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The Effects of pH on Alkali-Swellable Latex Binder Coating Systems

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The Effects of pH
On Alkali-Swellable Latex
Binder Coating Systems

By

Larry N. Justen

A Thesis Submitted to the
Faculty of the Department of Paper Science
and Engineering in Partial Fulfillment
of the
Degree of Bachelor of Science

Western Michigan University

Kalamazoo, Michigan

Dec. 1976

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Introduction

In recent years there has been a growing demand for the use of synthetic latexes as sole binders in coating formulations. This has been brought about by the shortage of supply and changing prices of natural binders like casein and protein. Synthetic latex binders require no cooking; this increased energy saving over starch becomes more important as fuel prices rise. Synthetic latex systems are easy to handle and they can be combined easily to fit different requirements.

Most synthetic latex systems need a thickener and water retention aid to achieve the right viscosity and flow properties. The new alkali-swellable latexes will produce a thickening effect upon alkali addition. These latexes are alleged to have better water retention and binder control than the other non-reactive latex binders.

Water retention is a direct indicator of binder migration in a coating application, since some latex binder travels with the water into the paper substrate. Water retention determines leveling of the coating after application. The hold-out qualities of the dried coating and the rate of drying are also affected by water retention. Physical and optical properties will vary with changing water retention of the coating color. It is generally accepted that water retention is dependent on viscosity and solids content.

This study examines alkali-swellable latex systems to determine how pH levels of the coating color can affect physical and optical properties

of the coated paper. An all alkali-swellable system and an alkali-swellable/standard unreactive latex system was applied to a groundwood stock at varying pH levels. Coat weight and percent solids were held constant, and coated samples were tested for any physical or optical changes. Viscosities were measured at the different coating color pH levels using high and low shear equipment.

Literature Survey

Latex



Synthetic polymer latices are comprised of submicroscopic polymer spheres, colloiddally suspended in water. This description covers all the styrene-butadiene, acrylic, and polyvinyl acetate latices. The water is called the continuous phase and the spheres, the dispersed phase. The latin word latex means fluid or emulsion. The solids content of most commercial latexes ranges from 40% to 65%, with a particle size ranging from .10 microns to .30 microns. Early latexes were about .25 microns compared to a modern carboxylated styrene butadiene (SBR) particle size of .15 microns. Alkali-swellable latexes have a particle size of .1 microns. Compared to clay particles, latex particles are about 1/25 the size.¹

These milky, opaque latex emulsions remain a fluid at normal solids content. During drying, coagulation of particles starts at around 75% solids. Surface tension forces resin particles tightly together, which transforms the fluid to a tough, transparent continuous film.

The basic unit of a latex polymer is the monomer. Monomer means one part, and is the term applied to the building blocks of the latex. Polymer means many parts, and consists of a whole chain of monomers, which have chemically reacted together. Almost all latex polymers are very long chains of carbon atoms, connected either by single or double bonds. A homopolymer is a polymer with molecules made up of one repeating unit or monomer. A copolymer has two different repeating monomers in each molecule.

Polymers with double bonds in their backbone are called "diene" rubbers. Natural rubber, all styrene butadiene (SBR), acrylonitrile-butadiene rubbers, and polybutadienes are in this class. Under extreme heat and pressure, and with use of a catalyst, their monomers are transformed to copolymers. These copolymers tend to form a very elastic "rubbery" film.

Polymers with no double bond in the backbone tend to form a more plastic film which recovers more slowly from stress than the double bonded copolymers. The acrylics and polyvinyl acetates belong to this class. The composition of some of the common monomers and copolymers are drawn below.²

<u>Monomer</u>	<u>Repeating Unit</u> (hydrogens omitted)
Butadiene	$-C-C=C-C-$ 
Styrene-butadiene copolymer	$-C-C=C-C-C-C-$ 
Natural rubber	$-C-\overset{\text{CH}_3}{\underset{ }{C}}=C-C-$
Acrylate R ₁ = H, Acrylic acid R ₂ = CH ₃ , Methyl acrylate	$-C-\overset{\text{C}}{\underset{\begin{array}{c} \\ \text{C}=\text{O} \\ \\ \text{OR}_1 \end{array}}{\text{C}}}-$
Polyvinyl Acetate	$-C-\overset{\text{C}}{\underset{\begin{array}{c} \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}}{\text{C}}}-$

Monomer units coupled together in straight linear fashion are called linear polymers. Molecules with branched repeating units are called branched polymers. By "crosslinking" molecules, primary covalent bonds are established between each molecule. A three-dimensional structure is created which is very resistant to heat. Polymers of this sort, after curing, will not melt and are termed thermosetting. Thermoplastic polymers will melt when heated. These polymers are usually linear polymers, although some branched polymers will also melt. Polymer molecular chains of a few thousand molecules are low weight molecular polymers which form soft films. High weight polymers are composed of many thousand molecules and form harder, tougher films.

Polymerization is the process of forming polymers out of monomers. Condensation polymerization usually produces thermosetting polymers, by the reaction of two similar functional molecules with each other. Water is usually the medium of exchange. Addition polymerization usually produces thermoplastic polymers, by chain reactions of vinyl monomers.

Polymerization is aided by the emulsification process, which stabilizes monomers, through chemical coupling of water to oil. An emulsifier is a chemical compound which has one end polar, or water loving, and one end organic, which likes oil. In a latex emulsion, this emulsifier coats the polymer spheres. Emulsifiers usually are soap types, like alkyl sulfates or sulfonates. This process usually gives higher molecular weight latexes, with smaller particles. Large particles are not as good for adhesion or optical properties, but are more stable.¹

Plasticizers are added to polymers to induce more flexibility in the film. By destroying secondary bonds between molecules, and linking itself between them, the plasticizer reduces brittleness. By adding chemically reactive functional groups at different places on the polymer chain backbone, the properties of the polymer can be changed. "Carboxyl" groups were first to be used in the early 1960's. Carboxylated acrylic emulsions and carboxylated styrene butadienes had low viscosity, less odor, better mechanical stability, and better ink holdout than the non-carboxylated latexes. The carboxyl functional group not only gave better adhesion between pigment particles, but it also had an affinity for the cellulose fiber.³

Latexes have certain advantages in paper coating functions.

- a. strength
- b. high degree of flexibility
- c. water resistance
- d. high gloss
- e. dimensional stability
- f. low viscosities at high solids

With rising protein and casein costs, latexes are becoming more profitable to operate with starch in paper coatings. The table on the following page shows the consumption of starch and synthetic latex between 1968-1972.¹²

<u>Adhesive</u>	<u>Consumption</u>		<u>% Increase</u>
	<u>1968</u>	<u>1972</u>	
Starch	315,000 Tons/yr.	500,000 Tons/yr.	63%
Synthetic Adhesives	138,000 Tons/yr.	230,000 Tons/yr.	60%
Protein	--	50,000 Tons/yr.	--

These figures show the increased trend towards synthetic latexes. Just recently protein has come back into the market with prices dropping to the same level as synthetic latexes. These binders are still twice as expensive as starch, but the increased cooking costs, because of climbing fuel prices, have reduced the economical edge.

The relative low "adhesion" of starch reduces optical and glossing properties while giving the coating film less water hold out.¹² Starch adhesion is produced by chemical reaction of hydroxyl groups, which creates a low specific adhesion (.6-1.0). Although most latexes have a low specific adhesion (1.0-1.25), the high flexibility of the bonds gives the coating better water hold out and less adhesive demand. This means coating colors can be formulated with higher percent solids. The reduced water consumption helps increase drying efficiency. By using more clay and less binder, increased optical properties can be observed. Latex is finding use in more coating formulations every day - but it does have some disadvantages.

- a. Expensive - twice as expensive as starch
- b. Foaming
- c. Freeze and heat sensitive

- d. Poor pigment disperser
- c. Reduces opacity on calendering
- f. Sensitive to pH
- g. Poor water retention

The last three factors will be examined in this experiment.

Synthetic Latex - Costs

The majority of synthetic latex used in the coating industry today is styrene-butadiene. Over 140,000 tons of carboxylated styrene-butadiene was used in 1972. They cost roughly .38¢ per pound. Vinyl acetate copolymer latexes are used somewhat in the industry. Over 80,000 tons were consumed in 1972 and present cost is .37¢ per pound.¹² Acrylic copolymers are the third category, but high costs (.52¢ per pound) keep their use low in the industry. Butadiene-acrylonitrile latex is used also because of its high grease proofing, but it too is expensive, along with being mechanically unstable. Alkali-swellaable latexes have lower molecular weights and molecular control additives to induce viscosity thickening, and increase water retention over other latexes. Certain styrene-butadiene and acrylic latexes are modified to make them highly pH sensitive and alkali-swellaable.

This report will analyze a common carboxylated styrene-butadiene latex and an alkali-swellaable styrene-butadiene latex, so their depth will be covered more thoroughly.

Styrene-Butadiene

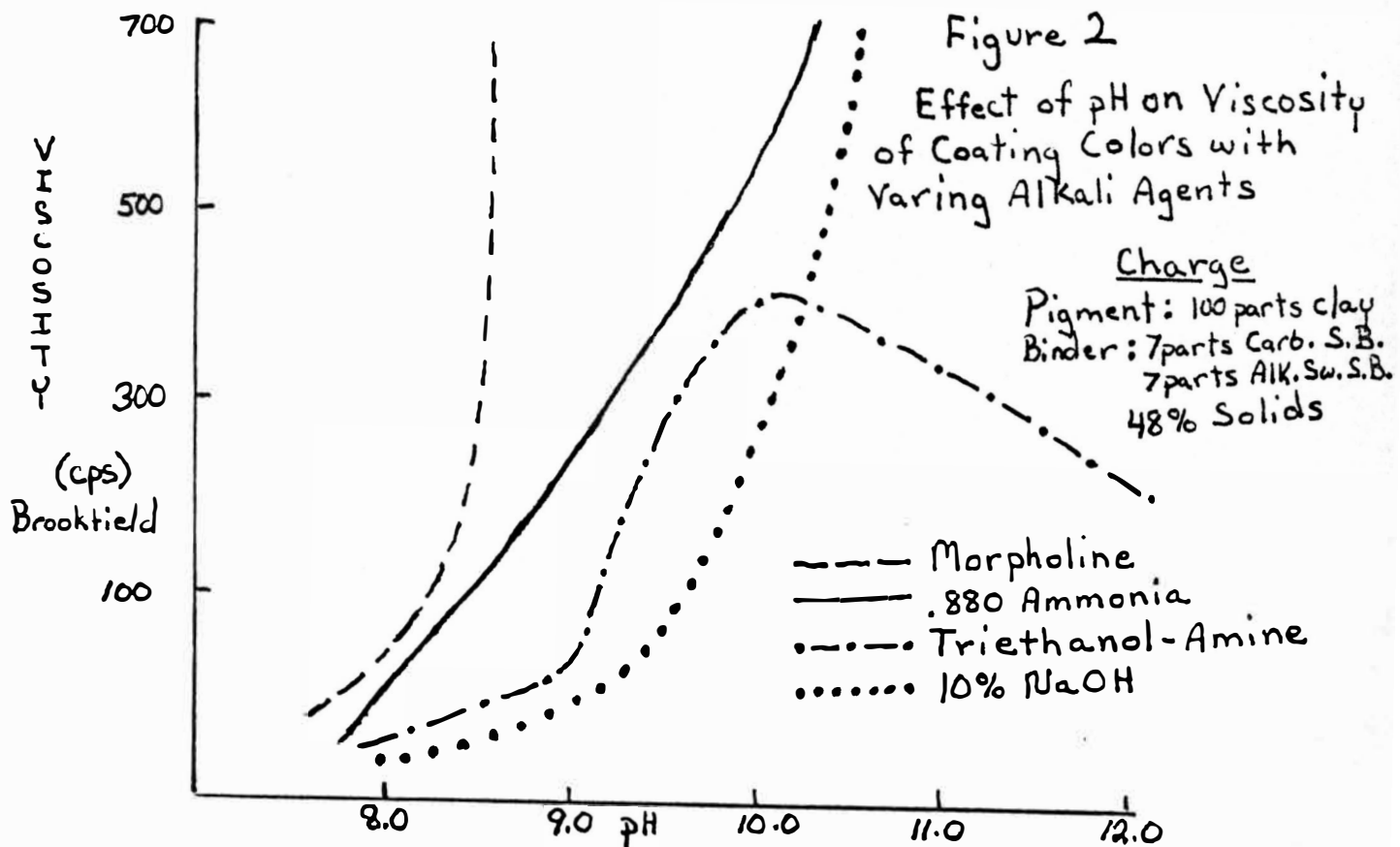
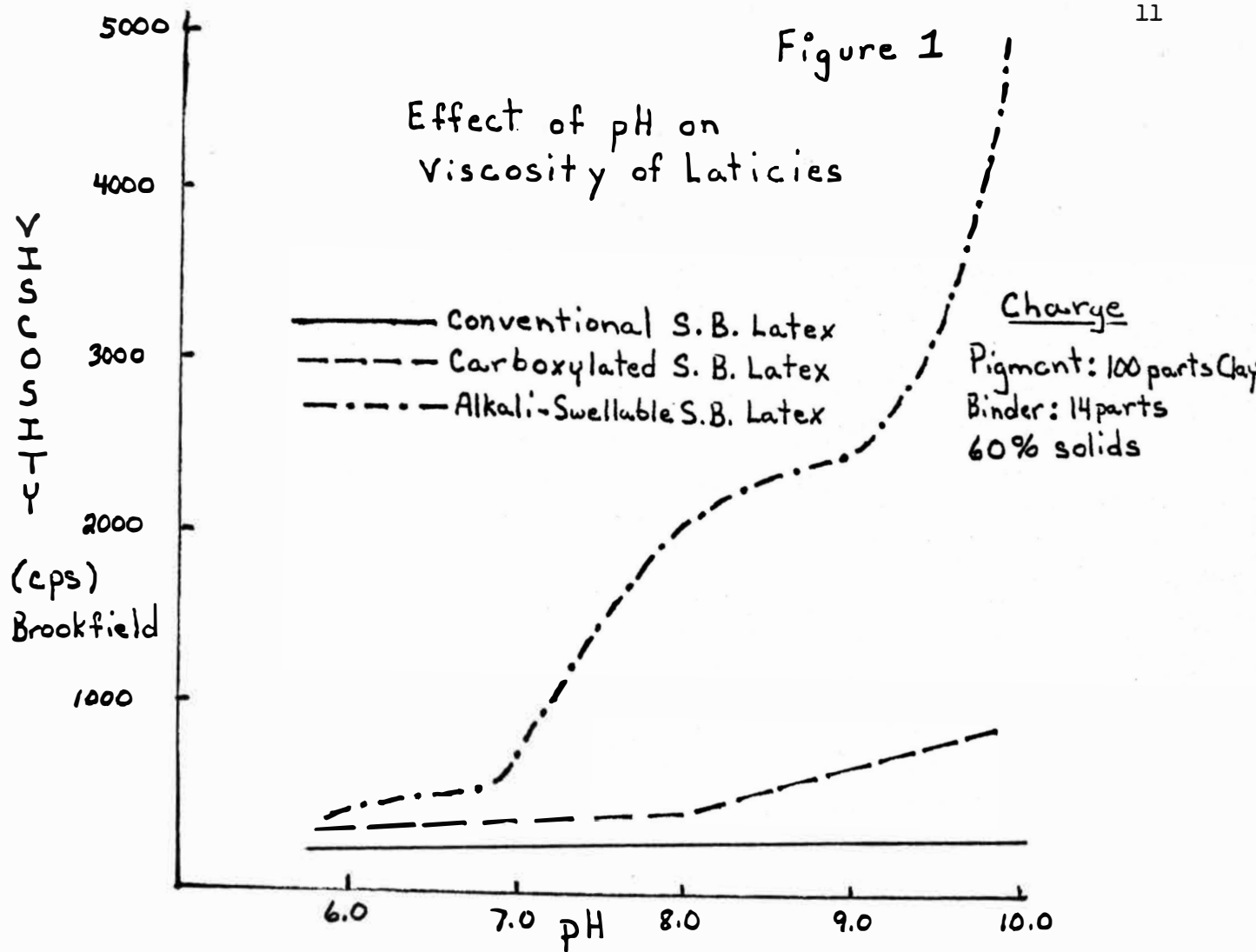
Styrene-butadiene is still the major synthetic binder used in paper coatings. It was first introduced in the late 1940's as a cobinder with natural binders and was used in very small amounts. The problems with early styrene-butadiene latexes were that they yellowed with ultraviolet light and upon drying, the residual butadiene monomer gave off strong odors. This was very bad for the bread wrap papers at the time, so work was done to overcome the problem. During the 1960's, carboxylated styrene-butadiene latexes came into the picture. By adding small amounts of carboxylic acid, and by varying molecular weights of the copolymer, the residual odor and yellowing resistance was improved. Less emulsifier was needed, which increased the water retention, along with having better adhesive strength and increased stiffness.³ Almost all carboxylated latexes are pH sensitive. They thicken slightly around the neutral to 8 pH level and generally produce higher viscosity coating colors. Some degree of viscosity control can be obtained by using these latexes. Most carboxylated styrene-butadiene latexes are sold at pH near the neutral point.

The ratios of the monomers in the styrene-butadiene polymer gives control over the latex flexibility. A ratio of 80% styrene - 20% butadiene will produce a non film forming emulsion, whereas a 75% butadiene - 25% styrene ratio will produce a soft rubber. Styrene gives the film hardness and dimensional stability, while butadiene gives the film elasticity, flexibility, and softness. By blending these monomers, the character of the film can be altered. Normal paper coating ratios are about 60-66% styrene to 34-40% butadiene.⁷

Alkali-Swellable Styrene-Butadiene Latex

In the alkali-swellable styrene-butadiene latex, a functional group is added which thickens the latex with increasing pH. The alkali-swellable latexes will take on water at a pH increase above seven. The carboxyl groups oriented on the surface react with the base to form a salt. This reduces the mobile water and increases the viscosity and water retention of the color. Some viscosity control can be achieved by pH control.⁴ In Figures 1 and 2, viscosity is plotted against pH for a conventional styrene-butadiene latex, a carboxylated styrene-butadiene latex, and an alkali-swellable styrene-butadiene latex.⁶ The effect of alkali-agent on alkali-swellable latex is also shown. Although the coating color is only 48% solids, changes in viscosity with different bases can still be observed. Ammonia will be used in this study as the alkali-agent.⁵

Alkali-swellable styrene-butadiene latexes are gaining wide use in the paper coating area. The comparable price of protein (37¢ to 40¢ per pound) and increased energy costs of cooking starch have made its use possible. Cationic starch, which is a good replacement for protein, cannot be used on low solids coatings, or an air knife system. Mottle occurs because of the high viscosity starch creates and the high water retention it has. Alkali-swellable latexes are being used more and more as replacements for protein in conjunction with other nonswellable latexes. Conventional styrene-butadiene latexes are priced between 38¢ to 40¢ per pound. Carboxylated styrene-butadiene latexes are a little higher at 43¢ to 45¢ per pound, and the alkali-swellable styrene-butadiene latexes are about 43¢ per pound.^{6, 12}



Acrylic Latexes

Acrylic monomers can be polymerized in many ways and into many combinations of latexes just like the styrene-butadiene monomers. In an alkyl-acrylate or vinyl ester family of monomers, the lowest family member usually gives the hardest and toughest polymer. The polymer gets more flexible, softer, and more resistant as the carbon content of the copolymer increases.

Acrylic monomers can be varied by adding certain functional groups to the polymer chain. Some common monomers are listed below:¹

Methyl methacrylate

Ethyl acrylate

Butyl acrylate

Acrylic acid

Vinyl acetate

The ratios of hard to soft monomer is in the range of 40:60 in most latexes. Particle size and type of emulsifier will affect the properties of the latexes.

Acrylics first came into the market in the late 1950's. Early latexes did not have the binding strength so the industry turned to carboxylated acrylic emulsions. They had low odor, low viscosity, and good stability. Their high price and short supply moved the industry towards carboxylated ethylene-acrylic acid copolymers. These latexes displayed the same low viscosities and low water resistance as the carboxylated styrene-butadienes.

An alkali-swellable acrylic vinyl-acetate which displays the same characteristics as the swellable butadiene latex, has been developed and

is proposed to be a replacement for casein and protein. By adding a vinyl acetate functional group to the copolymer, the latex becomes pH swellable. It is presently being used as a synthetic protein in combination with a conventional styrene-butadiene latex in all synthetic binder systems. It is priced at 36¢ per pound. A viscosity comparison with a conventional styrene-butadiene latex is shown in Figures 3 and 4, along with a Hercules rheogram showing high shear viscosities of each. An expected alkali-swellable acrylic latex rheogram is also shown.⁸ An alkali-swellable vinyl acetate will be tested in this study for viscosity variations with increasing pH.

Poly Vinyl Acetate

About 80,000 tons of poly vinyl acetate were marketed in 1972. Vinyl acetate can be polymerized with itself to form a homopolymer. This emulsion is very water sensitive, hard, and brittle. PVAc is composed of a vinyl acetate copolymer and an ethylhexyl acrylate copolymer. Although it is given the name poly vinyl acetate, it is really a derivative. This polymer does have fairly good binder properties and is used somewhat with carboxylated styrene-butadiene in all synthetic systems.¹ The price of PVAc is at 36¢ to 38¢ per pound. A 10% increase is expected this year because of acetic acid shortages. Acetic acid is the basic unit of the emulsion.⁹

100% Synthetic Binder Systems

There are presently six basic synthetic binder systems in use today. They are listed on the following page with recent market values.⁵

Figure 3

Effect of Per Cent Solids on Viscosity of non swellable binder systems

VISCOSITY

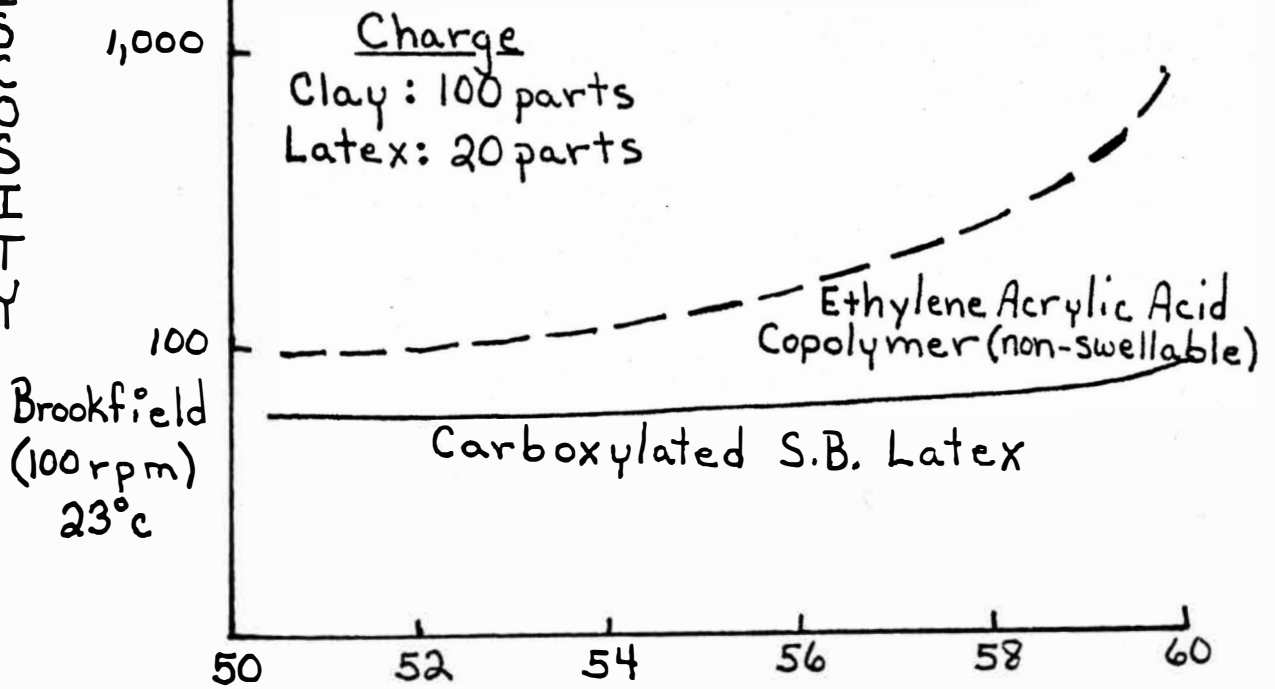
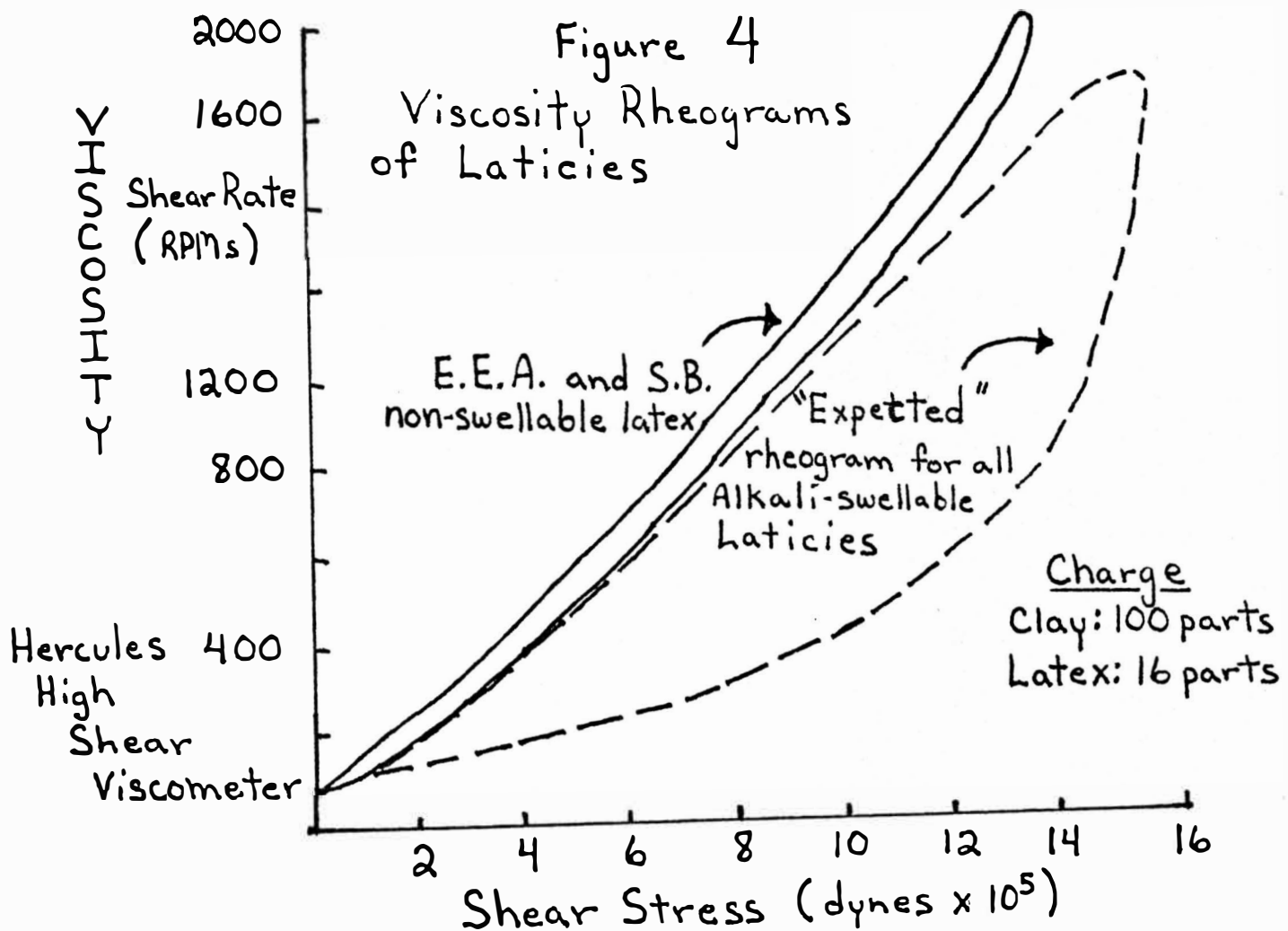


Figure 4

Viscosity Rheograms of Laticies



-- 1.	<u>Alkali-swellable vinyl acetate</u>	36¢ per pound
	Carboxylated styrene-butadiene	45¢
-- 2.	Carboxylated styrene-butadiene	45¢
3.	<u>Carboxylated styrene-butadiene</u>	45¢
	High styrene styrene-butadiene	42¢
4.	<u>Carboxylated styrene-butadiene</u>	45¢
	Vinyl acetate	38¢
-- 5.	<u>Carboxylated styrene-butadiene</u>	45¢
	Alkali-swellable styrene-butadiene	43¢
6.	Alkali-swellable styrene-butadiene	43¢
--	Works well on board coatings.	
	All prices based on mill delivery 5,000 pounds.	

Their finished coating properties are all about the same and are much like a protein/latex or starch/latex system. The viscosities of the alkali-swellable systems must be watched because viscosity increases with pH. All papers coated with these systems reach maximum water resistance and wet pick after approximately twenty-four hours. The 100% synthetic systems will have coatings of higher gloss and better light stability than those of protein/latex mix systems. By changing the blend ratios of the mixed synthetic systems,^{1,3,4,5} the coating properties can also be changed to suit the manufacturer's needs. Conventional styrene-butadiene latexes have very poor water retention properties, which make them unsuitable as an all synthetic binder system. They produce paper coatings which are limp and flexible. Carboxylated styrene-butadiene is used in the board coating area because it requires the least total binder. The 100% binder system using a carboxylated styrene-butadiene, and an alkali-swellable styrene-butadiene, does produce a board coating with satisfactory gloss and wet pick.

The 100% alkali-swellable styrene-butadiene system in coated board does not work well. The coating can be applied easily, but glueability decreases after three months to a point where it cannot be glued. By using an alkali-swellable vinyl acetate instead of the swellable styrene-butadiene latex, aging characteristics can be improved.⁵ For this study, a conventional styrene-butadiene latex will be used instead of a carboxylated styrene-butadiene, in conjunction with a swellable latex. The conventional styrene-butadiene latex will have less effect on the alkali-swellable latex as the carboxylated styrene-butadiene would.

Water Retention

Water retention is the capacity of a coating color to hold back its water and not release it to the paper substrate. If water escapes too fast into the paper, adhesive will also follow. This has a serious effect on binder migration. Binder migration, either into the substrate or heated surface, affects coating properties. Three important effects are listed below.¹

Ink receptivity - too much migration to surface

reduces ink absorbency

- ink mottle

Glueing - too much migration to surface

reduces glueability

Pick resistance - excessive migration into substrate

causes picking and binder starved areas

Figures 5 and 6 show the effect of pH and temperature on water retention. Samples were tested on a Thomin conductivity and S.D. Warren

Current Testers.^{10,11} Binder levels were varied using a conventional styrene-butadiene and carboxylated styrene-butadiene latex. Water retention can be seen to decrease with increasing temperature, so this study was conducted at room temperature (24 degrees centigrade). From the second chart, the effect of pH upon water retention can be shown. Using a carboxylated styrene-butadiene latex as the binder, water retention increases with increasing pH. Taller and Dill, using a sonic water retention tester, concluded that coatings with high water retention values will give a strong uniform coating.¹¹

In a trailing blade application, the "snap back" effect, of water being forced out of the coating, at the nip, causes solids buildup at the blade. This creates scratches on the paper and starved coating areas. Coatings with high retention are alleged to counter this effect.⁴

Figure 5

Effect of Temperature
on Water Retention of
Coating Colors

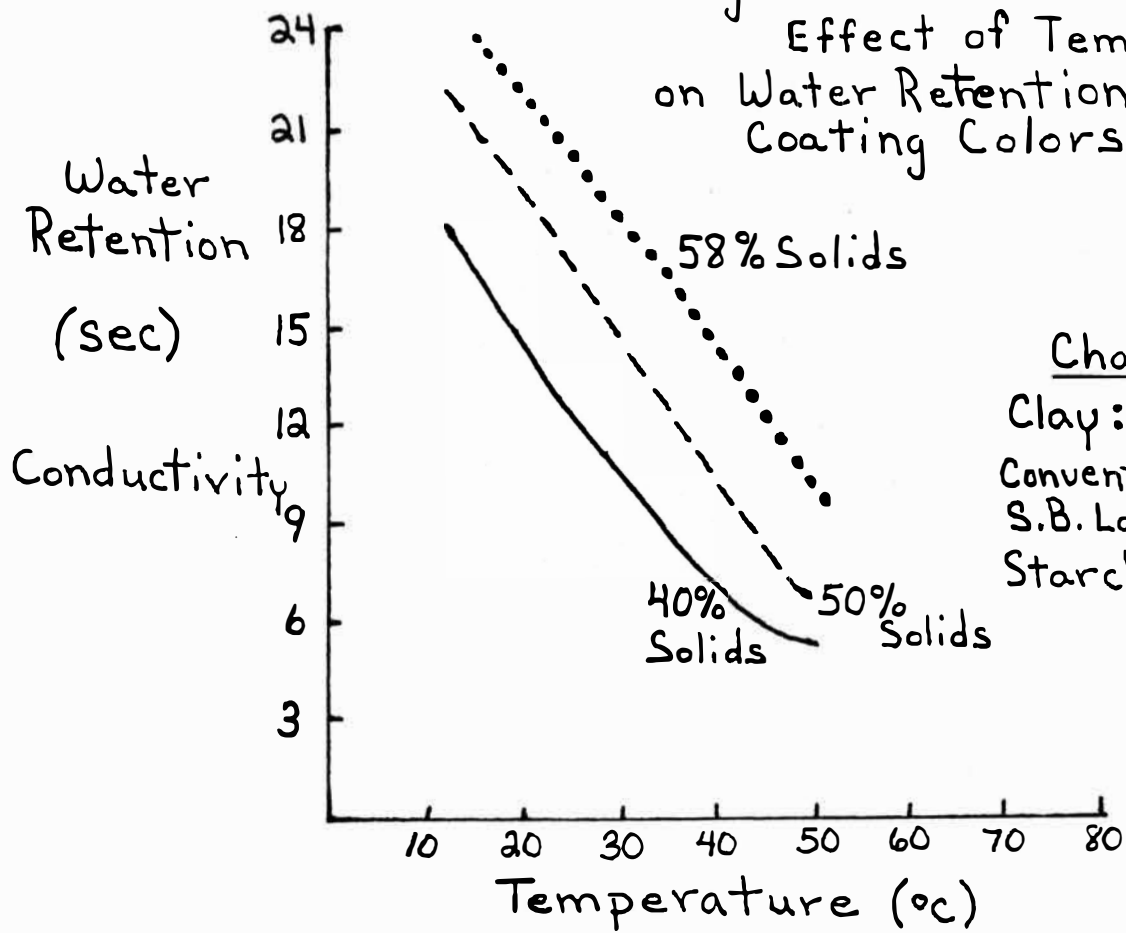
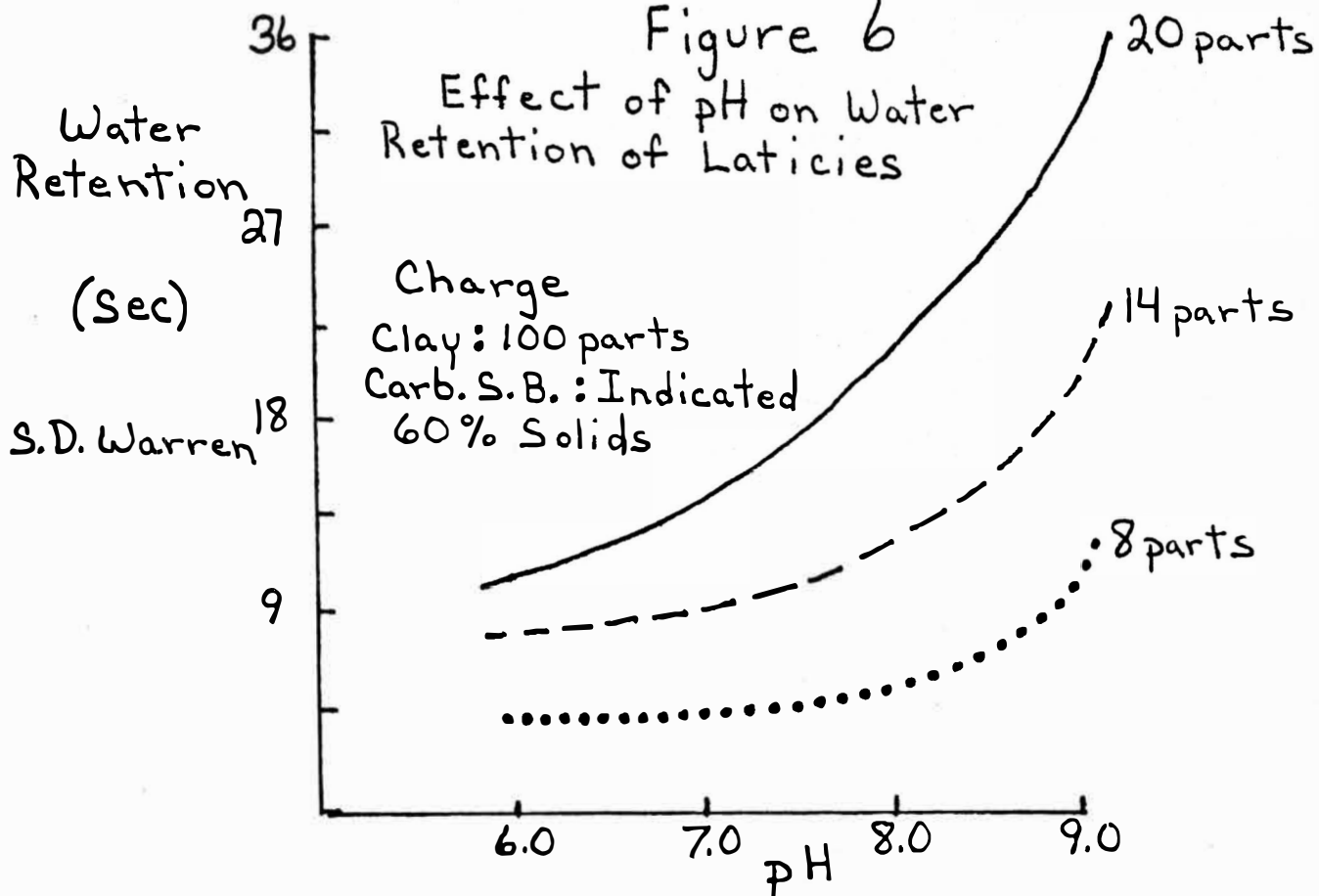


Figure 6

Effect of pH on Water
Retention of Laticies



Experimental Procedure

Materials

Coating formulations:

--Alkali-swellable styrene-butadiene -- Dow Latex 635

price - 43¢ per pound, 48% solids, pH 5.4

Brookfield vis. 96 cps (no. 2 spd., 100 rpms)

--Alkali-swellable vinyl acetate -- Rohm and Haas AR74

price - 36¢ per pound, 45% solids, pH 4.7

Brookfield vis. 104 cps (no. 2 spd., 100 rpms)

--Carboxylated styrene-butadiene -- Dow Latex 673

price - 46¢ per pound, 46% solids, pH 6.2

Brookfield vis. 60 cps (no. 2 spd., 100 rpms)

--Conventional styrene-butadiene -- Dow Latex 620

price - 38¢ per pound¹², 50% solids, pH 6.0

Brookfield vis. 95 cps (no. 2 spd., 100 rpms)¹³

--Engelhard HT predispersed

--TSPP dispersant

--Ammonia

Coating machine trial

--Base stock -- Niagara groundwood

B.W. 31.8, Sheffield porosity 73, Tappi brightness 71.7, Tappi opacity 87.0

--Binder

Used alkali-swellable styrene-butadiene latex -- 1st run

Used alkali-swellable styrene-butadiene/conv. styrene-butadiene -- 2nd run

--Calender (lab model at Western Michigan University 30 psi, 6 pass)

Testing equipment

Viscosities: Low shear -- Brookfield viscometer

High shear -- Hercules viscometer

TAPPI T648 su-64

Pick: IGT pick tester

TAPPI T499 su-94

Gloss: Hunter Lab Model D16, 75 degrees

Opacity: B&L 2 Opacimeter

Brightness: Automatic Color-Brightness Meter

K & N: 2-minute ink penetration
Brightness reduction measured

Procedure

--Latexes were "viscosity tested" at high and low shear.

--Coating formulation using alkali-swellable styrene-butadiene 100%
binder was calculated.

<u>Charge</u>	<u>Parts per hundred weight</u>	<u>Grams</u>
Engelhard HT predispersed clay	100	200
Alkali-Swellable Styrene-Butadiene	12, 15, 18	24, 30, 36
TSPP - dispersant	1	2
H ₂ O	to 55% total solids	

- Coating color was treated with ammonia for pH adjustments.
- High and low shear measurements were taken at several pH levels (7.0, 7.5, 8.0, 9.0, 10.0).
- The alkali-swellaable vinyl acetate was also tested as above, only TSPP was not used in the formulations.
- The carboxylated styrene-butadiene (673) was mistaken for an alkali-swellaable latex and after first test was dropped.
- A coating formulation using 50% conventional styrene-butadiene and 50% alkali-swellaable styrene-butadiene was made and tested. Only one test was completed at 55% color solids. This formula was duplicated for the coating machine.
- The alkali-swellaable styrene-butadiene binder formulation was remade without TSPP and tested. This formula was also duplicated for the coating machine. 18 parts binder level was used.
- Tables I and II include coating machine charge for two runs.
- Coating demand:

paper: $700 \text{ ft/min} \times 26'' \times \frac{1'}{12''} = 1,517 \text{ ft}^2/\text{min}$

$\frac{30 \text{ lbs}}{3300} \times 1,517 = 13.8 \text{ lbs/min}$

coat
weight: 8 lbs

$\frac{8}{3300} \times 1,517 = 2.8 \text{ lbs/min}$

$2.8 \times 5 \text{ runs} = 14 \text{ lbs coating}$

Start with 250 lbs clay and mix at 71% solids in Cowals disperser.

Add water and latex while raising the water content to 55% solids.

--Coating run on flooded nip coater using a blade applicator.

Coat weight was kept at 8 pounds, with about 2-3 psi blade pressure. Machine speed was set at 600 ft/min.

--Coating color pH was raised with ammonia. Samples were taken before and after each addition for a percent solids check.

--Coated paper was super calendered on the lab calender at 30 psi, 6 pass.

--Coated paper was tested for Tappi brightness, opacity, gloss, K & N ink receptivity, pick, and basis weight. Percent solids of the coating colors were determined for water retention comparisons.

Coating Machine Color Formulations

23

TABLE I - Total Alkali-Swellable System

	Parts	% Solids	Dry weight	Wet weight	H ₂ O
E ₁ Englehardt HT Clay	100	100	200, lbs.	—	—
Alkali Swellable S.B. Latex	18	48	36, lbs.	75, lbs.	39, lbs.
H ₂ O	—	—	—	154, lbs.	154, lbs.
Total	118	55	236, lbs.	229, lbs.	193, lbs.

pH: Adjusted with Ammonia; 7.0, 7.5, 8.0, 9.0, 10.0

TABLE II - Alkali-Swellable S.B. Conventional S.B.

	Parts	% Solids	Dry weight	Wet weight	H ₂ O
Englehardt HT Clay	100	100	250, lbs.	—	—
Alkali Swellable S.B. Latex	9	48	22.5, lbs.	47, lbs.	24.5, lbs.
Conventional S.B. Latex	9	50	22.5, lbs.	45, lbs.	22.5, lbs.
H ₂ O	—	—	—	194, lbs.	194, lbs.
Total	118	55	295, lbs.	286, lbs.	241, lbs.

pH: Adjusted with Ammonia; 7.0, 7.5, 8.0, 9.0, 10.0

Results and Discussion

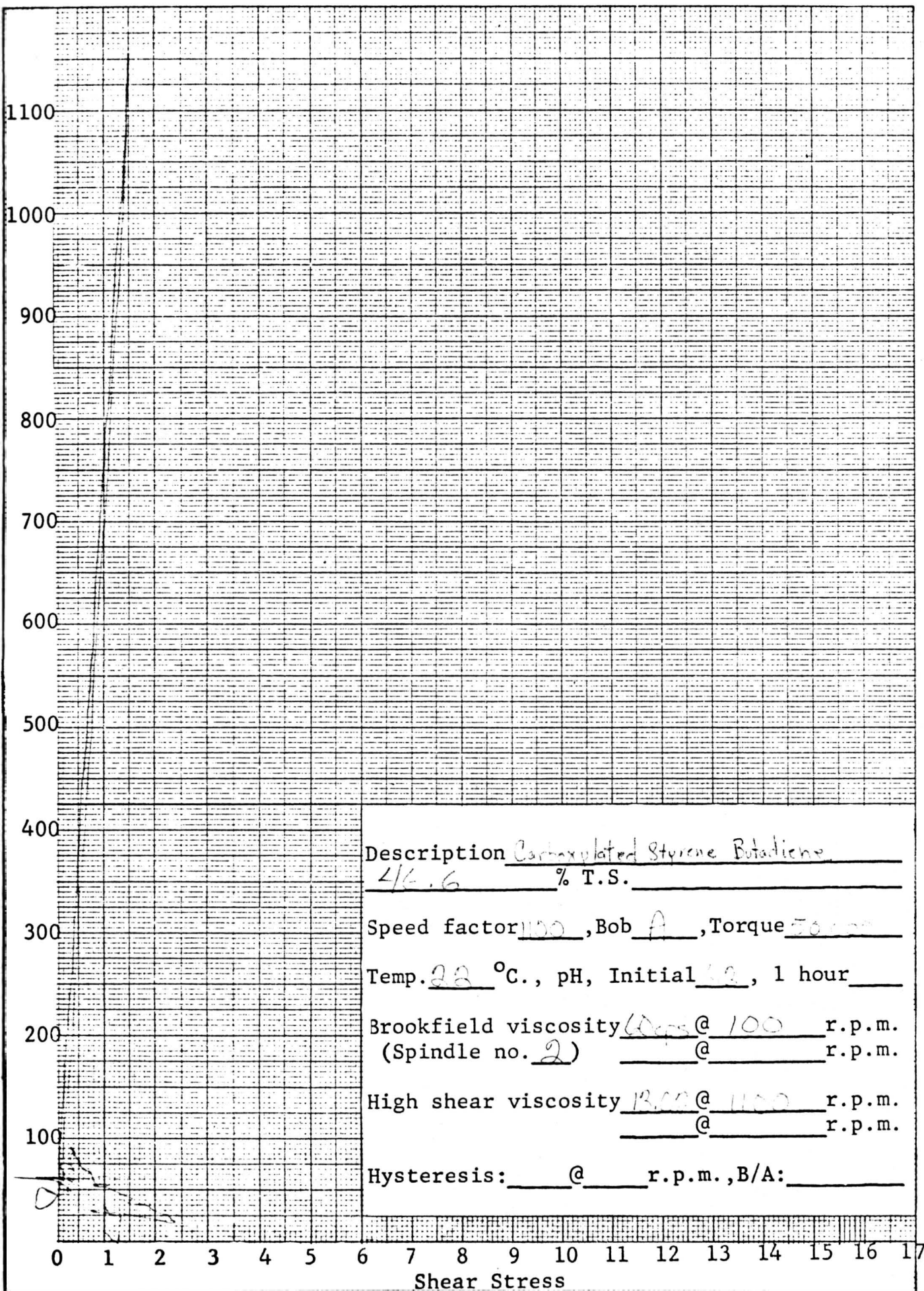
The Effect of pH on

Viscosity

Hercules rheograms 1, 2, and 3 show high shear viscosity characteristics of three latex binders at their storage state. The acrylic vinyl acetate, 3, shows a more plastic nature and a higher degree of thixotropy than the alkali-swellaable styrene-butadiene latex or the carboxylated styrene-butadiene latex. Because these latexes have no double bond in their backbone they become more plastic. This means it reforms more slowly under decreasing shear. In a blade coating operation a coating color must reform slowly, after the high shear imparted to it, or a buildup of dry color may result. This characteristic was also noted in the coating color samples.

Viscosities of the coating colors, at different pH levels were recorded. Viscosities of the alkali-swellaable latex systems did not compare with the graph in Figure 1. These systems showed increasing viscosity with increasing pH until 7.5-8.0 pH level. At this stage, all the alkali-swellaable systems began to decrease. Figures 7, 8, and 9 show the viscosity/pH graphs for two alkali-swellaable systems. Figure 7 shows the enormous viscosity difference between the alkali-swellaable acrylic vinyl acetate and the alkali-swellaable styrene-butadiene. The vinyl acetate polymer peaks in viscosity around 8.0 pH whereas the styrene-butadiene polymer peaks around 7.0 pH. Figure 9 shows the viscosity changes using

R. P. M.



Description Carboxylated Styrene Butadiene
46.6 % T.S.

Speed factor 100, Bob A, Torque 50.000

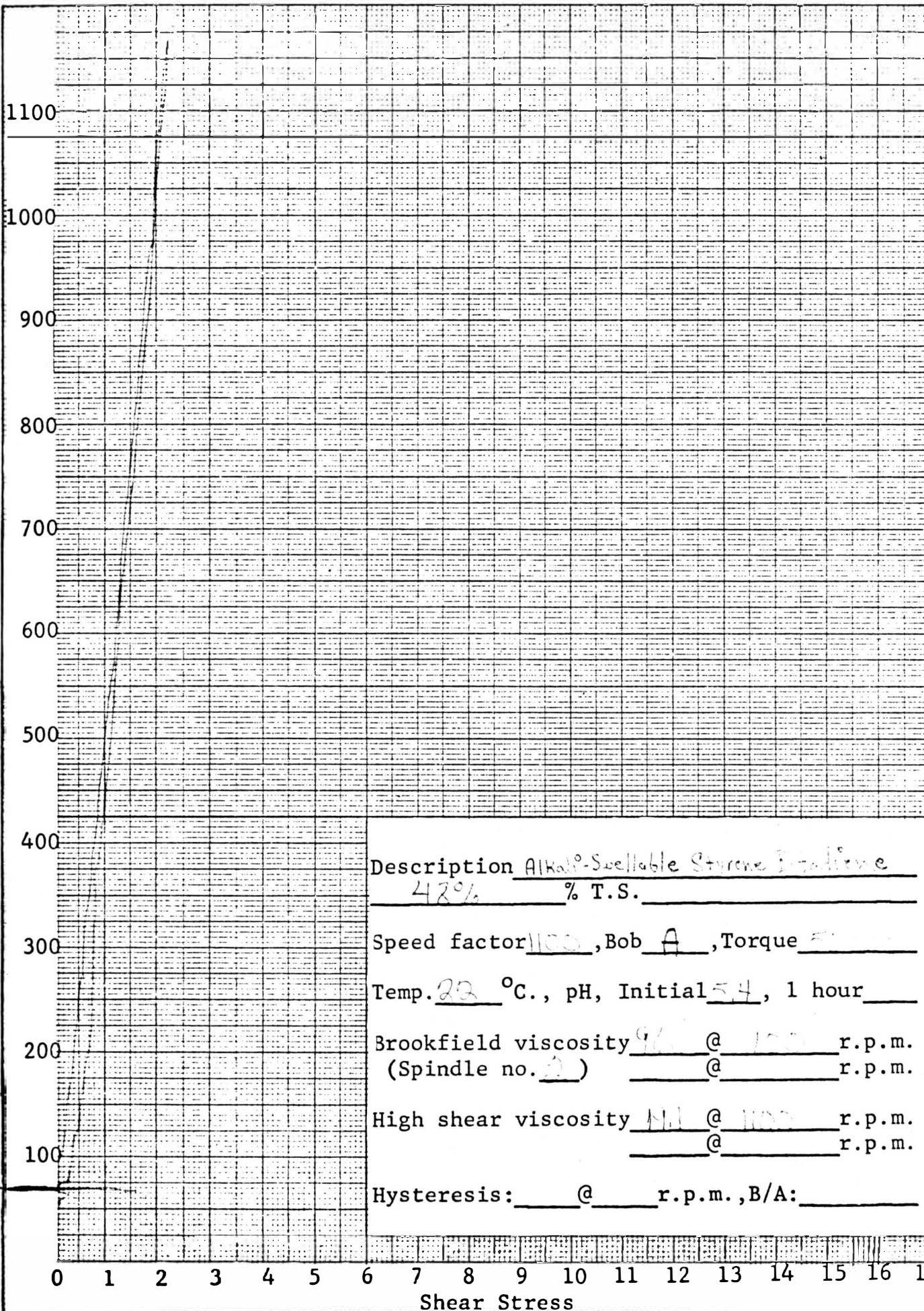
Temp. 22 °C., pH, Initial 52, 1 hour

Brookfield viscosity 600 @ 100 r.p.m.
 (Spindle no. 2) @ r.p.m.

High shear viscosity 1300 @ 1100 r.p.m.
 @ r.p.m.

Hysteresis: @ r.p.m., B/A:

R. P. M.



Description Alkal^o-Swellable Styrene Emulsion
48% % T.S.
 Speed factor 100, Bob A, Torque 5
 Temp. 22 °C., pH, Initial 5.4, 1 hour
 Brookfield viscosity 96 @ 100 r.p.m.
 (Spindle no. 2) @ r.p.m.
 High shear viscosity 111 @ 100 r.p.m.
 @ r.p.m.
 Hysteresis: @ r.p.m., B/A:

R. P. M.

1100

1000

900

800

700

600

500

400

300

200

100

Description Alkal^o Swellable vinyl acetate
45 % T.S.

Speed factor 100, Bob A, Torque 50,000

Temp. 28 °C., pH, Initial 4.7, 1 hour

Brookfield viscosity 154 @ 100 r.p.m.
 (Spindle no. 2) @ r.p.m.

High shear viscosity 45.5 @ 100 r.p.m.
 @ r.p.m.

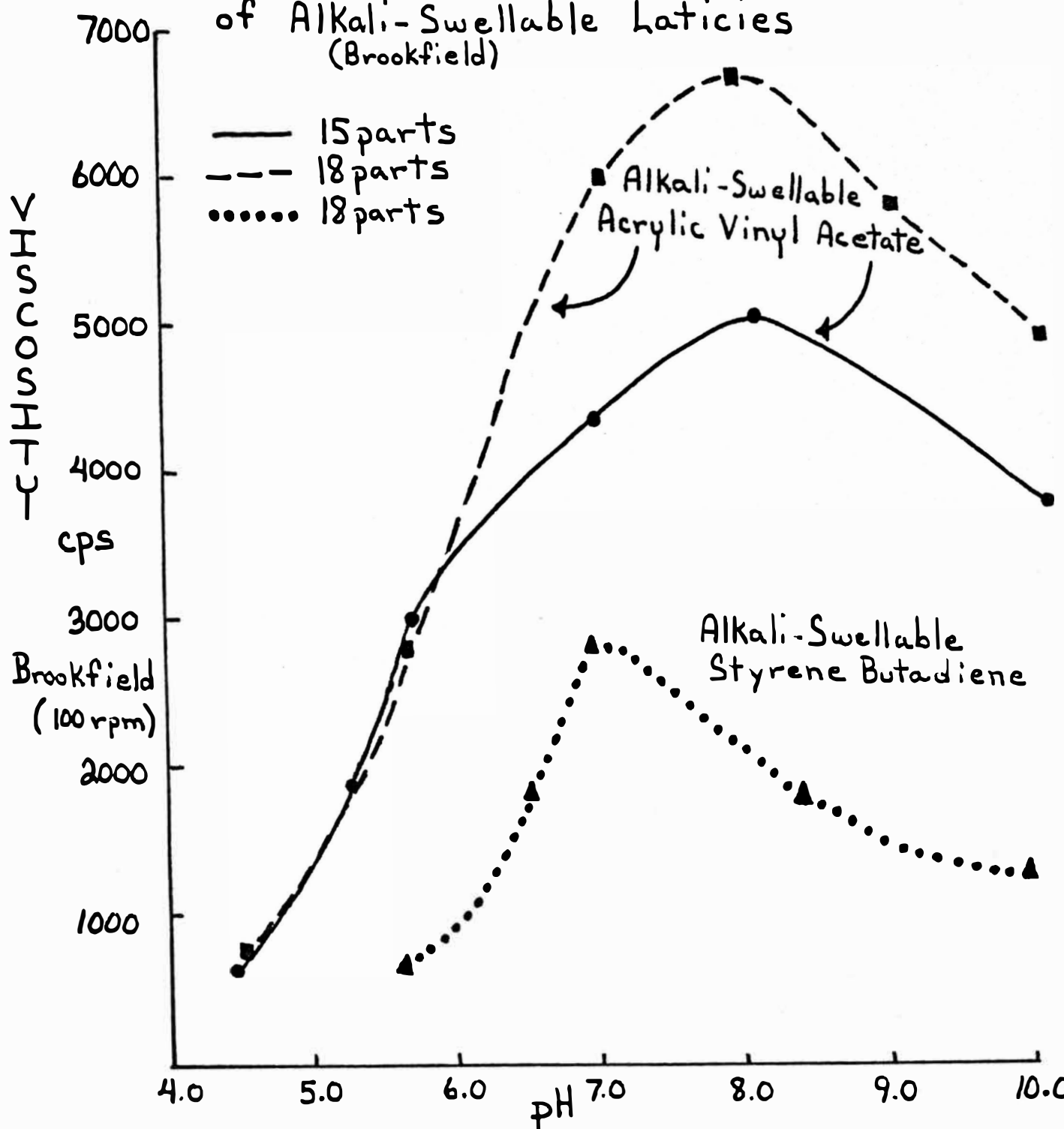
Hysteresis: @ r.p.m., B/A:

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

Shear Stress

Figure 7

Effect of pH on Viscosity
of Alkali-Swellable Laticies
(Brookfield)



Charge

Clay: Predispersed Englehardt HT

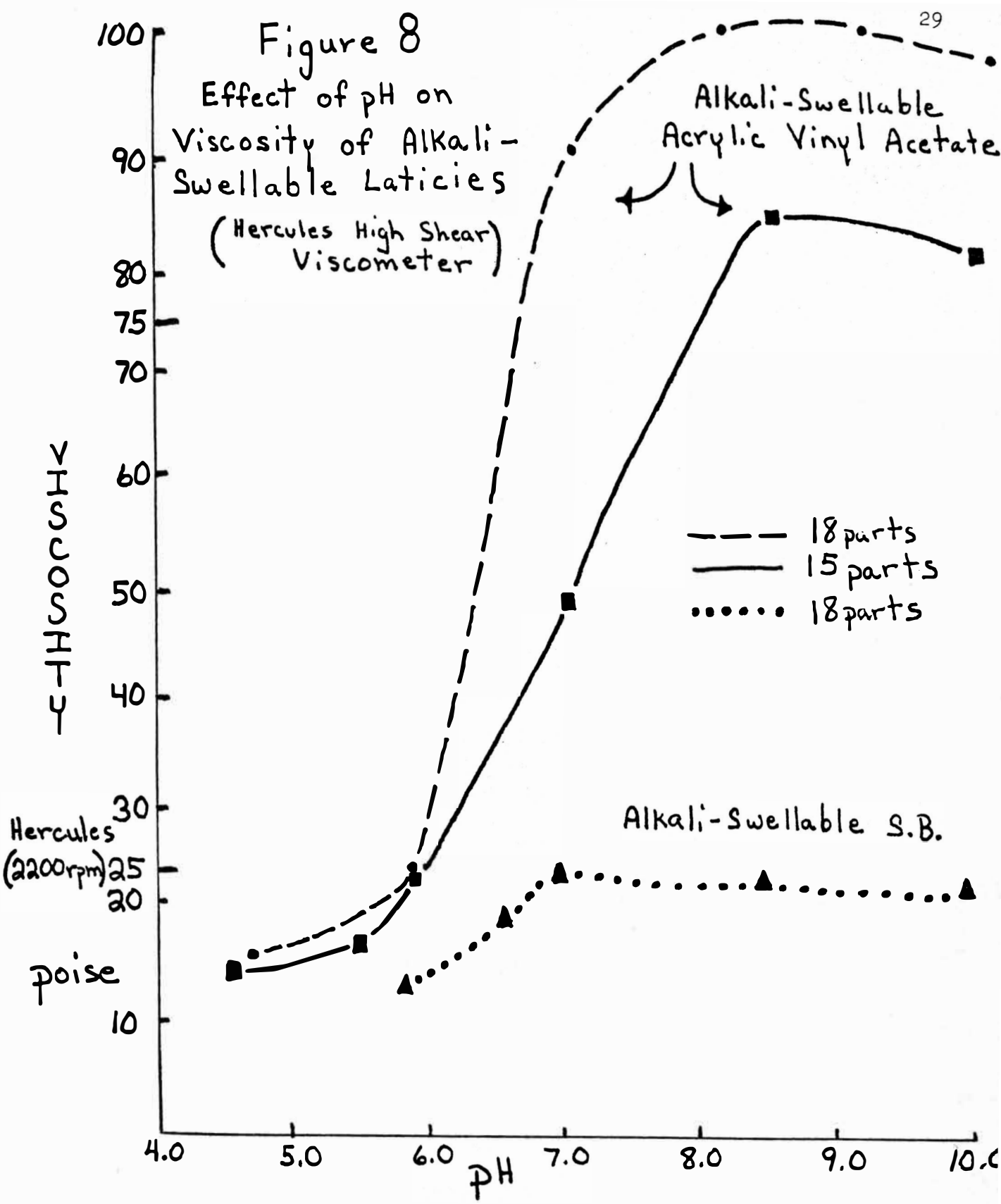
Binder: Alkali-Swellable Laticies; 15, 18 parts

No TSPP

55% Solids

Figure 8

Effect of pH on
Viscosity of Alkali-
Swellable Laticies
(Hercules High Shear
Viscometer)



Formula

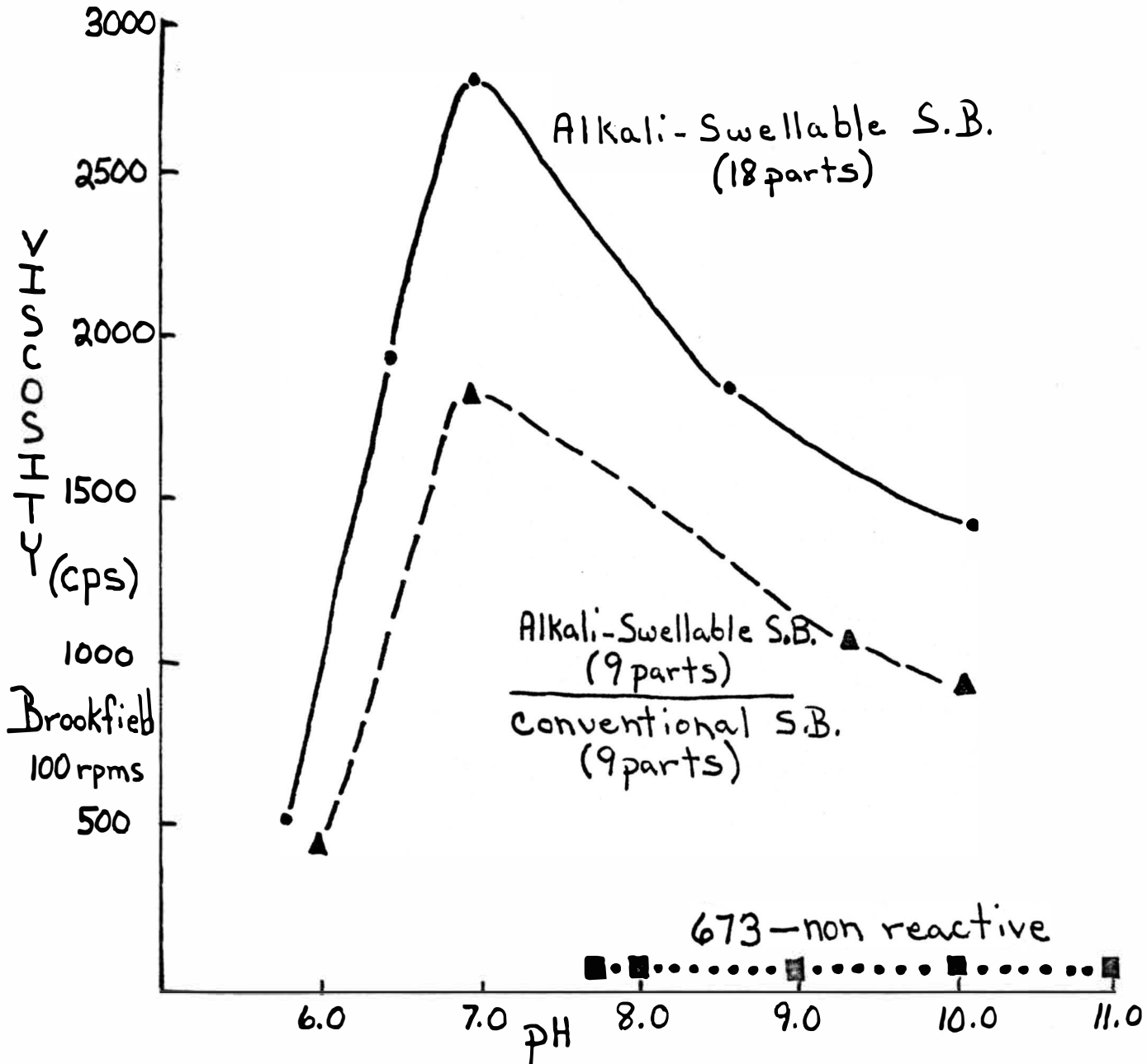
Clay; No. 2 HT — 100 parts

Binder; Alkali-Swellable Laticies — 15, 18 parts

55% Solids

Figure 9

Effect of pH on Coating Trial
Color Systems
Viscosity



Formula

Clay: Englehardt HT (predispersed)	100 parts
Binder: Alkali-Swellable S.B. (Run I)	18 parts
Alkali-Swellable S.B. (Run II)	9 parts
Conventional S.B.	9 parts

55% Solids

the coating machine formulation colors. The high point in viscosity falls around 7.0 pH and from there on decreases. The styrene-butadiene latex is much less pH sensitive towards viscosity than the acrylic vinyl acetate polymer, which is why it was used on the coating machine.

Rheograms 4 through 8 are the high shear results for the alkali-swellaable styrene-butadiene 100% binder system. In the neutral pH range, the rheograms show an increasing resistance to initial shear breakdown. This plastic nature is increased until about 7.5 pH where upon it begins to decrease. Thixotropic patterns also increase until around 7.5 pH where they too decrease. Rheograms 9, 10, and 11 are results of the vinyl acetate latex binder system, and although the values are much greater, their patterns are the same.

TSPP is often used as a disperser for pigment dispersion. Latex is a poor disperser, so TSPP was used in the alkali-swellaable styrene-butadiene formula. The results, Figures 10 and 11 as compared to Figure 7, show that the viscosities for the TSPP formulations are lower than the colors without it. TSPP, as a solid form, is very difficult to dissolve in water and complete initial dissolving was not possible. TSPP, or any disperser, was not used for this study, so a predispersed clay was used.

A percent solids analysis was determined before and after each pH adjustment, so an idea of the colors' water holding ability could be determined. This test is not very conclusive because the very small differences in percent solids are subject to error. The coating color was sampled from the bottom of the puddle coater and not from the blade. Improper mixing and circulation could also have affected the results.

R. P. M.

1100

1000

900

800

700

600

500

400

300

200

100

Alkali-Swellable
Styrene butadiene

Description Alkali-Swellable 18
117 % T.S.

Speed factor 100, Bob E, Torque 1

Temp. 24 °C., pH, Initial 5.9, 1 hour

Brookfield viscosity 515 @ 100 r.p.m.
(Spindle no. 2) @ r.p.m.

High shear viscosity 100 @ 2000 r.p.m.
@ r.p.m.

Hysteresis: @ r.p.m., B/A:

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

Shear Stress

R. P. M.

1100
1000
900
800
700
600
500
400
300
200
100
0

Description Alkal^o - Swellable
Styrene-butadiene 18pph
% T.S. 45

Speed factor , Bob 5, Torque

Temp. 24 °C., pH, Initial 5, 1 hour

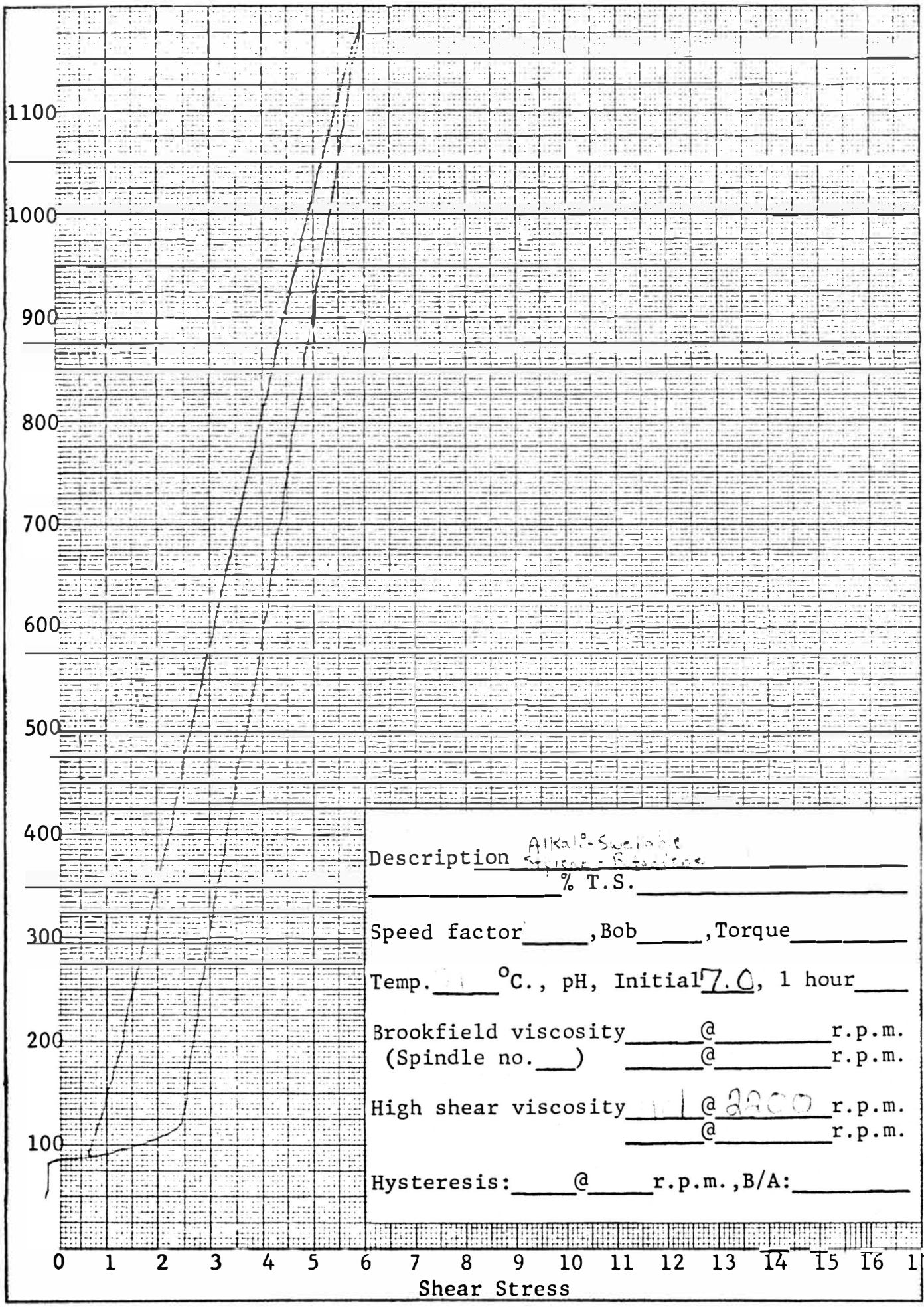
Brookfield viscosity 170 @ 1 r.p.m.
(Spindle no. 1) @ r.p.m.

High shear viscosity 15 @ 200 r.p.m.
@ r.p.m.

Hysteresis: @ r.p.m., B/A:

Shear Stress

R. P. M.



Description Alkali-Swellable
Styrene-Butadiene
 % T.S. _____

Speed factor _____, Bob _____, Torque _____

Temp. _____ °C., pH, Initial 7.0, 1 hour _____

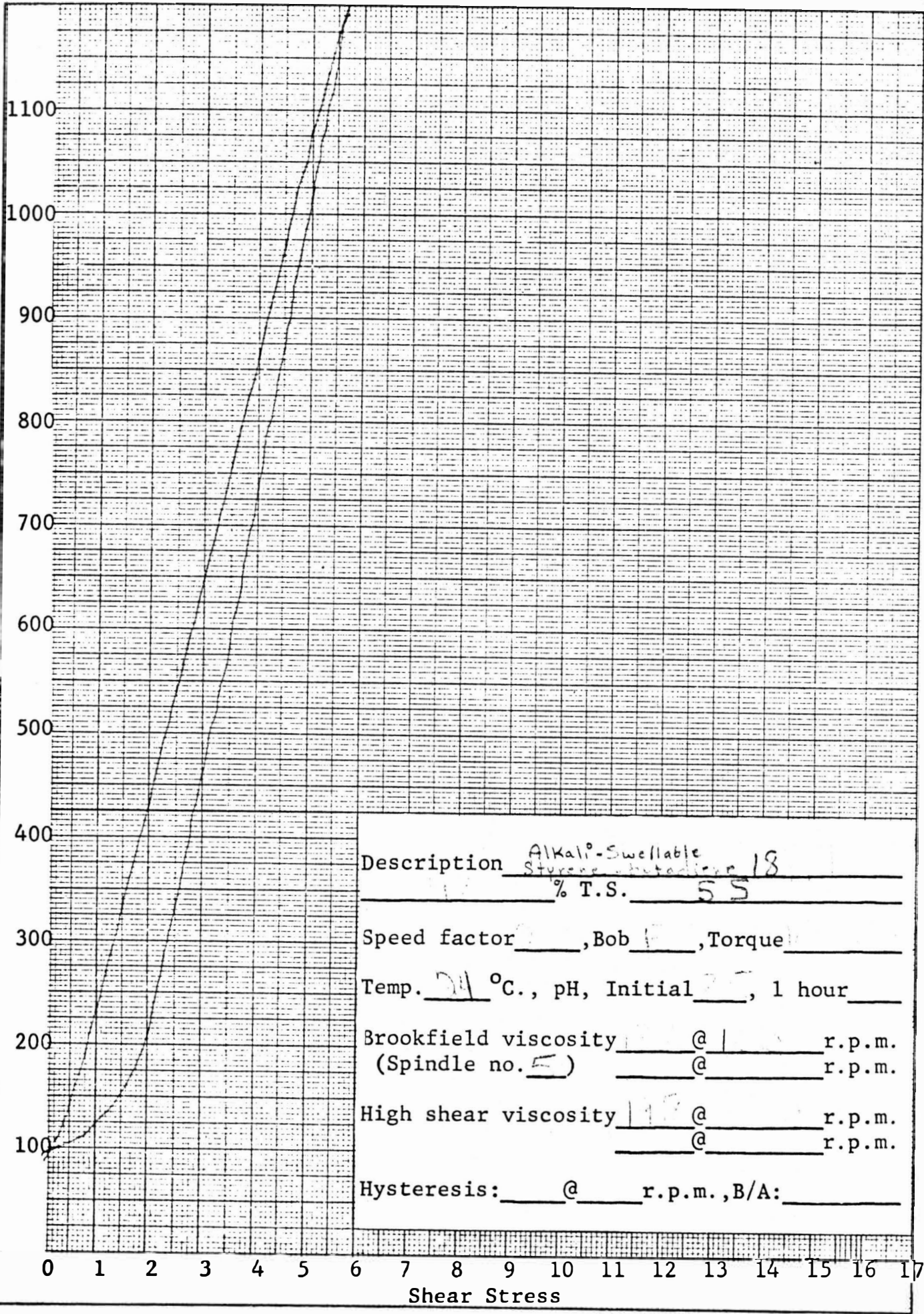
Brookfield viscosity _____ @ _____ r.p.m.
 (Spindle no. _____) _____ @ _____ r.p.m.

High shear viscosity 11 @ 2200 r.p.m.
 _____ @ _____ r.p.m.

Hysteresis: _____ @ _____ r.p.m., B/A: _____

Shear Stress

R. P. M.



Description Alkali-Swellable
Styrene-butadiene 18
 % T.S. 55

Speed factor 2, Bob F, Torque 1

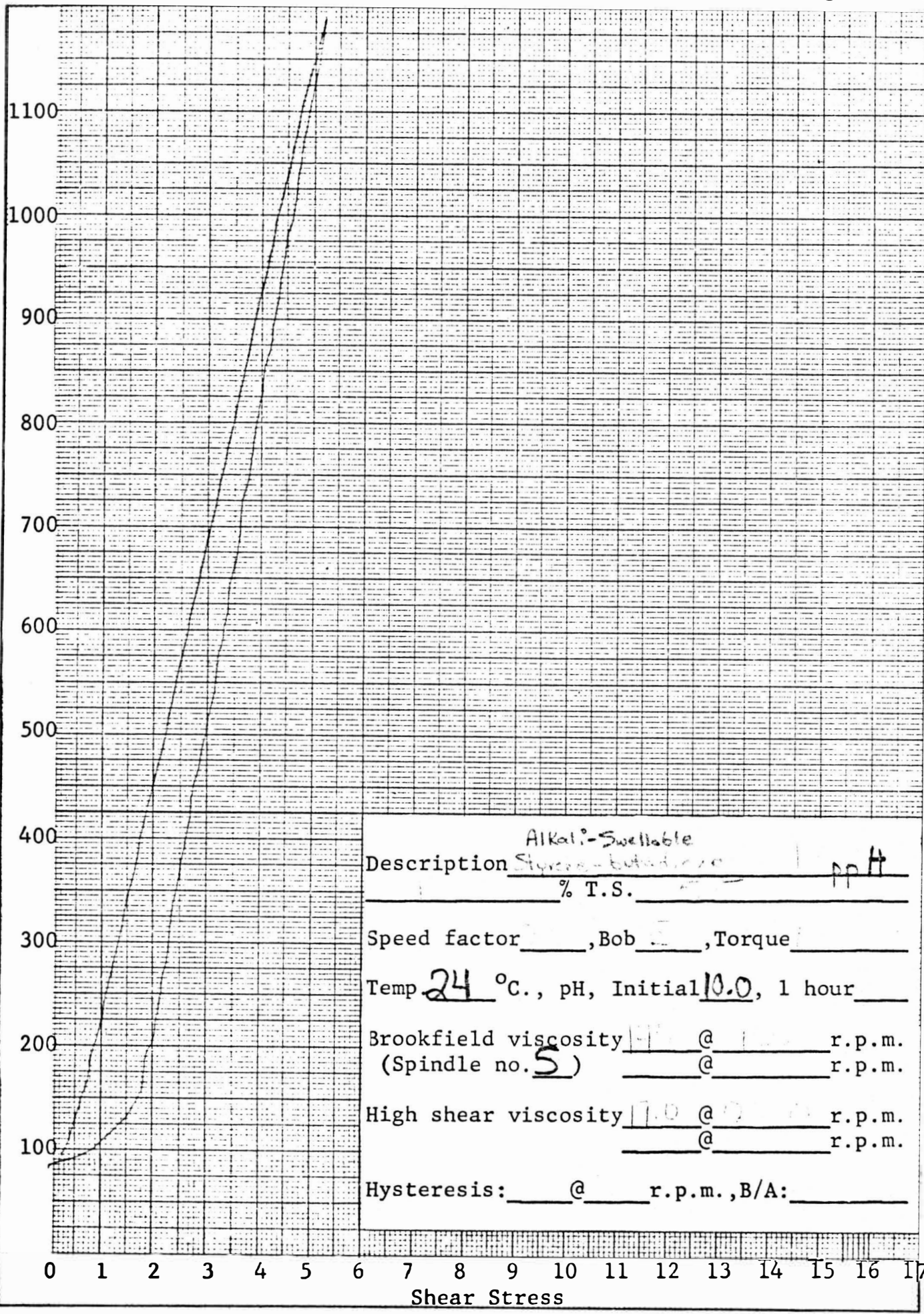
Temp. 24 °C., pH, Initial 25, 1 hour 1

Brookfield viscosity 150 @ 1 r.p.m.
 (Spindle no. 5) 150 @ 1 r.p.m.

High shear viscosity 117 @ 1 r.p.m.
117 @ 1 r.p.m.

Hysteresis: 1 @ 1 r.p.m., B/A: 1

R. P. M.



Description Alkali-Swellable Styrene-butadiene ppH
 % T.S. _____
 Speed factor _____, Bob _____, Torque _____
 Temp 24 °C., pH, Initial 10.0, 1 hour _____
 Brookfield viscosity 17.0 @ _____ r.p.m.
 (Spindle no. 5) _____ @ _____ r.p.m.
 High shear viscosity 17.0 @ _____ r.p.m.
 _____ @ _____ r.p.m.
 Hysteresis: _____ @ _____ r.p.m., B/A: _____

Shear Stress

Alkali-Swellable
Acrylic Vinyl Acetate

R. P. M.

Description Alkali-Swellable
Acrylic Vinyl Acetate
% T.S. _____

Speed factor _____, Bob _____, Torque _____

Temp. 14 °C., pH, Initial _____, 1 hour _____

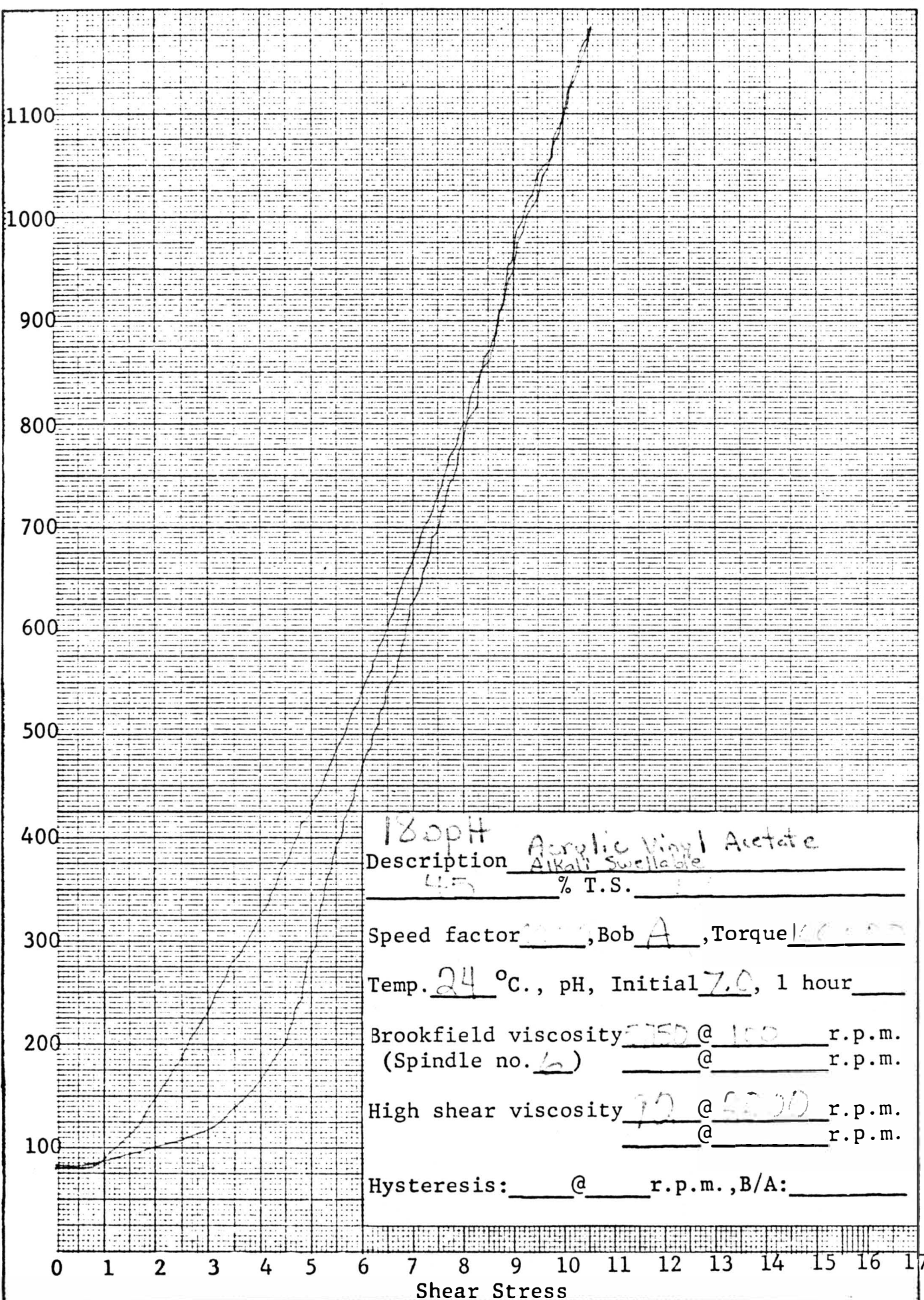
Brookfield viscosity _____ @ _____ r.p.m.
(Spindle no. _____) _____ @ _____ r.p.m.

High shear viscosity _____ @ _____ r.p.m.
_____ @ _____ r.p.m.

Hysteresis: _____ @ _____ r.p.m., B/A: _____

Shear Stress

R. P. M.



180pH
 Description Acrylic Vinyl Acetate
Alkali Swellable
4.5 % T.S.
 Speed factor 300, Bob A, Torque 100.00
 Temp. 24 °C., pH, Initial 7.0, 1 hour
 Brookfield viscosity 750 @ 100 r.p.m.
 (Spindle no. 6) @ _____ r.p.m.
 High shear viscosity 70 @ 5000 r.p.m.
 @ _____ r.p.m.
 Hysteresis: _____ @ _____ r.p.m., B/A: _____

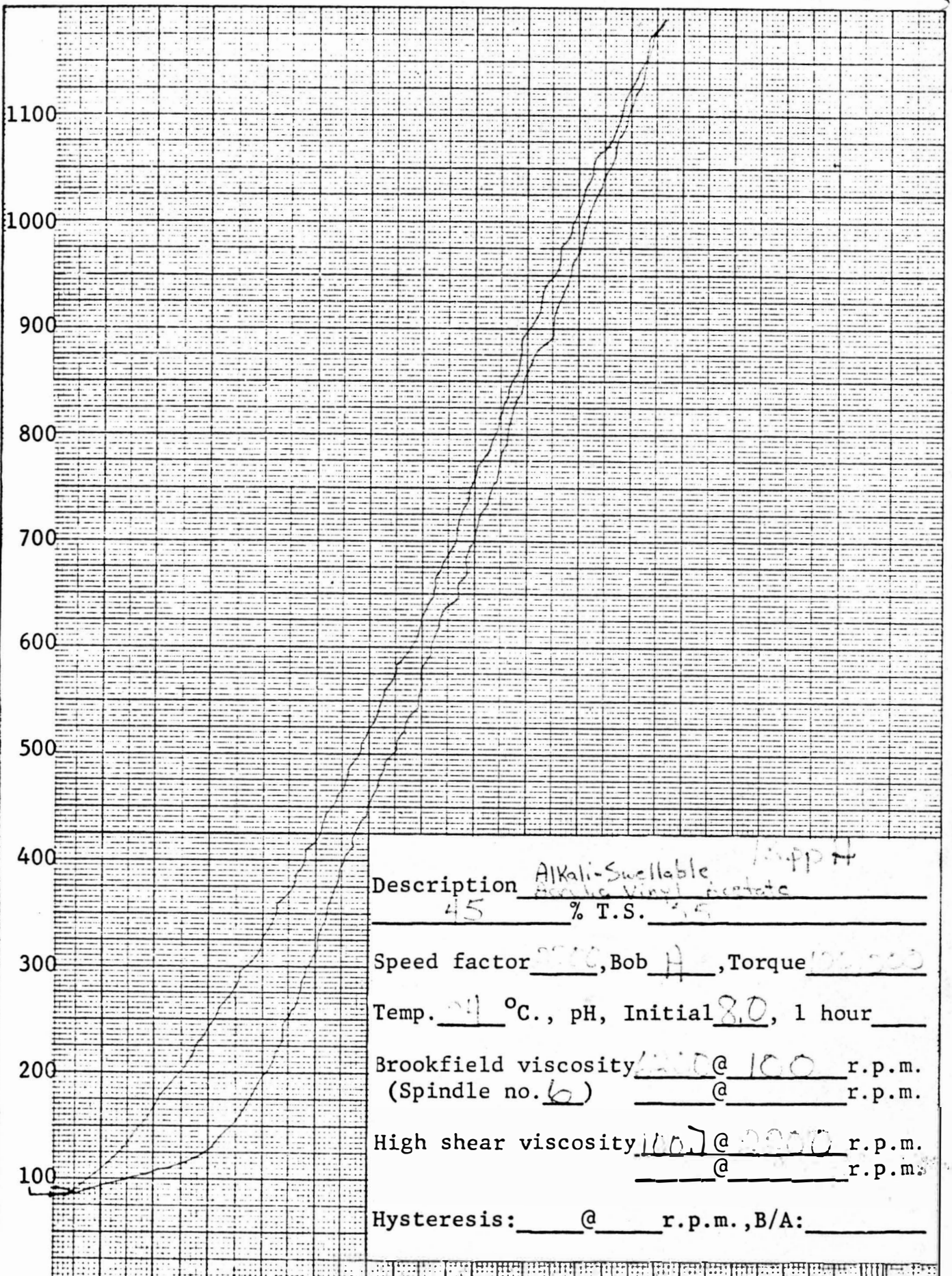
Shear Stress

R. P. M.

1100
1000
900
800
700
600
500
400
300
200
100

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

Shear Stress



Description Alkali-Swellable
45 45 % T.S. 4.5
Speed factor 5000, Bob A, Torque 100000
Temp. 24 °C., pH, Initial 8.0, 1 hour
Brookfield viscosity 1200 @ 100 r.p.m.
(Spindle no. 6) @ r.p.m.
High shear viscosity 100 @ 2000 r.p.m.
@ r.p.m.
Hysteresis: @ r.p.m., B/A:

Figure 10
Effect of Binder Level
on Viscosity of Coating
Colors

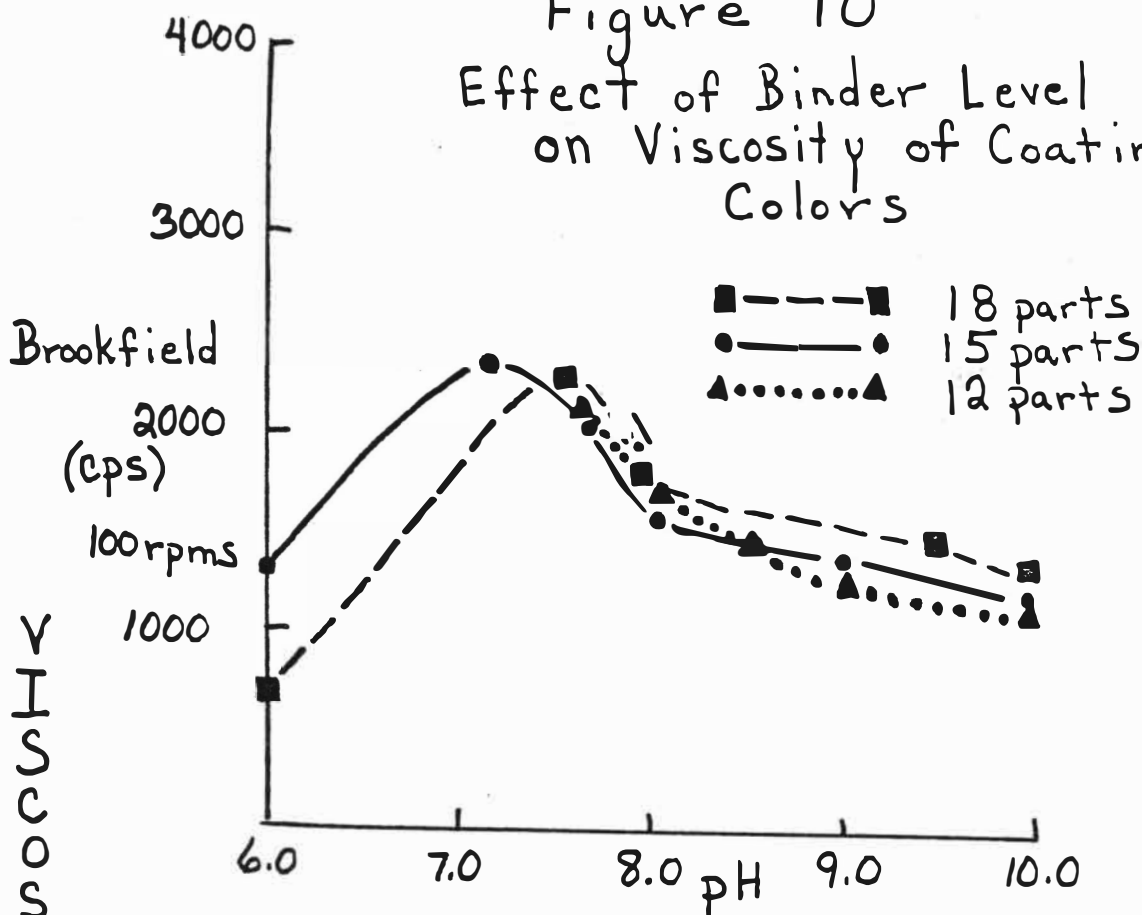


Figure 11

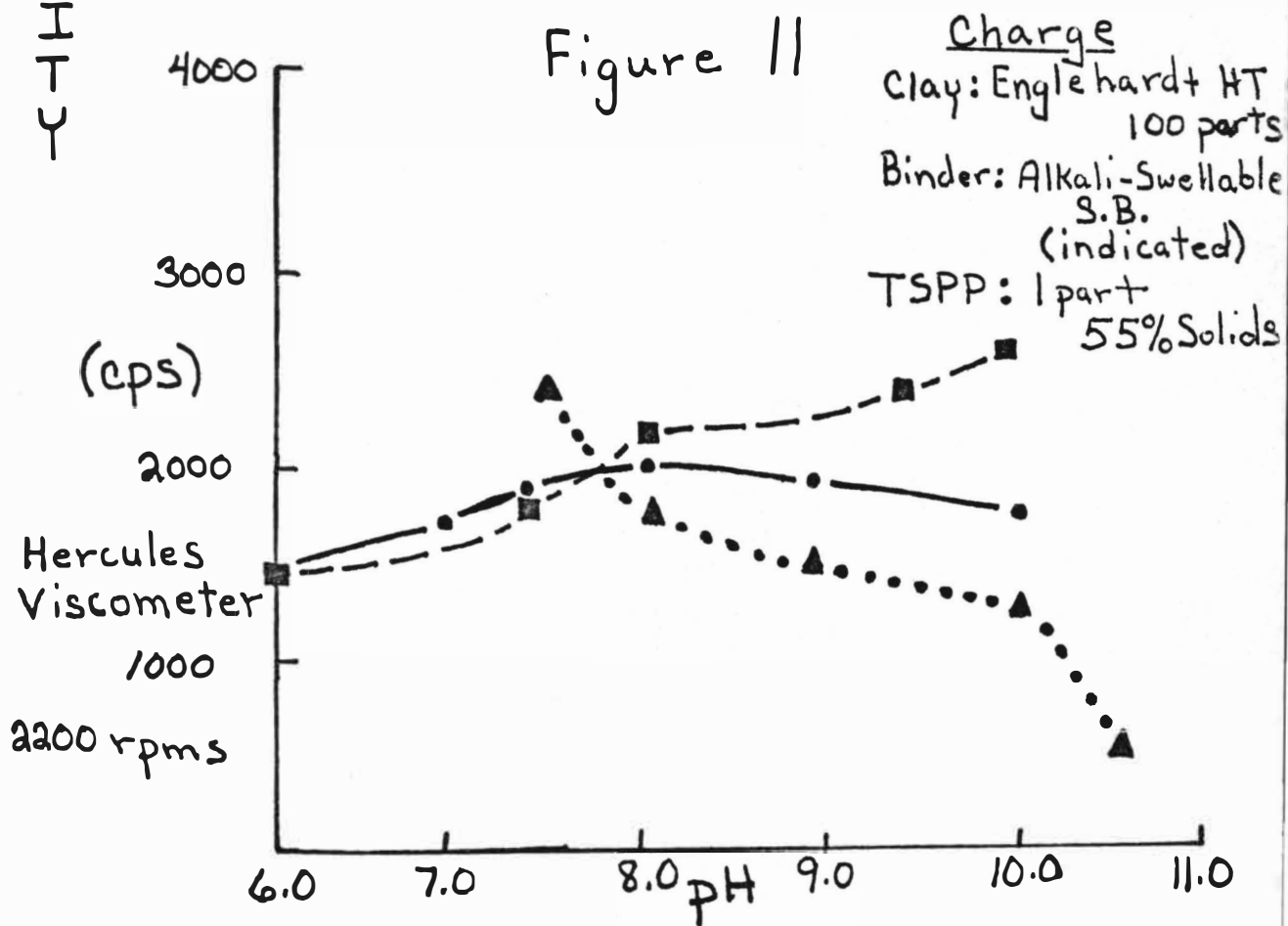


Figure 13 shows these results. The mixed latex system had a higher water retention than the complete alkali-swellable latex system, which was not to be expected. By increasing color pH, the water retention of the mixed system decreased while the sole alkali-swellable latex system increased. This test is very general and cannot be considered as absolute.

Figure 12 shows gloss results for the two coating machine systems. The mixed system has the higher gloss values, but only in the neutral pH area. The sole alkali-swellable system has higher gloss values after 8.0 pH. By comparing Figure 12 with Figure 9, it can be seen that the higher gloss values are obtained at about the highest viscosity levels, but from there on the comparison ends. Gloss values for both systems peak at the 7.0 pH level and the 10.0 pH level. Between these two points the gloss values are the lowest, which would indicate reduced water retention.

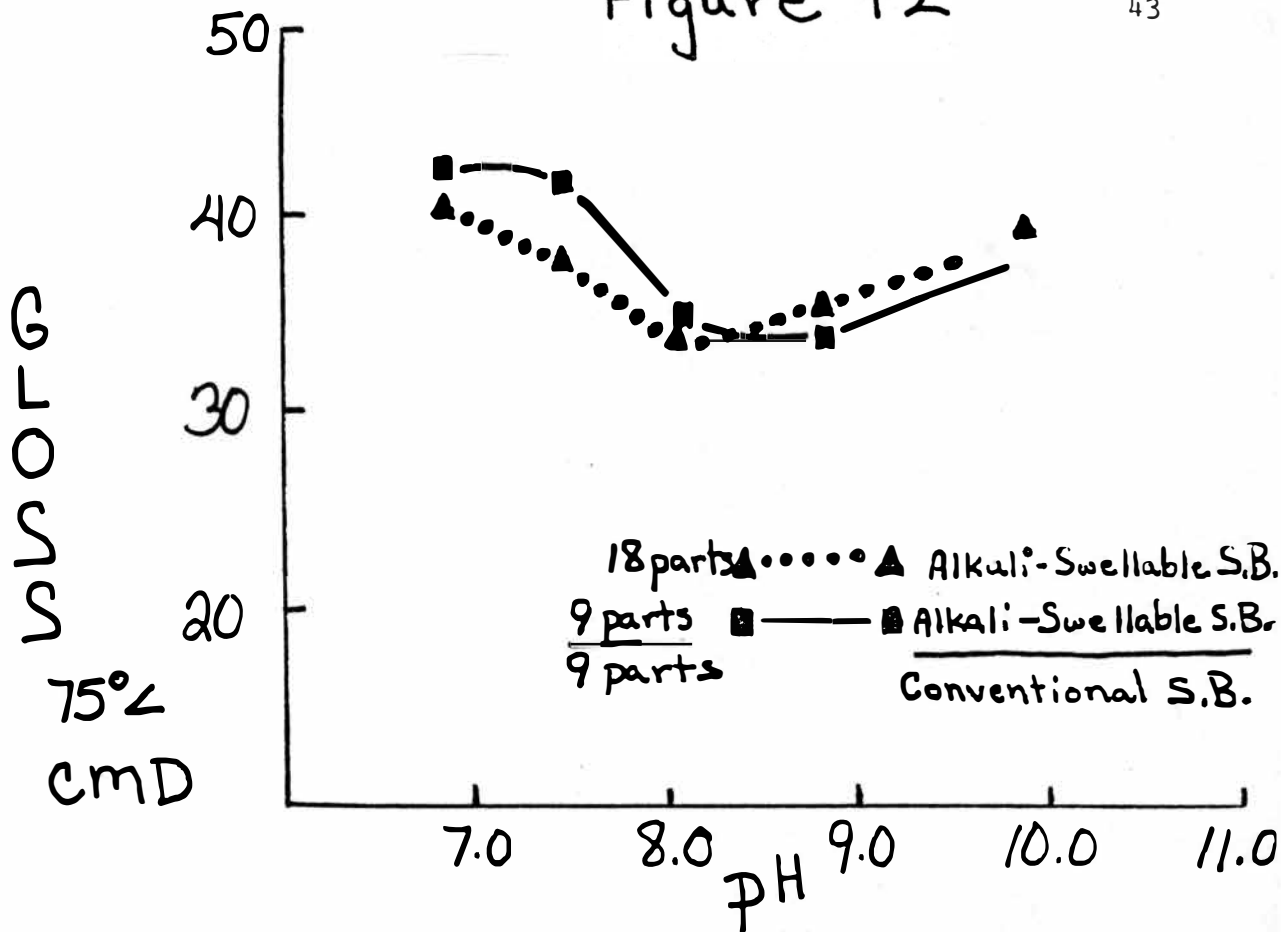
Optical properties of both systems are shown in Figure 14. The total alkali-swellable system had the higher opacity and brightness readings, but the differences between them were no more than two points. Opacity for both systems peaked between 8.0 pH and 9.0 pH, which would also indicate less water retention in these areas. Brightness values for both systems were also very similar. The total alkali-swellable system had the higher brightness values, in the neutral range, with the lowest in the alkaline range. The mixed system also followed this same pattern which would also indicate higher water retention in the neutral pH range.

Figures 15 and 16 analyze the coating colors' strength by the K & N ink receptivity test and I.G.T. pick test. Ink receptivity was higher for

the mixed system, but again only in the 8.0 pH to 10.0 pH range. The total alkali-swellable system had slightly lower K & N values which would indicate less migration of binder into the substrate. By analyzing the pick test, it can be seen that this decreasing migration into the paper helped to increase pick strength. Although the mixed system has much higher pick values, it also follows the same pattern as the total alkali-swellable system. Water retention is higher in the 7.0 pH to 8.0 pH range, which results in higher pick values and lower K & N values. This effect is reduced as pH is increased.

Figure 12

43



Effect of pH on Gloss and % Solids

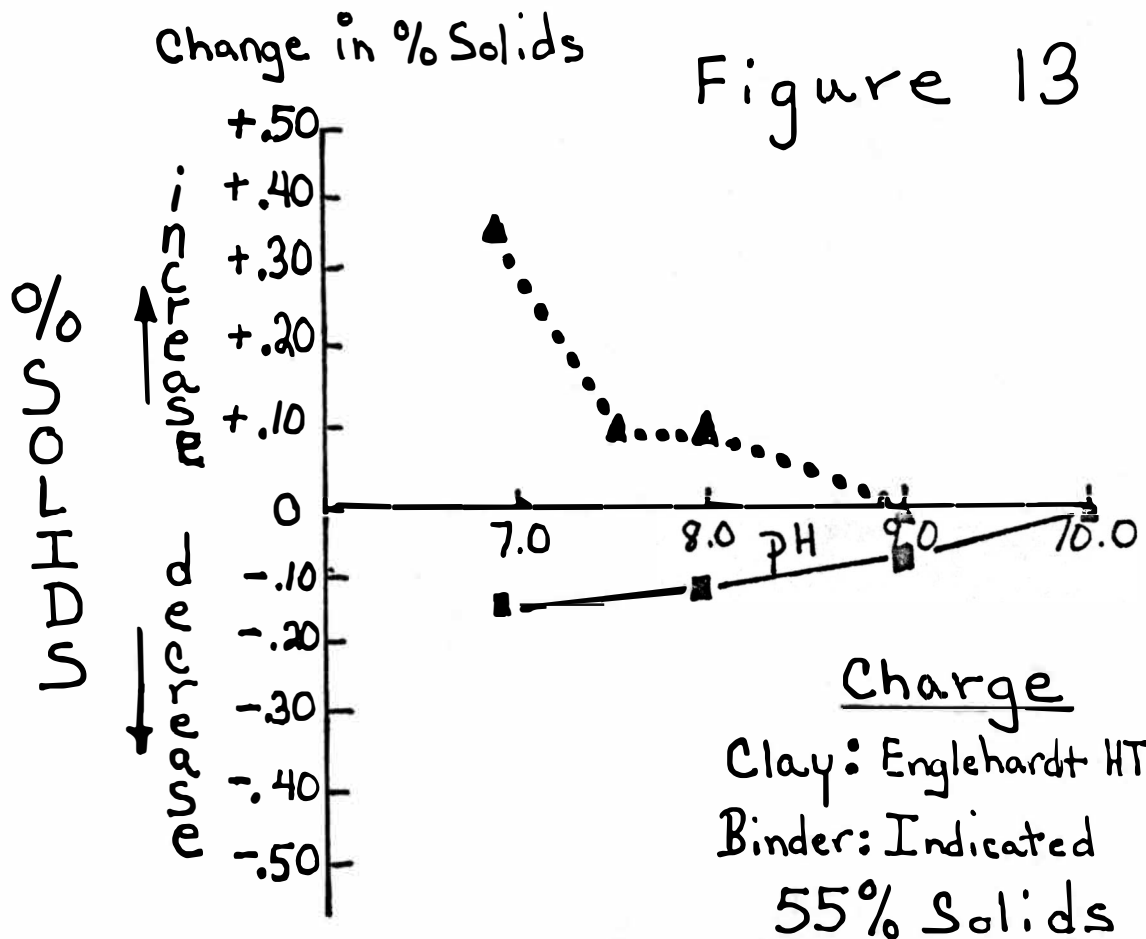
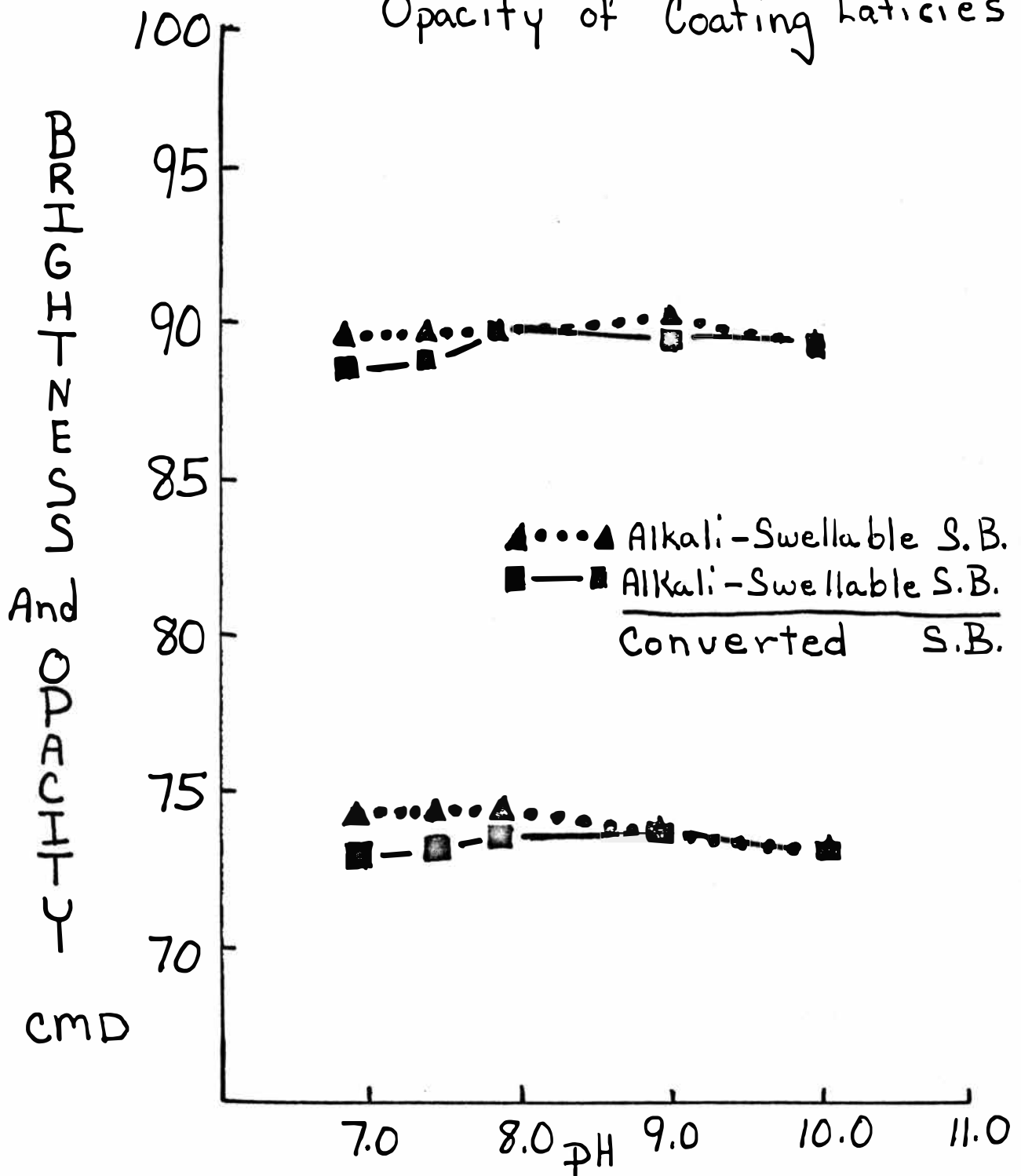


Figure 14

Effect of pH on Brightness and Opacity of Coating Laticies



Charge

Clay: Englehardt HT 100 parts

Binder: Indicated

55% Solids

Figure 15

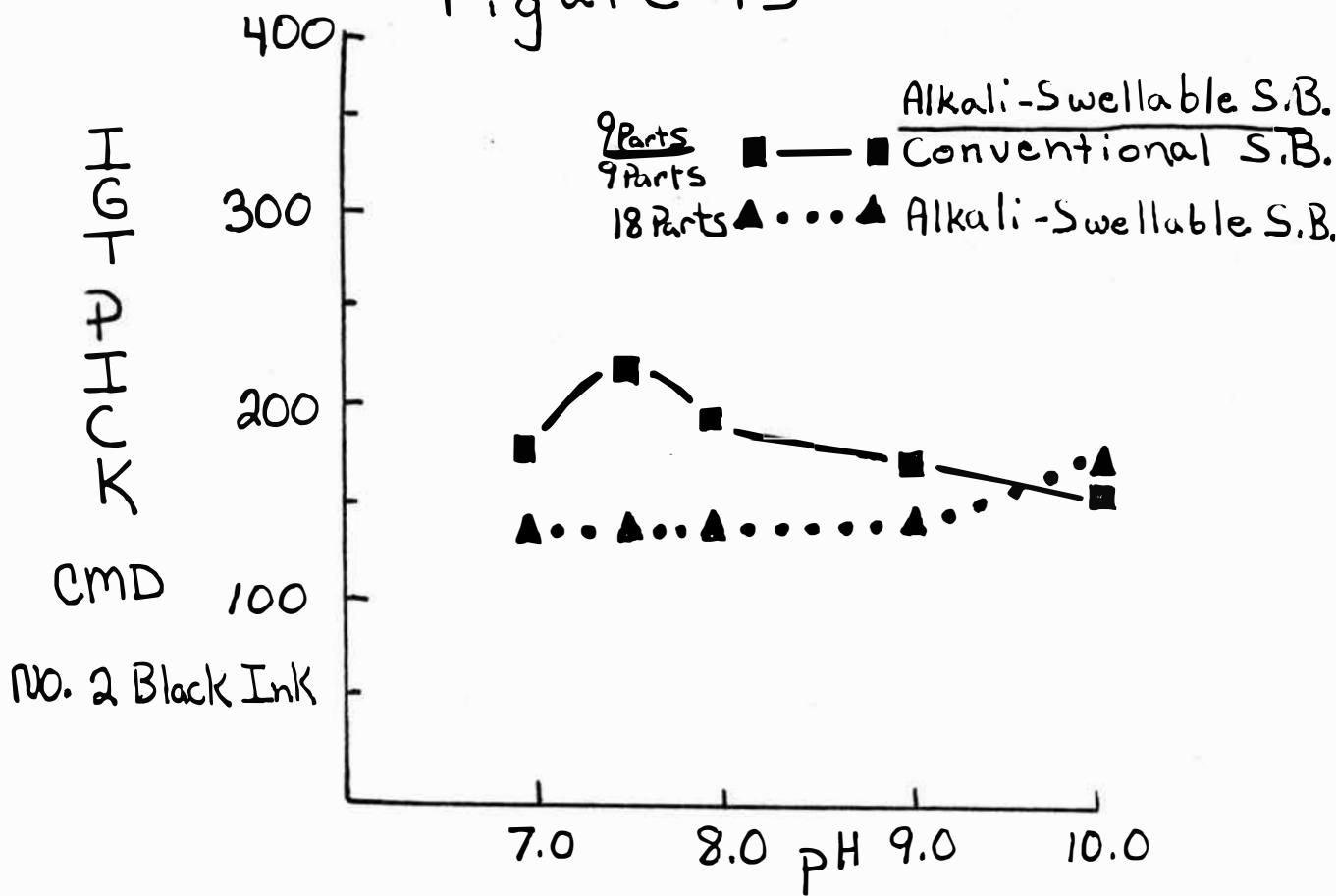
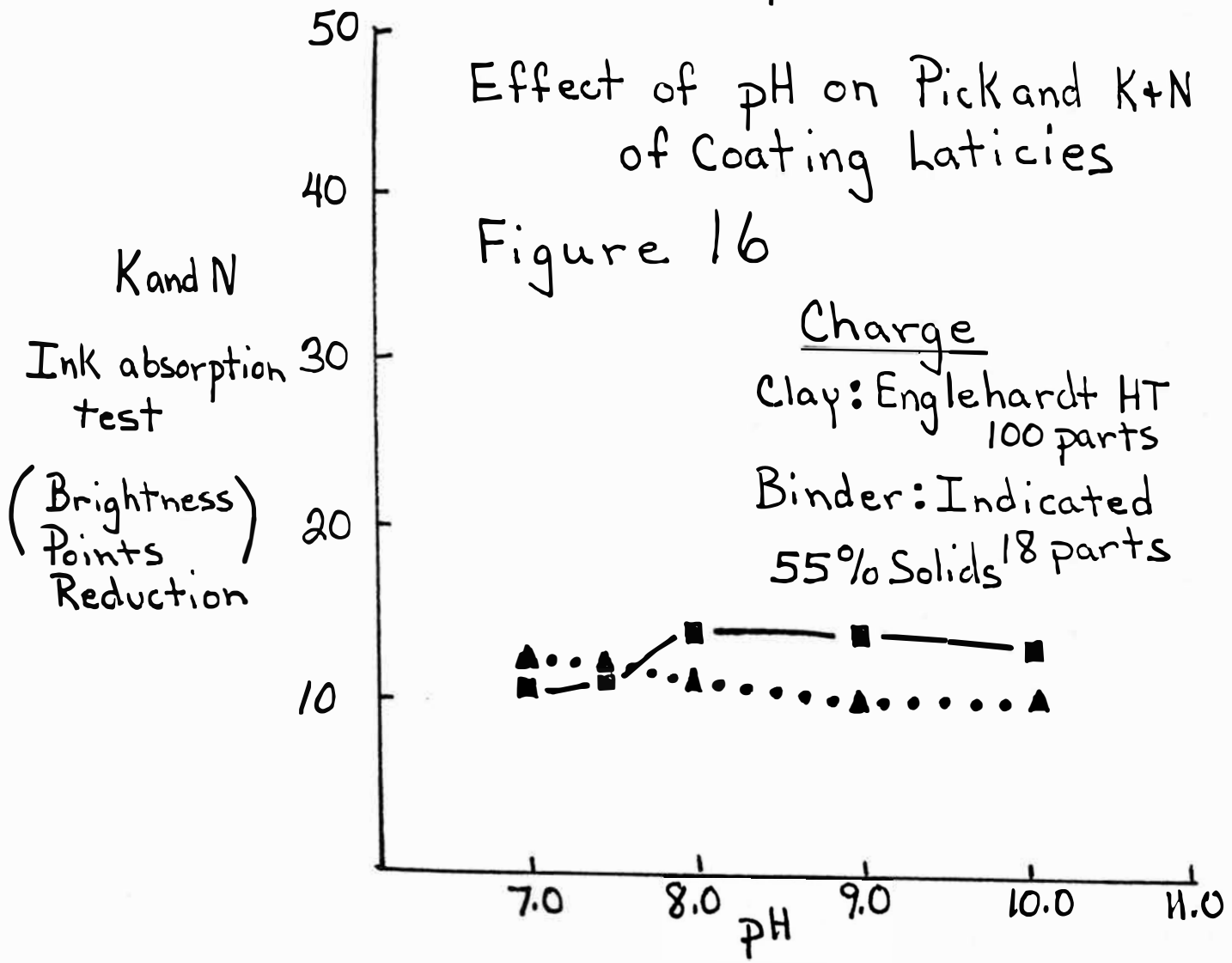
Effect of pH on Pick and K+N
of Coating Laticies

Figure 16



Data Tables

Run I

Tests

	<u>(Alk.sw.S.B.)</u>	<u>Opacity</u>	<u>Brightness</u>	<u>K & N</u>	<u>Gloss</u>	<u>Pick</u>
pH	7.0	89.4	74.0	12.7	40.8	150
	7.5	89.1	74.3	12.8	35.8	160
	8.0	89.8	74.1	11.4	35.1	160
	9.0	90.4	74.0	10.4	38.9	170
	10.0	90.0	73.7	10.4	40.1	190

Run II

	<u>(Alk.sw.S.B.)</u> <u>(Conv.S.B.)</u>	<u>Opacity</u>	<u>Brightness</u>	<u>K & N</u>	<u>Gloss</u>	<u>Pick</u>
pH	7.0	88.0	73.3	11.9	42.9	190
	7.5	89.3	73.9	12.7	40.8	220
	8.0	90.3	74.0	13.6	36.9	200
	9.0	90.0	74.0	13.6	36.8	185

Conclusion

The new alkali-swellable latex systems do have a slight effect upon coating strength with changing pH. This slight variation in coating strength could be attributed to water retention. In the neutral pH range, the addition of an alkali agent will increase viscosity and very possibly water retention. With additional pH adjustment between the 8.0-9.0 pH range, this thickening effect is reduced, which would reduce water retention also. At this point, the plasticity of the color is reduced. Although viscosity continues to decrease with pH levels over 9.0, the water retention of the color would seem to rebound slightly, but not completely.

By mixing reactive latexes with unreactive latexes, slightly increased optical properties will be noticed, but the effect on the physical properties of the coating depends more on the unreactive latex. The total alkali-swellable system gave comparable results with the mixed system. The increased viscosity makes it more economical to use because less or no thickener is needed. The alkali-swellable styrene-butadiene latex is less viscosity sensitive than the swellable acrylic vinyl acetate latex, which would make it easier to run on an air-knife coater.

There are many other additives which are used in paper coatings today. Thickeners, dispersants, defoamers, and water retention aids

are used increasingly more and these all have an effect on the operation of an adhesive binder. By using alkali-swellable latexes as binders, these other additives may be reduced or eliminated. These types of latexes will find more and more use in paper coating formulations in the future.

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pp 41 + 42 you say brightness
and $K+N$ are larger you should
say higher.

p 47 3rd from bottom line disperses into
"increasingly more" is
repetitively redundant —

p 22 what is a Kowal mixer?
do you mean the Cowles dispenser?

— if you ran on our coater you used a
flooded nip, blade coater not a
puddle coater. —

— did you use the pilot calendar or Lab?

Table II Same as before — move to right
also —
change pph to parts

P 24 enormous

~~Table~~ ~~Stick to~~ Roman Numerals and
move →

Actually this is not a Table; it is a
figure and should be : Figure 1

NOTE: for figures you use arabic numerals not roman —

031 discrepancy

Table of Contents

Alkali-Swellable
Procedure

spell it out
Styrene Bu

~~References~~ use ~~Literature~~ Bibliography

P2

pH

not ph

"dine"

P4

line 3 are called "diene" or "~~diene~~" ?

P5

Curing not curing

P8

pH

9

flexibility (check earlier Page)

P11

(Table I)

your left margin will be too small - the legend will be lost in ~~the~~ binding -

13

& Rheogram not ~~Plot~~

14

(table II) Same as Table I -

15

Flexible

16

Less effect ~~to~~ than ?

18

Table III Same as I and II

19

Bottom line

Sheffield Smoothness

Tappi Brightness

" Opacity

20

Hunter Lab, model D16 75 degrees

(L)

why the L ?

See page

Opacity - R & L

for most smoothness & L

2/10/77

2

all tables & figures need titles and
Tables use Roman Numerals and figures use arabic -

Content is good - but you do have a
tendency to make strong statements for which
you have no support:

Example: Conclusions: First Sentence -
you have no data on water retention. You
have pick data, which you are assuming
has been affected by ~~water~~ adhesive
migration which you assume is related
to water retention. All of your assumptions
may be correct, but you have no proof
and should not be so positive about
your claims.

Call if you have questions -
the enclosed sheets are some spelling
and other corrections needed.

Jim Klein

2/10/77

①

Larry - in general your effort is good -
but here comes that old however -
I'm afraid almost all Figures
will have to be re-done -.

for Example: (1) you need a left
margin so it can still be read
when it is in a folder.
(2) colors are nice on the
original but are lost on copies.

Specifics TABLE I is not a table
at all: it is, or should be;

Figure 1. Effect of ~~var~~ pH on Viscosity of
AND. Laticies

Figure 2. Effect of pH on Viscosity
of coating colors

TABLE II

+ Figure 3
Figure 4

Table III figure 5
Figure 6

TABLE IV is really TABLE I. Formulation for ----
AND Table II. Formulation ---- →

ETC. -