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## The Effect of Hydrocolloids in Control of Water Retention in Coating Systems

Gordon C. Bentley Jr.  
*Western Michigan University*

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THE EFFECT OF HYDROCOLLOIDS  
IN CONTROL OF  
WATER RETENTION IN  
COATING SYSTEMS

by

Gordon C. Bentley Jr.

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

The purpose of this study was to observe how three hydrocolloids (Kelgin Q series, Procoat 150, and Dow 650) function in their control of water retention in clay systems. The water retention values were measured on a modified Warren tester. It was found that the three hydrocolloids are viscosity modifiers. However, their control of water retention is not due to their effect on viscosity, but rather, to their good water holding capabilities. Therefore, viscosity is not the primary parameter in control of water retention when using these hydrocolloids.

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## INTRODUCTION

One of the major problems associated with the coating of paper is the excessive migration of the continuous phase of the coating color into the base sheet. This is referred to in industry as binder migration, vehicle migration, water holdout, water retention and a variety of other names.

Before water retention can be fully understood, one must understand the basis of pigment coating. The basis for any pigmented coating is the application of a pigment that is held to the surface of the substrate by a suitable adhesive which is generally dissolved in a liquid. The dissolved adhesive and the water in the pigment slurry, serve as the vehicle for the application of the pigment. This vehicle is referred to as the continuous phase. A certain amount of penetration into the substrate by the continuous phase is necessary for the pigment to be bound to the substrate. When there is an excess of migration, dewatering may occur causing rheological scratches on blade coaters. It may also cause gloss mottle which leads to poor printing. However, if there is not enough penetration into the substrate, the pigment may not adhere causing picking and linting in printing presses.

There are basically two mechanisms by which the continuous phase of the coating color penetrates into

the base stock. These are capillary action of the fibers and hydraulic pressure. Capillary action can be considered to be a static occurrence, whereas hydraulic pressure is a dynamic occurrence.

There are three parameters of the coating system which are thought to control water retention. These are percent solids, viscosity, and the water holding capabilities of the coating color.<sup>1</sup>

Percent solids has been found to be a very determining factor in water retention. Krishnagapalm and Sernard in 1976 found that the use of high solids eliminated excess migration of the continuous phase.<sup>2</sup> Heiser and Cullen in 1965 also tested the theory of percent solids and determined that the higher the percent solids of the coating color the less prone the continuous phase was to migrate.<sup>3</sup> This is due primarily to the formation of a filter cake which contains the remainder of the continuous phase on the surface of the sheet.

Water retention can be controlled by viscosity and by changing the water holding capabilities of the coating color. This is achieved by the addition of modifiers. These modifiers are hydroscopic polymers known as hydrocolloids. Hydrocolloids are generalized as solubles, semisolubles and swellables. Solubles consist of carboxymethylcellulose (CMC), hydroxyethylcellulose (HEC) and polyvinylalcohol (PVA). Semisolubles include protein, starch and sodium alginate (Kelgin). The swellables

include alkali sensitive laticies and sodium polyacrylate.

The hydrocolloids function by ionic attraction, dipole absorption and hydrogen bonding between carboxyl and hydroxyl groups of the pigment particles, binder and the water in the coating color.<sup>4</sup> As the polymer associates with the pigment particles, a Helmholtz double layer is formed resulting in the immobilization of the continuous phase.<sup>5</sup>

Water retention of the coating color is measured and reported as a water retention value or WRV. A coating with a high WRV has the ability to prevent the continuous phase of the coating from penetrating into the base stock. A variety of methods have been developed over the years for measuring water retention. The first of these was based on the boat sizing test. Dry indicator was placed on a sheet of paper which was floated on the coating color. The time required for the continuous phase of the coating color to penetrate the paper and wet the indicator was recorded as the WRV value. However, this test was limited to coating with low percent solids.<sup>6</sup>

The next tester introduced was the roll inclined plane tester. It consisted of a plate of glass inclined at an indicated value on which the coating color was placed at predetermined positions. The substrate is mounted on a roll which is rolled down the glass plate. Knowing the velocity of the roll moving down the inclined

plane and knowing the viscosity of the coating, a value for the wet film thickness can be calculated which is considered a WRV value. There are many disadvantages to this tester. Two of these are the placing of the drops and the change in velocity of the roll due to the slowing action exerted by the coating. The relationship between water retention and film thickness could also not be determined.<sup>7</sup>

The first test to measure water retention directly was the sonic tester. It consisted of spreading the coating onto the substrate which was between two sonic probes. As the water penetrated the substrate, the speed of sound through the sheet decreased. This is due primarily to the swelling of the fibers.<sup>8</sup>

Other testers introduced in recent years rely on the fact that the conductivity of the paper is a function of the moisture content of the paper. The first of these was the static terminal ring cell. This tester consists of placing the coating color in a ring cell that has been placed on the paper stock which is covered by plastic. When the plastic is pulled out, a timer is activated and the time required to reach a .1mA current flow is reported as the WRV value.<sup>9</sup>

The test that is most used in industry is the S.D. Warren tester. It consists of connecting a steel plate and a weight to a power supply. The coating color is applied to the steel plate and the paper and weight are



placed upon it. The time required for a .5mA current to occur is reported as the WRV value. Many sources of error exist in this tester. These include the conductivity of the paper, polarization of the electrodes, temperature of the coating color, weight and area of the top electrode. However, these can be overcome.<sup>10</sup>

The above background was to show how water retention functions, is controlled and measured. The primary concern of this project is to determine how sodium alginate, protein and an alkali sensitive latex function in their control of water retention.

Kelgin is sodium alginate that is derived from brown seaweed by ion exchange. Kelgin functions rheologically as a pseudoplastic fluid.<sup>11</sup> Kelgin and protein are semi-solubles and it is not generally known whether they function as viscosity modifiers or alter the water holding capabilities of the coating. However, they are theorized to be found as coiled molecules in solution. These coils are thought to act as feet which hold water within its structure by ionic attraction. Alkali sensitive laticies are theorized to function as water holding agents through their ability to imbibe water and swell. Although this action will also affect viscosity, it is believed that water holding is the main effect on water retention.

By comparing the WRV values of high, medium and low viscosity samples of each additive at the same viscosity, one can determine whether the additive functions as a

viscosity modifier or has good water holding capabilities. If the WRV values are the same at equal viscosities, then the additive is a viscosity modifier. However, if the WRV is not equal to viscosity, but is directly related to addition level, then it can be assumed that water holding or some other mechanism is the dominating factor.

## EXPERIMENTAL PROCEDURE

Twenty coatings were made and tested in the following manner. The hydrocolloids that were used were Kelgin Q series (high, medium and low viscosity), Procoat 150 (high, medium and low viscosity), and Dow 650, an alkali swellable latex.

The WRV values that are reported here are calculated from a modified Warren tester. The values are an average of ten tests and were conducted at room temperature using Allied 12 lb. bible paper. The modifications on the tester included adding a strip recorder to measure the change in current and the top electrode was weighted to give a pressure of .214 PSI. To avoid the problem of conductivity of the paper, a wet sheet of paper was placed between the electrodes and the recorder was adjusted to full scale.

The addition levels were calculated in preliminary work and were also based on the continuous phase of a 50 percent solids clay slip. A number 2 clay (hydrasperse) was slurried at 70 percent solids and then reduced to 50 percent solids by the addition of the dissolved hydrocolloids and water.

The kelgins were dispersed under medium agitation in warm water for thirty minutes. The low viscosity was dissolved at 6 percent solids, the medium at 3 percent solids, and high at 2 percent solids. Once these were

dissolved, they were added to the clay slips under medium shear at three different levels. The low viscosity levels were 3%, 2.5% and 1.6%. The medium levels were 1.3%, 1.25% and .8%. The high levels were .95%, .8% and .5%. After the addition of the kelgins, the clay slips were agitated under medium shear for approximately 20 minutes. After the kelgins were thoroughly dispersed, Brookfield viscosity and WRV were taken. WRV was also run on the Kelgins before they were added to the clay.

The proteins were slurried under medium agitation and soaked for 30 minutes in cold water. They were then heated to 115-120 degrees F, at which time a cutting agent of 5% Borax and 24%  $\text{NH}_4\text{OH}$  based on the dry weight of the protein was added. The temperature of the protein was then brought and held at 130-140 for 30 minutes. The low viscosity was cooked at 27% solids, the medium at 22% and the high at 18%. They were then added to the clay at addition levels of 1 to 10 percent using medium agitation and were agitated for approximately 20 minutes. At this time Brookfield viscosity and WRV were run on the clay slips and the protein solutions.

Dow 650 is received at 46% solids. It was added to the clay at 15% solids under medium agitation. The pH was then changed to 6, 8, and 10 by the addition of 28%  $\text{NH}_4\text{OH}$ . Brookfield viscosity and WRV were taken at each pH.

## RESULTS

The basic preliminary work referred to in the experimental procedure consisted of calculating addition levels of the hydrocolloids. These were to be calculated by plotting concentration of the hydrocolloid to viscosity and picking three addition levels of each additive. This was used in determining addition levels of the Kelgin. However, this did not work with the protein and the latex. The protein in levels that are applicable to industry had virtually no viscosity. This too was the case with the latex. Therefore, the protein and latex were added at levels most commonly used in industry.

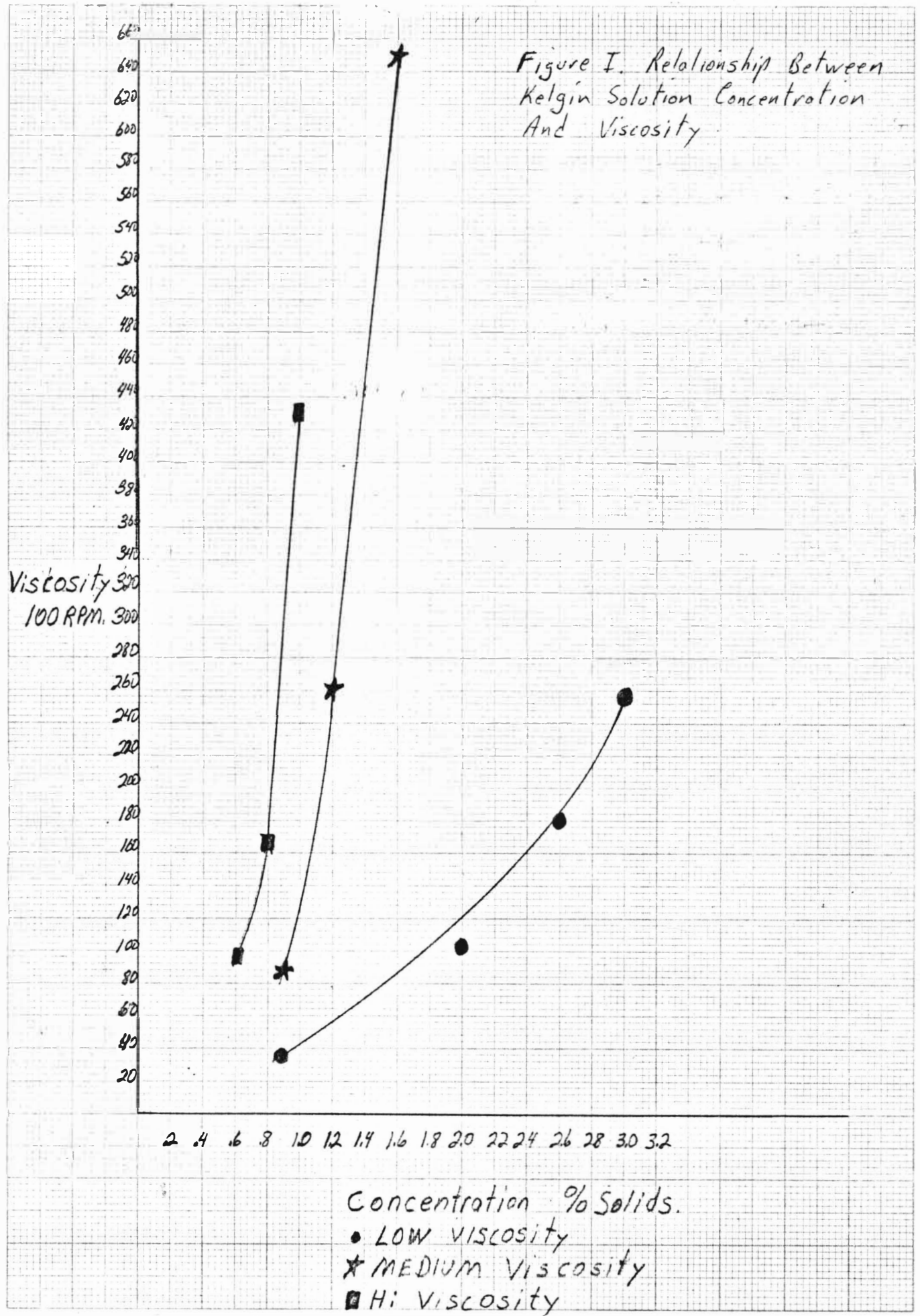
The kelgins as can be seen in figure 1, increase in viscosity as the concentration in percent solids increases. As the concentration of kelgin increased, the viscosities of the three also increased. However, the viscosity when added to the clay, was inversely related to the samples. Therefore, the low viscosity sample had the highest viscosity and the high viscosity, the lowest. This can be seen in figure 2. WRV acted differently than viscosity. The low viscosity had the highest WRV value and the medium the lowest (figure 3). However, the WRV values for the kelgin solutions, were less than .5 seconds.

The protein solutions at levels that are applicable to industry had viscosities that were nearly the same as that of water. Therefore, the addition levels of 1 to 10%

were chosen due to their use in industry. When the protein was added to the clay, there was observed a decrease in WRV of approximately one second. (figure 4 and 5). There was also observed an interaction which, as the concentration of the protein solution increased, the viscosity of the clay increased. (figure 6). WRV also followed this pattern. As the concentration of the protein solution increased and also viscosity increased, WRV increased (figure 5 and 7). The high viscosity also recorded the highest viscosity and WRV values, whereas, the low viscosity, the lowest viscosity and WRV values. (figure 6 and 7).

The addition level of the latex was also chosen by its use in industry. The latex showed virtually no change in viscosity as the pH was increased from 6 to 10. Once the latex was added to the clay and the pH changed, there was a slight increase in viscosity (figure 8). The WRV values of the latex at 15% solids were less than .5 seconds. However when the latex was added to the clay and the pH changed, the WRV values increased until the pH reached 9. Above that point, the WRV values began to decrease (figure 9).

Figure 1



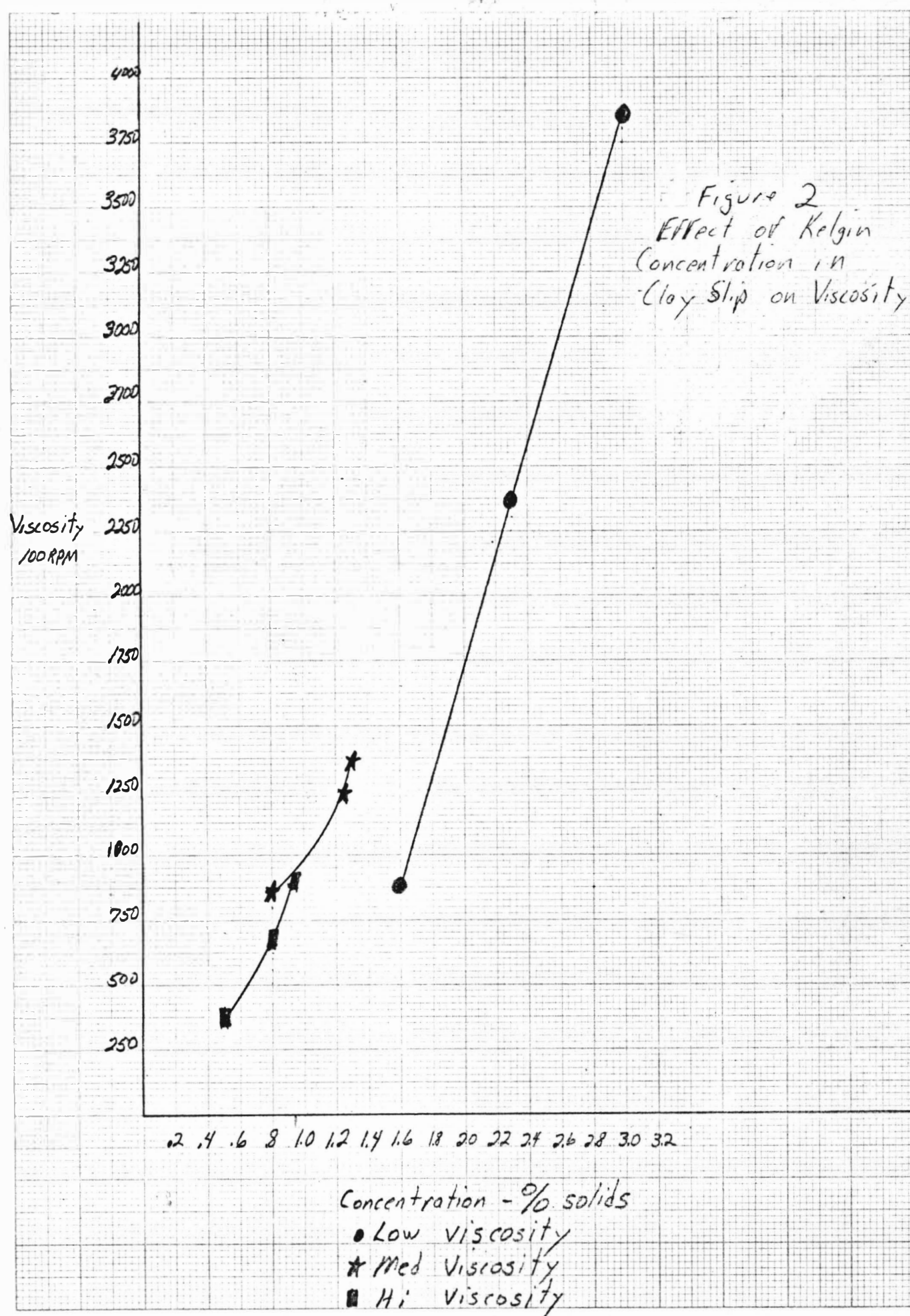




Figure 3  
The Effect of Kelgin  
Concentration in Clay  
Slips on WRV.

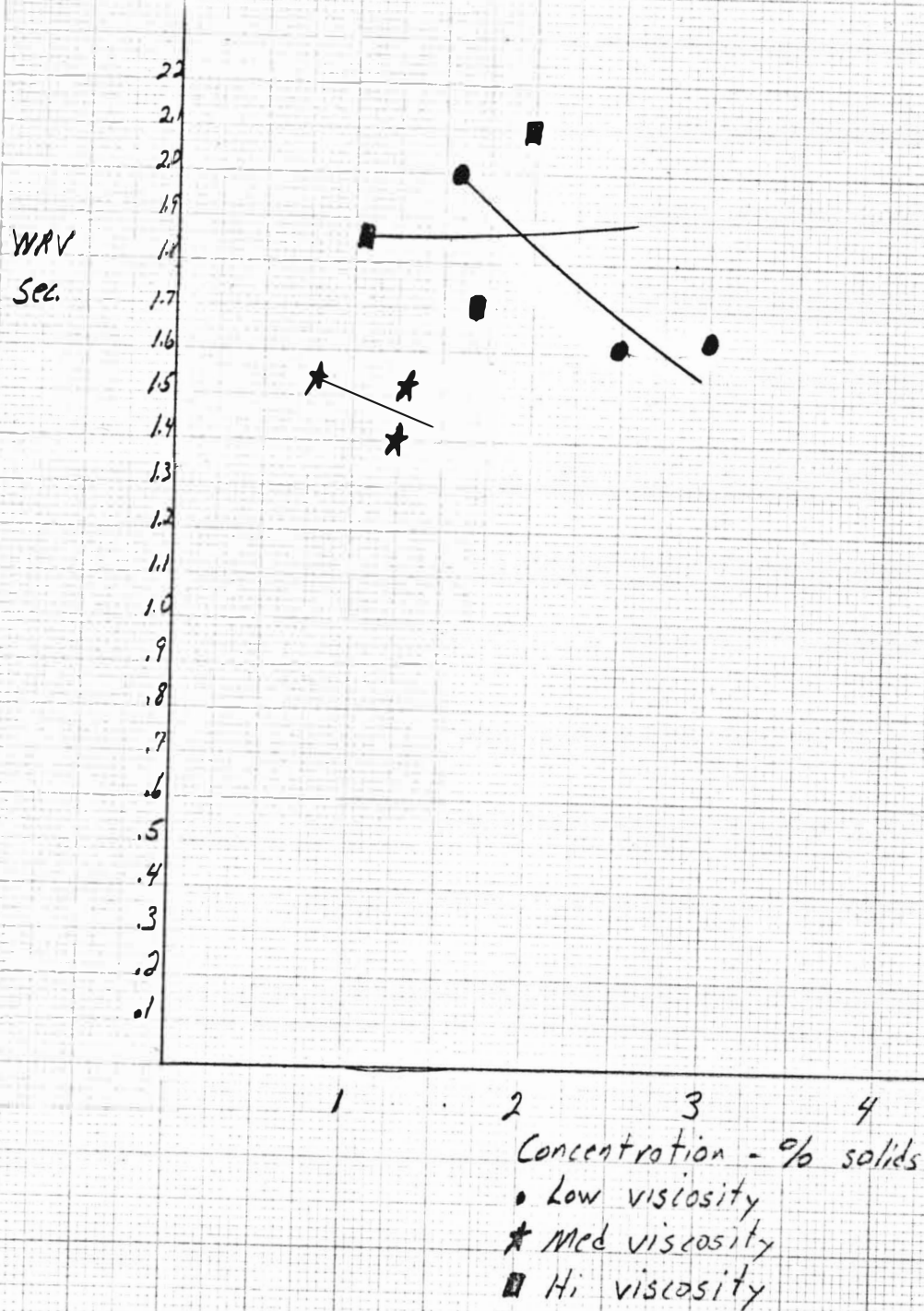
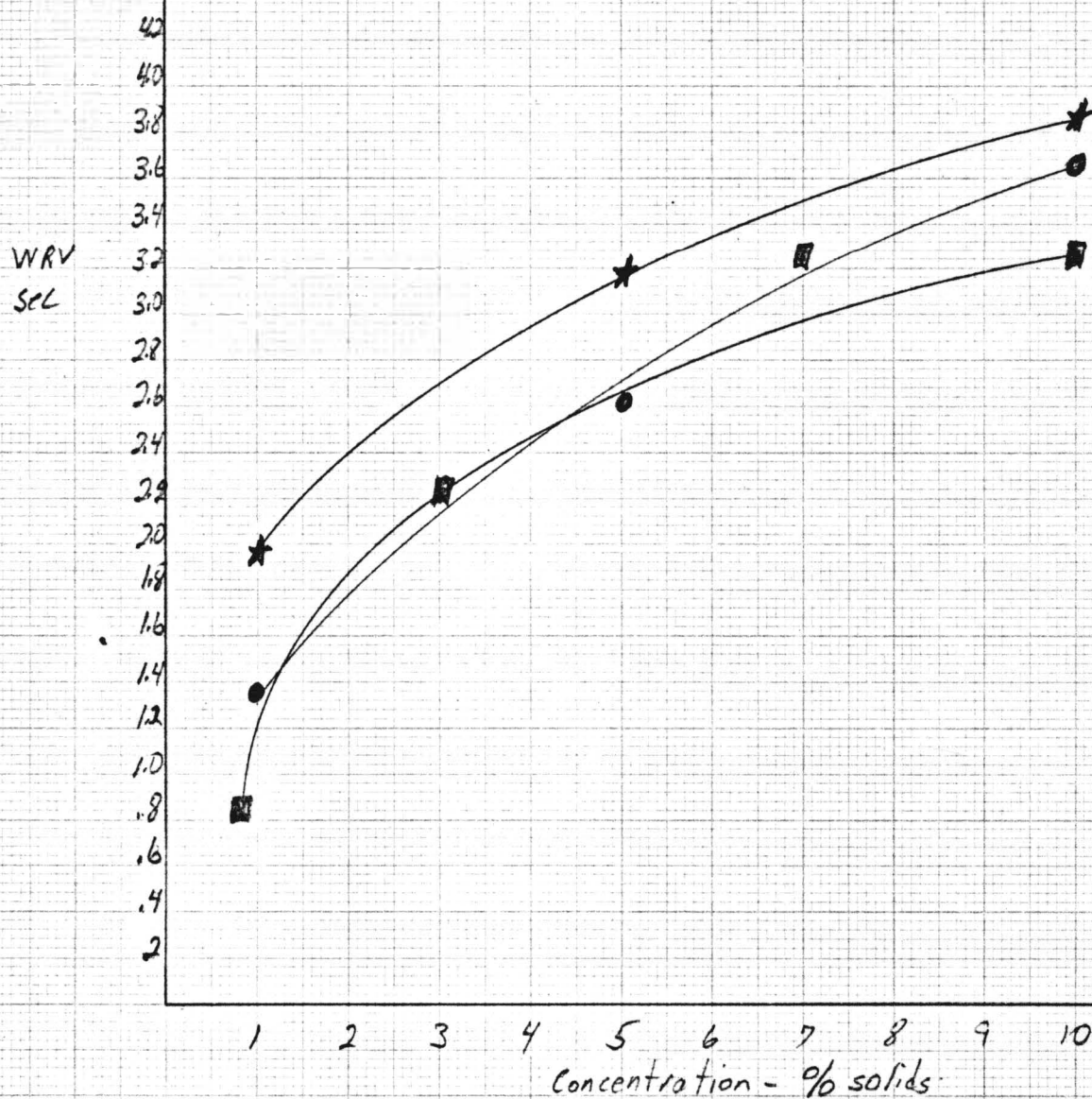
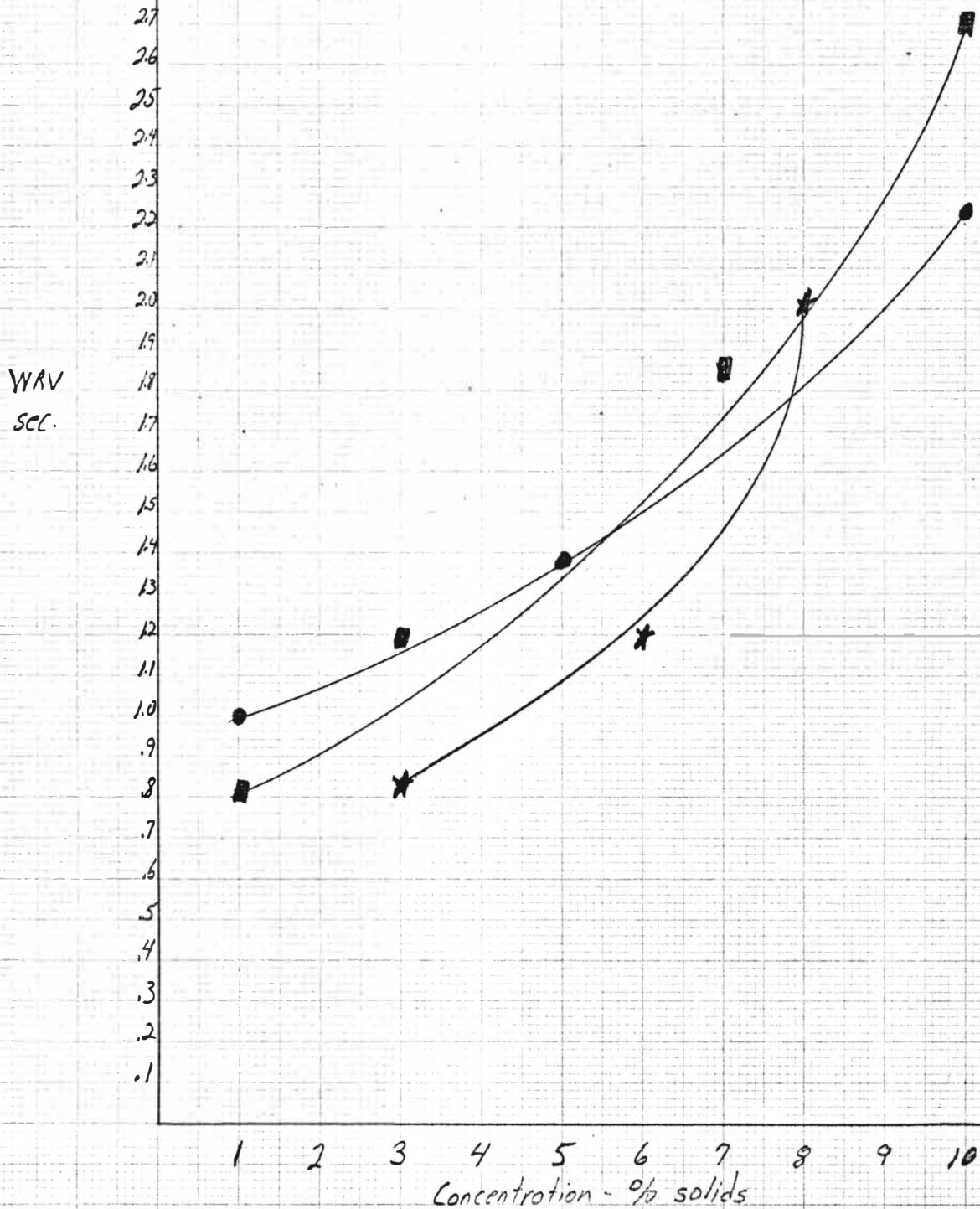


Figure 4.  
The effect of Protein  
Solution Concentration  
on WRV



- Low - viscosity
- ★ Med. viscosity
- Hi. viscosity

Figure 5  
The Effect of Protein  
Concentration in Clay Slips  
on WRV



• Low viscosity  
\* Med. viscosity  
■ Hi. viscosity



Figure 6.  
The Effect of Protein  
Concentration in Clay  
Slips on Viscosity

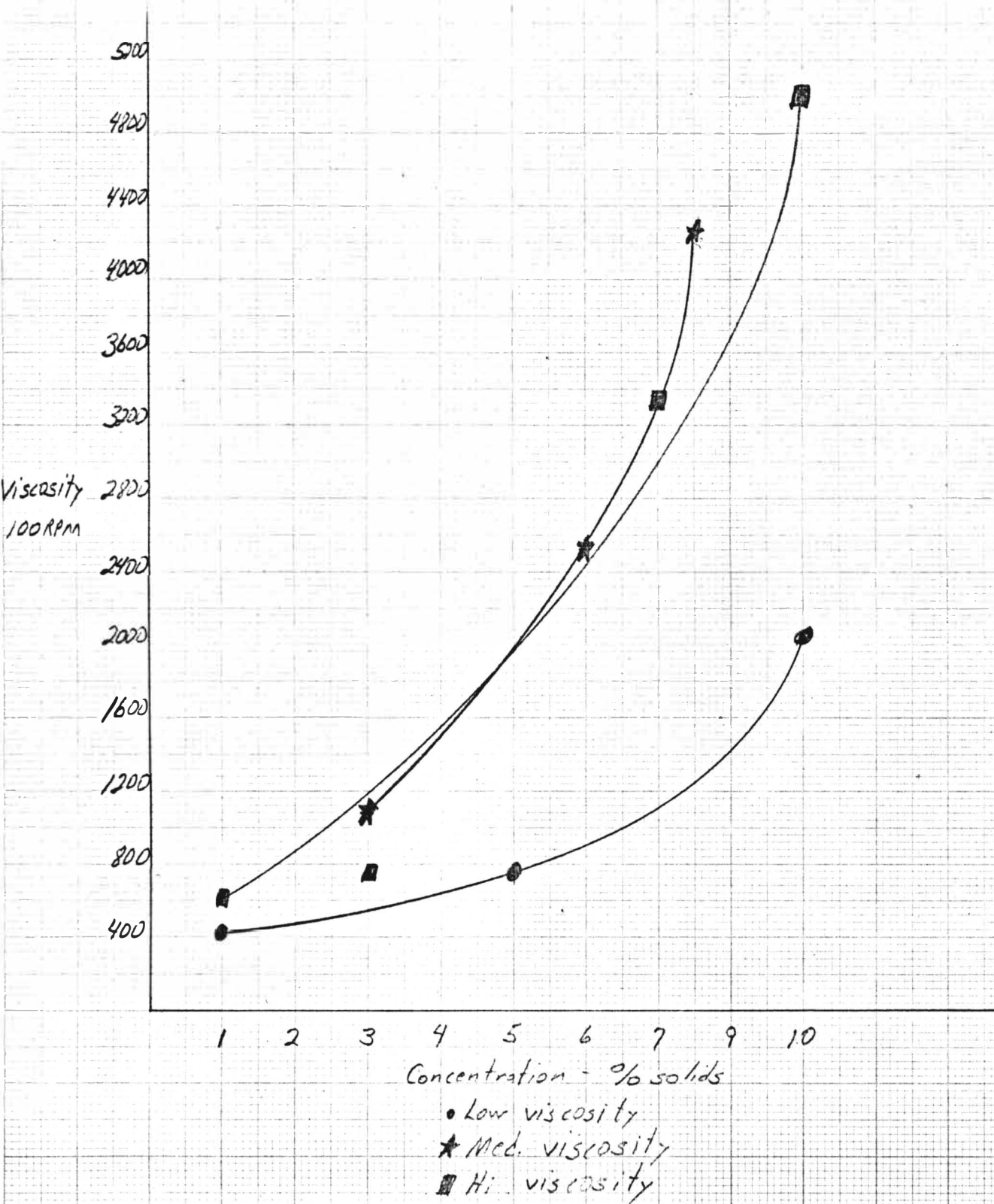


Figure 7.  
The Effect of Viscosity  
of Clay Slips With  
Protein Solution on WRV

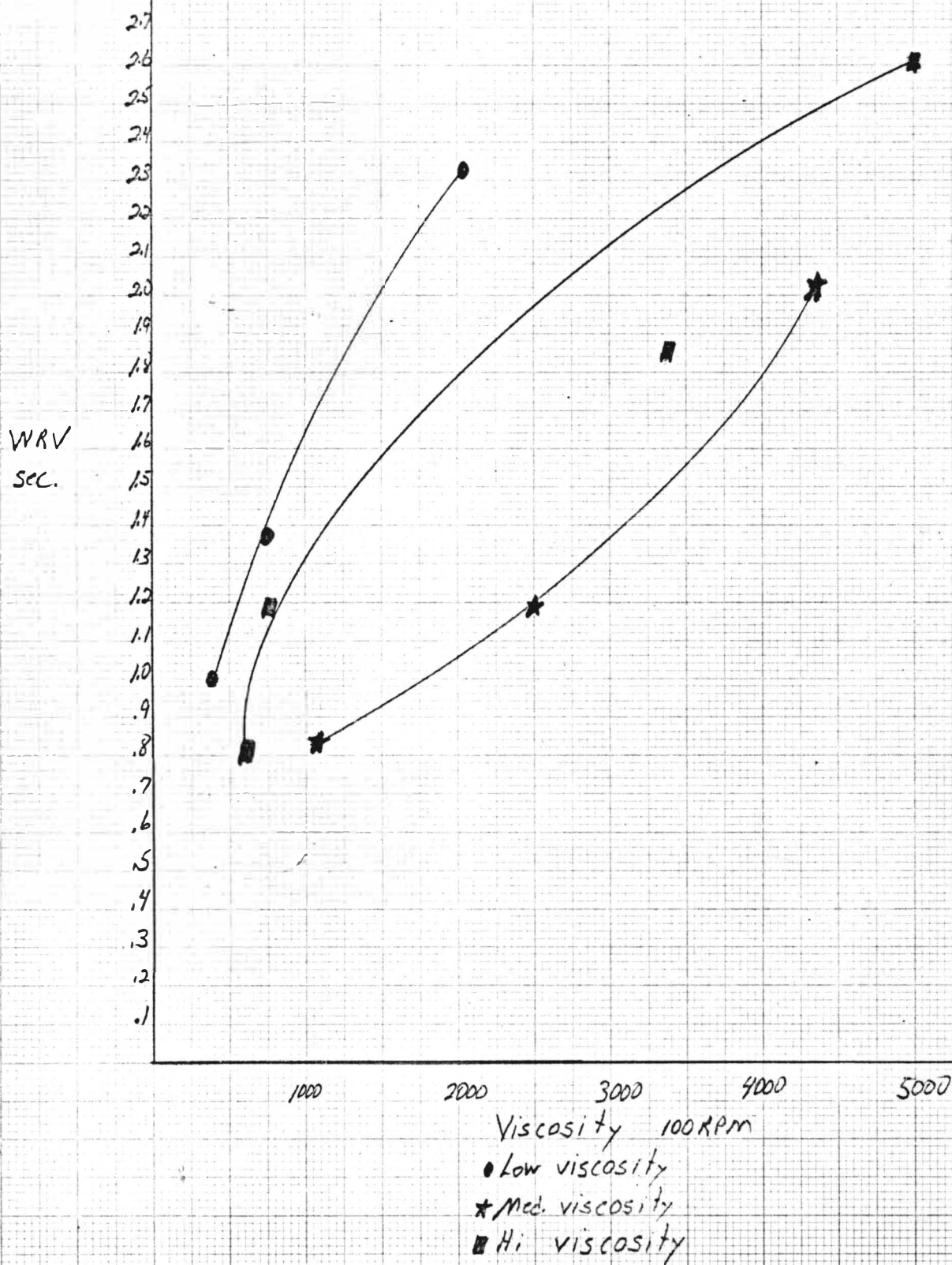


Figure 8  
The Effect of Viscosity  
of clay slips with  
Latex at 15% solids  
on WRV

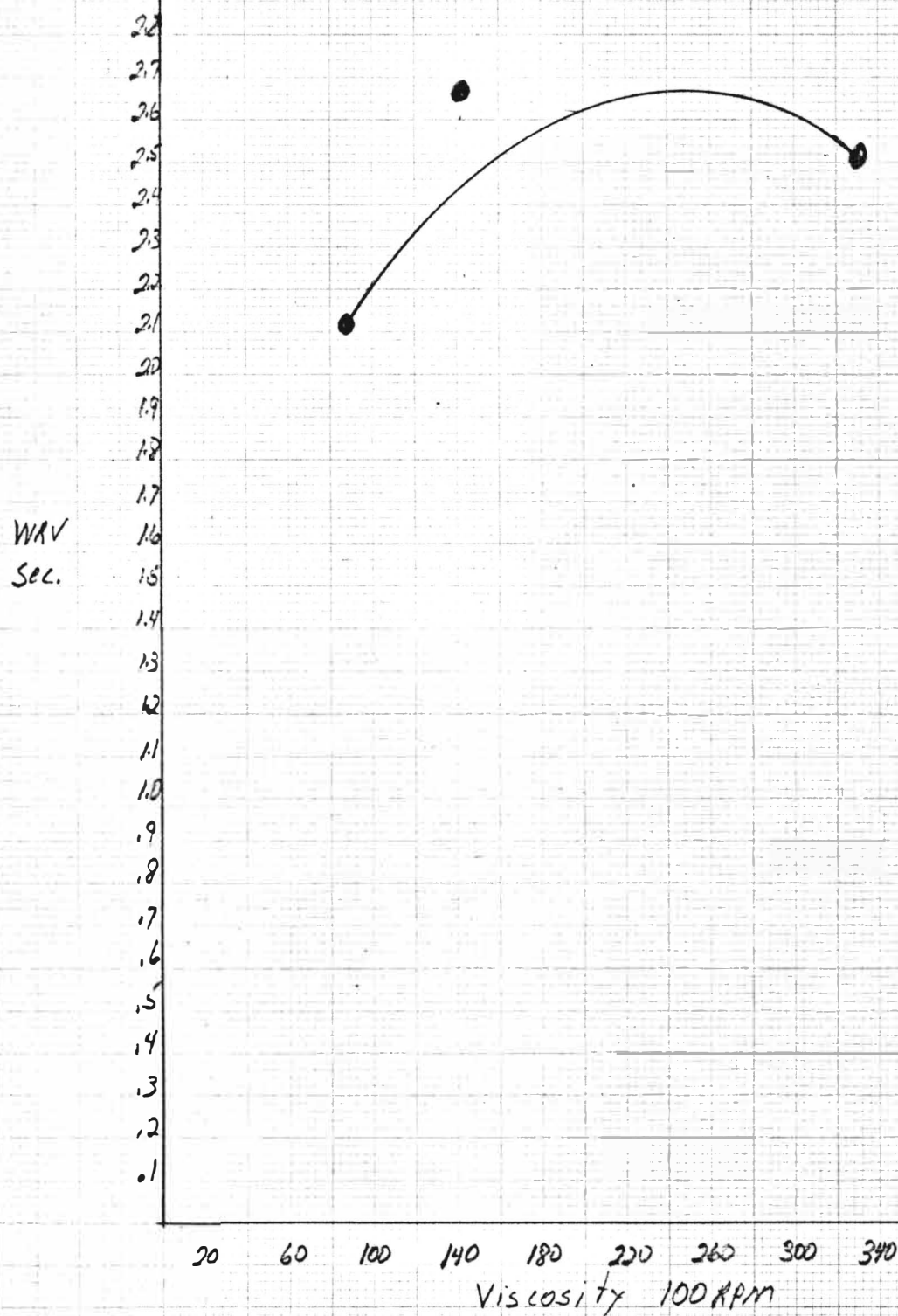
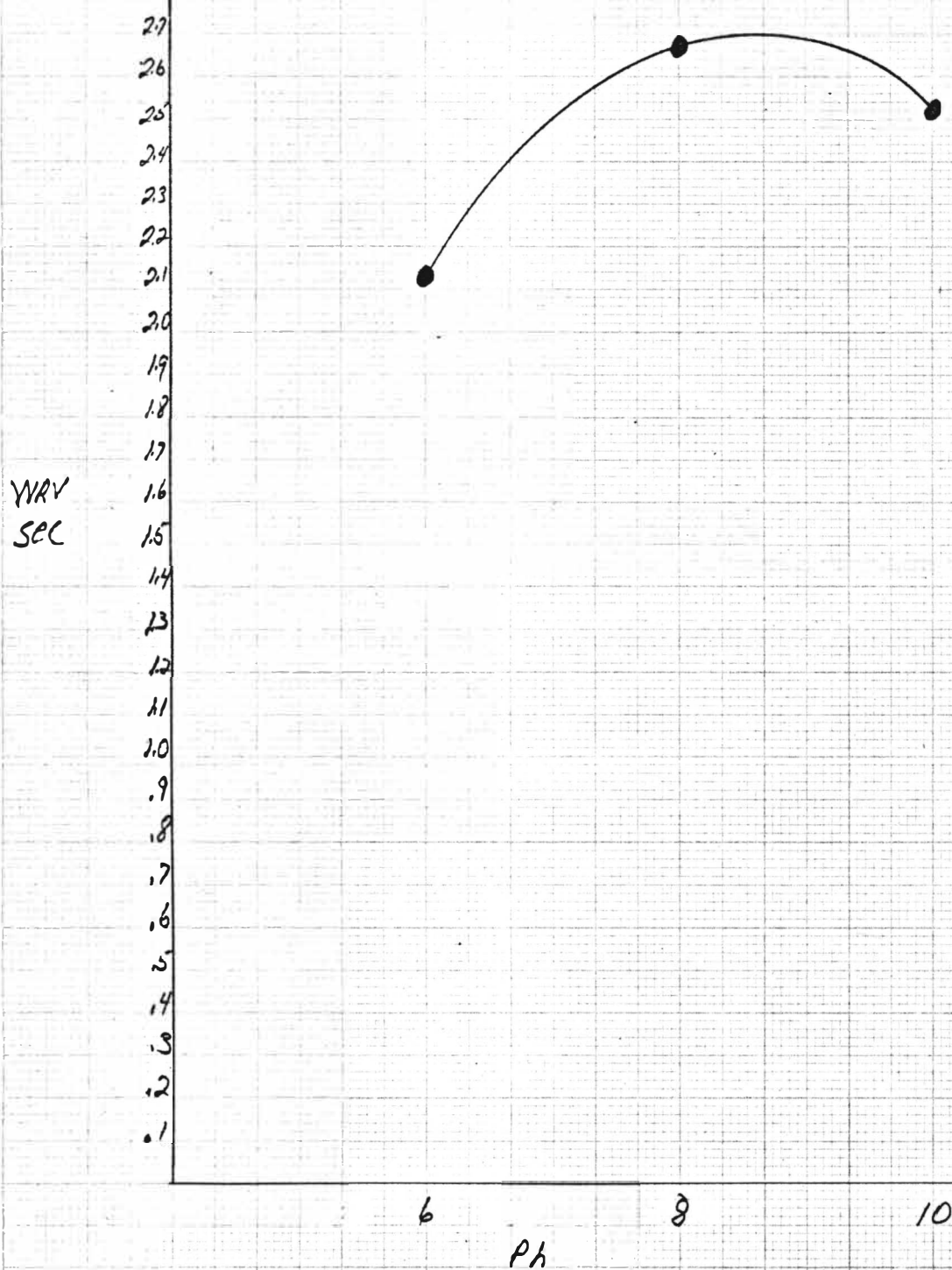


Figure 9.  
The Effects of pH of Clay  
Slips with latex of 15%  
Solids on WRV.





## DISCUSSION OF RESULTS

As stated earlier, if the high, medium and low viscosity kelgin and protein are added to the clay slips at concentrations which are the same viscosity, and the WRV values once added to the clay are the same, then they are viscosity modifiers. However, if the WRV values are not equal to viscosity, but are related to addition level, then it can be assumed that water holding or some other mechanism is the dominating factor.

Kelgin has been theorized to be a viscosity modifier. However, by choosing a viscosity of 900 from figure two, it can be seen that the levels of addition of the high viscosity sample would be approximately .9%, the medium viscosity .8% and the low viscosity 1.6%. If the kelgin was a viscosity modifier then the WRV values at these concentrations would be the same.

### CLAY AND KELGIN AT 900 CPS.

	%SOL	WRV sec.
Low	1.6	2.0
Medium	.8	1.5
High	.9	1.8

However, as can be seen above and in figure 3, this is not the case. There is however a relationship to concentration. The concentration of the low viscosity kelgin was higher than the concentration of the high viscosity. When added to the clay, this produced higher viscosities (figure 3) and also higher WRV values. Therefore, Kelgin has good water holding capabilities and is not a



viscosity modifier.

The Protein has also been theorized to be a viscosity modifier. By choosing a viscosity of 2000 in figure 6, addition levels of 5% of the high and medium samples and 10% for the low viscosity can be found. If, as in the kelgin, the protein was a viscosity modifier, then the WRV values would be the same at these concentrations.

CLAY AND PROTEIN AT 2000 CPS.

	%SOL	WRV sec.
Low	10	2.2
Medium	5	1.1
High	5	1.35

As can be seen in figure 5, and above, these concentrations do not produce the same WRV value. This can also be seen in figure 7 where 2000 cps. of each sample does not produce the same WRV value. Since the WRV values are not the same at equal viscosities, the protein is not a viscosity modifier but rather, has good water holding capabilities.

The latex had to be treated in a different manner. It is assumed that if the latex was a viscosity modifier, then as the pH was changed which could cause an increase in viscosity, then the WRV value would also increase. In figure 8, it can be seen that as the pH rises, the WRV value also rises. However, at pH 9 the WRV value decreases. This is also the case in figure 9 where the WRV drops at 250 cps. This drop can be attributed to the latex molecule dissociation once the molecule has swollen to its maximum size. If the latex were a viscosity modifier, there would

not be a change in WRV when the molecule dissociated, rather a continuous increase as viscosity increased. Therefore, the latex has good water holding capabilities.

## CONCLUSIONS

Kelgin, Protein and alkali swellable laticies are viscosity modifiers. However, their control of water retention is not due to their effect on viscosity, but rather, to their good water holding capabilities which are related to concentration. As the level of addition of the hydrocolloids increases, the water retention values increase, indicating the clay slip is better able to contain its continuous phase on the surface of the sheet. Therefore, viscosity is not the primary parameter in water retention. Of the three hydrocolloids, the protein solution had the highest water retention values. When added to the clay, Dow 650 at 15% solids and pH 8 had the highest water retention values.

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# APPENDIX

## KELGIN SOLUTION

	%SOL	VISCOSITY	WRV
Low	1.60	65	--
	2.50	160	--
	3.00	256	--
Medium	.80	69	--
	1.25	160	--
	1.30	300	--
High	.50	78	--
	.80	163	--
	.95	280	--

## KELGIN WITH CLAY

Low	1.60	800	1.99
	2.50	2070	1.61
	3.00	3600	1.63
Medium	.80	686	1.54
	1.25	1280	1.40
	1.30	1330	1.52
High	.50	300	1.85
	.80	686	1.70
	.95	866	2.09

## PROTEIN WITH CLAY

Low	1.00	400	.99
	5.00	750	1.37
	10.00	2040	2.32
Medium	3.00	1080	.82
	6.00	2500	1.18
	8.00	4350	2.01
High	1.00	600	.81
	3.00	760	1.19
	7.00	3360	1.85
	10.00	5000	2.70

# PROTEIN SOLUTION

	%SOL	VISCOSITY	WRV
Low	1.00	--	1.37
	5.00	--	2.62
	10.00	--	3.67
Medium	1.00	--	1.96
	5.00	--	3.18
	10.00	--	3.85
High	.80	--	..83
	3.00	--	2.21
	7.00	--	3.26
	10.00	--	3.26

	LATEX	VISCOSITY	WRV
15% Solids	pH		
	6	88.0	2.13
	8	141.6	2.67
	10	330.0	2.52
10% Solids	10	86.0	2.29
5% Solids	10	75.2	1.58