	77.2	75.3	75.5	75.5	76.4

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	35.4877			
Blks (Binder)	3	1.2427			
TRTS (Clay)	4	13.7065	3.4266	4.63	2.87 *
Blk X TRT	12	5.7336	0.4778	0.6	2.28
Error	20	14.8050	0.7403		

LSD .10 = 1.48
(for comparison between clays)

LSD .10 = 0.74
(for comparison between TRTS)

Caliper (O-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	4.09	4.09	4.26	4.42	4.24
	4.12	4.09	4.28	4.39	4.37
PVAC	4.07	4.48	4.26	4.40	4.23
	4.01	4.15	3.85	3.85	4.10
Starch	4.09	4.05	4.06	4.15	4.15
	3.95	3.96	4.01	4.06	3.92
Protein	3.97	3.93	4.06	3.91	3.91
	4.06	3.92	3.97	3.96	4.00

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	.96456			
Blks (Binder)	3	.42582			*
TRTS (Clay)	4	.05259	.01315	0.9	2.87
Blk X TRT	12	.20356	.01696	1.2	2.28
Error	20	.28260	.01413		

LSD .10 = 0.21

(for comparison between clays)

Caliper (6-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	3.03	3.02	3.11	3.08	3.07
	3.12	3.08	3.11	3.19	3.01
PVAC	2.98	3.13	3.03	3.05	2.96
	3.02	3.09	3.02	3.05	3.02
Starch	2.96	2.91	2.98	3.05	3.00
	3.07	3.07	3.08	3.08	3.07
Protein	3.15	3.05	3.05	3.07	3.05
	3.17	3.07	3.03	3.03	3.03

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	.12491			
Blks (Binder)	3	.02129			*
TRTS (Clay)	4	.01034	.00259	1.14	2.87
Blk X TRT	12	.04778	.00398	1.75	2.28
Error	20	.04550	.00228		

LSD .10 = 0.08

(for comparison between clays)

Gloss (0-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	41.6	24.0	29.0	28.5	20.6
	34.7	37.6	27.5	24.0	21.9
PVAC	28.4	26.5	27.6	31.0	23.7
	33.9	33.0	29.1	25.2	23.3
Starch	13.7	13.7	13.0	12.3	10.8
	13.5	12.7	14.0	12.0	10.3
Protein	25.6	20.1	20.7	20.1	13.8
	23.1	21.8	20.9	18.7	14.0

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	2479.7698			
Blks (Binder)	3	1784.5488			
TRTS (Clay)	4	384.5360	96.134	10.15	2.87 ✓
Blk X TRT	12	121.2500	10.1042	1.07	2.28
Error	20	189.4350	9.347		

LSD .10 = 5.27
(for comparison between clays)

LSD .10 = 2.64
(for comparison between TRTS)

Gloss (6-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	74.5 77.0	76.8 71.8	74.3 74.3	70.6 74.3	69.7 67.9
PVAC	67.0 71.9	69.7 72.1	69.7 70.8	73.2 65.7	67.2 66.3
Starch	50.3 45.8	49.5 51.0	56.1 46.2	52.6 54.9	46.1 48.0
Protein	70.7 67.2	60.5 62.7	67.3 67.5	61.9 58.8	52.5 52.6

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	3701.94			
Blks (Binder)	3	3083.03			
TRTS (Clay)	4	257.04	64.260	8.62	2.87
Blk X TRT	12	212.78	17.73	2.38	2.28 ★
Error	20	149.09	7.455		

LSD .10 = 4.71

(for comparison between clays)

Opacity (0-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	91.6	92.0	92.6	92.7	91.5
	91.1	92.4	92.6	93.2	91.8
PVAC	90.8	92.9	91.9	91.9	91.2
	92.5	93.5	93.4	93.5	93.2
Starch	90.6	90.4	90.6	90.8	90.7
	91.9	91.3	91.7	91.3	91.0
Protein	92.6	91.8	92.8	92.2	92.0
	92.1	92.3	92.9	91.9	91.9

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	28.8097			
Blks (Binder)	3	12.5427			
TRTS (Clay)	4	2.9785	0.7446	1.7	2.87
Blk X TRT	12	4.5536	0.3795	0.8	2.28
Error	20	8.7350	0.4368		

LSD .10 = 1.14

(for comparison between clays)

Opacity (6-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	91.1	91.3	92.3	93.0	90.9
	91.2	92.7	92.3	93.8	90.9
PVAC	91.5	92.9	92.3	92.7	92.4
	91.5	93.1	92.6	92.8	91.9
Starch	90.3	90.3	91.1	90.8	90.4
	90.6	90.3	91.2	91.0	90.1
Protein	91.7	91.0	91.4	91.4	90.6
	91.6	91.2	91.6	91.6	91.0

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr) 39		32.3760			
Blks (Binder) 3		17.7320			
TRTS (Clay) 4		6.7535	1.6884		2.87
Blk X TRT 12		6.1305	.5109	5.81	2.28 *
Error 20		1.760	.088		

LSD .10 = 0.51

(for comparison between clays)

Smoothness (0-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	41.4	40.8	46.0	67.6	63.9
	41.5	27.6	46.2	85.3	67.6
PVAC	45.0	83.5	65.3	76.7	64.5
	40.0	55.5	54.6	60.7	62.2
Starch	58.8	69.7	76.9	86.6	71.6
	55.5	71.2	75.0	76.8	70.0
Protein	48.0	58.3	62.5	54.5	66.0
	46.7	59.3	62.7	60.7	70.7

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	7283.351			
Blks (Binder)	3	1759.149			
TRTS (Clay)	4	2716.096	679.024	14.57	2.87
Blk X TRT	12	1875.776	156.3147	3.35	2.28 ★
Error	20	932.330	46.6165		

LSD .10 = 11.78

(for comparison between clays)

Smoothness (6-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	15.0	12.5	12.0	12.1	14.5
	16.0	12.5	12.0	12.3	14.2
PVAC	15.2	17.0	13.3	13.7	13.7
	12.5	13.0	11.5	15.7	13.4
Starch	13.7	18.7	19.8	14.2	17.2
	19.3	19.2	19.0	22.0	18.8
Protein	15.7	14.2	17.8	17.8	15.8
	15.8	20.5	17.8	17.8	16.7

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	296.0498			
Blks (Binder)	3	167.7428			*
TRTS (Clay)	4	1.7310	0.4328	0.1	2.87
Blk X TRT	12	42.6210	3.5518	0.8	2.28
Error	20	83.9551	4.1978		

LSD .10 = 3.53

(for comparison between clays)

Porosity (O-Nips)
Sheffield

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	48.4	45.6	42.7	43.4	40.8
	46.1	36.1	42.9	46.2	35.2
PVAC	49.1	80.3	64.8	50.5	60.0
	50.5	70.2	59.2	64.0	52.5
Starch	42.2	51.5	55.7	50.0	56.5
	39.0	36.0	36.0	58.0	71.0
Protein	51.3	72.0	79.0	71.0	65.3
	71.3	65.8	52.0	75.5	64.3

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr) 39		6428.1297			
Blks (Binder) 3		3435.8627			★
TRTS (Clay) 4		312.7685	78.1921	1.20	2.87
Blk X TRT 12		1374.4336	114.5361	1.76	2.28
Error 20		1305.0649	65.2532		

LSD .10 = 13.93

(for comparison between clays)

Porosity (6-Nips)
Sheffield

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	17.5	18.0	13.0	15.0	16.0
	16.2	14.5	14.2	16.5	14.4
PVAC	19.2	30.8	24.3	18.3	21.0
	22.8	27.2	26.3	29.1	24.3
Starch	19.5	22.0	20.7	20.2	21.8
	16.7	15.6	16.0	18.2	27.0
Protein	27.3	27.2	19.2	29.2	21.2
	23.2	29.8	19.2	29.1	21.5

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	1009.784			
Blks (Binder)	3	565.832			
TRTS (Clay)	4	75.6965			2.87
Blk X TRT	12	221.1355	18.428	2.51	2.28
Error	20	147.12	7.356		

LSD .10 = 4.68

(for comparison between clays)

IGT Pick (6-Nips)

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	71.0	92.0	56.0	34.0	30.0
	56.5	48.0	56.0	36.0	30.0
PVAC	68.0	20.0	33.0	23.5	4.0
	57.5	34.0	41.0	49.3	8.0
Starch	34.3	17.5	21.8	14.8	13.0
	26.3	31.0	27.5	23.9	22.9
Protein	27.0	56.0	45.5	40.0	51.0
	21.0	46.0	31.5	34.5	77.0

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	14421.738			
Blks (Binder)	3	4178.007			
TRTS (Clay)	4	1462.782	365.5954		2.87
Blk X TRT	12	6296.4785	524.7062	4.22	2.28 ★
Error	20	2486.475	124.3238		

LSD .10 = 19.23

(for comparison between clays)

K&N Ink (6-Nips)
% Loss of Brightness

---Treatments---

	Hydra	C1	C2	C3	C4
Dow 620	25.2	28.1	33.4	33.7	27.6
	23.8	30.2	33.3	35.5	28.9
PVAC	26.9	35.1	31.0	27.3	28.8
	28.3	36.1	35.2	34.5	33.9
Starch	21.8	22.8	24.8	24.6	25.7
	23.0	22.3	25.3	26.7	25.0
Protein	31.7	27.0	30.3	29.4	25.8
	30.8	28.8	30.6	29.1	26.1

AOV Table

<u>Source</u>	<u>d.f.</u>	<u>SS</u>	<u>MS</u>	<u>F_{calc}</u>	<u>F_{.05}</u>
Total (Corr)	39	628.356			
Blks (Binder)	3	309.902			
TRTS (Clay)	4	89.8735			2.87
Blk X TRT	12	165.1205	14.01	4.63	2.28 ★
Error	20	60.460	3.023		

LSD .10 = 3.00

(for. comparison between clays)