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Andrew R. Knoll Western Michigan University

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THE EFFECTS OF VARIOUS ADHESIVES AND ADHESIVE LEVELS ON THE SCATTERING COEFFICIENT OF PIGMENTED COATINGS: AN ATTEMPT TO PREDICT SCATTERING COEFFICIENTS

BY

ANDREW R. KNOLL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OP THE COURSE REQUIREMENTS FOR THE BACHELOR OF SCIENCE DEGREE '

WESTERN MICHIGAN UNIVERSITY KALAMAZOO, MICHIGAN APRIL 19?8 "

ABSTRACT

The object of this study was to determine the effect of various levels of different adhesives on the scattering coefficients of a coating. Once the relationship of the adhesive effect on the scattering coefficient was determined an equation was to be devel0ped to predict the optical properties of the coated sheet. This study shows that there is an increase in scattering coefficient from *5* to lOpph adhesive and after lOpph a steady decrease in the scattering coefficient **as more** adhesive is added. The increase is theorized to be due to flocculation of fines within the coating and the decrease due to the filling of voids in the coating. The scattering coefficient of the coating can be predicted for the adhesive addition range of 10 to 30pph by a linear equation. The data obtained in this work correlates with results of other workers using black glass and foil substrates.

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THEORETICAL

Several attempts have been made using the Kubelka-Munk Equation to predict the optical properties of coated paper. Theoretically, brightness of the coated sheet (R_{∞}) and opacity of the coated sheet, (Co.gg) can be determined if the scattering and absorption coefficients are known for all the materials within the sheet. Applying this idea to predict coat weights and coating formulas necessary to achieve specitications could be a valuable tool in the area of cost optimization. The present procedure of extensive laboratory testing to determine the final properties could be done by a computer.

Gartagnis and Cleland (1) have gone so far as to design a computer program to figure out the cheapest combination of basestock and two sided coating to achieve a certain set of specifications. Crouse ant Zabel (2) used the Kubelka-Munk equation to predict coat weights. With this technique they were able to get within \pm 5% of the actual coat weights in $75%$ of their samples. The remaining $25%$ of the samples were within \pm 12 $\frac{2}{3}$ of the actual coat weights. Some of the variance was attributed to adhesive **levels** and **adhesive** ratios. • •

The Kubelka-Munk Theory, upon which all the work done in this area of optical properties has been based, was adapted for uncoated paper by Steele (4) and Judd. These equations are based on the concept that when light enters a diffusing medium part of it is reflected back, part of it

 $-1-$

is absorbed and part of the light passes through the medium. Paper is one such diffusing mediwn, because light is reflected when it passes through a medium of different refractive indices. Paper therefore produces reflected light because cellulose fibers and air differ in refractive index. The light reflected is given by the Fresnel equation, Equation 1 from Robinson and Linke (5) :

$$
R = (n - 1)^2 / (n + 1)^2 \tag{1}
$$

where R is the light reflected and n is the refractive index of the medium in contact with air, air having a refractive index of one.

Kubelka and Munk theorized that this reflected light could be explained in terms of scattering coefficients, s, ' and absorption coefficienta, K, for the materials making up the paper. These materials' coefficients are additive as shown in Equation 2 from Steele (4) :

 $S_{\text{total}} = S_1 X_1 + S_2 X_2 + S_3 X_3 + --- S_n X_n$ (2) where X is the weight per unit area of the material.

The S and K values are related to the measured quantities of R , brightness given by Equation 3, Ro.₈₉, reflectance with a background of 89% of total reflectance, given by Equation 4, Ro, reflectance with a black background, **given** by Equation 5 and Co.₈₉, Tappi opacity, given by Equation6. Equations J, 4, and *5* all come from Steele (4). Equation 6 is the Tappi Standard definition of opacity.

$$
R_{\infty} = 1 + \frac{K}{S} - \sqrt{\frac{K^2}{S^2} + 2\frac{K}{S}}
$$
 (3)

-2-

$$
Ro.89 = \frac{\frac{1}{R_{\infty}}(0.89 - R_{\infty}) - R_{\infty}(0.89 - \frac{1}{R_{\infty}}) e^{SX (\frac{1}{R_{\infty}} - R_{\infty})}
$$
(4)

$$
(0.89 - R_{\infty}) - (0.89 - \frac{1}{R_{\infty}}) e^{SX (\frac{1}{R_{\infty}} - R_{\infty})}
$$

$$
Ro = \frac{e^{SX(\frac{1}{R_{\infty}} - R_{\infty})} - 1}{\frac{1}{R_{\infty}} e^{SX(\frac{1}{R_{\infty}} - R_{\infty})} - R_{\infty}}
$$
\n
$$
Co._{89} = \frac{Ro}{Ro.89}
$$
\n(6)

The interaction of these equations ties $R\infty$, Co. g_Q and SX together such that if any two of the properties are known, the third can be determined.

In Crouse and Zabel's (2) study the coatings scattering coefficient was treated as a filler in the basestock and assumes the coating's scattering coefficient is additive. The Equations $7, 8,$ and 9 used to calculate the scattering power, SX:

$$
a = \frac{1}{2} \left(1/R_{\infty} + R_{\infty} \right) \tag{7}
$$

$$
Ro = (R - Rg)/1 - Rg (2a - R)
$$
 (8)

$$
SX = \frac{\ln (1 - (Ro \times Ro_{0})) / (1 - (Ro/R_{\infty}))}{(1 - R_{\infty}) / R_{\infty}}
$$
 (9)

where Rg is the basestock reflectance and R is the reflectance of a layer with background reflectance Rg.

These equations have been used with great success, but they were designed for uncoated papers. Applying a coating to paper adds a non-homogenous layer to the system. Clark and Ramsey (3) took Kubelka's work on non-homogenous layers. explaining what happens to incident light thusly. As the incident light strikes the coated paper, some of the light is absorbed, some reflected and some transmitted. The transmitted

$$
-3-
$$

light enters the paper substrate where some of this light is absorbed some reflected and the remainder is reflected back towards the coating. Here in the coating this reflected light splits into the factions of absorbed light, reflected light and transmitted light, with the reflected light reentering the substrate to continue the process.

This process is shown in Figure 1.

Incident

Light

This concept led to the following equations for reflectance, Ro, Equation **10** and transmission, **T,** Equation **11** from Clark and Ramsey (J), *tor* a coated one **side** sheeta

$$
Ro = \frac{1}{2} \left[\alpha - \sqrt{\alpha^{2} - 4 \cos \theta} \right]
$$
\n
$$
\alpha = \cos \theta \left[\frac{1}{R_{\infty}} + R_{\infty} - 1.1236 \right] + 1.1236
$$
\n
$$
T = \left[1 - Ro \left(\frac{1}{R_{\infty}} + R_{\infty} \right) + Ro^{2} \frac{1}{2} \right]
$$
\n(11)

With all this work improving the ability to predict the optical properties of a coating, the effect *ot* the **adhesive** on the final properties has been ignored. Robinson and Linke (5) studied two **cases** of pigments and **adhesives.** One **case** involves the pigment and **adhesive** having air filled voids between them. The second case exists when the pigment is completely imbedded in the **adhesive. The** first **case is** similar to what is believed to **exist** in a pigmented coating. • Robinson and Linke varied the amount of coating and pigment in a coating color to get a graphical analysis of what the

-4-

scattering coefficient is for an adhesive. They determined a value for the absorption coefficient in a similar manner. Their conclusion was that the adhesive they used, starch, has a negligible effect on the scattering coefficient of the mixture, and it also has no effect on the absorption coefficient of the mixture.

The purpose of this study is to determine whether this treatment of adhesives and their effect on the Kubelka-Munk equation holds true for other **adhesives,** both soluble and *^I*" insoluble. If it is determined that adhesives do effect the S value of the pigment, a modification of the Kubleka-Munk equation will be developed. This determination will be based on whether the S and K values for different **adhesives** differ. If there is a difference, then the **adhesives** absorb and reflect light differently. If the values are the same for the different adhesives, then the phenomenon is not a case of the adhesives absorbing light. The phenomenon then cannot be explained by the Kubelka-Munk equation. If this is the case one possible source of explanation is Trader's (6) concept of the pigment surface area being covered by the adhesive.

To test these concepts, coatings will be made from two different pigments and four different adhesives. The adhesives used will be two soluble adhesives, starch and protein, and ' two insoluble adhesives, an S.B.R. and a P.V.A.C. The pigments and adhesives will be combined in single pigment, single binder systems and coated on the same basestock. The adhesives will be added at four separate levels of addition,

 $-5-$

5, 10, 20, and 30pph. Coat weights, G.E. Brightnesses and opacity values will be obtained for each sheet.

Once this data is obtained the scattering coefficients will be determined for each coating using the Crouse and Zabel method. This method will be used because of its ease of application. The scattering coefficients will then be plotted against adhesive level to determine whether different adhesives do effect the scattering coefficients differently. Regression analysis of this data will give an equation of how scattering varies with adhesive level. This **regression** • equation will be used to determine the scattering coefficient of the mixture at 0% pigment, therefore giving a value for the scattering coefficient of the adhesive. Direct experimentation will not give the correct value for a pure adhesive since there are no voids or pigment interaction.

EXPERIMENTAL PROCEDURE

The pigments studied in this project **were** a #1 coating clay, MCP Spray Satin and a precipitated calcium carbonate, Missippi Lime M60. Both of the pigments **were prediapersed** at 70% solids.

Four different adhesives were studied. The adhesives used were an ethylated starch, Penford Gum 280, a protein, Pro-Cote 200 MV, an S.B.R. latex, Dow 620, and a polyvinyl acetate, National 1105. The starch was dispersed in distilled water at 20?' aolida by weight, heated in **a steam** jacketed beaker to 75% ± 5⁰C and held at this temperature for 10 minutes with constant stirring. The protein was also dispersed in distilled water at 20% solids and allowed to wet out for 20-JO minutes. The protein solution was heated with a steam jacketed beaker to 48⁰± 1⁰C where a cutting agent was added. The cutting agent used was 14% ammonium hydroxide and *5�* borax by weight. Heating was continued to 56° + **2 ° c** and this temperature was held for 15 minutes with stirring. The S.B.R. latex and the P.V.A.C. were used as a water emulsion.

The pigments and adhesives were combined as single • pigment, single adhesive systems. The combinations **were** then blade coated one side on a paper substrate by a Keegan coater. Coat weight variation was achieved by varying blade pressure. The paper substrate **was a** Niagara groundwood-coater basestock with basis weight of 47.24 g/m^2 ,

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a G.E. Brightness of *7?.35,* an opacity of 87.02, and a scattering power of 3.007.

Coat weight determinations were made by cutting a rectangle of air dried coated paper with a template and gaining the weight by difference. The brightness figures were obtained from a G.E. Brightness meter using filter $#15$. having a wavelength of *5?5wn.* This filter was chosen because it correlates **beat** with the opacimeter data. The opacity testing was done on a Diano Opacimeter. •

A computer program was used to figure the scattering coefficient of the total sheet. The equations used in this program are Equations 12, 13, 14, and 15.

G.E. Briefhtness =
$$
R_{\infty}
$$
 Oparity = C

$$
a = 0.89/C \tag{12}
$$

$$
b = (1 - \frac{1}{C} - 0.89 \left(\frac{1}{R_0} + R_\infty \right))
$$
 (13)

$$
Ro = \frac{-b - \sqrt{b^2 - 4 \times a \times 0.89}}{2a}
$$
 (14)

$$
SX = \frac{\ln \left[(1 - \text{Ro} \times \text{Ro}) / (1 - \text{Ro/R}_{\infty}) \right]}{(1 - \text{Ro}^2) / \text{Ro}} \tag{15}
$$

The scattering power of the coated sheet minus the scattering power of the uncoated **sheet** divided by the coat weight gives the scattering coefficient of the coating as shown in Equation 16:

$$
Sc = \frac{(SX_t - SX_p)}{C.W.}
$$
 (16)

where Sc = the scattering coefficient of the coating, m^2/g ${\tt S}{\tt X}_{\tt t}$ = the scattering power of the coated sheet SX_{p} = the scattering power of the basestock C.W. = the coat weight, g/m^2

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RESULTS

TABLE I

CLAY SYSTEMS

where $SX = total scattering power from the coated sheet$ Sc = scattering coefficient of the coating, m^2/g

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TABLE II

CLAY SYSTEMS

TABLE III

CaCO₃ SYSTEMS

$CaCO₃$ SYSTEMS

 $-13-$

 \overline{z}

 -47

 \mathbb{Q}

TABLE V

Results of Linear Regression Run on Points 10 - 30pph

Clay Systems: Sc vs % Pigment

TABLE VI

Results of Linear Regression Run on Points 10 - 30pph

CaCO₃ Systems Sc vs % Pigment

DISCUSSION OF RESULTS

Looking at the graphs of scattering coefficients vs. adhesive level for both systems, the scattering coefficient increases in both the clay and the calcium carbonate **systems** to a maximum value at 10pph addition. After that value the scattering coefficients decrease at separate rates for each adhesive. The decrease after the maximum value appears to be a linear relationship. These two trends will be treated separately.

EFFECT OF ADHESIVE ABOVE 10pph

A linear regression was run on each pigment's adhesive system in the range of 10 to JOpph adhesive. the linear regression data can be found in Tables 5 and 6. The intercepts for each adhesive correlate with the same adhesive with the different pigment. • These should be the scattering coefficients of the adhesive. Since they are different for **each adhesive,** the theory proposed earlier in this paper that different adhesives affect the scattering coefficients differently holds true. Calculating the scattering coefficients for the pigments using **these** lines at� **adhesive** gives an average scattering coefficient for CaCO₃ of .207m²/g. The value for the $\#1$ clay was .177m²/g which compares to Trader's (6) figure of .136m²/g, which was determined with a 100% pigment system. The difference is due to

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the system of pigment and adhesive. The constants determined in this study apply to a pigmented coating system held together with an adhesive and having air voids in the coating that are gradually being filled by the adhesive. This system is in a relatively steady state which exists as long as there are separate air voids in the coating. **When** all the voids are filled the system changes to a state **where** the pigment particles are imbedded in the adhesive film. **Thie was** reported by Robinson and Linke (5) **as Case** II.

EFFECT OF ADHESIVE BELOW lOpph

Looking now at the area of *5* to lOpph adhesive it appears that the scattering phenomena in this area is affected by some other mechanism than **what is seen** in the 10 to JOpph region. This use in scattering coefficient occurs in an area of adhesive level **where** other researchers have proposed structural changes in the I coating.

GRAFTON'S ENCAPSULATION THEORY

Grafton (8) studied the effect of adhesive level on the coating's structure. He noted that the film volume of the coating **went** to a maximum at 4pph starch and 2.5pph polyvinyl alcohol in combination with an experimental clay with a narrow particle **size** range.

-1?-

Once this maximum film level was achieved it remained the same until about 22pph starch and 4pph polyvinyl alcohol. Grafton attributed this phenomena to the adhesive encapsulating the entire pigment particle and this encapsulated particle would then have a thickness greater than the uncoated particle. This thicker particle would **cause** more voids within the coating structure which should cause an increase in scattering coefficient. The film volume decreased after 22 and 4pph respectively, due to the voids in the film being filled.

Grafton tested his theory by using a machine delaminated clay with a particle thickness 10 times that of the previous clay. The purpose of this was that if the delaminated clay absorbed as much adhesive on the surface as the thinner clay. the increase in film volume would be much smaller. This smaller increase in film volume was in fact observed.

THE SPOT WELD THEORY

Another theory could explain the film volume increase in Grafton's work. The particles do not necessarily have to be encapsulated to see the effect of the increased amount of voids in the coating. As the coating dries the water is evaporated **away** and because of capillary action the adhesive is drawn to the points where the pigment particles touch. When the adhesive

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dries it has wedged the particles further apart creating voids in the same manner as Grafton's Encapsulation Theory.

KALISKI'S FLOCCULATION THEORY

The phenomena of the scattering coefficient going to a maximum as initial amounts of adhesive are being added has been reported by Kaliski (7). He applied #1, #2 and machine 4elaminated clay to black **glass** • varying the level of starch adhesive. The **maximum** scattering coefficient of $#1$ clay was achieved with a level of 5pph starch, and additional **levels** of starch beyond this point caused a decline in scattering. The mechanism that he **used** to explain **these** results was .. that as the adhesive was added, clay **fines were** bound • together. These aggregates would scatter light more effectively. Increasing the adhesive level beyond Spph causes the further aggregation, and the optimum dimensions of the aggregates are exceeded. Kaliaki chose this mechanism because #1 clay **showed** a greater increase in scattering coefficient with adhesive addition than the #2 clay, and the machine delaminated clay **showed** no increase at all. The $#1$ clay has higher degree of fines than the $#2$ clay and much more than the delaminated clay.

Looking at Kaliski's results with the $#1$, $#2$ and machine delaminated clay, both Grafton's Theory and the Spot Weld

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Theory would predict an increase in scattering coefficient for all three types of clay due to an increasing amount of voids created with the increase in adhesive. More voids. no matter how large, would increase the scattering coefficient due to more sites for a change in refractive indices. Therefore an increase should have been **seen** in the delaminated clay's scattering coefficient **as a** small amount of • • adhesive was added. Kaliski reported a steady decrease with increasing adhesive. Thia therefore leaves only the flocculation of fines to explain the increase in scattering coefficient for the $#1$ clay.

In this study both the #1 clay and the CaCO₃ have about the same number of fines and following the flocculation theory, should have reacted the same to adhesive addition. They did show the same general trend, so the floeculation of fines is the reason attributed to the increase in scattering coefficient from *5* to lOpph adhesive addition. The Spot Weld or the Encapsulation Theories might be the cause of the film volume increase, but not the increase in scattering coefficient.

In summary, the data in this study can be explained by the following mechanisms, From O **adhesive** to approximately • lOpph, the fines in the coating are flocculated to give increased scattering. The coating film volume also increases due to either encapsulation of the particles, or the spot welds in the latice expanding, This is Case Ia. After the flocculation has achieved its maximum at lOpph, Case Ib exists, Thia is a system where a relatively fixed latice of

-20-

pigment particles has its voids gradually being filled by adhesive. When no more voids exist, Case II now takes over. The pigment particles are now imbedded in the adhesive.

CONCLUSION

From the data presented in this report it was determined that different adhesives do effect coatings differently. A rise in the scattering coefficient of #1 clay and CaCO₃ coatings in the range of 0 to lOpph adhesive was observed and was attributed to the flocculation of fines in the coating. After this flocculation period has reached its maximum a linear equation can be used to predict the scattering coefficient of a coating between 18 to 3Opph **adhesive.** • •

The results of this report can be explained by the coating going through three phases as adhesive is added to the coating, ending at lOpph adhesive, Case lb, a steady state where the voids in the pigment latice are being tilled by adhesive, lasting from lOpph adhesive until all the voids are filled in the coating. At this point Case II exists, where the pigment particles are imbedded in the coating.

This report also indicates that the same general trends observed for coatings applied to black glass or foil substrates can also be observed with coatings applied to a paper substrate.

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RECOMMENDATIONS

To determine whether the rise in scattering coefficient is due to the flocculation of fines in the pigment, a study should be conducted using pigments with various fine fractions. Coatings with more fines would increase more in scattering coefficient with minor adhesive additions. This study should be done with pigments having controlled amounts of fines and be run in the range of O to lOpph adhesive addition.

A further extension of this report would be to take the linear equations and the scattering coefficients of the adhesives and pigments determined tor Case lb and determine their ability to predict scattering coefficients for coatings in this report. If this proves successful with single pigment, single adhesive systems, multiple pigment, multiple adhesive systems should be tried.

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