



Western Michigan University
ScholarWorks at WMU

Paper Engineering Senior Theses

Chemical and Paper Engineering

4-1996

Coating Insolubilization: A Comparison of AZC and KZC

Scott Brigham
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/engineer-senior-theses>

 Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation

Brigham, Scott, "Coating Insolubilization: A Comparison of AZC and KZC" (1996). *Paper Engineering Senior Theses*. 11.

<https://scholarworks.wmich.edu/engineer-senior-theses/11>

This Dissertation/Thesis is brought to you for free and open access by the Chemical and Paper Engineering at ScholarWorks at WMU. It has been accepted for inclusion in Paper Engineering Senior Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



Coating Insolubilization

A Comparison of AZC and KZC

by:
Scott Brigham

Advisor: Dr. Ellsworth Shriver

April 9, 1996

INTRODUCTION

The prime function of a paper coating insolubiliser is to reduce the water solubility or sensitivity of the pigment binders used in the coating composition. The degree and amount of water solubility will depend on the type and amount of binder used (1). This is important in many applications of coated paper or paper board. Tags, instruction manuals, poster board and wall paper all require varying degrees of resistance to water.

Coating insolubilisers can be broken into two main categories: waterproof and water resistance. Waterproof refers to products that have been rendered impervious to water by hydrophobic materials such as wax.

Water resistance refers to coatings that slow the rate of or amount of liquid penetration. Most coated paper and paperboard is printed with water base inks so coatings must be somewhat porous to receive ink. However, the critical factor is how much the coating binder becomes solubilized and particles loosened.

There are a three main methods to obtain water resistance in a paper coating. The first is method utilizes the incorporation of highly water-repellent materials such as waxes of metallic soaps. The second is incorporating binders of low water sensitivity into the coating composition. The last method and the method that I

will be studying involves the formation of insolubility through cross-linking reactions of coatings with an added metal salt, amino group, or aldehyde (2).

BACKGROUND

Historically, the two most common cross linking/curing agents have been melamine formaldehyde and glyoxal-based resins due to their strong cross-linking ability with starches and proteins. Both melamine formaldehyde and glyoxal-based resins cross-link well with the hydroxyl (OH) groups of natural binders. However, synthetic binders, such as latex, have few OH sites and therefore are not as effective as are starches and proteins.

These synthetic binders have been increasing in use throughout the paper industry for several reasons. These binders do not require special treatment before addition to coating formulas, they have high binding strength, and good coating flexibility. Due to the increasing use of synthetic binders a new family of cross-linkers have evolved from Zirconium chemicals (3).

Zirconium is a surprisingly common and widely distributed element. Due to the element's high charge to radius ratio, the aqueous chemistry of zirconium is characterized by hydrolysis in the presence of polymeric species. The range of

species present depends on the zirconium and hydrogen ion concentration, the nature and concentration of anions present, the temperature and the history and age of the solution. This gives zirconium the ability to react strongly with oxygen containing species, which is the reason zirconium chemicals are finding use with organic polymer systems (4).

A commonly used form of Zirconium is Ammonium Zirconium Carbonate (AZC). AZC is a soluble alkaline salt of zirconium which is available as an aqueous solution. This has been a known insolubiliser for coating binders since the early 1960's. However, little work has been done to assess its performance and true capabilities compared to other insolubilisers.

If evaporation of water is carried out in the presence of organic polymers, reaction occurs between the zirconium and the polymer to produce cross-linked structures with the rest of the solution leaving as carbon dioxide and ammonia. The molecular size and complexity provide the insolubility in water. This is the reason for the use of AZC as an insolubiliser in paper coating binders (4).

However, one of the major problems with AZC is the release of ammonia. Some companies prohibit the use of ammonia based chemicals which makes AZC an impossible choice. In the past the only other choice was to resort to the less

reactive aldehyde and glyoxal based resins. Now there is an alternative Zirconium chemical that does not release ammonia: Potassium Zirconium Carbonate (KZC).

AZC and KZC are both possible zirconium compounds capable of supplying the insolubilisation of coating. KZC is new on the market compared to AZC. It is thought that the ammonia in AZC reacts with the clay dispersion and causes viscosity increases during storage times. An inhibitor of ammonium tartrate slows this reaction between the ammonia and clay. However, studies have shown that KZC does not result in viscosity increases.

KZC appears to be a viable replacement for AZC due to its rheology characteristics and ability to stay stable without ammonia.

PURPOSE

My thesis will compare and contrast the insolubilisation performance of KZC and AZC. The areas that will be evaluated include rheology and insolubilisation.

EXPECTED FINDINGS

I expect that KZC will perform equally as well as AZC and will eliminate the environmental problems associated with AZC.

EXPERIMENTAL DESIGN

Coating Formulation

My experiment uses a simple coating formulation of styrene/butadiene latex as a binder, carboxy methyl cellulose as the flow modifier and an insolubiliser. The coating solutions are to be made using .57, 1.6, and 3.7 parts each of AZC and KZC on coating pigment. Also a control group will be run using 0 parts insolubiliser. The formulations are as follows:

- 100 parts #2 Clay (Hydrasperse)
- 18 parts latex binder (dow 620)
- 1 part carboxy methyl cellulose
- .57, 1.6, and 3.7 part insolubiliser
- .25 parts dispersant (Dispex N40)- KZC only

After make-down of the coating formulations, the pH of the coatings were adjusted to 8.5. Dispersant was added to KZC coating formulation due to its high viscosity upon addition.

Application

Each of the coatings were applied to a base stock using a laboratory CLC coater. The coater was run at the lowest power level and drying time to limit the curing of the sheet. The sheets were then transferred to an oven and cured at 102

C for varying times of 0, 20, 40, 60, and 300 seconds. This allows the cure rate for both insolubilisers to be examined.

Testing

These formulations were then measured for initial viscosity to determine the effect the insolubiliser may have upon addition. Viscosity readings were continued for 1, 5, and 24 hours on both coatings to determine the effect time may have on the coatings.

The cured samples were then tested for insolubiliser performance using the Adams Wet Rub test following TAPPI Standards. This test was run for 90sec testing times. The resulting solutions were then tested for turbidity to measure the amount of solubilised coating.

RESULTS

(See following Table and Graphs)

DATA TABLE I

AZC

	.57pph			1.6pph			3.7pph		
	6.9 g/m2	9.9 g/m2	17.5 g/m2	8.5 g/m2	10.6 g/m2	18.0 g/m2	6.8 g/m2	10.8 g/m2	13.7 g/m2
0sec	420	452	475	402	420	439	240	320	392
20sec	362	327	326	207	315	352	220	280	297
40sec	289	260	245	165	250	295	180	124	180
60sec	237	174	187	145	155	158	120	95	113
300sec	155	98	103	110	91	98	75	80	90

KZC

	.57 pph			1.6 pph			3.7 pph		
	7.4 g/m2	11.3 g/m2	17.3 g/m2	6.7 g/m2	10.7 g/m2	17.9 g/m2	7.6 g/m2	10.6 g/m2	19.8 g/m2
0sec	510	500	590	500	310	510	290	380	471
20sec	410	470	420	180	283	450	190	275	400
40sec	300	400	340	150	205	300	140	160	300
60sec	210	300	265	140	180	250	120	112	240
300sec	160	65	98	110	83	90	74	90	80

CONTROL

	6.7 g/m2	11.0 g/m2	16.7 g/m2
0sec	513	587	632
20sec	436	489	607
40sec	425	457	588
60sec	421	398	591
300sec	388	410	490

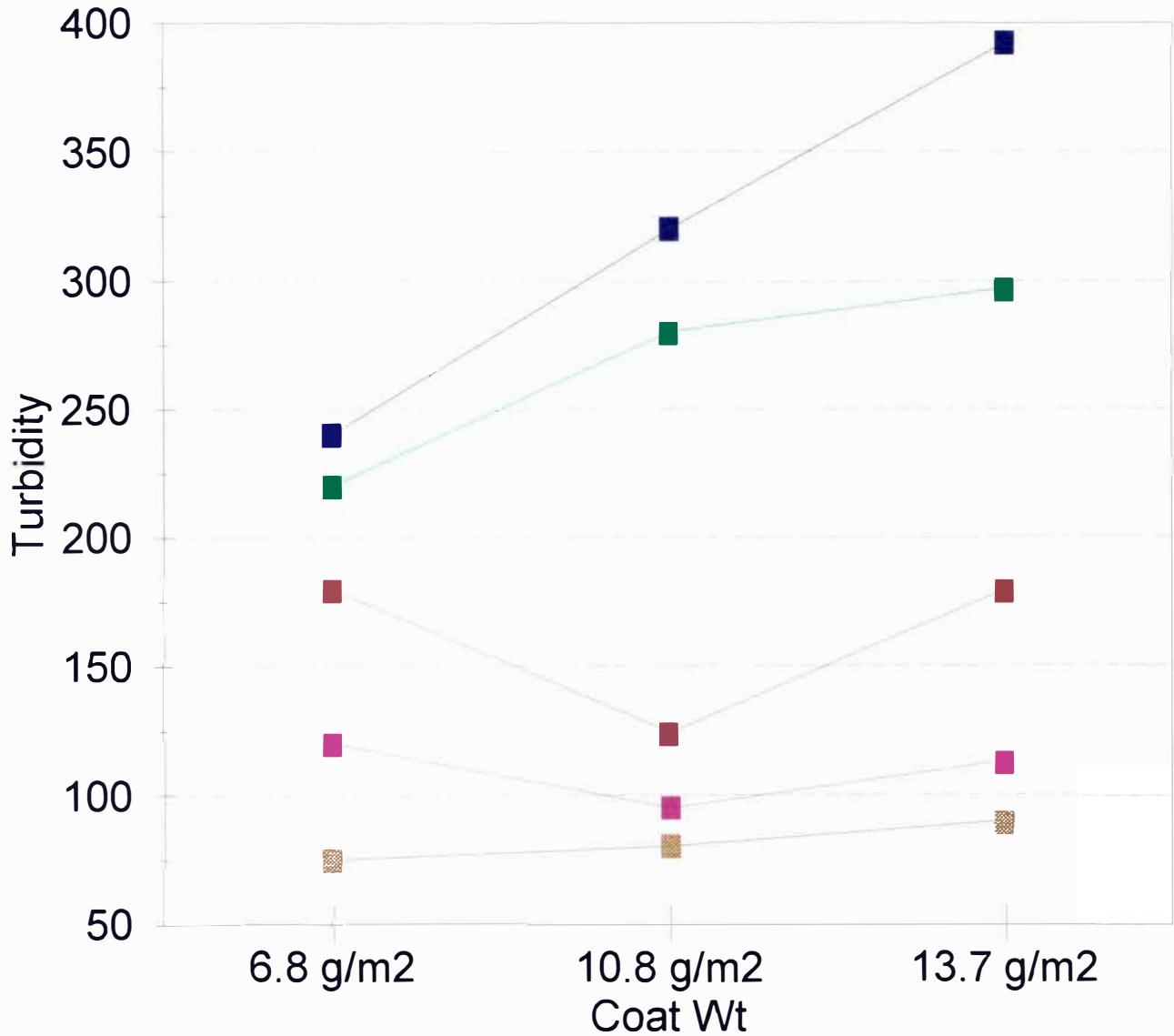
VISCOSITY

(cP at 100 rpm)

	AZC	KZC
INITIAL	1200	3450
1 HOUR	1220	2450 (With Dispex)
5.0 HOUR	4990	1620 " "
24 HOURS	11100	1444 " "

Effect of Coat Wt.

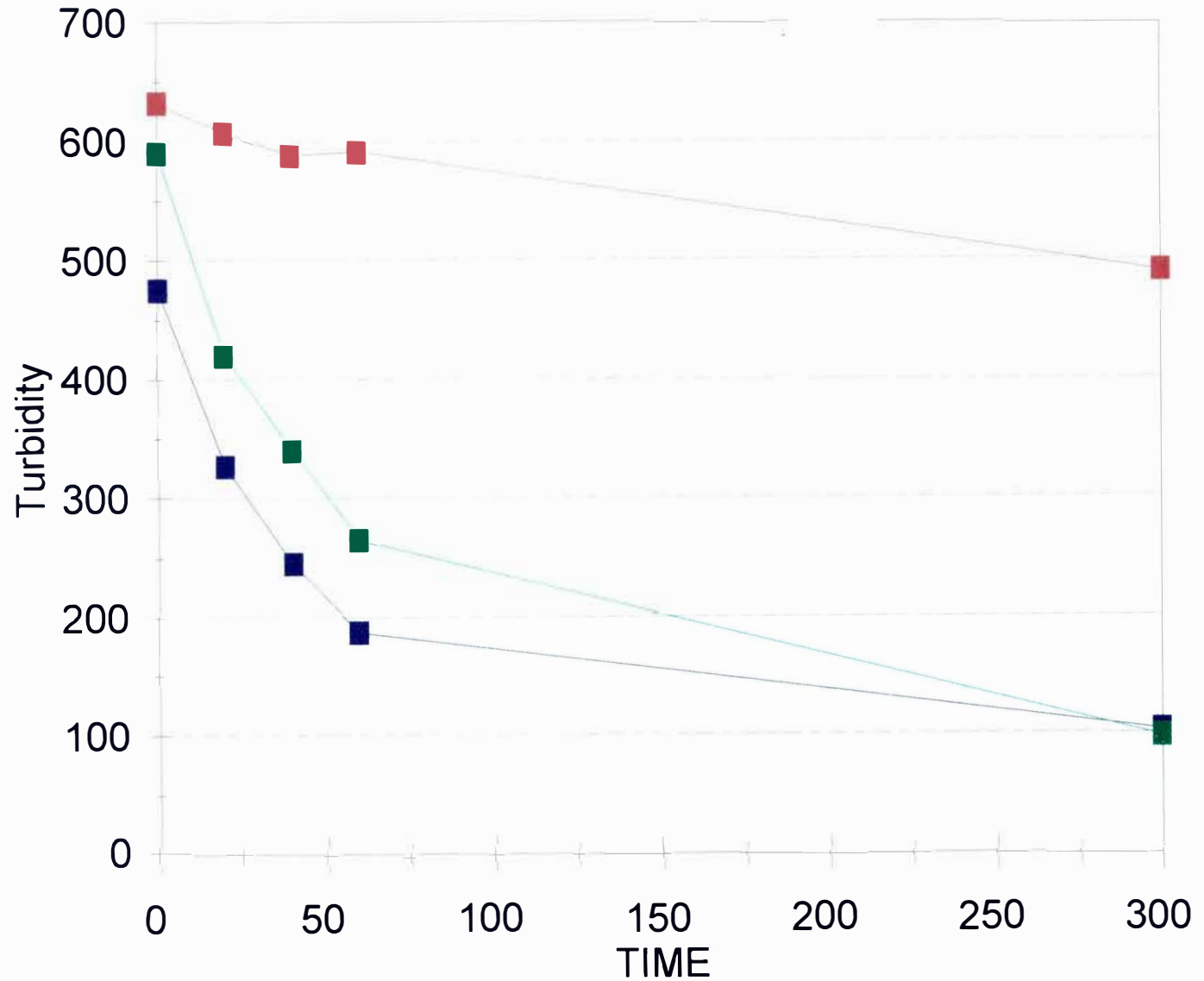
3.7 pph AZC



■ 0sec ■ 20sec ■ 40sec ■ 60sec ■ 300sec

Cure Rate

.57 pph AZC & KZC

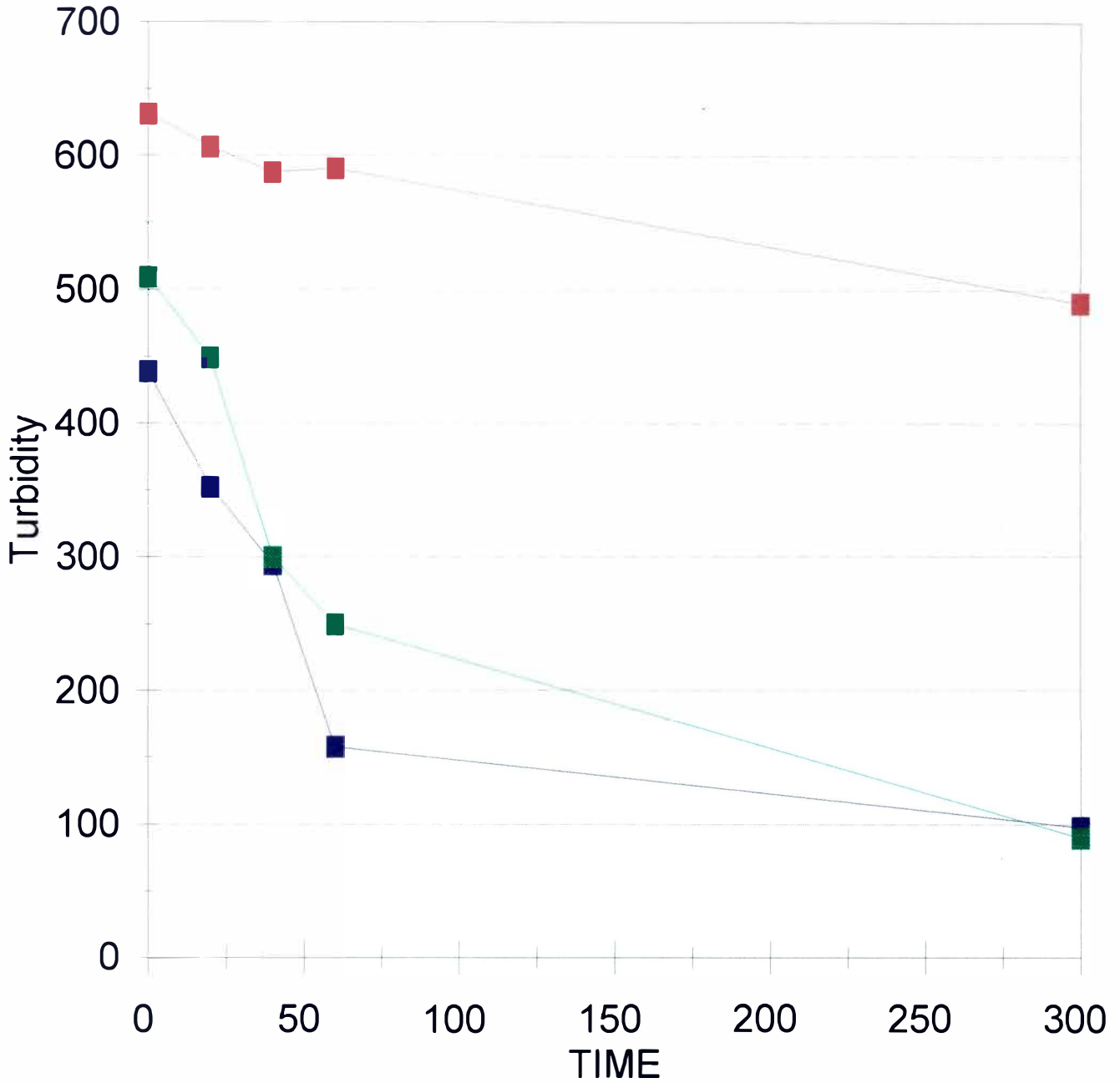


AZC KZC CONTROL

■ 17.5 g/m² ■ 17.3 g/m² ■ 16.7 g/m²

Cure Rate

1.6 pph AZC & KZC

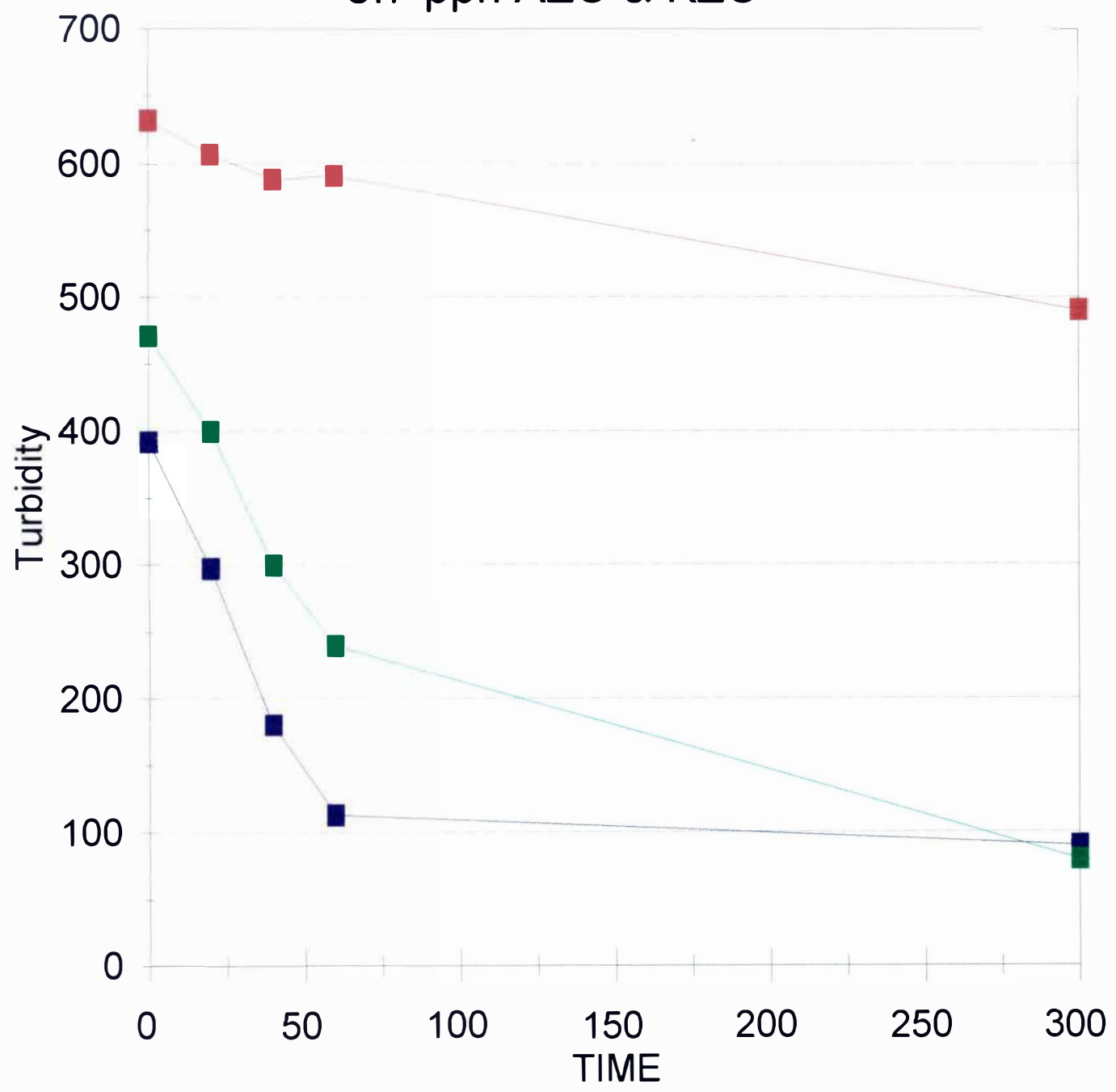


AZC KZC CONTROL

■ 18.0 g/m² ■ 17.9 g/m² ■ 16.7 g/m²

Cure Rate

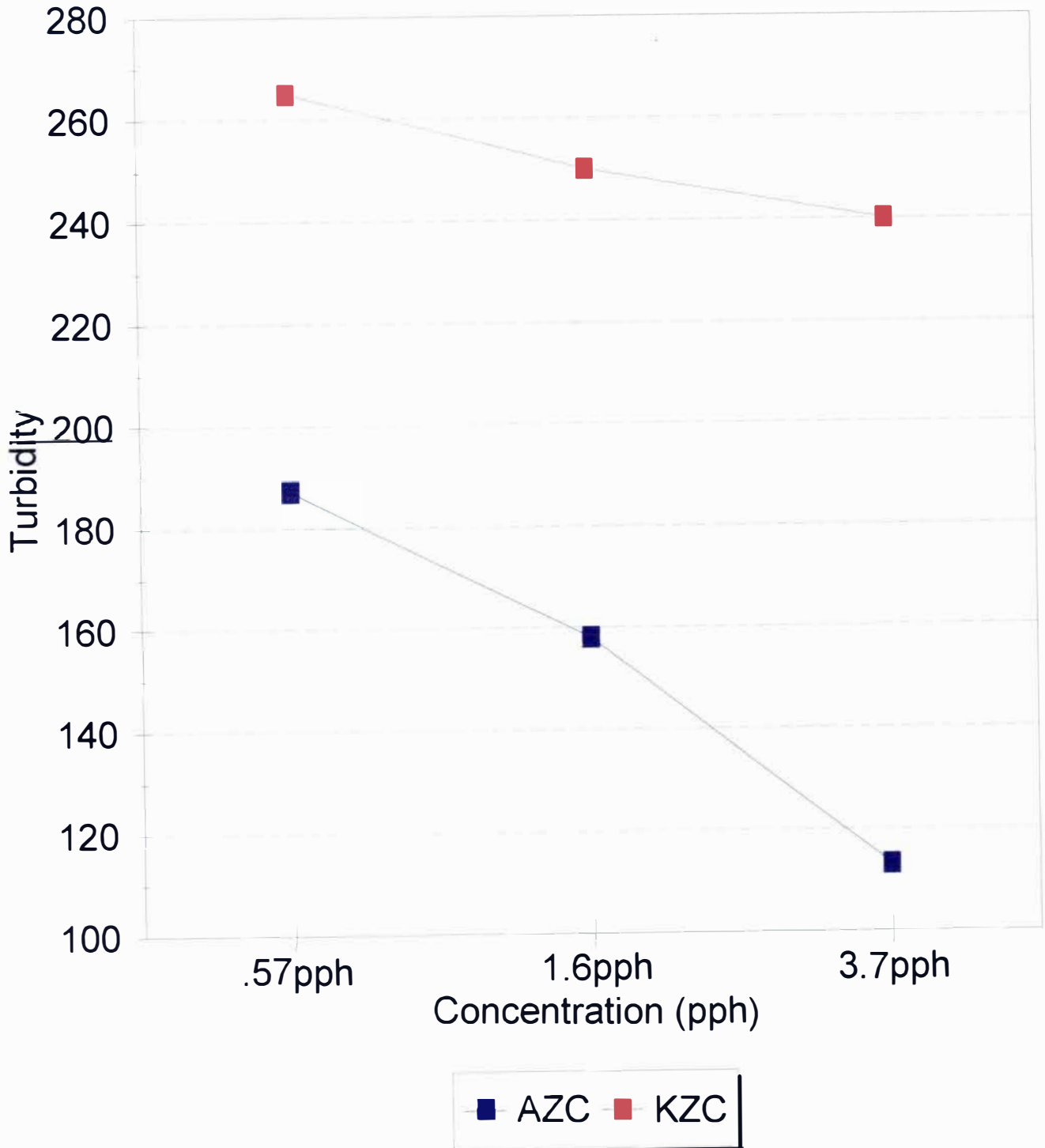
3.7 pph AZC & KZC



AZC	KZC	CONTROL
■ 13.7 g/m ²	■ 19.8 g/m ²	■ 16.7 g/m ²

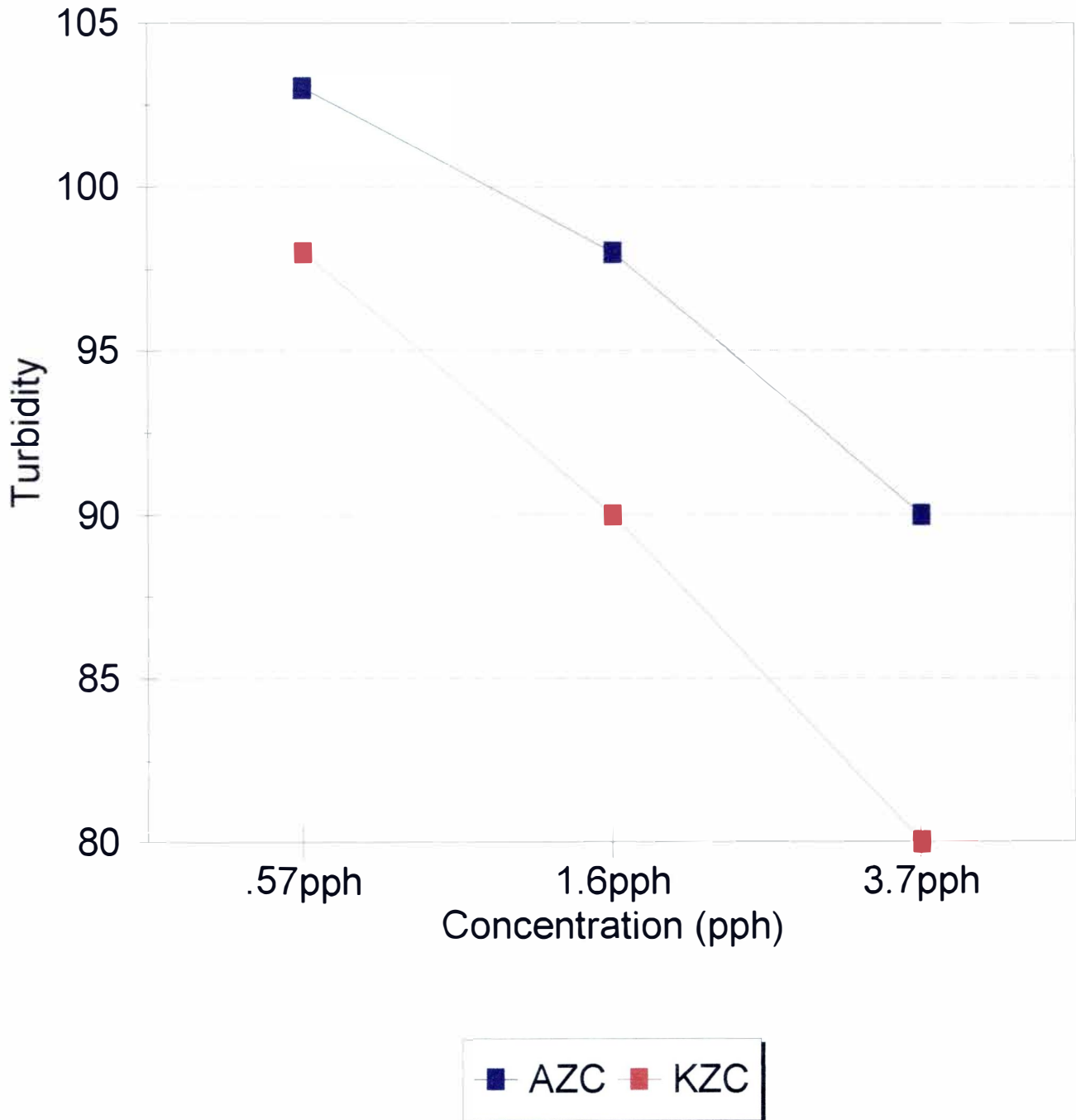
Insolubiliser Performance

High Coat Wt./60 sec Cure Time



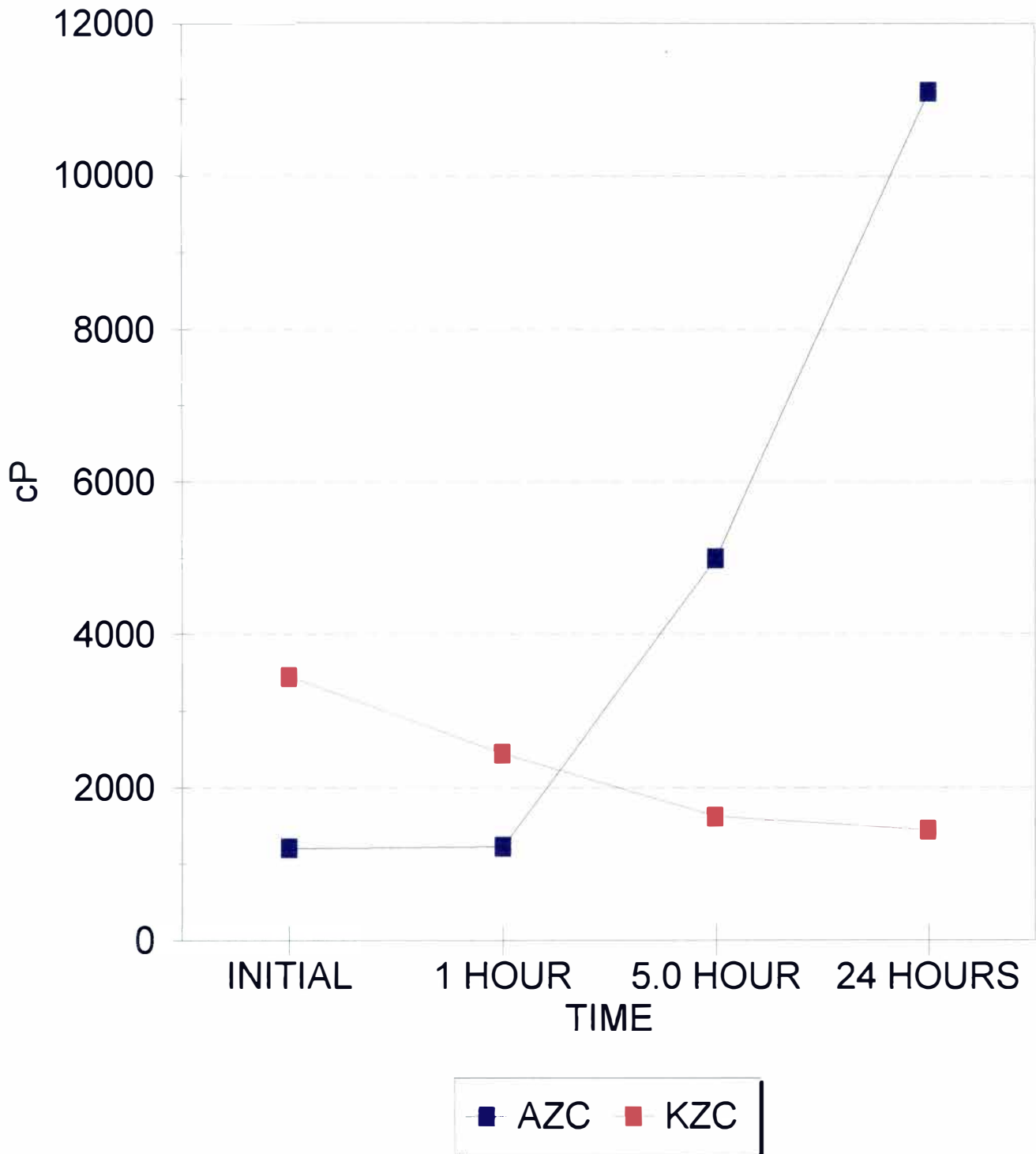
Isolubiliser Performance

High Coat Wt./300 sec Cure Time



Effect of Time of Viscosity

KZC and AZC



DISCUSSION

The experiment was based on the premise that sufficient coating would prohibit the Adams Wet Rub test from reaching the base sheet. Once the basesheet was reached the results can no longer be compared due to the fact that the wet rub spent a duration of the 90 second test time rubbing the base sheet instead of the coating itself. This created a significant problem at low cure times as there was insufficient insolubilisation to prevent this occurrence.

Graph I demonstrates the effect that coat weight has on the amount of coating that is rubbed off for AZC as measured by the turbidity of the solution. At low cure time there was distinct differences between the coat weights. This demonstrates that at each coat weight the Adams Wet Rub reached the base sheet. However, the 300 second cure time had sufficient resistance to wet rub as proved by almost even turbidity numbers for all three coat weight. This demonstrates that this data is viable.

Graph II demonstrates a similar trend to Graph I. At low cure times the coating was unable to resist the penetration of the wet rub. This again shows that the base sheet was reached and the amount of coating rubbed off changed when the coat weight was increased. These graphs show similar trends between AZC and

KZC as coating insolubilisers.

Graph III demonstrates the cure rate of AZC when compared to KZC at .57 parts per hundred parts binder insolubiliser concentration and the high coat weight. The graph demonstrates that AZC and KZC have similar cure rates. With the low addition levels, the coatings still double the insolubilisation level, after 60 seconds of cure, as compared to the control group. There is an evident cure rate shift between the two which is thought to be caused by the addition of the dispersant. The dispersant is thought to interfere with the cross-linking between the latex binder and the Zirconium. However, the fact that KZC is capable of performing insolubilisation properties is well demonstrated.

Graphs IV and V again further demonstrate the ability of both insolubilisers to decrease the amount of coating solubilised in the wet rub test. Coat weight variations were caused by the CLC coater and are inherent in its operation. This is expected to cause slight variations but as above mentioned, if the wet rub never reaches the base sheet no variation will occur.

The purpose of the experiment was to prove that AZC and KZC reacted similarly as coating insolubiliser. Due to the unforeseen viscosity problem the formulations of the two insolubilisers differ by the addition of the dispersant to

KZC and can not be directly compared. However, Graph VI and VII due show both insolubilisers provide increased insolubilisation when their concentrations are increased. Graph VII shows that at the high cure time the performance of the two only differ by at most 10 turbidity units. This suggests that the performance difference may be due to differences in cure rates.

The last figure is Graph VIII. This demonstrates the differences between the two insolubilisers with respect to viscosity. It can be seen that AZC showed little to no increase in viscosity one hour after addition. However, after five hours the KZC, still at the same pH, increased drastically. The viscosity increased from 1220 to 4990 cP after five hours and from 4990 to 11100 after 24 hours. This is expected to be decreased by the addition of an ammonium tartrate.

Looking at the KZC curve we can see that the viscosity was high upon addition but decreased with time. This may be due to the further mixing of the dispersant or rheology differences between KZC and AZC.

CONCLUSION

- 1.) KZC has shown to be an effective insolubilising agent
- 2.) KZC and AZC follow similar curing rates at the tested concentrations
- 3.) Most curing for both insolubilizers occurs during first 60 seconds
- 4.) Insolubilizing properties increase steadily with an increase in concentration
- 5.) Large concentrations must be used to obtain incremental increases in insolubility
- 6.) KZC causes an increases in viscosity upon addition, but remains constant with time
- 7.) AZC causes only slight increases in viscosity upon addition, but increases with time

RECOMMENDATIONS

- 1.) Larger Coat Weights-
Insufficient coat weights caused the Adams wet rub to reach the basesheet before the end of the test. This causes significant error in the test results
- 2.) Lower KZC Coating Viscosity-
The coating containing KZC should be ran first under conditions that can then be applied to the AZC coating (solids, thickener content, dispersant etc.). This would enable proper evaluation of performance between the two.
- 3.) More Insolubilizer Concentrations-
Three concentrations are not adequate to determine optimal concentration levels for insolubility. More levels would demonstrate the trend more clearly.

REFERENCES

- 1) Athney, R.D. Jr., (eds). "Water Resistance in Paper Coatings" TAPPI PRESS, Atlanta, 1983.
- 2) Landes, C.G. and Kroll, L. (eds). "Paper Coating Additives", TAPPI PRESS, Atlanta, 1978.
- 3) Cox, J. "Technology Produces the Edge for Coating Binder Supplies", American Papermaker 52(12):54-55.
- 4) McAlpine, I., 1982 TAPPI Coating Conference Proceedings, TAPPI PRESS, Atlanta, p.165.