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THE EFFECT OF VISCOSITY ON BINDER MIGRATION

by

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A Thesis submitted to the
Faculty of the Department of Paper Technology
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University

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ABSTRACT

Binder migration has caused many problems in practical applications. There are many variables involved in this field including the base stock, percent solids, the type of pigment and adhesive, and the coat weight.

Binder migration seems to be a function of three almost simultaneously occurring events. These are, migration due to capillary action, pressure, and redistribution during drying.

The procedures used to determine migration in this study included an embedding technique, an infrared technique, and a technique using the IPC brightness meter. The first two techniques failed and only limited information was obtained using the other technique. The most important development was the embedding procedure. Combining this and the right equipment, valuable results may be obtained.

INTRODUCTION

Coatings are made up of three basic materials suspended in water. These three components are pigments, adhesives, and miscellaneous chemicals called additives.

Coating pigments are inorganic materials which are insoluble in water. Pigments represent the largest portion of the dry coating; approximately 78 - 80 percent by weight. There are many types of pigments, but the main ones are clay, calcium carbonate, and titanium dioxide.

In order to prepare a coating the pigment must be dispersed. Pigments in their natural state consist of agglomerates and aggregates. These aggregates must be broken down mechanically. Even though the particles are dispersed, they will reflocculate when the mechanical agitation ceases. Therefore, a chemical is added to the system; called a dispersant.

The viscosity of the coating mixture is very important when the coating is applied on a commercial machine. The viscosity is dependent upon the composition of the coating. Coating pigments, adhesives and dispersants all have an effect on the viscosity.

LITERATURE REVIEW

Rheology of Clay-Water Systems.

The particle size of clay affects the viscosity of the coating color. Particle sizes of less than two microns increase the viscosity. When these smaller sizes are not included in the suspension, the viscosity and the degree of thixotropy decrease. The structural geometry of a clay particle is flat and plate-like. This is true only of the smaller particle sized clays.

It has been shown that particles larger than two microns are not flat plates, but stacks of plates laminated together (1). These larger particles tend to yield dilatant systems; therefore, the smaller flat particles are best for coating purposes.

The plate-like particles determine the flow properties of clay-water systems. This particular structure allows the particles to glide along each other without losing contact. This gliding process, plus the rotational movement of the particles, represents the basic features of the rheology of clay-water mixtures(2). These systems are typically plastic. According to Weyl and Ormsby; "plasticity requires separation of the particles by water and loose packing (2)." It is believed that clays adsorb water on their surface, thereby keeping the particles separated. This feature, plus the anisodimensional shape of clays, are the main factors which yield plasticity.

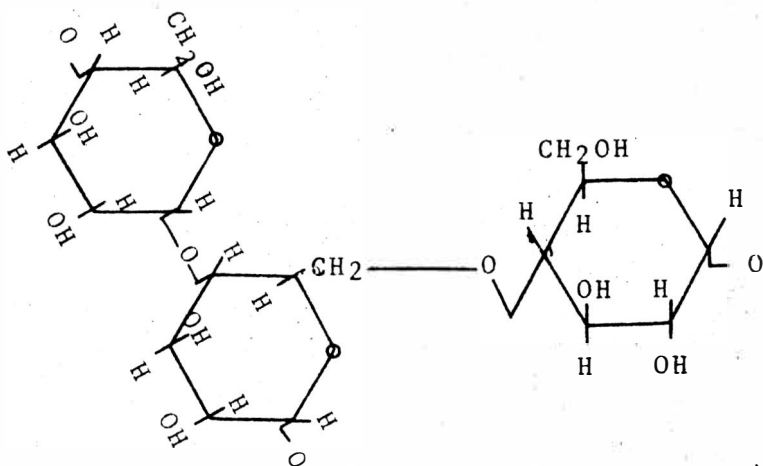
The Effect of Adhesives on the Coating Color.

Another material in the coating composition is the adhesive. Adhesives bind the pigment particles together, as well as the coating to the sheet.

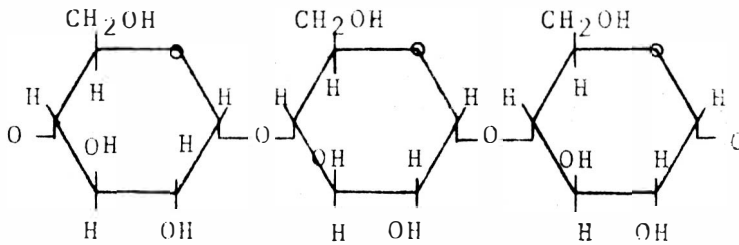
The function of the adhesive is to help carry the pigments in a dispersed condition, to influence the flow behavior of a coating mixture, and to regulate water retention (3).

There are basically two types of adhesives, natural and synthetic. Natural adhesives include starches, starch and cellulose derivatives, casien, soy protein, and animal glue. Synthetic adhesives include a variety of latices, polyvinyl alcohol, polyvinyl acetate, plus many others.

Starch is made up of two fractions, a branched amylopectin fraction and a linear amylose fraction. Approximately 70 - 75 percent of the adhesives used in the coating industry are starches or starch derivatives.



AMYLOPECTIN



AMYLOSE

Starch contains approximately 22 - 26 percent amylose, and 74 - 78 percent amylopectin (4).

As heat is applied to a starch-water system, the starch granules swell and the mixture thickens. Near the boiling point, the mixture reaches its "peak viscosity" (4). If the temperature is held constant the starch will break up and lose its viscosity. When it cools the starch will back up.

Commercial processes try to lower the peak viscosity and the set back point. There are many types of converted starches, such as: oxidized starches, dextrins, derivatized starches, enzyme converted, thermal conversions and other minor processes.

Adhesive strength is usually a result of the type and degree of conversion. Adhesive strength depends on four criteria (5).

1. The amount of starch in the coating
2. The molecular dimension to which the starch has been fragmented.
3. The extent to which the starch is dispersed.

4. The nature of the substituent groups on the molecule.

Adhesion demands intimate contact and will be enhanced if the adhesive is evenly distributed over a large area of the pigment particles. This means that adhesion will be greater if the adhesive is well dispersed.

Better dispersion may be obtained by cooking for longer periods of time. This yields a higher degree of substitution and in the case of hydroxyethylated starches; a stronger adhesive.

In an aggregated molecular solution the structure contributes highly to water retention. Also, a molecular dispersed structure yields adhesive and pigment binding power.

When hydroxyethyl groups replace the hydroxyl groups of the starch, followed by acid hydrolysis, a converted starch is obtained which is well dispersed and behaves like a molecular aggregate. This combination yields good water retention and high pigment binding power.

As stated before, the adhesive is one of the factors that influences viscosity. Starches cooked at low solids level (4 - 8 percent) exhibit pseudoplastic flow. Starches cooked at high solids (12 percent and higher) exhibit thixotropy, as well as pseudoplasticity. If a high viscosity starch is used, the resulting color will have a higher viscosity than if a low viscosity starch was used.

Also, as stated before, the adhesive binds the pigments to each other and the coating to the substrate. Daum and Benninga felt that hydrogen bonding between the hydroxyl groups of the clay and of the starch is the most probable mechanism of binding starch to clay. It was also felt that much work still needed to be completed on this subject (6).

The Effects of a Dispersant

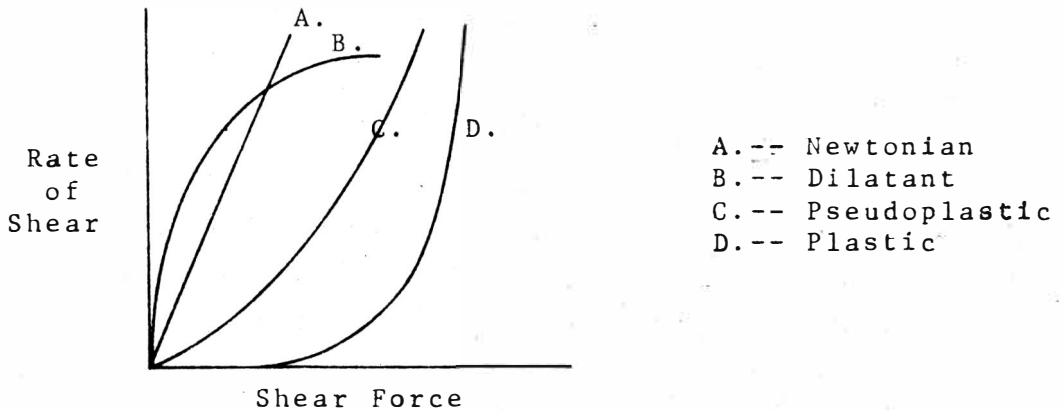
Most coating colors will reflocculate if and when the mechanical shear ceases. To keep this from occurring, a dispersant is added to the system. Tetrphosphates, silicates, organic surfactants, proteinaceous polymers are dispersants, but the polyphosphates are probably the best.

A dispersant surrounds the clay particles with a "cloud" of ions referred to as the diffuse double layer. It seems that clay particles have negative charges on their faces and positive charges on the edges. The deflocculant anion is adsorbed on the crystal edges and the cations surround the particle as a swarm of "counterions" (7). This layer of counterions form an integral part of the particle. When the particle moves, the counterions move with it. In this way the particles are able to move independently to each other.

A dispersant will generally reduce the viscosity of the total color.

Rheology of Coating

Coating colors also follow the basic types of flow. They are plastic, pseudoplastic, dilatant and Newtonian. The following graph illustrates these flow properties.



In addition to the basic types of flow, the term thixotropy should be introduced. It is not a type of flow but describes the behavior of the types of flow. For thixotropy to exist the rate of destruction of the clay slurry must be greater than the rate of recovery. This difference in the destruction and recovery cycles yield a hysteresis loop. The speed of restoration of the material determines the degree or extent of thixotropy. The larger the area covered by the loop the greater the extent of thixotropy.

The viscosity of a coating color can be measured by a variety of viscometers. Diehm and Hamerstrand demonstrated

that all viscometers will correlate if shear rate is plotted against viscosity (8). Unfortunately, the most widely used viscometers do not yield such an answer directly.

One of the most widely used viscometers is the Tecton Hi-shear viscometer. It is one of the best instruments for rapidly determining the rheological properties of a coating mixture. A curve is obtained directly from the machine. This curve plots rate of shear versus torque. The viscosity can be calculated from these flow curves by using the equation below:

$$\frac{9.55 TS}{\text{RPM's}}$$

Where T = Torque
S = Bob constant
9.55 = Machine constant

The Brookfield viscometer is also widely used in the industry. Even though it is widely used, it contains very serious limitations. These limitations are due to varying annular gap between the cup and bob. Therefore, the shear rate can only be estimated. For non-newtonian flow more than one reading should be taken because the viscosity is not constant. The Brookfield is excellent for routine control measures, but has numerous drawbacks as shown above.

The coating color affects the viscosity in a number of ways. Low solids coatings are generally Newtonian with viscosities in direct proportion to the solids content.

Lowering or raising the solids content is usually sufficient to modify the mixture. This is not the case with high solids coatings because the adhesive and pigment particles are closer together. Viscosity can be reduced by adding water, but only at the risk of changing other rheological properties (9).

Binder Migration

During the coating process the sheet goes through a series of operations. These operations are applications, metering and drying. All of these operations affect the final coating structure. These variables affect binder migration which in essence determines the structure of the coating. There are three main types of binder migration:

1. Capillary action.
2. Pressure due to application and metering.
3. Redistribution during drying.

The final distribution of the adhesive is a function of all three variables.

Migration due to capillary action is controlled by the surface tension and wetting angle of the migrating phase (10). This takes into account the wetting characteristics of both the paper and the pigment. Molecular weight is inversely proportional to capillary migration. The migrating phase is mainly water, because the polymer chains of the adhesive are held securely by the pigment.

Particle size plays a part in capillary migration.

Clays are known to absorb water on their surface. Finer clays absorb water more readily than coarser clays. This directly affects capillary migration. That is, capillary water migration is less for finer particle size clays than for coarser clays.

Pressure migration is also dependent upon the molecular weight of the binder. Water and polymer chains move together toward the substrate. As pressure is applied, the particle size of clays and binders come into play. Larger particle size will pack more and reduce pressure migration; whereas smaller particles have less tendency to pack, thereby creating an easier passage through the color and an increase in pressure migration.

The bulk of the migration is due to drying. As drying takes place, the water molecules in the coating rush to the surface to replace those evaporated off. If this rushing water is fast enough, there exists what is called the "streaming vehicle" which can carry with it suspended pigments and adhesive (11). The smaller the particle and the lower the specific gravity, the more easily it can be carried by the streaming vehicle. Since binders have lower specific gravities than pigments, they will migrate to the surface easier. If evaporation is slow, much adhesive is lost into the base stock. If vaporization is high, the penetration is

reduced and the coating becomes adhesive rich. Another thing that should be taken into account is whether the water absorbed by the substrate evaporates through the substrate or through the coating (12).

The properties of the base stock also affects binder migration. The degree of water absorption by the substrate depends on the degree of internal and external sizing, porosity, and the overall makeup of the paper. The size of the pores also affects the migration of the vehicle. Adhesive penetrates further into the substrate with the larger pores than with small pores. But, more adhesive is lost to the substrate which contains small pores (13). This indicates that depth of penetration is not directly proportional to the amount of adhesive lost from the color.

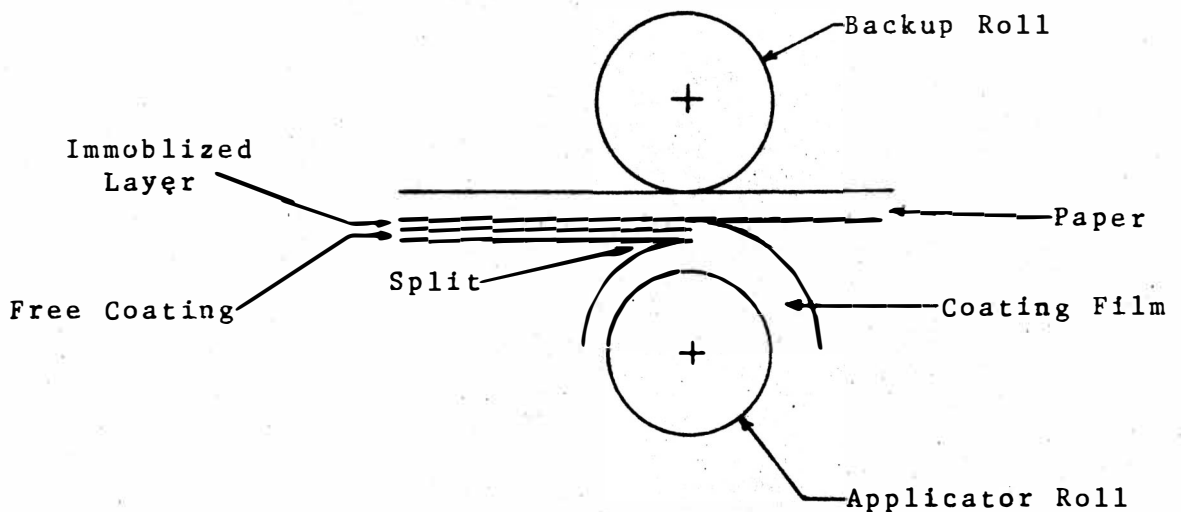
If the base stock is anisodimensional, the substrate will absorb water at different rates across the sheet. If the sheet is extremely anisodimensional, the coating surface may become mottled. This is, of course, an undesirable feature in the coated surface.

Water Retention

Water retention of the coating depends on the combined effects of viscosity, percent solids, the water holding ability of the starch, the chemical structure and the molecular weight of the starch, type and particle size of the pigment, and many other miscellaneous factors.

Water retention increases with increasing solids and the amount of starch present. It increases with increasing temperature. It also has been said that viscosity has little direct effect on the water retention (14).

The water retention of a coating is important because its immediate effect is an increase in percent solids content of the coating at the instant of application, due to absorption by the substrate. This thin layer, at the coating - substrate interface is called the immobilized layer. The rest of the coating is called the free coating and is in a fluid state. The free coating will split and transfer some fraction of the coating to the paper; roughly 50 percent.



The type and structure of the starch effects the water retention values. A starch, which has an aggregated structure, tends to hold more water in much the same way as a sponge.

A hydroxylethylated starch gives a high water retention value. This is due to the special influence of the hydroxyethyl groups, which has a beneficial effect on water retention because of its hydrophilic nature and formation of a loose aggregate structure (5).

EXPERIMENTAL DESIGN

Binder migration is controlled by the properties of the base stock, the solids content of the coating, the type and amount of pigment and adhesive used in the coating, and the coat weight.

The basic idea of this particular study was to closely control the above variables, and vary only the viscosity of the coating. This was done by using different viscosity starches. Penford Gum 280 is a low viscosity starch, and Penford Gum 200 is a high viscosity starch.

The starches were cooked at approximately 7.0 percent solids to 185°C. in a double boiler. The solids content of the starches were maintained by adding water to compensate for evaporation losses after the cooking was

completed.

The clay used was a number two coating clay. It was slurried at approximately 62 percent solids without the aid of a flocculant. After fifteen minutes of constant agitation, the starch was added slowly to the clay slurry. This, the coating color, was mixed thoroughly for thirty minutes.

The freshly prepared coatings were used immediately, and were applied to the sheet with a number 26 rod. The coated papers were air dried. In no case was forced air drying used.

The properties of the coating and the base stock are listed below.

Coating properties

Penford Gum 280.

100 parts clay

16 parts starch

30.2% solids

Viscosity -- 55Cp

Coat weight -- 15.4 # (25x38-500)

Penford Gum 200.

100 parts clay

16 parts starch

30.0% solids

Viscosity -- 1669Cp

Coat weight -- 16.6# (25x38-500)

Properties of the Base Stock

Porosity -- 15.2 sec./ 100cc.

Hercules size test -- 13.8 sec. (Reflectance 70%)

Caliper -- .0039 in.

Ash -- 6.1%

Basis weight -- 45.83# (25x38-500)

After the samples were dry it became necessary to evaluate them. This was done using three different approaches.

The first procedure included a sample embedding procedure using a polymer called Butyl Methacrylate. This procedure is included in the appendix. After the samples were ready, they were cross-sectioned on a microtome to 5 microns. These cross-sections were placed on a slide, stained with an iodine stain, and examined with a microscope. It was hoped that the stain would selectively indicate starch, this however did not occur. Instead the stain spread completely over the sample and no differences in color could be seen. Therefore, this technique was put aside in favor of an infrared technique.

The infrared technique used, included a Multiple Internal Reflectance apparatus used as an attachment to the infrared spectrophotometer. The idea behind the use of this equipment was to obtain a spectrum indicating the presence and amount of starch on the surface of the

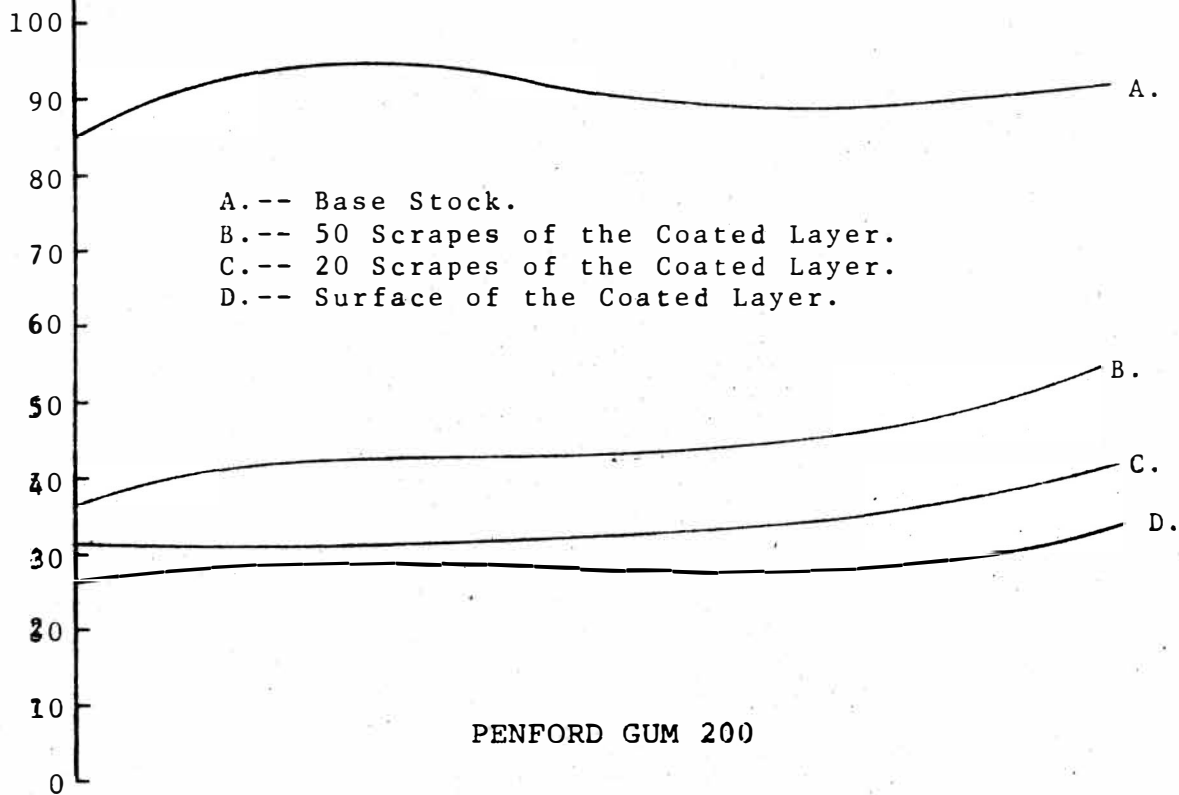
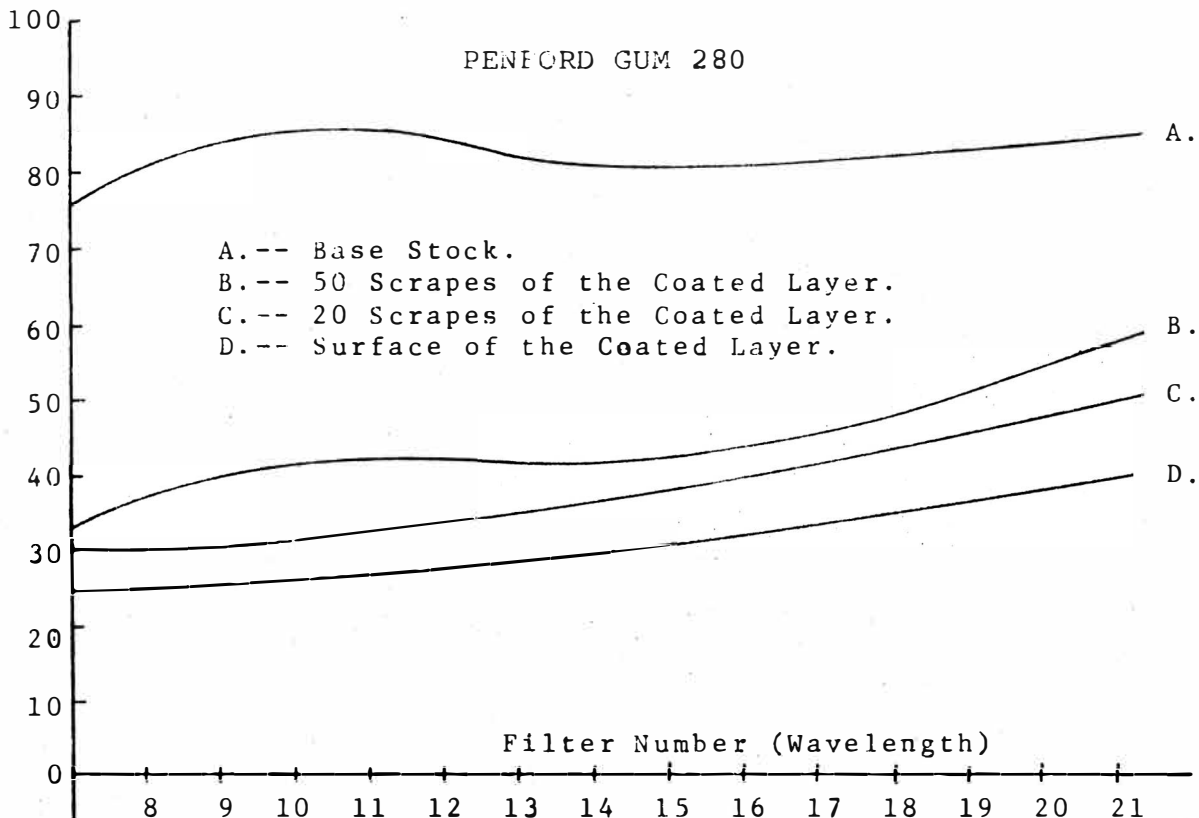
coated layer. This technique failed when an integral part of the apparatus was damaged. This technique would probably have been of limited use anyway, since the spectrums of starch and cellulose are very close.

The last technique used was a staining procedure using an IPC brightness meter. The samples were stained on the surface of the coated layer and readings were taken at each filter of the brightness meter. Then using a fresh sample, the surface of the coating was scraped twenty times with a blade, stained, and readings were obtained from the brightness meter. Using the same technique, readings were obtained for a sample scraped fifty times. The same procedure was applied to the base stock with no coating on it.

DISCUSSION of the RESULTS

The first two techniques listed above were of very little use in obtaining results. From the third technique some very qualitative results were obtained. These results are the graphs found on the following page.

When comparing these graphs, we find that the curves of the coated layers and those of the base stock are quite different. The curves of the coated layers have a definite upswing to the right, whereas the base stock does not. This fact in itself yields only



qualitative results. This is due to the lack of precision in the procedure itself. There are simply too many question marks involved with this procedure to obtain quantitative results.

The placement of the curves on the graph might indicate a differing amount of starch between the coated layers. That is, it may be possible to say that since curve B is displaced higher on the graph than curve D, less starch was indicated. But here again we are dealing with procedural questions, such as consistent staining techniques, and placement of the sample on the brightness meter etc. Therefore the results are again in question, and at best qualitative.

CONCLUSIONS and RECOMMENDATIONS

The study of binder migration is far from finished, and it can be seen from this paper that more advanced techniques are required to study this problem.

Possibly, the most important technique developed was the sample embedding procedure. Combine this and the right equipment, such as an electron microscope, valuable information may some day be obtained.

Appendix.

EMBEDDING PROCEDURE

Removal of inhibitors.

Use twenty parts by weight of a five percent sodium hydroxide - twenty percent sodium chloride solution per one hundred parts of monomer. Stir or shake for ten minutes. Draw off bottom layer in a separatory funnel. add a small amount of sodium carbonate, stir and filter.

Addition of a catalyst.

The catalyst used was benzoyl peroxide. The catalyst may be added in any amounts desired so long as it does not exceed one percent by weight. The catalyst is added to the monomer and dissolved by stirring. Filter the solution if necessary.

Preparing a partially polymerized monomer casting syrup.

Heat the catalyst containing monomer on a steam bath, stirring continually, until the solution obtains a consistency like that of glycerin. At this point remove the vessel from the bath and cool. The consistency should approximate that of molassis when it is cooled.

Saturating the specimen with monomer.

Specimens should be impregnated with catalyzed, inhibitor free, liquid monomer. This is done by placing the specimen in the catalyzed monomer. Saturation is complete when the specimen sinks to the bottom.

Embedding the specimen.

Thoroughly wet the mold with the catalyzed monomer. Pour the desired amount of the casting syrup into the mold. Now, remove the specimen from the liquid monomer and carefully place it into the mold containing the casting syrup. It is now ready to be cured in an oven at 110 -115 °F. The time the polymer takes for curing depends on how much catalyst was used.

Note: The mold used in this study was an ordinary gelatin capsule, size 000.