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The Effects of Pigment and Adhesive on Strength Development in Coated Paper

By

Henry G. Brink

A thesis submitted in partial fulfillment of the course requirements for the bachelor of science degree

Western Michigan University Kalamazoo, Michigan April, 1980

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Abstract

The application of a coating is expected to increase basepaper strength by a mechanism of adhesive penetration and enhancement of interfiber bonding similar to the strength improvements seen with size press treatments. It was felt, therefore, that the amount of strength improvement could be used as a measure of binder migration into the sheet. Pigmented and nonpigmented coatings were applied to a basepaper with a keegan coater. The pigment used was a predispersed clay, and the adhesive was a low viscosity polyvinyl alcohol. Both types of coatings produced statistically significant strength increases (up to 15% increase in tensile strength) over the levels of adhesive application. However, the amount of increase was not directly related to the amount of adhesive applied, and could not be used to measure binder migration. This study did, however, lead to a new theory to explain the strength increase. The results suggested the possibility of strength improvement due to coating film formation and PVA-clay bridging.

Background

Binder Migration:

Pigmented paper coatings are composed mainly of water, pigments, and adhesives. The water is very important since it acts as a vehicle for the application of the pigments and adhesives to the paper. The tendency of the binder to follow the movement of water in the coating and into the base paper during the coating process has been termed "Binder Migration", and is especially pronounced with soluble binders (3,4,5,6,7,8,9,10,11). Movement of water into the basepaper may also partially "de-bond" the sheet(1). This may cause loss of strength, and allow the fibers to reorient under stress.

The function of the pigment is to improve the optical and printing characteristics of the base paper. Small particles of pigment may however, migrate with the water throughout the coating, and also into the basepaper (5, 12, 13). The pigment may also tie-up the adhesive to a certain extent, and reduce its mobility.

The adhesive is added to hold the pigment particles together and to the basepaper. If the adhesive migrates, certain problems may arise depending on the extent and direction of migration. A certain degree of binder migration

is necessary to bind the coating to the basepaper. However, excessive migration into the paper will cause the coating to be poorly bound. This has been attributed to a loss of binder from the coating--paper interface (16). Excessive migration to the coating surface has similar effects (4, 8, 19).

The extent and direction of binder migration are affected primarily by the percent solids of the coating, the rate and method of drying, and the base paper absorbancy (17). Eklund and Palsanen (4) have shown that the type of binder has no effect on the direction of migration, but only on the magnitude of migration. Percent solids increases have been shown to inhibit binder migration. A higher degree of binder migration has been observed with low solids coatings than with high solids coatings (4, 7, 17, 18). Davidson (18) showed that coating at low solids produced a weaker coating than coating at high solids, with the same composition.

These three factors (percent solids, rate and method of drying, base paper absorbancy) influence binder migration in four stages of the coating process: application, doctoring or pressure, capillary, and drying.

In the first stage, application of the coating to the basepaper, it is primarily the basepaper absorbancy which governs: binder migration (8, 9, 10, 11, 17). The basepaper absorbancy, in turn, is influenced by many

factors. These include: degree of sizing, temperature, porostiy, percent moisture, percent groundwood (3, 4, 13, 20). Fifi and Arendt (19) have also shown migration in this stage to be an inverse function of the coating applicator gap. The degree of migration in this stage is very important for two reasons. First, it controls the rheology for the next stage; and second, it influences the final position of the binder in the coated sheet.

After the application stage the basepaper web, covered with a relatively thick layer of coating, travels through the doctoring or pressure zone. Here the excess coating is removed. As the paper-coating composite passes under the blade, the pressure of the blade forces the fluid phase into the basepaper (8, 9, 10). It has been shown that solids content, binder level, and binder type are the major factors governing binder migration here (8, 9, 10). Also, it has been shown that penetration increases with blade pressure (4, 5, 17, 22). If a considerable portion of the fluid phase is lost to the base sheet during the application stage, the coating may become dilatant at the doctoring stage. This may cause scratching under the pressure of a blade coater, or poor coat weight control on air knife coaters (4, 8, 19, 21).

The next stage of binder migration in the coating process is in the draw between the metering and drying stages. Here, capillary action draws more of the fluid

phase of the coating toward the base paper (5, 22, 23). Increased water retention by the coating would reduce this form of migration.

The final stage of migration is in the drying stage. Much work has been done in this area (4, 5, 6, 7, 15, 17, 23, 24). These workers have shown migration to be in the direction of the coating surface and to be a function of drying rate. The drying stage has also been shown to be the final control on migration. They have also shown that the method of drying is the most important parameter governing the magnitude of migration; although, solids level, viscosity, coat weight, and binder type also have an effect.

The use of infra-red drying all but eliminates binder migration in the drying stage due to its ability to heat the coating and the paper evenly throughout (4, 6, 7). Several workers have shown that the initial drying rate governs the extent and direction of binder migration in the drying stage. With high intensity drying in the initial stage the binder migrates to the surface. With low initial intensity, migration is toward the basepaper (7, 17, 24). Holtman (24) found a critical time or "set point" at which the final properties of the coating are determined by drying rate. He also determined that the overall rate of drying is less important than the initial rate.

Water Retention:

There are several factors which govern the degree of water retention, or resistance to migration in coating systems. These include the percent solids, the type of binder, and the viscosity of the coating. The effect of percent solids was discussed in the section on binder migration. There it was shown that coating at low solids promoted dewatering of the coating (4, 7, 17, 18).

The effect of binder type is based on the hydrophobic nature of synthetic binders, and the hydrophilic nature of soluble binders. Soluble binders, such as starch, protein, and polyvinyl alcohol, generally impart a higher degree of water retention due to their hydrophilic nature. Synthetic binders, on the other hand, generally lower the degree of water retention. Hagerman, et.al. (26), stated that the percent latex in a coating was inversely related to the degree of water retention, and concluded that this relation was due to the hydrophobic nature of the latex.

Water retention agents are generally used in alllatex systems, or systems where a considerable portion of the binder is latex. The water retention agents, or hydrocolloids, serve to inhibit the relatively free migration of the water in a latex system.

The most common hydrocolloids used for water retention agents in coating systems are carboxymethylcellucose (CMC), hydroxyethylcellulose (HEC), and sodium alginate (kelgin).

These polymers are of high molecular weight and are water soluble. They are generally added to a coating at 0.1 to 1.5 parts per 100 parts of pigment. At this level of addition they can control rheology and excess binder migration for better optical, physical, and printing properties. They also allow the coating to be applied at a higher solids content (21).

The water retention of a coating color is measured on a conductivity tester. The instrument most widely used is the S.D. Warren tester. This tester consists of a metal plate and a weight connected across a milliammeter and an AC power supply. Coating is poured over the metal plate, and the paper sample and weight are simultaneously placed on top of it. The time is then measured for a 0.5 MA current to flow, and is recorded as the WRV (water retention value).

This instrument is affected by many variables, but the most important variable is the temperature of the coating color. Stinchfield, et. al.(28) showed that the WRV drops off quickly as the temperature of the coating color is raised.

Statement of Problem:

The application of pigmented coatings to a basepaper may influence the final coated paper strength. Interactions of the continuous phase (water and adhesive) with pigment particles and the basepaper could cause a strength development to occur. Any strength development was expected to be due to migration of the adhesive into the basepaper. Once in the basepaper, the adhesive could replace weakened or hydrated bonds, or create new interfiber bonds. The purpose of this study was to quantify any strength changes of a coating basepaper caused by the migration of the continuous phase of a coating into the basepaper. It was also of interest to note any interactions of the pigment and adhesive. Therefore, coatings were run with and without pigment.

Experimental Procedures:

Choice of Basepaper:

This experiment placed several requirements on the coating basepaper. Absorbtivity was required in order to obtain penetration of the basepaper by the continuous phase of the coatings. Uniform strength properties were also required so that small increases in strength would be larger than the variability within the basepaper itself.

The coating basepaper from Consolidated Paper Co. met these requirements. It was an approximately $70g/m^2$, slack-sized coating rawstock. The Hercules size tester showed there to be no sizing at all, and a statistical analysis of the tensile data proved the variability in the basepaper strength to be small enough.

Keegan Coater:

A laboratory scale keegan coater was used to apply the coatings. It was a blade coater with infra-red drying.

A device was constructed which placed a clean, welldefined ink mark on the unrolling web of paper. This devise consisted of a tricycle wheel mounted to roll on top of the paper and place the ink mark at exact intervals. Measurement of the distance between marks on a blank and on the coated paper produced a measure of the dimensional change due to wetting.under tension. Such a dimensional change would affect the tensile properties of the paper independent of adhesive penetration. The coater was run with an air pressure to the tensioning brake of 20 psig. Coating Formulations:

Both non-pigmented and pigmented coatings were applied to the basepaper at various adhesive levels. The coating components used were:

> Pigment: Hydrasperse (clay) Adhesive: Elvanol (71-30, low viscosity) (Polyvinylalcohol) Dye: Methylene Blue (direct dye) Water: Distilled water

The non-pigmented coatings contained only water, adhesive, and dye. The dye was added at 1% in order to distinguish the coated area of the paper from the uncoated. These non-pigmented coatings were applied initially and 1, 3, 7, and 8,7% adhesive. The next run was made with adhesive levels of 2, 5.2, 13, and 11.4% The PVA was prepared at about 15% solids.

The pigmented coatings contained clay, adhesive, water, and dye. Each pigmented coating was made up at 50% solids. Three replications were run at each of four adhesive levels (0, 0.5, 1.5, 3.5% PVA of solution). Higher adhesive levels were not possible due to viscosity problems.

After application of the coatings the quantity of adhesive applied, in g/m^2 , had to be determined. The following procedures were followed:

Procedure for determining grams/meter² of PVA applied for non-pigmented coatings:

- 1) A weighed amount of coating was applied with the keegan coater.
- 2) The coated paper was unrolled and conditioned in the constant temperature and humidity room.
- 3) The machine direction dimensional change was measured.
- 4) The entire coated area was cut out with scissors and weighed.
- 5) The basis weight of the uncoated paper was determined from punches taken before and after the coated area.
- 6) The weight of the cutout without coating was determined by subtracting off the weight of PVA applied.
- 7) The weight of the cutout minus coating (grams) was divided by the basis weight (grams/meter²) to obtain the square meters coated.

8) The grams/meter² of PVA applied was obtained by dividing the weight of PVA applied by the square meters coated.

<u>Procedure for determining grams/meter² of PVA applied</u> for pigmented coatings:

- 1) The coating was applied with the keegan coater.
- 2) The coated paper was unrolled and conditioned in the constant temperature and humidity room.
- 3) The machine direction dimensional change was measured.
- 4) Basis weight punches were cut from the coated paper and from the uncoated paper.
- 5) The coat weight was calculated by difference.
- 6) The grams of PVA applied per square meter was obtained by multiplying the coat weight by the percent PVA of the dry coating.

These two procedures were required for several reasons: 1) Coat weight punches could not be used to determine the slight coat weight differences with the non-pigmented coatings since the relative error would be too large. The larger coat weights with the pigmented coatings reduced this relative error. Better results were obtained for the non-pigmented coatings by weighing a larger area. The pigmented coatings appeared to be more viscous 2) and adhered to and dried on the blade of the coater. As the nip ran empty the pigmented coatings began 3) to skip; making it nearly impossible to cut out the coated area accurately.

Testing:

Several tests were run on both the coated paper and the coatings:

Paper Tests:

- 1) Tensile, elongation, TEA
- 2) Z-Direction tensile
- 3) Basis weight
- 4) Coat weight
- 5) Machine direction dimensional change

Paper Tests:

Coating Test:

- 1) water retention value
- 2) Hercules high
- shear viscosity
- 3) Percent solids

The tensile strength, percent elongation, and tensile energy absorption were determined on the instron instrument for the first set of coatings run. From these results it was found that the variation in determining the percent elongation and the tensile energy absorption was too large for the data to be useful. It was also found that the increases in tensile strength in the cross-machine direction were too small to be of statistical significance. After these findings only the machine direction tensile factor was determined to be of statistical significance and useful. Ten values were obtained for each coating, and for a blank for each run.

The Z-Direction tensile was also determined on the instron instrument in an effort to measure the penetration' of the paper by the adhesive. Three strips one inch wide and several inches long were run for each coating, and for a blank for each run.

Procedures for determining basis weight, coat weight, and machine direction dimensional change have already been described.

Coating Testo:

Coating Tests:

The water retention value for each coating was measured on a modified S.D. Warren tester. The plate of the tester was replaced by a metal screen. Three readingswere averaged for each coating. The Hercules high shear viscosity and the percent solids were also determined for each coating.

Presentation and Discussion of Results:

The results of the testing were summarized in table I for the non-pigmented coatings, and table II for the pigmented coatings. Each run for the non-pigmented coatings consisted of four coating formulations and a blank. Table I shows the data for only two replications. Atthird replication was run, but the coat weights were not determined properly, and the third replication was discarded. Each run for the pigmented coatings consisted of four coating formulations. One formulation of each run was a blank which contained no PVA. Three replications were run at each of four adhesive levels. The PVA applied was lower for the pigmented coatings because a smaller percent of the coating was PVA. With higher percentages of PVA the pigmented coatings became too viscous to run with the Keegan coater.

The machine direction tensile values were recorded as the averages of ten tests each. The tensile factors were calculated by dividing the tensile values by the basis weight of the paper for that run. The tensile

factor increase was the increase over the tensile factor for the blank. Paired t-tests were run on these values and their respective standard errors. The t-tests showed each increase to be statistically significant.

The water retention values were shown to increase with both viscosity and percent PVA of solution. The Z-direction tensile showed no significant change over the levels of PVA applied. This suggested that penetration into the basepaper was minimal. However, the Z-direction tensile test may not have been sensitive enough to measure penetration. The Z-direction data for the pigmented coatings was of little significance since the blanks could not be tested. The coatings for the blanks contained no PVA, and the tape used for the test would not adhere to them. The machine direction dimensional change was measured for each coating. It was found that this measurement was highly dependent on the width of the coated area. Therefore, measurements were made on coated areas of comparable width. The change in dimension was a loss of about 3mm in each case. This represented a loss in the machine direction dimension of about 0.38%. The Relationship Between Tensile Factor Increase And Grams of PVA Applied Per Square Meter:

This relationship is shown in Figure I for both pigmented and non-pigmented coatings. The curve for the non-pigmented coatings appears to be exponential. A

sharp increase in strength occurred over theldowerlievels of adhesive application, and then leveled off as more adhesive was applied. This plateau effect may have suggested that at low levels of adhesive application the soluble PVA penetrated the paper, along with the water, to replace hydrated bonds, and create new interfiber bonds. The rate of increase in tensile factor with adhesive application, or the slope of the curve, was reduced at higher levels of adhesive application. This reduction in slope probably paralled a reduction in the penetration of the basepaper by adhesive. Increased viscosity and solids percent might limit the fluid phase migration as indicated by increased water retention values. With increased water retention by the coating (reduced penetration), fewer interfiber bonds could have been created or reinforced within the paper. The level of strength development attained could then have been due to highly increased bonding near the surface of the paper and the strength of a PVA film formed on, and bonded to the surface.

Adhesive levels above 2.3 g/m^2 were not studied since the viscosity would be too high to run with the Keegan coater. If more adhesive had been applied; however, less of the PVA would have penetrated the paper. This may have resulted in the curve turning downward toward a lower tensile factor increase which would correspond to the additive strengths of the paper and coating; with little enhanced interfiber bonding.

The curve for the pigmented coatings in Figure I appears to be linear, and to increase much faster than the curve for the non-pigmented coatings. The line shown was generated by linear regression, and has a correlation coefficient of 0.772. Although the WRV's were of the same order as those of the non-pigmented coatings, the mobility of the PVA molecules was most likely reduced due to the presence of the clay particles, The clay may also have contributed to a bridging effect. Such an effect could have caused a continuous film of coating to be formed faster than without pigment; with minimal penetration of adhesive. The strength increases observed could have been primarily due to the strength of the clay-PVA film bonded to the paper; with some strength due to reinforced interfiber bonds near the surface of the paper.

The Relationship Between Tensile Factor Increase And Percent PVA In The Coating Solution:

The relationship, shown in Figure II, is similar to the relationship between tensile factor increase and adhesive applied shown in Figure I. The tensile factor increase for the pigmented coatings was much steeper than that for the non-pigmented coatings (nearly four times the slope), and both curves increased linearly. Again, the bridging effect between the clay particles may have contributed to faster formation of a coating film. This could have caused the tensile factor for the pigmented coatings to increase faster and to higher levels than for the non-pigmented coatings.

The Relationship Between Tensile Factor Increase And Water Retention Value:

This relationship, shown in Figure III, suggests only a general increase in tensile factor with increasing WRV. This result was contrary to what was initially expected. Increasing WRV was expected to lower the tensile factor increase since migration into the basepaper would be retarded. However, as suggested by Figures I and II, the formation of a coating film may have been the primary cause of strength development, and not adhesive penetration as initially expected. Therefore, the increase in tensile factor with increased WRV would be consistant with the other results.

Conclusions and Recommendations:

Increases in coated paper strength were expected to be due to penetration and reinforcement of the basepaper by the adhesive. The data, however, suggested that another mechanism may have also been involved.

With increased water retention value the increase in strength was expected to be reduced. When plotted against WRV, however, the tensile factor displayed a general increase. The Z-direction tensile showed no significant change over the levels of adhesive application. This suggested that very little of the PVA penetrated or increased the strength of the basepaper itself. However, the Z-direction tensile test may not have been sensitive enough to measure penetration.

When tensile factor increase was plotted against grams of PVA applied per square meter a plateau effect was observed with the non-pigmented coatings. The sharp initial increase for this curve may have suggested penetration and reinforcement as the mechanism of strength improvement at low levels of PVA application (low solids coatings). At higher levels of PVA application (higher solids coatings), the strength increase may have been caused by the additive strengths of a PVA film and increased interfiber bonding near the surface of the paper. This was suggested since at higher solids, viscosities, and WRV's the mobility of the PVA may have been reduced.

With pigmented coatings, the coated paper strength increased linearly and more quickly than the non-pigmented coated paper strength. This suggested the possibility of faster film formation due to a bridging effect between the pigment particles and the adhesive.

In order to further study these phenomena, non-pigmented coatings should be run at the same viscosity and percent solids. The coat weight could then be controlled

by blade pressure and coater speed. This would possibly eliminate the WRV as a source of variation in strength development.

The strength of the coating films should also be determined. This might be done by applying the coatings to either a non-adhering surface or to a very thin paper. It might also be of interest to study higher adhesive applications and strength after calendering.

TABLE 1

Results For The Non-Pigmented Coatings

	1				 A second sec second second sec	and the second se				
run	coat weight g/m ²	PVA percent of soln	PVA grams per meter	MD tensile k grams	tensile factor	tensile factor inc. (X1000	WRV seconds	viscosit) poise	2-dir. tensile	MD dimen. change mm
1	.1202	1	.1202	15.65	.2192	9.0	1.37	-	.20	3
2	.3346	3	•3346	16.51	.2312	21.0	2.47	-	.19	3
3	.7692	7	.7692	16.45	.2304	20.2	4.40	-	.19	3
4	1.2744	8.7	1.2744	17.08	.2392	29.0	5.93	-	.19	3
lank 1	0	0	0	15.01	.2102	-	-	-	.19	0
1	.1913	2.0	.1913	15.35	.2182	15.8	4.57	.0226	.20	3
2	.4358	. 5.2	.4348	15.38	.2186	16.2	8.13	.2920	.19	3
3	2.279	13.0	2.279	16.04	.2280	25.6	11.03	.4510	·19	3
4	1.9629	11.4	1.9629	15.97	.2270	24.6	11.10		.19	3
lank 2	0	0	0	14.14	.2034		-	200 -	.19	0

Results For The Pigmented Coatings

3.									and the second sec	in the second
run	coat weight g/m ²	PVA % of Soln.	PVA grams per meter	MD tensile k grams	tensile factor	tensile factor inc. XI000	WRV seconds	viscosity poise	2-dir. tensile	MD dimen. change mm
lank 1	5.779	0	0	15.98	.2239	-	1.87	0.0632	-	3
1	7.684	0.5	.0768	16.32	.2287	4.8	2.27	•3790	.19	3
2	6.816	1.5	.2045	16.80	.2354	11.5	5.57	.8737	.20	3
3	7.558	3.5	.5571	16.86	.2362	12.3	7.0	3.179	.20	3
Lank 2	6.017	0	0	15.84	.2209	-	1.67	.0534	-	3
1	7.235	0.5	.0724	17.16	.2393	18.4	1.87	.3530	-	3
2	6.047	1.5	.1814	17.50	.2440	23.1	3.70	.8420	.21	3
3	7.006	-3.5	.4904	18.32	.2550	34.6	5.60	-	.21	3
lank <i>3</i>	6.920	0	0	15.99	.2230	_ >	2.00	.0538		3
1	5.954	0.5	.0595	17.30	.2412	18.2	2.10	.4050	.21	3
2	6.585	1.5	.1976	16.78	.2340	11.0	5.40	.8420	.21	3
3	5.713	3.5	•3999	18.11	.2526	29.6	6.93	-	.21	3

Interval
 Operation







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