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Thomas P. McKeel
Western Michigan University

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An Investigation of the Relationships between Water Retention Additives and the Water Retention Mechanism

by

Thomas P. McKeel

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the course requirements for
The Bachelor of Science Degree

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Abstract

The purpose of this study was to examine how CMC, HEC and Kelgin QL function in their control of water retention. It is proposed that their performance can be related to the presence of hydroxyl and carboxyl groups on the hydrocolloid molecule. It was also proposed to study the effect of pigment selection on water retention. Water retention values(WRV) were measured on a modified S. D. Warren conductivity tester. It was concluded that the proposed theory represents a valid explanation of the water retention mechanism involving these additives. Differences in WRV of the additives was attributed to structural differences between the additive molecules. It was also concluded that no single factor- hydrophilic tendency, particle size, shape or distribution- could be identified to account for differences in WRV or improvement when pigment selection was varied.

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Theoretical Background

A major problem in coating color application is the control of penetration of the continuous or liquid phase. The continuous phase consists of water and binder, the primary purpose of which is to anchor the coating to the basestock. Although some penetration is desirable, Rowland and others have shown that excess penetration can have a detrimental effect on ink receptivity, smoothness and printability(1,2,3).

Water plays a dominating role when a coating color is brought into contact with the rawstock. It determines the rate of dehydration and solids increase along with rheological changes during the coating application. Dill and Taylor defined water retention as the capacity of a coating color to hold back its water and not release it to the paper substrate(4). Water retention(WR) is commonly referred to as: water holding, water loss, vehicle retention, water holdout and vehicle holdout. The ability to release this fluid is reported to be dependent on the number of hydrophilic attractions between the components and other factors such as liquid phase viscosity and coating percent solids(5,6).

Heiser and Cullen in 1965 determined that as the percent solids of the coating color was increased the continuous phase exhibited less tendency to migrate(7). Jones and Hetherington in 1980 reported similar results with their puddle blade WR-measuring device(8).

Hydrocolloids, more specifically, synthetic thickners, have been used in the paper industry, at concentrations of 0.1 to 0.5 parts per 100 parts pigment, to improve the water holding capabability of many coatings(5). These additives are known to be viscosity modifiers, however, studies by Somers(9) in 1970, Bently(10) in 1979 and others(11) indicated that concentration of additive is more important to WR than changes in viscosity as a result of the additive. Bartell has stated that the mechanism be which they function is dependent on the presence of certain functional groups, such as hydroxyl and carboxyl groups(5). Eklund attributed greater WRV with CMC and Kelgin to the presence of carboxyl groups not present on HEC(12). These additives react thru dipole adsorption, ionic attraction and hydrogen bonding with the binder, pigments and water present in the coating(5,8,13,14). These water soluble polymers can absorb on to the surface of the pigment acting as a protective colloid by extending the effective radius of the particle outward. This interaction suggests the formation of a Helmholtz double layer, which can immobilize a water layer around the particle.

A wide variety of methods have been developed to measure water retention. The first of these was the blotter permanganate test(15). The time for the liquid phase to penetrate the paper and wet the indicator was recorded as the WRV. This method was limited to low percent solids coatings.

Several other tests were developed but later discarded due to endpoint determination inaccuracies.

Stinchfield, Clift and Thomas developed an electrical conductivity test, known as the S. D. Warren tester, which measured the time required for the vehicle to penetrate the substrate and lower its resistance to a pre-determined level(16). The longer the time required to reach the set point, the greater the water retention of the coating. Temperature was reported to be the most important variable affecting this test, however, the type and amount of adhesive and pigment and percent solids also needed to be considered. Stinchfield, Clift and Thomas also reported decreased WR with $CaCO_3$ as compared to clay. This reaction was theorized to be related to differences in the particle size, shape and hydrophilicity.

Taylor and Dill devised a sonic velocity device to measure WR(4). Using this device, they concluded that viscosity changes as a result of hydrocolloid addition is not the sole factor causing increased WR. They suggested a network formation between the additive and the pigment particles could also contribute to improved WR.

The first dynamic WR test was the rolled inclined-plane technique(17). The amount of penetration could be calculated from the Arnold equation by comparing the patterns generated on a sheet of paper as a coating was smeared out by a steel roll.

A significant dynamic WR device was developed by Jones and Hetherington at Dow Chemical(8). Their puddle blade device was designed to simultaneously compare the WR capability of two coatings. They reported that at 70% solids, void of any binder, smaller particle size increased WR. However, the lower WRV of precipitated $CaCO_3$ as compared to clay was attributed to the lower hydrophilic nature of the $CaCO_3$ particles.

The thesis of this study is that CMC, HEC and Kelgin function by interacting with the water and pigments, present in the coating, to immobilize the continuous phase, preventing excess penetration. By comparing the coating WRV, at equal levels of additive concentration based on the percent in solution, with and without pigments present, a change in WRV would indicate an interaction between the additive, the water and the pigments.

Previous studies have reported the effect of pigment selection on WRV. Various factors including particle size, shape and hydrophilicity have been mentioned as being influential with respect to WRV. It is hoped that by varying the type of pigment selected, it will be possible to determine which, if any, factor stands out as the most important factor affecting the WRV of coatings.

Experimental Procedure

In the first segment of this experiment, 9 coatings were prepared and tested. The hydrocolloids evaluated were Hercules 7L1 CMC, Union Carbide QP-09 HEC and Kelgin QL.

The WRV that are reported here, are calculated from a modified S. D. Warren tester. The values are an average of five tests and were conducted at room temperature using Allied 12 lb. bible paper. Figure 1 illustrates the test equipment set-up.

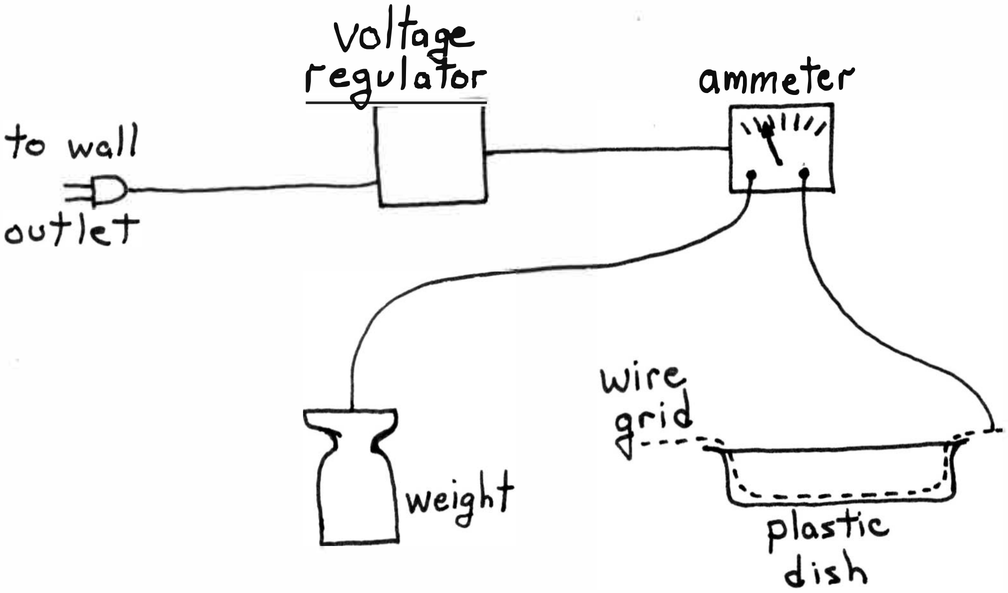


Figure 1

A coating was prepared and an amount was poured into the plastic dish to just cover the wire grid in the bottom of the dish. A piece of bible paper was suspended across the dish. The top electrode, weighted to give a pressure of .214 psi, was then placed on the paper forcing it down into the coating and against the wire grid. A change in the current was measured directly off the ammeter, with the time recorded being the time to reach 1/2 scale on the meter.

The coatings prepared in this study represent simplified models of industrial coatings. They were purposely designed to be void of any binders, defoamers and other chemical additives that might interfere with the variables to be studied. The method of concentration based on percent in solution contradicts the normal industry practice of concentrations based on pigment. It was felt that the industry practice does not allow WRV to be compared independent of percent solids. Utilizing concentrations of additive actually in solution it is possible to compare WRV at equal levels of concentration independent of the pigment solids.

The addition levels were based on the continuous phase of a 36.8% solids #2 clay slip. Sample calculations are shown in Figure 2.

Clay	35g.	35g.	35g.
Additive	1.8g.	1.2g.	0.6g.
Water	60g.	60g.	60g.
% Solution	3.0	2.0	1.0
% Solids	36.8	36.8	36.8

Figure 2.

4.0 percent solids solutions of Hercules 7L1 CMC and Union Carbide QP-09 HEC were prepared by dispersing 10g. of the respective hydrocolloid into 240g. of vigorously agitated tap water. In a similar manner, a 4.0 percent solids solution of Kelgin QL was prepared, except that distilled water was used in place of tap water.

In the second portion of this study, 16 coatings were prepared and evaluated in the Warren tester. Master solutions of the individual components were prepared from which the required amounts, illustrated in Figure 3, were withdrawn.

Pigment	35g.	35g.	35g.
CMC	1.8g.	1.2g.	0.6g.
Water	60g.	60g.	60g.
% Solution	3.0	2.0	1.0
% Solids	36.8	36.8	36.8

Figure 3.

The procedure for preparing the 4.0% solids solution of CMC and measuring the WRV is the same as that used in part 1.

The #2 clay slurry was the same as that used in part 1. Ti-Pure(TiO_2- rutile form) at 82% solids was diluted to 70% solids with the addition of tap water. The ground $CaCO_3$ used was Hydrocarb 65 pre-slurried to 70% solids. Precipitated $CaCO_3$(Albagloss) was slurried to 70% solids with tap water and 0.5% Dispex N-40 using the Disersator high shear mixer.

Discussion of Results

It was theorized earlier that the presence of carboxyl and hydroxyl groups, functioning as water holding sites, enable CMC, HEC and Kelgin to modify the WR of coating colors. If the water retention values(WRV) of CMC, HEC and Kelgin without a pigment are higher than the WRV of CMC, HEC and Kelgin with a pigment, at equal concentrations of additive actually in solution, this would indicate that the pigment particles are interacting with the additives, to tie up the functional groups and reduce the number of available water holding sites.

The data as shown here and in Figures 4,5 and 6 indicates that at equal levels of concentration, WRV is decreased by the presence of a pigment, thus supporting the theory that CMC, HEC and Kelgin function due to the presence of carboxyl and hydroxyl groups.

2% solution of additive

	WRV (sec.)
CMC	8.4
CMC + Clay	3.5
HEC	2.96
HEC + Clay	2.0
Kelgin	4.4
Kelgin + Clay	2.3

The water holding capability of the functional groups can also be used to explain the higher WRV of CMC and Kelgin, shown in Figure 7, as compared to HEC. While CMC, HEC and

Figure 4

Effect of CMC Solutions on WRV

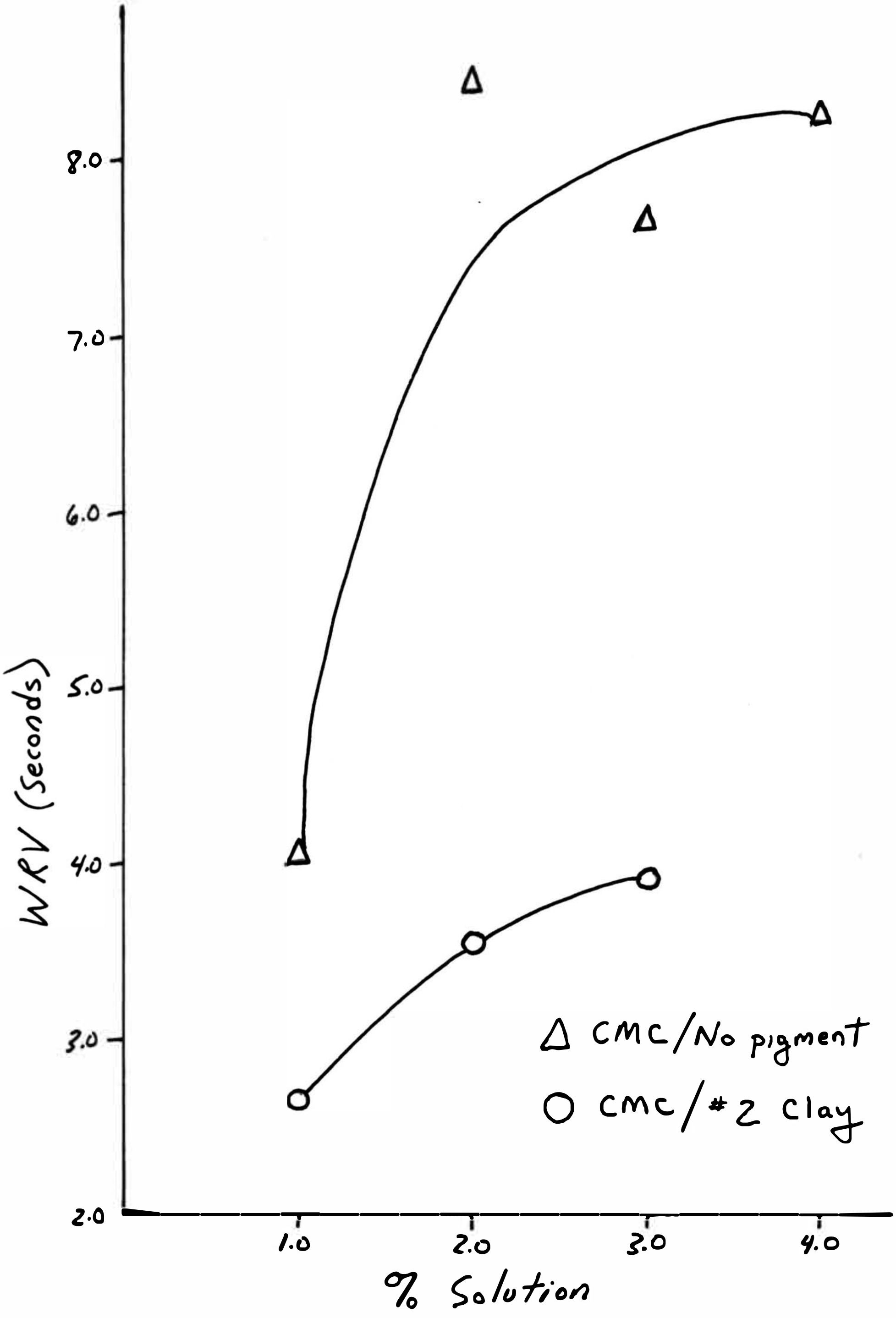
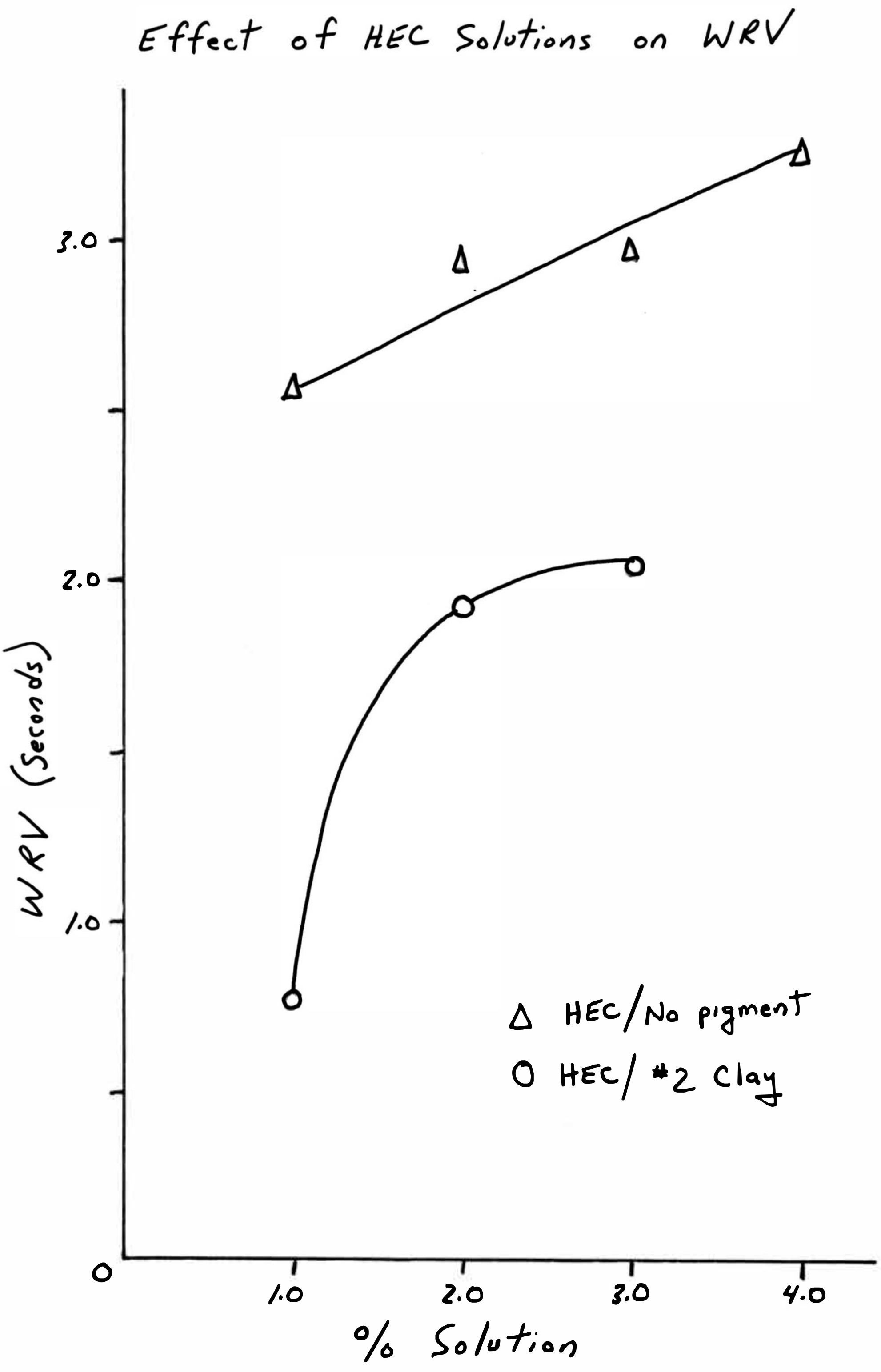


Figure 5



Effect of HEC Solutions on WRV
WRV (Seconds)
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
% Solution
△ HEC/No pigment
○ HEC/ #2 Clay

Figure 6

Effect of Kelgin Solutions on WRV

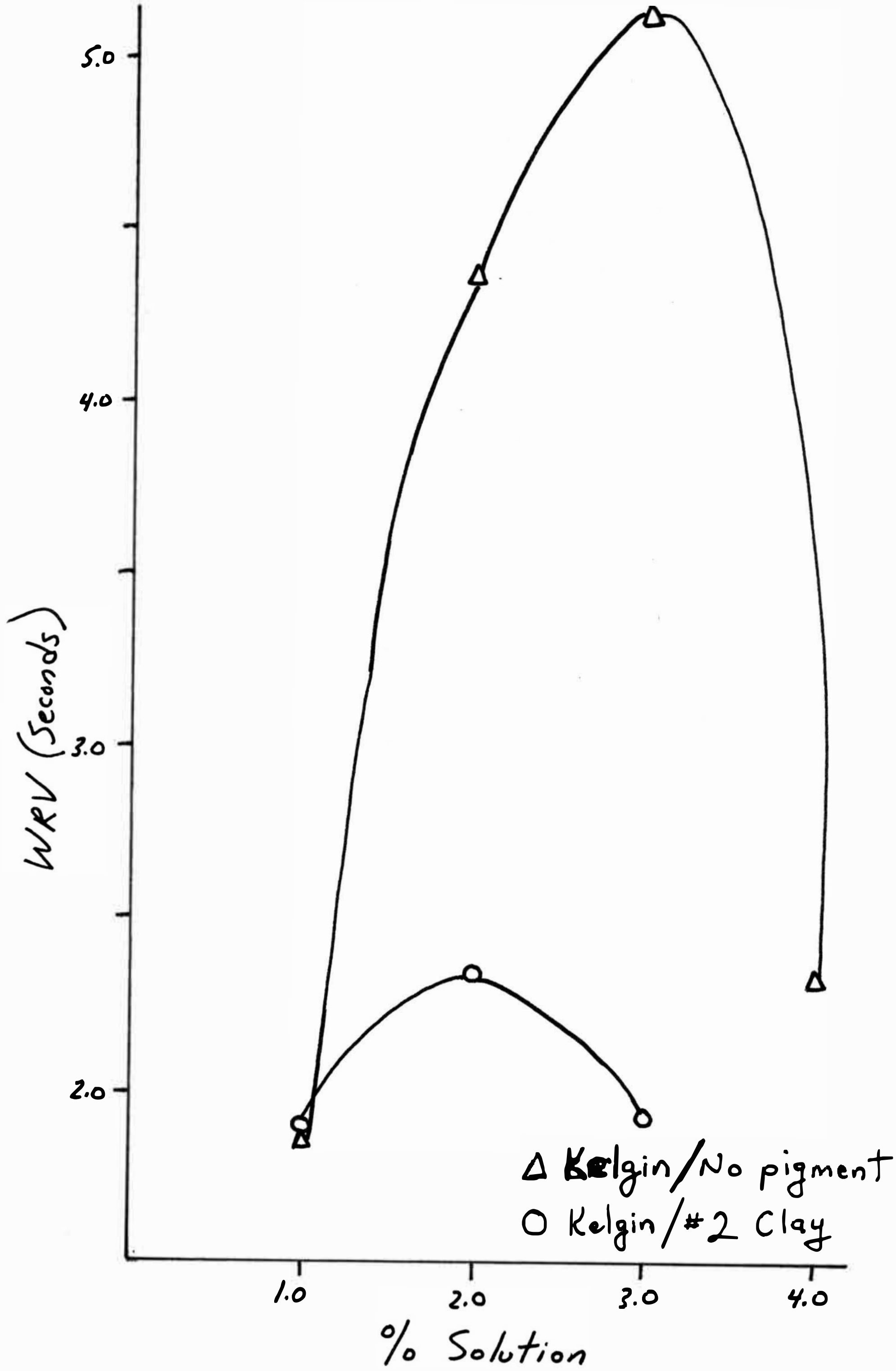
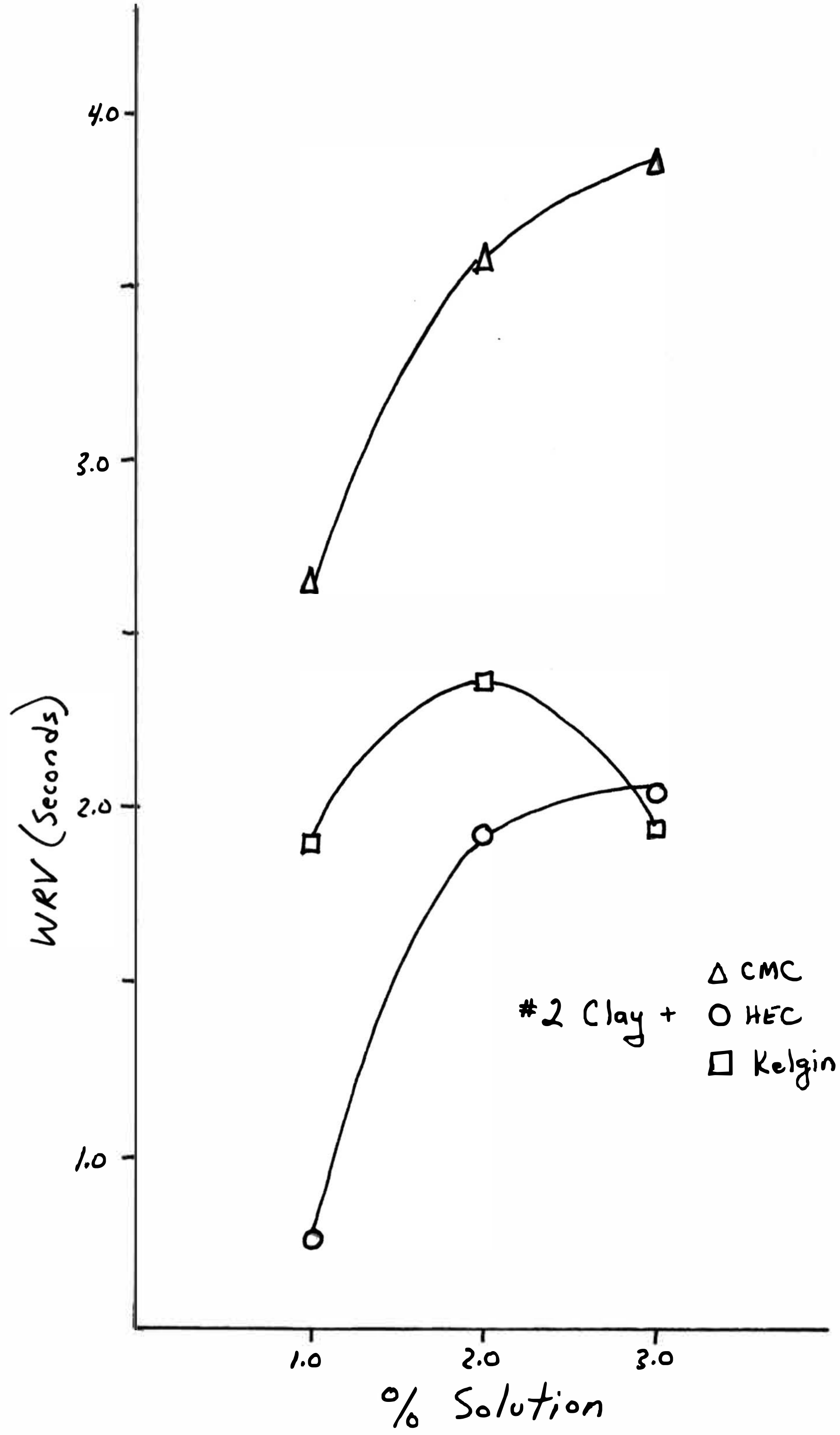


Figure 7

Effect of WR Additives on WRV



Kelgin all contain hydroxyl groups, only CMC and Kelgin contain carboxyl groups which can provide additional water holding sites. Similarily, we might expect CMC and Kelgin to produce a greater improvement in WR than HEC at equal concentration levels. However, Figure 7 indicates that between 1% and 2% solution concentration, CMC and HEC produce WR improements of a similar magnitude, with Kelgin giving substantially less WR improvement.

Figures 4,5, and 6 illustrate that WRV increases as the concentration of WR additive is increased. This improvement can be attributed to a greater number of available water holding sites as the additive concentration is increased. However, the graphs also show that WR improvement begins to level out above additive concentrations of 2.0% solution. Above 2.0%, CMC and HEC continue to improve WR, although the magnitude of the increase begins to decrease.

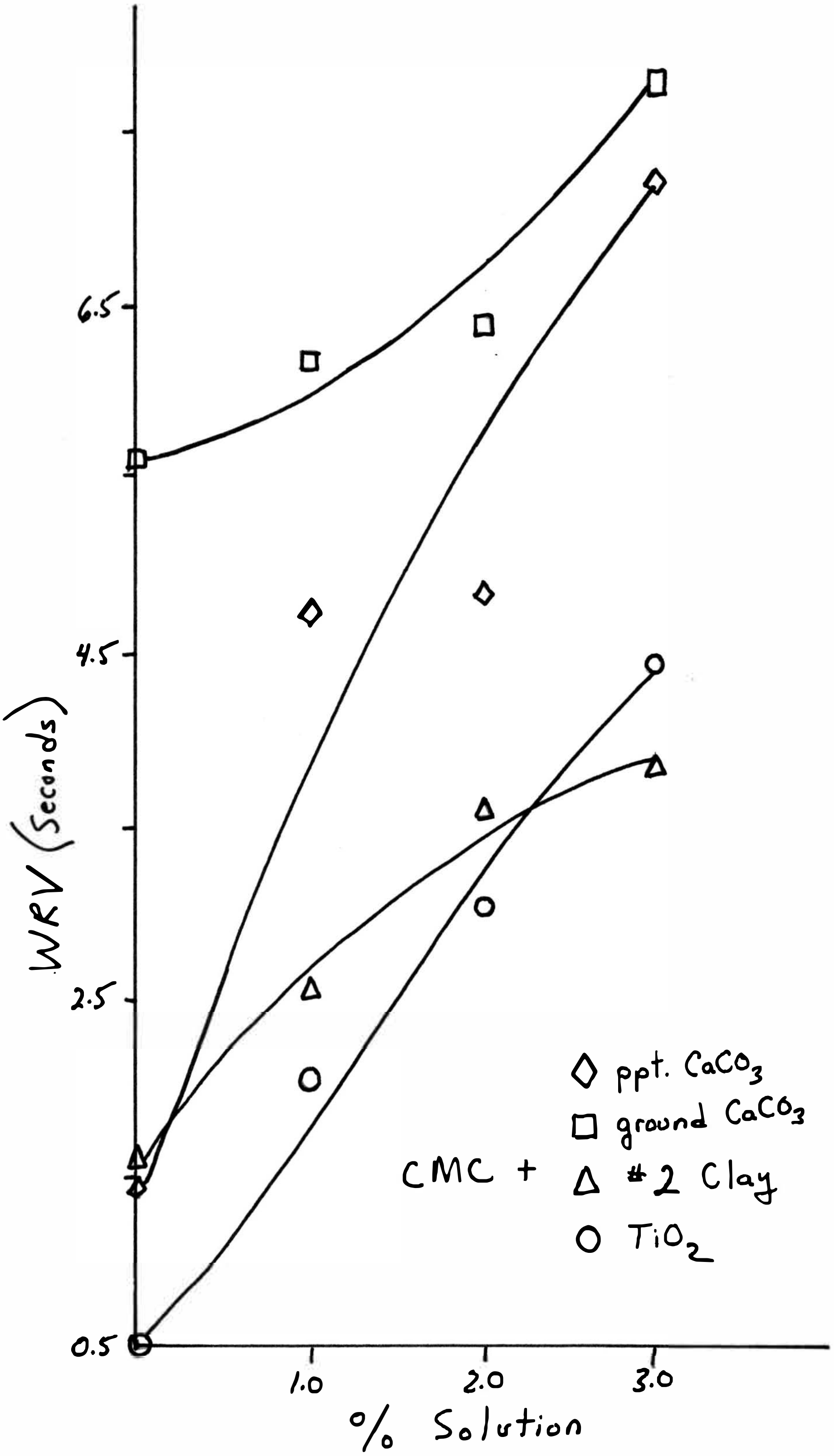
Between 2.0 and 3.0%, WRV was shown to decrease with Kelgin. WRV of Kelgin with and without clay, shown in Figure 6, indicated that the WRV of Kelgin without clay rises to a peak at approximately 3.0% and then decreases. Following the addition of a clay pigment, the point at which the WRV begins to decrease was found to be approximately 2.0% solution. It is possible that as the concentration of Kelgin is increased, the carboxyl and hydroxyl groups of the Kelgin molecules react more with each other rather than with the water in the coating. These reactions may occur to the point that the water is excluded from the reaction and thus reducing the WRV of the coating. The addition of a pigment may accelerate this reaction by providing a large surface area around which the Kelgin molecules may agglomerate. Applying this theory to CMC and HEC, it is evident that the additive concentration is still insufficient to totally exclude the water molecules from interacting with the functional groups, therefore WR continues to improve.

Interestingly, CMC, which also contains both carboxyl and hydroxyl groups, did not exhibit this type of behavior at similar levels of addition. This suggests that there may be other factors that, individually or in combination with the theory discussed above, could explain the reaction of Kelgin. One factor could be the sensitivity of Kelgin to multi-valent ions(18). Literature on Kelgin indicates that poly-valent cations can react and sometimes crosslink with Kelgin. This crosslinking of the Kelgin could tie up the water holding sites and reduce WR. Literature concerning CMC indicates that it is relatively insensitive to most poly-valent ions and does not crosslink or precipitate out of solution(19).

The second portion of this experiment was designed to study the effect of pigment selection on WR. The results, shown in Figure 8, indicate that WR, at equal levels of CMC concentration, is greatest with a fine ground $CaCO_3$

Figure 8

Effect of Pigment Selection on WRV



followed by precipitated $CaCO_3$, #2 clay and TiO_2. Although WRV increased as the concentration of CMC increased, the magnitude of WR improvement varied with the pigment being tested.

TiO_2, as expected, showed a substantial improvement in WR from 0.5 to 3.6 seconds. The chemical inertness of TiO_2 particles prevents them from reacting not only with water molecules but with CMC as well. This would suggest that increased WR is a result of the introduction of water holding groups, on the CMC molecule, into the TiO_2 coating.

The #2 clay, with its higher surface potential than TiO_2, and therefore greater hydrophilic tendency, produced higher WRV when tested alone(20). However, the hydrophilic attraction of the clay is also attractive to the carboxyl and hydroxyl groups on the CMC molecules. Although WR increased with CMC addition, the possibility of a reaction between the functional groups of CMC and the clay particles could gradually exclude the water from interacting with the CMC. The net result would be a gradual decrease in WR improvement until a point is reached at which additional amounts of CMC have either no effect or decrease WR.

An earlier study by Jones and Hetherington(8) stated that although precipitated $CaCO_3$ had a smaller equivalent diameter than a #2 clay, it dewatered faster, which they attributed to the less hydrophilic nature of the $CaCO_3$. The results of this study indicate that a #2 clay shows more WR than a precipitated $CaCO_3$ and less WR than a fine ground $CaCO_3$, when tested alone. If the hydrophilic nature of the pigments is important to WR, we should expect to find both $CaCO_3$'s having lower WRV than clay with no additive present and greater WRV than clay when CMC is added. The magnitude of WR improvement should also be greater with the $CaCO_3$'s due to fewer reactions between the pigment and the functional groups on the CMC. The precipitated $CaCO_3$ results correspond to this theory very well, however, the ground $CaCO_3$ do not. As can be seen in Figure 8, ground $CaCO_3$ exhibits higher WRV than clay when tested in the absence of CMC, yet the magnitude of WR improvement is similar to clay. Because these two pigments have very similar particle size distributions this suggests that particle size may have some effect on WR(<u>21</u>). If particle size is an important factor, then these two pigments should have similar WRV at equal concentrations of CMC. The data shows however that the WRV of ground $CaCO_3$ is greater than the WRV of the #2 clay, therefore particle diameter does not appear to be the controlling factor in WR.

Other factors which may have some effect on WRV of various pigments are particle shape, method of manufacture, and pH(<u>22</u>).

Conclusions

The ability of CMC, HEC and Kelgin to retain water in a coating color is a function of the hydroxyl and carboxyl groups present on the additive molecule. The absence of carboxyl groups on the HEC molecule may explain the lower WRV, as compared to CMC and Kelgin, which contain both functional groups. Water retention can be improved by increasing the concentration of additive, however, above a certain concentration WR appears to level off and may decrease.

No conclusive statement can be made concerning the controlling factors of WR as related to pigment selection. Although WR increases with additive concentration, pigment selection may effect the magnitude of this improvement. This appears to be related to the hydrophilic nature of the pigment, however, the results also suggest that particle size distribution, particle shape, method of manufacture and pH may influence WR and needs to be considered.

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Appendix 1

Water Retention Values

% Solution	0	1	2	3	4
Kelgin	-	1.88	4.38	5.12	2.32
Kelgin + clay	-	1.9	2.34	1.92	-
HEC	-	2.56	2.96	2.98	3.24
HEC + clay	-	0.76	1.91	2.03	-
CMC	-	4.04	8.44	7.64	8.3
CMC + clay	1.6	2.64	3.59	3.86	-
CMC + ppt. $CaCO_3$	1.46	4.72	4.86	7.2	-
CMC + grd. $CaCO_3$	5.6	6.2	6.4	7.8	-
CMC + TiO_2	0.5	2.08	3.02	4.4	-