

Modeling Latex Variables to Predict the Printing Properties of Coated Papers

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Abstract: A quantitative model of the interactions between latex variables and the end-use properties of coated paper is useful for engineering a latex to provide particular printing characteristics. The type of latex used in the coating formulation not only affects the strength of the coating, but also affects the pore structure and absorbency characteristics of the surface. These coating characteristics determine the rate of ink tack-build on the press and impact ink transfer and water interference problems. In this work, a response surface design was created to predict the impact of acrylonitrile (ACN) level, butadiene level, particle size and degree of crosslinking on the ink tack-build and ink transfer characteristics of coated paper. A series of polymers were carefully synthesized according to this design. Each latex was evaluated as the sole binder in model offset coating formulation that was applied to a woodfree basesheet with a wire wound rod. The coated papers were tested and a commercial statistical software program was used to generate the response surfaces for printing characteristics. The resulting models showed the addition of acrylonitrile reduced paper and ink stability slope, increased the number of passes-to-fail and increased printed gloss. The addition of acrylonitrile also reduced the unprinted gloss of the paper. The response surface models successfully predicted the printing properties of coated papers finished under similar conditions.

Introduction

The amount and type of latex used in the coating formulation significantly affect the offset printing properties of coated paper by influencing the ink absorption characteristics of the surface. The choice of pigments and binders to be used in the formulation, along with drying and finishing effects, impacts the pore structure in the coating. The absorption of ink components by the pores in the coating affects the rate at which the ink builds tack and affects the amount of ink transferred to the paper (Zang, 1995).

Aspler and Lepoutre (1991) noted that increased binder level reduced the rate of absorption of test inks. Triantafillopoulos and Lee (1996) showed that doubling latex concentration in an all latex formulation reduced the rate of ink tack-build from 28 g/cm-sec to 3.5 g/cm-sec. They also found that replacing latex with starch gave a significant reduction in the rate of ink tack-build. Increasing binder level or adding starch to the formulation closes the pore structure of the coating and reduces the rate at which ink vehicle is absorbed

Zang and Aspler (1995) also found that at higher printing speeds, increased binder levels reduced ink transfer to the substrate. They believed that this difference was due to the rate of formation of a high-tack ink layer on the coated surface that influenced the split of the remaining ink film. At slow printing speeds the amount of binder present did not affect ink transfer. The authors postulated that at slower printing speeds and longer nip residence times, the ink film-split was controlled by the rate of solvent transport through the high-tack ink.

The addition of acrylonitrile (ACN) to a styrene butadiene polymer has been shown to significantly affect printing properties (Hensel, 1996). Van Gilder and Purfeerst (1994) showed that the polymer solubility parameter influences the rate of ink tack-build. They found the rate of ink tack-build decreased significantly as the solubility parameter increased from 8.8 to 9.7 (cal/cm³)^{1/2}, indicating that the ink solvent had less interaction with the high solubility parameter polymer.

The solubility parameter, δ , is defined as:

$$\delta = (\Delta E/V)^{1/2}$$

where ΔE is the heat of vaporization and V is the volume of the material (Brandrup, 1966). The heat of mixing of two solvents or amorphous polymers is related to the square of the difference of their two solubility parameters. Two substances will be miscible if their two δ s are nearly equal.

Acrylonitrile has a higher solubility parameter than a styrene-butadiene copolymer as shown below in Table 1.

Table 1. Solubility Parameters (cal/cm³)^{1/2}

Material	δ	Reference
polyacrylonitrile	12.5-15.4	(Brandrup, 1966)
polybutadiene	8.05-8.60	(Brandrup, 1966)
polystyrene	8.5-9.7	(Brandrup, 1966)
poly(butadiene-co-styrene)	8.01-8.70	(Brandrup, 1966)
poly(butadiene-co-acrylonitrile)	8.66-10.45	(Brandrup, 1966)
long oil alkyd resin	9.4	(Meyers, 1976)
short oil alkyd resin	10.8	(Meyers, 1976)
linseed oil	7.3	(Meyers, 1976)
offset ink solvents	7.4-7.8	(Van Gilder 1994)
low odor mineral spirits	6.9	(Brandrup, 1966)

Solvents such as mineral spirits or offset ink solvents would be more readily absorbed by a styrene-butadiene copolymer than by a similar copolymer containing acrylonitrile. A drying oil such as linseed oil would also be more readily absorbed by a styrene-butadiene copolymer than by a styrene-butadiene-acrylonitrile copolymer. Alkyd resins, such as those used in some ink varnishes, would likely be absorbed better by styrene-butadiene-acrylonitrile copolymers.

The addition of acrylonitrile to a styrene-butadiene copolymer is expected to reduce the interaction of offset ink solvent with the latex polymer and reduce the rate of ink tack-build. Desjumeaux (1997) has shown that reducing the rate of ink tack-build increases printed gloss. If the addition of acrylonitrile increases the solubility parameter of the polymer, the rate of ink tack-build should decrease and printed gloss should increase.

Forbes and Ave' Lallemand (1998) have recently looked at the effect of latex characteristics on printing properties in starch co-bound coatings for sheetfed offset. In such systems the starch cobinder affects ink transfer and the rate of ink tack-build. The purpose of this work is to investigate the effects of latex properties on printing performance in all synthetic binder systems.

EXPERIMENTAL

Four latex variables were selected for this study. These were:

1. acrylonitrile content
2. butadiene content
3. particle size
4. degree of crosslinking (gel content)

A blocked Box-Behnken response surface design was chosen using statistical software to evaluate the effects of the four latex variables at three different levels. The Box-Behnken design was selected to reduce the number of conditions in the design from the full 3^4 factorial (81 different runs) to 27. Running three replicates at the center point of the design generated an internal estimate of the experimental error.

The latices were carefully polymerized in the polymerization miniwork facility to match each point of the design. The four variables listed above were tested for each latex and, if a characteristic was not within tight control limits of the design, the polymer was remade until all four of the design criteria were obtained.

The latices were tested in a sheetfed offset formulation. A master pigment blend was made of a 75/25 mixture of dry fine No. 1 clay / dry ultrafine ground calcium carbonate. Each latex was added to the pigment blend at 16 pph.





Dispersant, lubricant, and water were added to the coating to yield 63 percent total solids.

The coatings were applied via rod drawdowns to a 47 lb. woodfree basesheet at a 10 lb. coat weight. Drying was accomplished with a combination of forced air (from a heat gun) and infrared heating for 20 seconds which brought the coated surface to a temperature of 190°F. Many researchers and practitioners in the field have used this technique because it provides more intense drying, compared to IR alone. More intense drying often represents conditions closer to those encountered in manufacturing.

The coated samples were conditioned for 24 hours in a room controlled to TAPPI standard conditions of 73°F and 50% relative humidity prior to calendering. The coated sheets were calendered on a steel/cotton roll laboratory supercalender at constant conditions of 500 pli, 140°F, and three passes through the nip. After reconditioning, at least four sheets representing each of the design conditions were tested for:

- Paper & Ink Stability (Plowman, 1998a, 1998b)
 - a. Slope = rate of ink tack build
 - b. Passes to failure
 - c. Force at failure

- Water Sensitivity
 - a. Ink transfer
 - b. Ink refusal
 - c. Wet pick

- Gurley High Pressure Density (inverse of porosity)

- 75° paper gloss

- Prüfbau printed gloss
 - One split
 - Fast set cyan ink (10 tack)
 - 1.4 to 1.6 ink density

A low P&I slope represents slow ink tack-build rate, and consequently, high coated surface strength with regards to picking. High coating strength is also associated with a comparatively high numbers of passes before failure and a high force at failure.

Averaged values for each of the coated paper tests were entered into a spreadsheet and statistical software was used to determine the mathematical

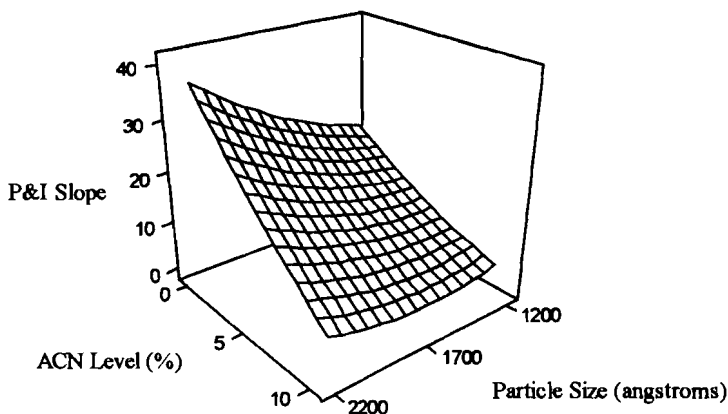
model that provided the best correlation (highest R^2 values) between the dependent properties and the significant latex variables. These quadratic equations were used to predict the values of the dependent properties from known latex characteristics.

Results and Discussion

Response surfaces can be drawn for any of the dependent properties in terms of any two of the four independent variables included in the study. For the purposes of this discussion we have chosen to examine the effects of ACN level in the styrene-butadiene-ACN (SBA) copolymer and latex particle size. The response surfaces were created while holding the butadiene (Bd) and gel variables constant at their midpoints.

Figure 1 shows that progressive addition of ACN in SBA latex reduces the P&I tack-build slope linearly for all particle sizes. This result is consistent with the results of Forbes and Ave'Lallemant (1998) for the addition of ACN to an SBA copolymer in a starch cobound system. For the all-latex formulations, the decrease in P&I Slope with ACN addition is twice that observed in the starch cobound system.

Figure 1. Effect of ACN and Particle Size on P&I Slope



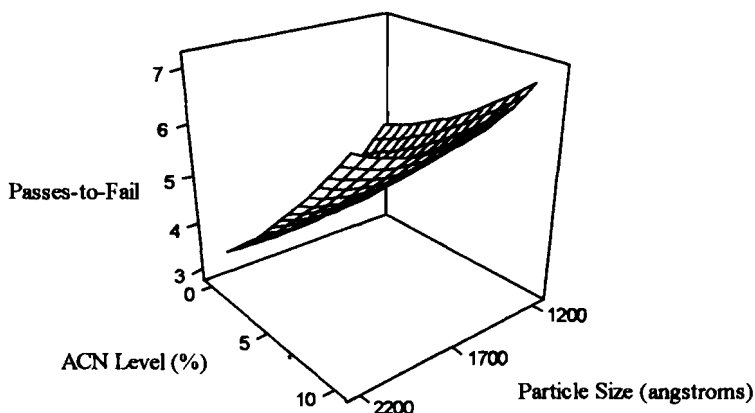
The rate of ink tack-build on a coated surface is likely due to the combined effects of ink solvent penetrating the pores of the coating and ink solvent being absorbed by the coating binder. The addition of starch will typically decrease the porosity of the coating and inhibit the penetration of ink solvent into the coating. The higher solubility parameter of the SBA copolymer will reduce the absorption of the ink solvents by the coating binder. Starch would be expected to

reduce the influence of ACN on ink tack-build because it would limit the amount of ink solvent penetrating into the coating and available for absorption by the SBA copolymer.

It is interesting to note in Figure 1 that the relationship between P&I slope and ACN content changes as the latex particle size increases. At small latex particle size, the incorporation of ACN has a less dramatic effect than at large particle size. We may view the smaller latex particles as producing a more uniform and dense latex film due to their larger surface area per unit weight that provides a better barrier to penetration of the ink vehicle. This effect is similar to the sealing of the surface with a soluble binder such as starch. Thus, the reduction in ink tack-build with the addition of ACN is less pronounced for a small particle-size latex because the small particle size has already contributed to sealing the coated surface.

Figure 2 shows the effect of ACN level on the P&I passes-to-fail is also more dramatic for large particle size latices. At low ACN addition, smaller particle-size latices provide greater coating pick-strength by providing a more uniform and dense film. The addition of ACN to the copolymer improves the passes-to-fail of the small particle latices by two passes, but increases the passes-to-fail of the large particle size latices by almost four passes. At the ten percent addition level of ACN, there is little difference in passes-to-fail of the small and large particle-size latices.

Figure 2. Effect of ACN and Particle Size on P&I Passes-to-Fail



It is likely that the same factors that reduce the tack-build slope for the large particle size ACN latices also allow the coating to survive a greater number of passes before picking is observed. If the coatings have nearly equal strength, a

coating that builds ink-tack more slowly would be expected to survive for more passes before picking is observed. Triantafillopoulos and Lee (1996) noted that this relationship does not necessarily hold when both the tack-build characteristics and the strength of the coating are changed. Changing the pigments in a formulation, or adding a soluble binder, can alter both tack-build and coating strength.

Figure 3 shows that the addition of ACN increases delta gloss for both small and large particle size latices. The increase in delta gloss is consistent with the lower tack-build slopes and lower ink setting rates with the addition of ACN. Slower ink setting offers more time for leveling of the ink split pattern produced during printing, which gives a higher printed gloss (Desjumaux, 1997).

Figure 3. Effect of ACN and Particle Size on Delta Gloss

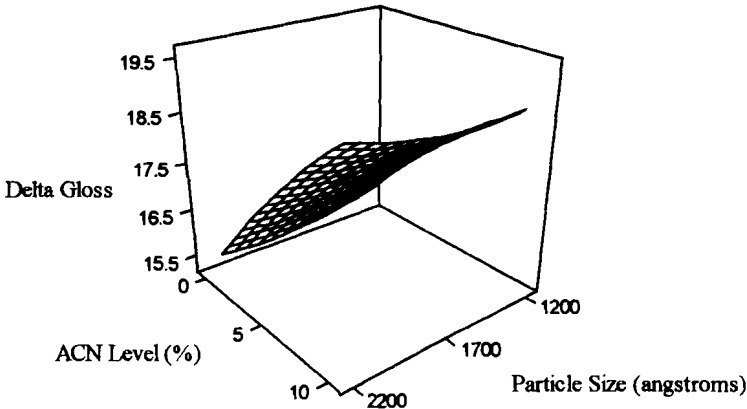


Figure 4 shows that ACN does have a small negative effect on paper gloss. This is contrary to the results obtained in a starch cobound system (Forbes, 1998) in which ACN had no effect on paper gloss. The reduction in paper gloss is more pronounced for smaller particle-size latices. Even for the small particle-size latices, the reduction in gloss is less than two points.

Figure 5 shows that ACN has no effect on ink transfer. The effect of particle size is clearly evident with the larger particle size latex giving higher ink transfer. This is consistent with the results of Zang and Aspler (1995) that showed a more open and porous coating gives better ink transfer during printing. The fact that ACN does not affect ink transfer indicates that the addition of ACN does not significantly affect the porosity of the coating.

Figure 4. Effect of ACN and Particle Size on Paper Gloss

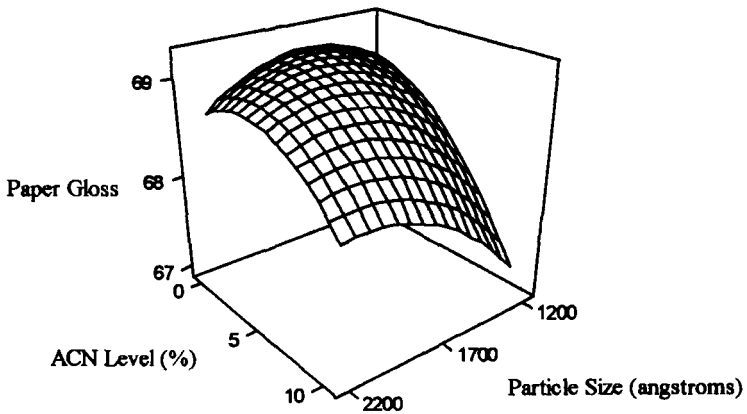
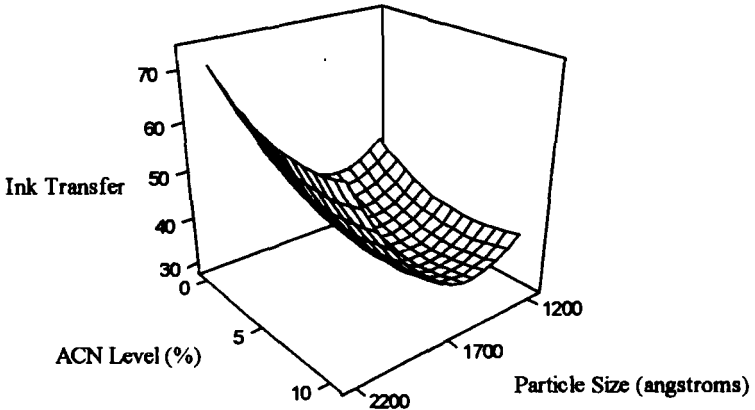
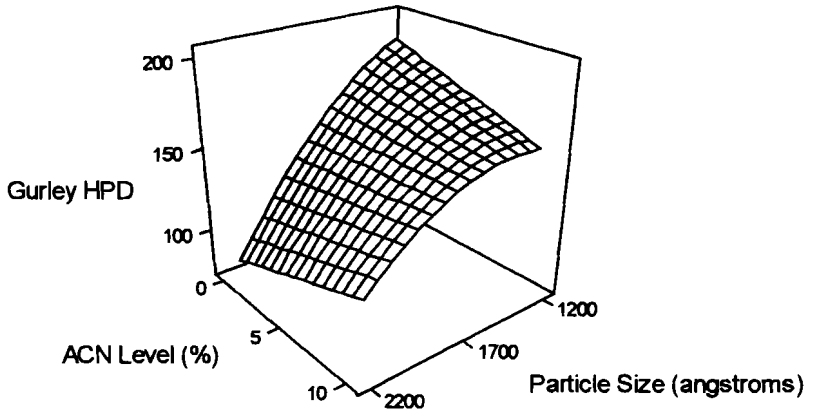


Figure 5. Effect of ACN and Particle Size on Ink Transfer



The response curve for Gurley high pressure density in Figure 6 also shows that the addition of ACN does not significantly affect coating porosity. ACN copolymers create the opportunity to independently change the P&I slope and passes-to-fail of the coating without significantly influencing sheet porosity. Although it is well documented that large SB latices give porous coatings at the expense of strength, SBA polymers expand the performance window by giving acceptable strength with a high coating porosity, i.e., by using large particle size SBA latices.

Figure 6. Effect of ACN and Particle Size on Gurley High-Pressure Density (HPD)



The mechanism for the effect of ACN on P&I slope is likely due to ink interaction with the latex. Due to its higher solubility parameter, ACN inhibits the interaction or absorption of the ink vehicle by the latex. A more open, larger pore volume coating layer (as provided by a larger particle size latex) would give greater access to the latex in the coating. The influence of latex solubility parameter would therefore be greater for a large particle size latex.

Figures 7 through 12 show the model predictions for the various print properties plotted against the actual experimental values. The solid lines in these figures represent a linear regression of the model predictions. The best fits were obtained for P&I slope and delta gloss and the lowest R^2 values were obtained for ink transfer and Gurley high pressure density.

These response surface models have only addressed the influences of four specific latex variables. A more general model for coated paper properties will need to address the effects of coat weight, calendering conditions, pigment composition, basesheet composition and ink formulation. Creating such model will likely require a more complex approach.

Conclusions

1. The addition of acrylonitrile to styrene-butadiene latex reduces P&I slope, increases the number of passes to fail and increases printed gloss.
2. The addition of acrylonitrile to a styrene-butadiene latex has a negative effect on paper gloss.

3. The addition of acrylonitrile has no effect on ink transfer or coating porosity.

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Figure 7. P&I Slope

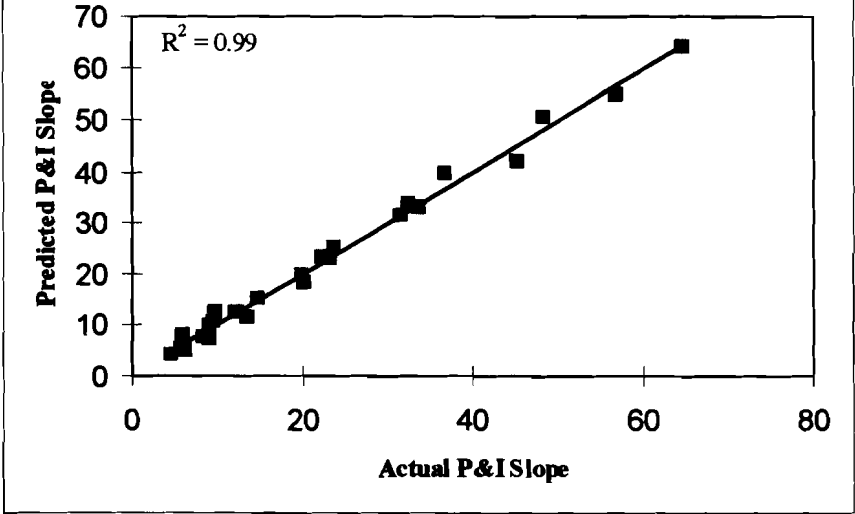


Figure 8. P&I Passes-to-Fail

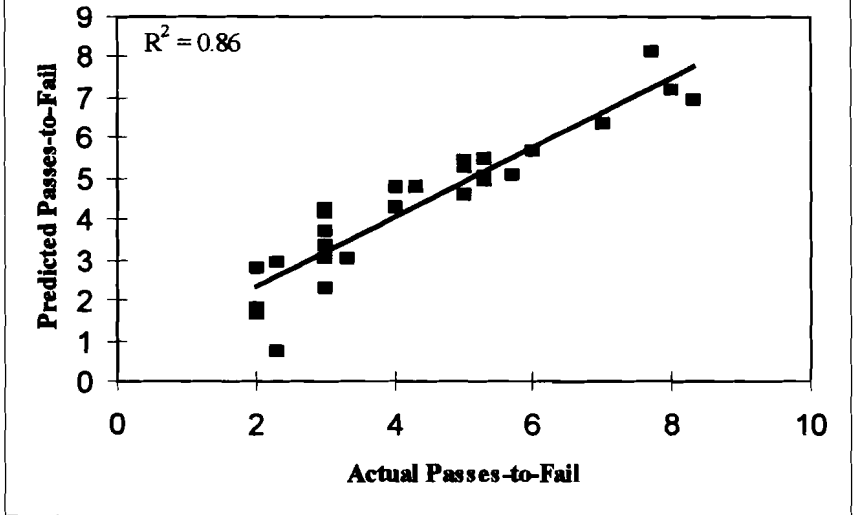


Figure 9. Delta Gloss

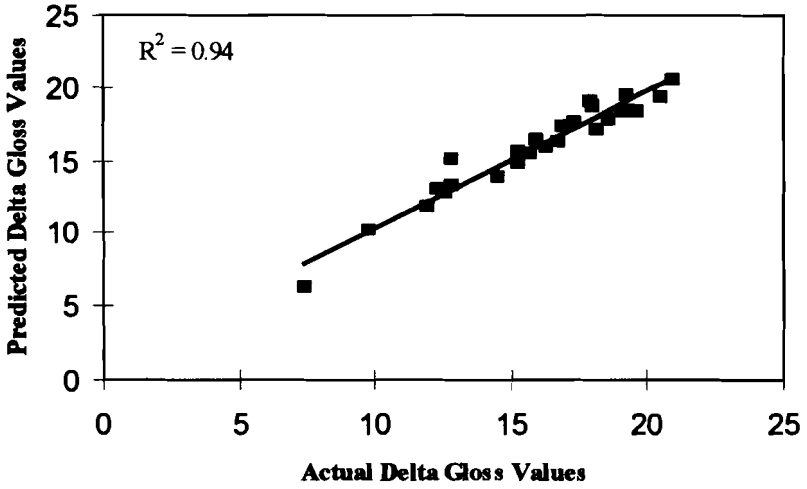


Figure 10. Paper Gloss

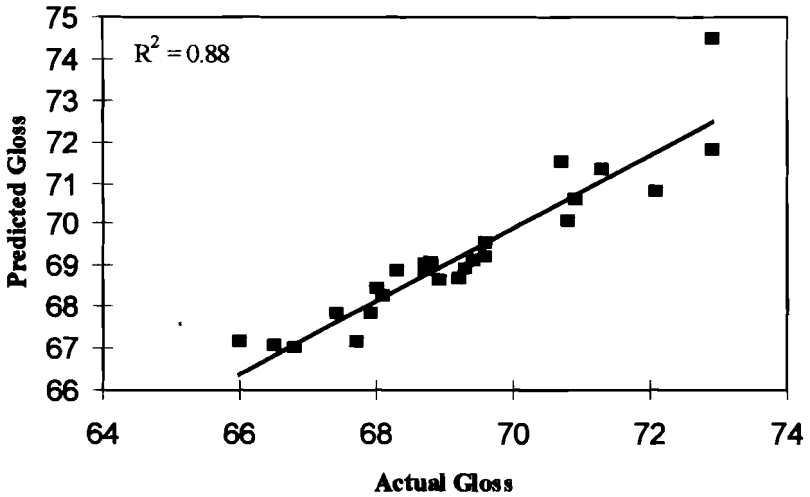


Figure 11. Ink Transfer

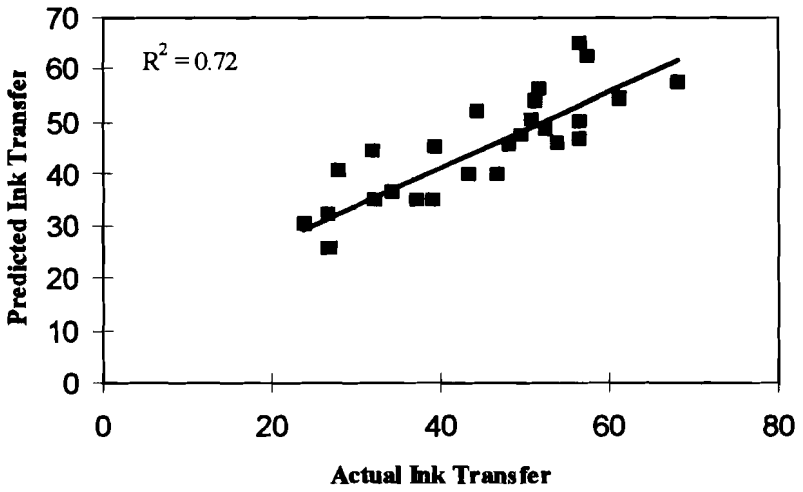


Figure 12. Gurley High-Pressure Density

