# "Effect of Polyacrylate addition on Coating Color Rheology, Water Retention and Runnability"

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**ABSTRACT:-** Five Commercial polyacrylates samples were used to study the effect on coating color rheology, water holding and runnability. Cylindrical Laboratory Coater was used to apply the coatings and study the runnability of the coating color. Healing tendency of coating was studied by inducing a streak under the blade and also immediately after the blade. Water retention of coating color was also measured. Coated paper was tested for physical properties. Healing of streaks after the blade was found to be dependent on the method of inducing the streaks. The streaks induced under the blade didn't show significant differences on the healing tendency of the coating color but it showed the same trend as that of hercules high shear viscosity. The higher acid level and cross-linking of Polyacrylate gave higher viscosity of the coating color. At low shear viscosity was more dependent on acid level but high shear viscosity was more a function of degree of cross linking for co-polymer type polyacrylate, but for terpolymer acid level was more effective in increasing the viscosity. Coating color containing polyacrylate were less sensitive to high shear. High acid level in the polyacrylate invariably gave higher water retention. Cross linking of the polyacrylate didn't show any effect on the water retention. Coated paper gloss decreased with increase of polyacrylate and showed good correlation high shear viscosity. The results could be explained with degree on interaction in the coating color. Increase in coating color solids reduced gloss and runnability was poor. At low solids, coating color with higher viscosity showed coating skips. At high solids streaking tendency was more prominent. Run in needed to maintain coat weight seems to have a significant effect on the runnability of the coating color.

**KEYWORDS:-** Polyacrylate, Coating Rheology, Water Retention, High Shear Viscosity, Streaks, Runnability, Coating Interactions.

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#### **INTRODUCTION**

Coating machine speeds are increasing along with the trend toward higher solids and low coat weight. Runnability problems increase with all these factors. Runnability problems include streaks, bleeding of the coating color and spits. In this study attention was focused on the development of streaks and also the effect of coating color rheology on coated paper properties. Generally, runnability is measured by running the coating color at high speed and then visually observing the coated paper for defects. The defects can originate either from the coating machine or from the coating color itself. A bad coating color could cause a scratch to form under the blade. However, a good coating color could heal after the formation of scratch. Accordingly the absence of scratch doesn't always mean the same thing. In the present study, a similar approach of inducing scratches was used as described by Adolfsson. (1) However, they only studied streak development for CMC as additive and no data for polyacrylate addition has been presented. Scratches were induced by the use of a plastic scraper of known width right after the blade and by the use of a "burr" of known size on the blade. The width of the resulting scratch in the dried paper was measured using an optical microscope and image analyzer. This way we were able to isolate the effect of machine conditions and coating color properties. This study was also done to evaluate the effect of the addition of different polyacrylates on coating color rheology, water retention and the runnability of the color using the Cylindrical Laboratory Coater. Runnability was also measured by running all the coatings at 750 m/min and examining the coated paper for defects.

The factors of primary importance affecting streak formation for the coating color are theorized or reported to be: Viscosity, rheology, water retention and visco-elasticity and interactions between the coating color components. A coating color must be sufficiently fluid (even at high solids content) to permit high speed application to the paper web and to spread smoothly to obtain complete coverage. Canard (2) studied the rheological behavior of the coating color. He found that dilatancy might not necessarily lead to a streaking problem. Dilatancy could be correlated with the appearance of streaks only in case of the high solids content, which he attributed to the formation of conglomerates.

Coating color exhibits stress relaxation due to the presence of visco-elastic materials. Adolfsson et al, (1) suggested that the flow rate during stress relaxation affects the manner in which blade streaks. induced at the blade tip in the wet coating layer during the coating operation subsequently level out. They explained that streaks are usually visible in the wet coating layer if the coating is immediately immobilized, but some of these (usually the coarser ones) don't flow out and they remain as severe quality defects in the dry coating layer. They found that both increasing the solids content and the addition of CMC increased shear modulus for both clay and CaCO<sub>2</sub>. But CaCO<sub>2</sub> showed lower viscoelasticity. Engstrom et al. (3) proposed that defects may arise from the inability of a coating color to spread evenly after the blade because elasticity retards spreading or levelling of the wet film after the blade. Subsequent drying freezes the defects on the coated paper. Bousfield (4) showed that the leveling of coating defects and irregularities is important to obtain a high quality coated surface. He found the absorption of the vehicle into the base sheet to be more important than drving with regard to the amount of irregularity leveling in the final coated sheet.

Sandas and Salminen (5) studied the effect of pigment-cobinder interactions and their impact on coating rheology, dewatering, and performance. They concluded that formation of strong aggregates in the coating color causes excessive high shear viscosity, which has a negative influence on runnability. Poor water retention also diminished blade runnability. They further found that pigment cobinder interaction affected coated paper properties.

Huang(6) reviewed the causes of scratches and bleeding and concluded that dewatering of the coating color under the blade is the major cause of rheological scratches and streaks. Aidun and Triantafillopoulos showed a correlation between the reynolds number of flow and the occurence of streaks. Flow instabilities in the short dwell coating pond seem to be responsible for the streaks (7)

### Effect of Polyacrylate Addition on Coating Color Properties

Polyacrylates are sodium salts of polyacrylic

acids. Polyacrylic acid is the simplest common synthetic polycarboxylic acid. Polyacrylic acid may be prepared in the atactic form by the polymerization of the monomer with conventional free radical initiators using the monomer. (8) The polyacrylate polymers are made by the copolymerization of (meth) acrylic acid and esters of (meth) acrylic acid. The properties of the polyacrylates vary widely depending on choice of the ester co-monomer(s), the acid/ ester ratio, and the molecular weight and branching degree. Water solubility of these groups depends on the number of carboxylic groups present.(9)

The polyacrylates used in paper coatings are alkali-soluble synthetic polymers. They are generally supplied as the sodium or ammonium salts. They are also available in emulsion form which converts to a clear, viscous solution on dilution and addition of a base. The Polyacrylates are compatible with most coating ingredients, but are sensitive to multivalent ions such as copper, aluminum, or iron. Temperature has little effect on viscosity, and the solutions show little sensitive to shear. Solutions of polyacrylates have little tendency to flocculate coating colors, and may tend to stabilize the viscosity and assist in keeping the pigments in suspension. They perform well in coating formulations with latex binders and are stable in storage.(10).

Jarnstrom et. al (11) studied the adsorption of CMC and polyacrylates on sodium kaolinite. They reported that both the polymers adsorb on clay and in all cases adsorption reaches a well defined plateau. They explained that adsorption is due to the electrostatic interactions between polyacrylate chains and between the polyelectrolyte and the surface. The latex binder is usually stabilized with anionic and non-ionic surfactant, typically sodium dodecylsulfate and a polyethylene oxide alkyl or alkyl/aryl ether. These compounds are adsorbed on the clay and latex surfaces. As a first approximation, it may be assumed that adsorption has reached equilibrium in individual clay and binder. The nature and extension of the surfaces available to the dispersant and stabilizers may be drastically changed when clay and latex are mixed. As a consequence, considerable redistribution of adsorbed species may take place. The result could be flocculation and/or drastic changes in viscosity. However, the actual extent of this redistribution at equilibrium will

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depend on the adsorption energy of each compound on the different surfaces, as well as on interactions between the compounds in the solution and on the surface. In addition, adsorption kinetics will probably be very important in particular for polymers or if chemisorption occurs. Hence predicting the result of mixing the two dispersions is quite difficult.

Charoenkitsupat (12) found that for capillary dewatering, cross-linked polyacrylates provided higher viscosity, and slightly higher water loss as compared to non-crosslinked polyacrylate. He also found that a high acid level polyacrylate gave higher viscosity and water holding. Terpolymer polyacrylates gave higher viscosity than copolymer polyacrylates. His work was all done using the lab drawndown technique. It was the initial intent of this project to extend his work to the CLC to evaluate the performance of these additives under conditions more closely related to actual coating systems.

#### **EXPERIMENTAL**

U.S.# 2 clay was dispersed at 70% solids without additional dispersant under high shear for 30 minutes. A styrene-butadiene copolymer was added at 12 pph. The specifications of the latex used are: particle size 1750 A, glass transition temperature(Tg)  $12^{\circ}$ C, and low level of acid modification. All coatings were prepared at 60% solids in the first phase and at 62, 64, and 66% solids in the second phase. Polyacrylates were be added to the coating color at 0.25 and 0.5 pph. Coating pH was maintained at 8.0 by addition of NaOH. The materials used are listed in appendix-A.

Appendix-A: Coating Color Components

Component		Commercial name		
Pigment	#2 U.S. Clay			
Polymer Dispersion	Styrene/Butadiene	Dow-620		
	Latex			
Water Holding Agents	СМС	Hercules-7LT		
	Polyacrylate #1	ALCOGUM L-29		
	Polyacrylate #2	ALCOGUM L-35		
	Polyacrylate #3	ALCOGUM L-31		
	Polyacrylate #4	ALCOGUM EXP-1695		
	Polyacrylate #5	ALCOGUM EXP-1873		

#### **Coating Color Analysis**

The coating color was tested for viscosity at different shear rates. The Brookfield viscosity was measured at 10, 20, 50 and 100 rpm. The Hercules high shear viscosity was measured using the E - bob at 6000 rpm with a ramp time of 2 sec using the DV-10. The Eklund Capillary Viscometer was used to measure viscosity at high shear rates. The water retention of coating color was measured by using. The Gravimetric Water Retention as described by Sandas et al.(13) An external pressure of 0.5 atm was applied on the coating color for a time period of 2 minutes.

Paper was coated using the coating formulations shown in Table-1

Table-1		
Coatin	ıg color	Formulations
Clay		100 pph
Latex	-	12 pph
PA#(1A-5A)	-	0.25pph
PA#(1B-5B)	-	0.5 pph
CMC A	-	0.25pph
СМС В	-	0.5 pph
Control	-	No additive

### Application of the coatings and induction of blade scratches.

The cylindrical Laboratory Coater was used to apply the coatings at a speed of 750 M/min. Coat weight was maintained at  $8.5\pm1$  gm/m<sup>2</sup>. The Blade run-in required to maintain the coat weight was noted. The operating conditions used for the CLC are given appendix-B. Coat weight was measured by ash method.

Appendix-B:	Operating	Conditions	for the
Cylindı	rical Labor:	atory Coate	<b>r.</b> ,

	and the second
Operating speed.	750 M/min.
Coating Blade Ext (in)	.04
Coating Bl. Thickness (in)	.018
Backing Bl. Thickness (in)	.035
Backing Bl. Free Ext (in)	1.25
Pre drying (sec/%)	20, 80%
Post Drying (sec/%)	35, 100%
Pond Angle degrees	50
Drying Delay Distance, meters	5

In order to study the levelling out of blade scratches, a scratch of 1.02 mm wide was deliberately induced immediately under the blade. The width of the resulting scratches on the dry coated paper was measured under a microscope with the help of an image analyzer. PA# 1,3 and 5 were run at 62,64 and 66% solids to evaluate runnability at higher solids. To further evaluate the runnability, scratches were induced immediately after the blade by mounting a plastic piece on the blade.

#### **RESULTS AND DISCUSSION**

## Effect of Additives on Rheology and Water Retention

Viscosity of coatings at low shear and high shear rates was measured with Brookfield and Hercules High Shear viscometer. The effect of Polyacrylate addition on Brookfield viscosity for different coatings is shown in figure-1. CMC, PA#1 & PA#4 showed the lowest viscosity, while PA#2 & 3 showed the highest viscosity.

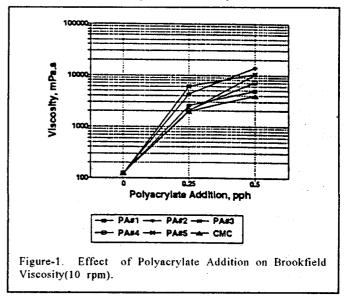
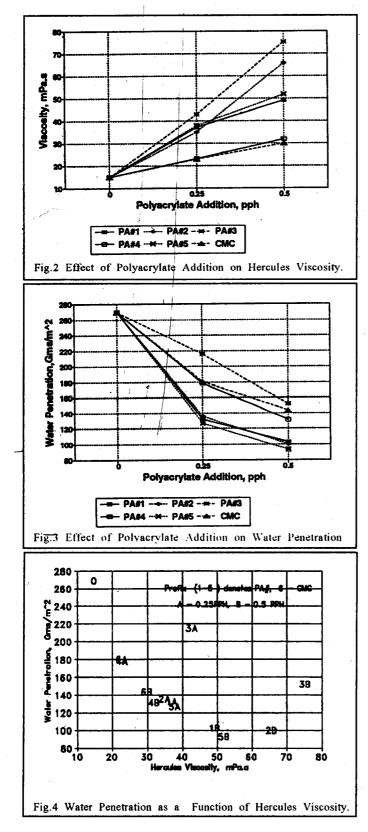


Figure 2 shows the effect of polyacrylate addition on Hercules Hi-shear viscosity at 6000 rpm. PA#3 & 2 showed the highest viscosity and PA#4 and CMC showed the lowest. The similarity in viscosity behavior between high and low shear rates fail to give any information related to the mechanism contributing to the viscosity increase.

Fig.3 shows the effect of polyacrylate addition on water penetration as measured with the Abo

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Akademi water retention meter. As evident from the figure PA#3 gave the highest water penetration. There is no significant difference in water penetra-

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tion for PA#1,5 &2. CMC showed water penetration characteristics similar to PA#4 &3. Fig.4 shows Water Penetration as a function of hercules viscosity. Water penetration decreases as the viscosity increases for all the polyacrylates, and PA#3 shows higher water penetration at any viscosity.

The implication from this data is that PA#3 might be creating the viscosity increase by interactions which build structure rather than by increasing the viscosity of the continuous phase.

Examination of the Hercules rheograms showed that PA#s 2 & 3 showed the plastic yield and thixotropic breakdown, which roughly agrees with the Brookfield data. The Eklund capillary data (at shear rates up to 5 x 10<sup>5</sup>) was in fairly good agreement with Hercules, except that PA#3 traded places with #5. The control was nearly Newtonian but slightly shear thickening in both and PA#4 and the CMC were slightly shear thickening in the capillary viscometer.

A general description of the properties of the different Polyacrylates is given in table-II and their respective rheological properties in table III.

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### Properties of Polyacrylates used in this study.

		• • • • • • • •			
	PA#1	PA#2	PA#3	PA#4	PA#5
Cross-linked	No	Yes	High	Slightly	No
Acid Level	High	High	Low	Low .	High
Type of Polymer	Co- polymer	Co polymer	Co- polymer	Ter polymer	Ter polymer
рН	2.2-3.5	3.0-4.0	2.2-3.5	2.2-3.5	2.2-3.5

#### **Table-III**

### Effect of polyacrylate addition on coating properties.

Properties	PA#1	PA#2	PA#3	PA#4	PA#5
Brookfield	L	H .	M/H	М	M/H
Hercules	M/H	M/H	Н	L	M/H
Capillary	М	Н	Μ	L	Н
Water Retention	Н	Н	L	М.	н

L-Low, M-Medium, H-High

Because of the large number of differences between the PAs used, it is difficult to isolate correlations between specific properties and coating behaviors. PA#3 had very low water retention while PA# 1, 2 & 5 had higher water retention. Accordingly, one could propose that the acid level had more influence on water holding than viscosity. PA#4, which distinguished itself by the lowest viscosity under almost all conditions, has no singular property to indicate the reason for this behavior. The striking differences between # 3 and 4 with respect to viscosity and water retention must stem from the cross linking or some other, unknown properties which allow # 3 to form the cross linking or some other. unknown properties which allow #3 to form high viscosity structures which readily release water.

#### **Effect of Additives on Coater Performance**

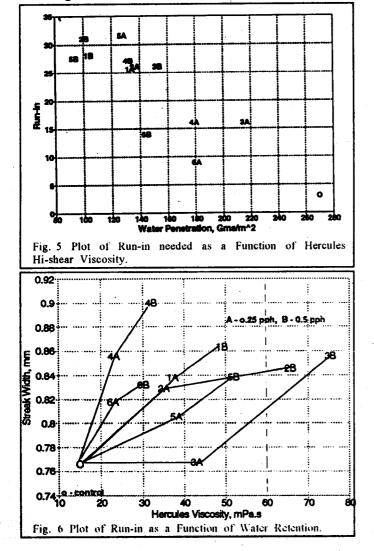
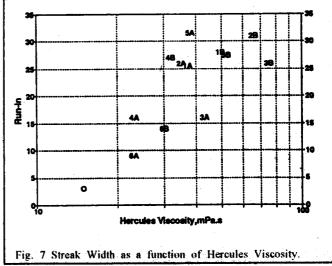


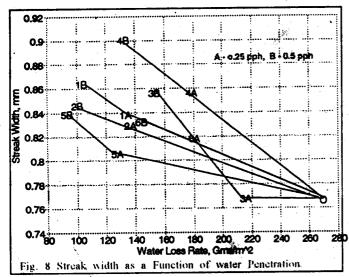
Fig. 5 shows the "run in" ( relative blade pres-

sure on the CLC which is expressed as "Run-in") needed to maintain 8.5 gm/m<sup>2</sup> coat weight, as a function of the Hercules viscosity. Generally, the higher the viscosity, the higher is the run-in needed to maintain the same coat weight. Fig. 6 shows the run-in as a function of water loss rate. It appears that the run-in needed decreased at higher dewatering rate, which is in contradiction to the expected behavior. At higher dewatering, there should be faster immobilization of the coating color and thus more blade pressure should be needed. The viscosity of the coating color seemed to be more important in affecting the run-in needed than water penetration of the coating color However, all the data points don't fall on a straight line, indicating the complex interaction of water penetration and polyacrylate properties.

When these coatings were applied to the wood free base, a blade was used which had a 1.02 mm. wide burr. The width of the resulting scratch in the dried paper was measured to asses the ability of the coating to heal. Figure 7 shows the scratch width as a function of Hercules viscosity for different polyacrylates. It shows that the addition of polyacrylate increased the scratch width, but at the same lavel of addition, higher viscosity polyacrylate gave more healing. Healing is indicated in this data by a lower scratch width. In this data it is seen that the control showed good healing and polymer addition was harmful. However, at the same level of polymer addition, higher viscosity led to more healing. PA#3 gave the highest healing and also showed highest thixotropy.



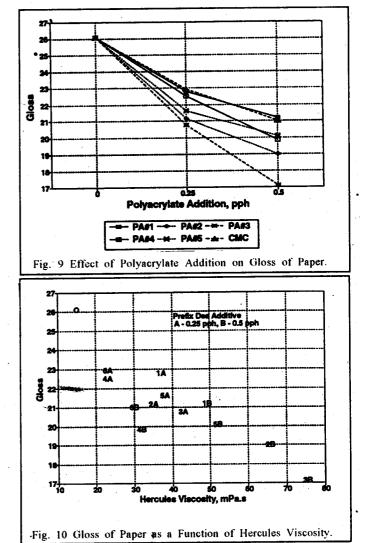
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The control did not show thixotropy, but it did show good healing indicating that thixotropy alone is not the only factor. Figure 8 shows the plot of scratch width as a function of dewatering rate and it appears that a higher dewatering rate gave more healing. This data is contrary to the common expectation that with higher dewatering the coating would increase in solids and not be able to heal. Higher dewatering should immobilize the coating faster and lead to less healing. Since there were no clear correlations between water holding, viscosity or thixotropy and the healing tendency, it is difficult to determine whether the technique is flawed or if the theories commonly used to explain scratching and subsequent healing are flawed. The best correlation seems to be with high shear viscosity, in that lower viscosity heals best.

#### **Effect of Additives on Paper Properties**

The coatings were applied to a wood free base stock using the CLC and the resultant paper tested. Fig-9 is the plot of effect of the polyacrylate addition on gloss of uncalendared paper for different coatings. It shows that with the addition of polyacrylates, the gloss of the paper dropped for all polyacrylates. PA#3 & PA#2 showed the highest drop while PA#1 the minimum along with CMC. In fact when gloss was plotted as a function of Hercules viscosity (fig 10), it can be seen that higher viscosity corresponds to lower gloss of the paper. In the second phase of this project, coatings were prepared at solids levels up to 66%. At the highest level, a higher gloss reduction was observed



corresponding to a tendency towards dilatancy in the capillary viscometer. These data imply that the higher viscosities originated from coating structures which also reduced gloss.

The type of polyacrylate didn't affect brightness or opacity appreciably. Initially, the addition of polyacrylate increased the brightness slightly, but increased addition didn't show any significant increase.

Figures 11 and 12 show the plots of roughness and porosity as a function of hercules viscosity. Roughness increased with the increase of viscosity, while porosity decraeased. Interestingly coating containing PA#3 at 0.5 pph didn't show the same trend.

Figure 13 also shows that scattering coefficient increased with the increase in viscosity if the data

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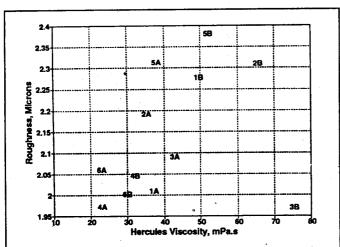
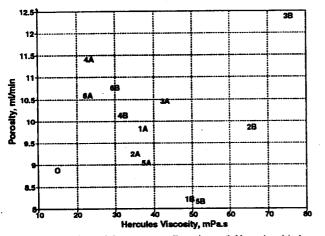
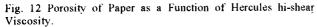
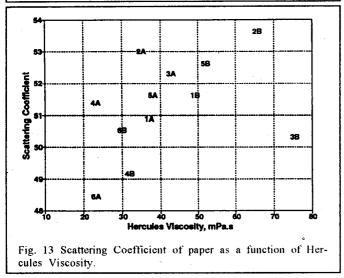


Fig. 11 Roughness of Paper as a Function of Hercules High-shear Viscosity.







for PA#3 is ignored. The implication of this data is that the higher hercules viscosity led to more structure in the coating, reducing gloss, increasing

roughness and the scattering coefficient. Unfortunately the reduction in porosity is not in support of this theory. The anomalous behavior of PA#3 is also contrary to theory in that increasing the viscosity by adding more polymer did decrease gloss but also decreased roughness and scattering coefficient. The data does demonstrate the ability of the additive to influence final sheet properties, but doesn't allow prediction through knowledge of the polymer properties.

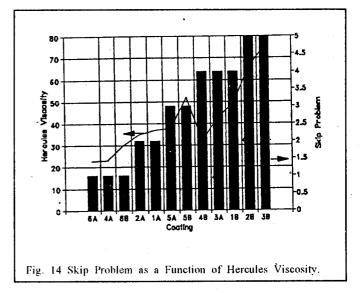
#### **RUNNABILITY OF COATED PAPER**

Runnability was analyzed by visually ranking all the samples for streaks and skips. Streaks were described as the non uniform distribution of coat weight, and skips as uncoated area. In Both cases the samples were ranked through visual examination and given a higher number for a higher frequency of the defect.

#### a. Skipping Tendency

Figure 14 shows the skip problem in comparison to the Hercules Viscosity. It is clear that there is an increased tendency of skipping at higher viscosity.

PA#2B, PA#3B showed the highest skipping problem at the highest viscosity. CMC, PA#4A and PA#IA showed the least skipping problem. It is also interesting that the skipping problem decreased with the increase of solids content. There was no skipping problem at solids higher than 62 % solids. However, skipping showed no correlation with water retention of the coating color.



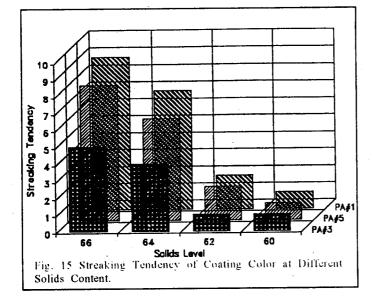
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#### **b.** Streak Development

There was no appreciable streaking at 60 % solids content and as the solids increased, the tendency of streaking increased. The figure 15 shows the streaking tendency at different solids. It is evident from the figure that the incraease in solids content invariably increased the streaking tendency of the coating color, but PA#3 showed the least streaking problem, while the PA#1 the most. Surprisingly enough the PA#3 gave the highest hercules viscosity and also highest dewatering, and hence it appears that both of these properties didn't negatively affect coating streak development. However, this problem showed the same trend as the heating tendency of the coating color, and thus it appears that the thixotropy of the coating color here also helped in reducing the streaking tendenciaes. This also corroborates that the healing tendency as measured by inducing streaking can be directly correlated to practical problem.

### Summary and Interpretation of Results

The preceding discussion of the results showed that different polyacrylate types and amounts had significant effects on viscosity, water penetration and coated paper properties. Increased amount of polyacrylate increased viscosity and water retention of coating color, but reduced the healing tendency of coating color. The properties of polyacrylate, such as; Cross-linking, acid level and polymer type affect the coating color properties significantly but not predictably.



High acid level Polyacrylates invariably gave high water retention, irrespective of degree of cross linking and polymer type. Carboxylic groups can create ionic cross-links between polymer chains which may give higher water retention.(14) It is claimed that a highly ionized polyacrylate contains so many like electrical charges that the normally random coil expands into a much stiffer, more rodlike structure.(15) Low acid level is expected to give lower viscosity. Hercules and capillary viscosity did show this trend, however PA#3 showed higher viscosity even at low acid level, and it is theorized that its high degree of cross linking might have helped it to build a network with the coating pigment. The higher viscosity of PA#2 over PA#1 also supports this hypothesis, that higher cross-linking can give higher viscosity, but not necessarily higher water retention.

Polyacrylate #3 showed an anomalous behavior as compared to all other polyacrylates in that it showed higher water penetration at higher viscosity, lower roughness, higher porosity and lower scattering coefficient at higher viscosity, which are opposite behaviors compared to all other polyacrylates. The results can be explained by the hypothesis that PA#3 did not build up continuous phase viscosity, but dynamic net work structure with the pigments, which were able to release water.

Run-in or blade pressure needed to maintain a constant coat weight increased with increase in hishear viscosity. It can be explained by increase hydrodynamic lifting force at the blade due to higher viscosity. However, dewatering of coating color didn't seem to affect the run-in in this study.

Healing of scratches in the coating color decreased with polyacrylate addition. However, at the same level of addition, higher viscosity gave higher healing. Healing of the coating color can be partly attributed to the thixotropy of the coating color. The Coating colors showed a streaking problem at higher solids, but coating colors which showed higher healing showed better runnability. Air entrapment in the puddle pond led to a skipping problem. Increase in the skipping tendency with increase in viscosity can be explained by its ability to trap air.

Coated paper properties are mainly dependent on coating structure i.e. the spatial arrangement of

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pigment particles. All the polyacrylates affected coated paper structure. Strong dependency of gloss and roughness on Hercules Viscosity presumably can be explained due to orientation effects of the clay particles. Kaliski(16) noted that clay particles had a tendency to align themselves parallel to the substrate during blade application. Increasing the viscosity of the coating, independent of other factors, would increase the opposition to this tendency. The result would be more random orientation of clay particles. Generally, the increase in Scattering coefficient with increase in viscosity can be explained by higher disorder and hence more microvoids for light scattering. The anomalous behavior of PA#3 can be explained by assuming it increased the viscosity through structure buildup and not through affecting continuum viscosity. Increase in solids content showed dilatency at 66 % solids, where a significant effect on coated paper properties was observed. The drop in gloss and smoothness at higher solids can be attributed to, as suggested by . Eklund(17), lower degree of orientation during high solids application as the tendency towards dilatancy.

#### **CONCLUSIONS**

- 1. Acid level of the ployacrylates was most important in affecting its water retention. Higher acid level gave higher water retention.
- 2. Healing tendency of coating color was affected by level of addition and thixotropy of the coating color. At the same level of addition, higher thixotropic breakdowns helps in healing of the streak.
- 3. Streaking problem increases with increase in solids content. Streaking tendency seems to be related to the healing tendency of the coating color. Coatings showing higher healing showed less streaking tendency.
- 4. Gloss and smoothness of the paper decreased with an increase in viscosity for all the polyacrylates. The affect of additives on opacity and brightness was negligible.
- 5. Run-in needed to maintain the desired coat weight showed correlation with high shear viscosity. Higher viscosity required higher run-in for all polyacrylates tested.

6. Coating color showed skipping at low solids and skipping problem increased with the increase in viscosity.

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