The Role of Water in the Starch-Clay-Paper Coating System

by John Mitchell McEwen

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THE ROLE OF WATER IN THE STARCH-CLAY-PAPER
COATING SYSTEM

A thesis submitted by

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INTRODUCTION AND HISTORICAL REVIEW

The development of the high speed machine coating process has greatly complicated the technical problems of the coated paper manufacturer. The advantage of improving the printing surface of paper by a low cost mineral coating is self-evident. However, the mechanical means of applying this coat have placed strict requirements on the physical and chemical properties of the coating materials used.

The use of high solids coating mixtures in machine coating has been dictated by the amount of time available to apply the coat and the necessity of rapidly drying the sheet after coating. Increasing the solids content not only increases the viscosity of the mixture, but also increases the sensitivity of the viscosity to small changes in the components. For example, increasing the solids content or amount of dispersing agent in a 60 per cent solids coating color affects the viscosity far more than the same change in a 50 per cent color. This means that minor variations in components may greatly change the viscosity and coating characteristics of the color. The problem is further complicated by the fact that most color components are natural colloids which vary at their source and are difficult to process so that a uniform product is obtained.

This discussion is confined to coating mixtures containing clay, starch, dispersing agent, and water although, in commercial practice, various other pigments, adhesives, and modifiers are used. Natural starches are too viscous to be used in coating mixtures and they must
be modified by chemical treatment or enzyme action to give less viscous solutions which still retain their adhesive characteristics. A raw clay may be any one or a mixture of a great number of mineral species but only certain of these, such as "kaolin," are suitable for coating. A coating clay should be separated from the extraneous material found with it, fractionated as to particle size, and washed with acid to give a uniform base exchange content before it is used. A dispersing agent must be added to the clay to reduce its viscosity before it can be used in high solids coating. However, the addition of too much dispersing agent may increase the viscosity of the mixture. Furthermore, some mixtures are dilatant and tend to become abnormally viscous when subjected to high rates of shear, whereas others are thixotropic and are abnormally fluid at high rates of shear. Thus, there are many variables, even in the simplest mixtures, which greatly influence coating properties.

The most comprehensive survey of the literature available in the starch, clay, and coating fields is given in West's Bibliographic Series (2-3). Another, more recent, source of information is the TAPPI monograph on starch for paper coating (4).
PRESENTATION OF PROBLEM

It has long been known that different clays give different properties to coating mixtures. Earlier investigators have shown that the hydrous nature of clay greatly influences the viscosity and coating characteristics of coating colors. Some (5, 6) have suggested that the distribution of water between starch and clay may have a great effect on the properties of the mixture. This seems reasonable, since both starch and clay are hydrophilic colloids, and they might be considered as competing for the water present in the system. It was thought that the properties of a color could be better predicted if the distribution of water between starch and clay could be determined for various mixtures. Results of such determinations indicated that, for coating type materials, the starch had such a great affinity for water that it was solvated by practically all the water present in the mixture. The investigation was continued in an attempt to devise means for determining the effect of clays and starches of varying hydrophilic nature on the viscosity and coating characteristics of the mixture.
DESCRIPTION OF MATERIALS AND TESTING METHODS

MATERIALS USED

Commercial starches and clays were used throughout this investigation. A description of materials, which will be hereafter designated by letter, is given below.


2. Clay B—a coating grade Georgia secondary clay with a sedimentation volume of 29.5.

3. Clay C—a coating grade Georgia secondary clay with a sedimentation volume of 43. The most hydrous of the clays used.

4. Starch A—a relatively viscous oxidized coating starch with a low degree of chlorination.

5. Starch B—a fluid oxidized coating starch with a high degree of chlorination.

6. Starch C—a fluid oxidized coating starch with a high degree of chlorination. This starch gave a thinner sol than Starch B.

7. Starch X—a relatively viscous coating dextrin.

8. Starch Z—a relatively fluid coating dextrin.
IMIBITION METER

In order to study the probably distribution of water between starch and clay in a coating mixture, it is desirable to measure the capacity of a colloid to hold or imbibe water. Sedimentation of starch by centrifuging was tried, but the starches tested did not settle if they were properly dispered. It was found that a starch sol would imbibe water through a membrane. The amount of water imibed in a given time seemed a good index of the hydrating capacity of starch. A meter similar to an osmometer was developed to measure this imbibing tendency of starch.

Description of Meter

The imbibition meter is similar to the Hersog and Spurlin osmometer as modified by Meyer (2). Figure 1 shows the disassembled meter and the assembled meter with filling tubes attached is shown in Figure 2.

Each half-cell is lathe turned from cast bronze. The solution compartments are 2 3/4 inches in diameter and 3/8 inch deep. One quarter-inch holes for the manometer tubes are drilled vertically, whereas the one quarter-inch filling holes are 45 degrees from vertical. Six one quarter-inch steel bolts, symmetrically spaced, draw the two halves together. The volume of each half-cell, including drilled holes and fittings, is 47 cc.

Manometer tubes are of the same and uniform bore, so that the volume change due to the rise of one solution and the fall of the other can be obtained from a linear measurement. Manometer tubes and filling
FIGURE 1. Component parts of imbibition meter
FIGURE 2. Assembled imbibition meter.
stopcocks are sealed to the cell by rubber gaskets fitted into brass tube fittings as shown in Figure 3. These gaskets are cut from one quarter-inch rubber tubing and are used in place of the brass ring furnished for copper tube connections.

The membrane is cut from unwater-proofed cellophane, such as viscose sausage casing. The membrane is slightly smaller in diameter than the bolt circle. Perforated brass disks, one on each side, hold the membrane in position while the cell is in operation. Perforations are one quarter-inch in diameter. Disks are not interchangeable and three pins in the body of the cell position each disk so that the holes will coincide. Disks are the same thickness (1/16-inch) as the recesses into which they fit. A thin gasket, cut from a rubber dental dam, is placed between the disks and their recesses. This acts as a seal between disks and cell and also causes the disk to protrude beyond the face of the half-cell so that the force holding the cell together is transmitted through the disks normal to the membrane between them, giving an effective seal.

Filling tubes are improvised as shown in Figure 2 from rubber and glass tubes and a powder funnel. Filling tubes must be long enough to provide sufficient head to drive the solutions the desired distance up the manometer tubes. The glass sections permit the operator to observe bubbles as they are worked out of the system. The unit is mounted in a wooden base having a semicircular slot to accommodate the body of the cell. Filling tubes are held by ring stands and clamps.

Operation of Meter

The meter is assembled with a fresh dry membrane and the stopcocks are closed. The solutions to be compared are poured into the
powder funnels. The imbibing solution is allowed to fill its half of the meter and ascend the manometer tube about 20 centimeters. After closing the stopcock, the filling tube is removed from the ring stand and lowered to below the level of the stopcock. The solution is then allowed to run back into the filling tube under the force of the head in the manometer tube. This forces out air bubbles which collect during filling. After closing the stopcock, the bubbles are eliminated from the filling tube by squeezing the rubber joint between the stopcock and the glass section of the filling tube. This operation is repeated until all bubbles are removed through the filling or manometer tubes.

The water side of the meter is filled in the same manner as the imbibing side. After the bubbles have been removed from both sides, the solution side is filled to a height of about 25 centimeters above the top of the brass fitting. The water is raised to a height of about 15 centimeters. This 10-centimeter head differential slightly bows the membrane toward the water side in all the disk perforations. It has been shown that further head changes due to imbibition of the solution cause only a slight further membrane displacement, whereas the effect is appreciable if the solutions start with equal heads. The water column should be high enough so that its fall can be checked against the rise of the imbibing side. Manometer heights are measured with a meter stick.

The initial height need not be recorded since the rate of change is measured after the materials have been in the meter for one hour.
This initial period permits the solutions to wet the membrane, come to final temperature equilibrium, and seep into cracks and crevices in the fittings. Solution heights are measured for a period of five hours after the initial one-hour period. The percentage inhibition is the rise of the imbibring solution multiplied by 100 and divided by the rise of a standard polyvinyl alcohol solution in the same apparatus for the same time. Heights at intermediate times may be recorded to determine if the inhibition rise is linear. The fall of the water manometer should be measured to see if the apparatus is leaking. If the manometer tubes are of the same diameter, the fall of the water side should be the same as the rise of the solution side.

Tests should be made at constant temperature. In this investigation a constant room temperature of 27 ± 1° C. was maintained by a thermostatically controlled, forced-circulation electric heater.

I03 SHEAR VISCOMETER

Viscosity measurements at low rates of shear were made with a MacMichael viscometer. A number 26 wire was used, usually with a three-centimeter cup and a two-centimeter cylindrical spindle. Measurements on 60-percent colors and their components were made with a one-centimeter cylinder. All measurements were made at 27 ± 1° C. Rotation rates were obtained by counting the number of revolutions in 30 seconds. The viscosity reading was made when two successive intervals gave the same rate.
HIGH SHEAR VISCOMETER

High shear viscosity measurements were made with a cylinder and plane viscometer similar to the one developed by Arnold (6) for the study of clays at high rates of shear. This instrument, shown in Figure 4, consists of a 16-pound chrome-plated steel cylinder which rolls down a 1/4 by 12 by 72-inch plate glass plane. The glass is supported by a heavy planed plank resting on a table. The desired slope is obtained by raising one end of the table on blocks. The cylinder used was approximately 4 1/2 inches in diameter and 4 inches long.

A drop containing 2 minims (0.1232 cc.) of the material to be tested is placed on the plane and the cylinder allowed to run over it at a known speed. The area of the pattern spread out on the glass is determined by the viscosity of the material and the velocity of the cylinder. The distance the cylinder should travel to strike the drop with a given velocity is calculated from the slope of the plane and the moment of inertia of the cylinder. A single slope and distances giving cylinder velocities of 40, 60, and 80 centimeters per second were used for this investigation.

The thickness of the film has been shown by Arnold (6) to be proportional to the viscosity of the material. This thickness is obtained by tracing the pattern on glassine, measuring the area with a planimeter, and dividing this value into the volume. The volume in cubic centimeters divided by the area in square centimeters and multiplied by $10^4$ gives the film thickness in microns.
FIGURE 4. High shear cylinder and plate viscometer.
HIGH SHEAR COATING ROLL

The high shear viscometer has been adapted to measure the spread of a coating mixture and its components on paper. A small square of Scotch tape was placed on the paper to prevent the drop of coating mixture from soaking into the sheet before the cylinder ran over it. This tape also secured the paper to the plane since it was placed on the end of the paper nearest the cylinder and extended to the glass plate. Although the area over which a coating spreads on glass depends on the viscosity, the area on paper gives an index of the spreading characteristics as influenced by the penetration of adhesive into the raw stock as well.

SEDIMENTATION VOLUME

The relative hydration of clays was estimated by the sedimentation volume test suggested by Comber (3). Suspensions were made by mixing 5 grams of clay with 100 ml. of distilled water in a 100-ml. graduated cylinder. One ml. of concentrated ammonium hydroxide was added to deflocculate the clay and the material was further mixed. After the mixture had stood for five minutes, 10 ml. of 0.1 M calcium nitrate were added, the mixture shaken, and the clay allowed to settle. The volume to which the clay settled was taken as an index of its “fatness” or hydrating capacity. The most hydrous clays have the greatest sedimentation volume.

"BLOTTER FRESHNESS"

The "blotter freshness" test was used to measure the rate at
which the liquid in a mixture penetrates a blotter laid on its surface. The mixture was placed in a shallow dish and stirred to prevent any surface orientation. The wire side of a square section of blotter was dusted with TAPI indicator and the blotter was placed on the surface, felt side down. The time required for the liquid to penetrate the blotter and change the indicator was measured with a stop watch.

FILTRATION RATE

The filtering characteristics of coating mixtures and their components were measured by the method suggested by Kerr (2). Thirty grams of clay were suspended in 95 grams of water and 45 grams of a 10 per cent starch sol. This gives 15 per cent of starch (based on the clay). The mixture was stirred 10 minutes with a variable speed laboratory stirrer and then poured into a funnel containing a standard filter paper. The number of milliliters of filtrate collected in 15 minutes was taken as an index of the filtering rate. Genco filter paper number 13255 was used.

In testing clay, the starch was replaced by water, making a slip of 30 grams of clay and 140 grams of water. Tests on starch alone were made by eliminating the clay, leaving 95 grams of water and 45 grams of 10 per cent starch sol.
STANDARDIZATION OF IMBIBITION METER

**General Discussion**

The imbibition meter was first used to compare starch and clay to determine which would take water from the other. It was found that the material having the greater affinity for water would dehydrate the other, as evidenced by the rise of the imbibing sol in its manometer tube. This imbibition was most pronounced when the starch or clay was compared with water; therefore, it was decided to compare the hydrating capacities of these materials by measuring their imbibing tendency against water. It will be shown later (Figure 7) that the imbibition of clay is apparently due to the osmotic pressure of the electrolyte added as a dispersing agent. However, dispersed starches cause water to flow through the membrane when no electrolytes are added. Different starches cause different rates of flow.

This pronounced ability of starch to pull water through a membrane may be due to several factors. Colloid osmotic pressure, osmotic pressure of electrolytes present, and hydration of the dispersed starch particles probably play their part. A measurement of the relative values of these factors was not attempted. However, it is believed that hydration of the starch is a major factor.

It will be shown later (Table III) that the ash content of the starch does not correlate with imbibition, as it should if the osmotic pressure of the electrolytes present were the major factor. The same
table shows that undispersed starch gives very little imbibition. If
the flow were due to the presence of electrolytes, it is thought that
a starch suspension stirred for 24 hours at room temperature would
give considerable imbibition.

Colloid osmotic pressure is generally considered to be very
low—in many instances, only 1 or 2 centimeters of water for a 20 per-
cent sol of a lyophilic colloid—and not even measurable for many
lyophobic sols (10). On the other hand, it has been reported by
Gortner (11) that starch will swell against a pressure of 2500 atmos-
pheres if heated in the presence of water.

Ostwald’s (12) equation for the pressure required to prevent
the taking of more solvent through a membrane is \( P = \frac{RTC}{M} + K\mu^2 \),
where \( C \) is the concentration, \( M \) is the particle weight, and \( K, R, T \),
and \( \mu \) are constants for the system. The first term represents the usual
electrolyte osmotic pressure, which increases in proportion to the ab-
solute temperature and the number of particles present. The second
term represents the solvation of the particles and is independent of
particle weight. For true solutions \( M \) is the molecular weight and this
is quite small as compared with the particle weight of colloids. Thus,
the osmotic pressure of electrolytes is very high, whereas that of
lyophobic colloids, which have no solvation, is very low. From a
consideration of these factors, it seems reasonable to assume that the
pressures observed for starch, a lyophilic colloid, are due in a very
large part to the second, or solvation, term.
Means of Expressing Imbibition

Figure 5 shows that the rate of flow through the imbibition meter membrane is fairly constant for several hours. The rate of volume increase between the first and sixth hours was taken as an index of the hydrating capacity of the sol. The volume change for the first hour was often erratic and, therefore, it was not included in the calculations. Possible explanations of this unpredictable behavior during the first hour are given in the section describing the operation of the meter.

The rate of change of the liquid level in the manometer tubes depends on a great many characteristics of the meter. These include the thickness and porosity of the membrane, the stretching of the membrane, the total volume of the meter, the size of the manometer tubes, the head applied at the start of the determination, and the size and arrangement of the perforations in the disks supporting the membrane. Since the membrane characteristics were found to vary from roll to roll of sausage casing used, an attempt was made to find a reproducible standard imbining substance with which an unknown colloid could be compared under the same conditions.

A 15 per cent solution of low viscosity polyvinyl alcohol (DuPont's Elvanol 70-A-05) was found to give reproducible imbibition values when dispersed under the conditions given in part C of the Appendix. Samples from three different lots of Elvanol 70-A-05 were found to give rates of rise of 1.00, 1.02, and 1.03 centimeters per
FIGURE 5
Variation in Height of 20% Starch Sol in Nanometer Tube of Inhibition Meter with Time
hour for a given membrane. The inhibition of other materials has been expressed in percentage of the inhibition of the standard polyvinyl alcohol solution. For example, if the observed rates of starch and standard polyvinyl alcohol sols were 0.49 and 0.98 centimeters per hour, the inhibition of the starch would be reported as 50 per cent.

Each determination of inhibition must be made with a fresh cellophane membrane. Each series of membranes cut from adjacent sections of a roll of sausage casing were checked against the inhibition of standard polyvinyl alcohol. The roll of cellophane used for most of the determinations gave a constant inhibition for standard polyvinyl alcohol throughout its length, but it was thought desirable to make sure that possible caliper and porosity variations did not alter flow rates.

Table I shows that the ratio of inhibition of a 20 per cent sol of Starch B to inhibition of standard polyvinyl alcohol was found to remain constant when a different thickness membrane, different diameters of manometer tube, and different cell volumes were used. It will be noted that a smaller meter volume had little effect, even though the change in concentration from water passing through the membrane was greater.
TABLE I

RELATIVE IMBIBITION OF 20 PER CENT STARCH B
AND 15 PER CENT POLYVINYL ALCOHOL SOLS

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Starch imbibition, cm./hr.</th>
<th>PVA imbibition, cm./hr.</th>
<th>Percentage imbibition (100 x starch) PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal meter</td>
<td>0.69</td>
<td>1.01</td>
<td>68.3</td>
</tr>
<tr>
<td>Meter with 2/3 normal volume</td>
<td>0.67</td>
<td>1.01</td>
<td>66.3</td>
</tr>
<tr>
<td>Meter with different membrane and manometer</td>
<td>0.64</td>
<td>0.94</td>
<td>68.1</td>
</tr>
</tbody>
</table>

Reproducibility of Imbition Values

The data in Table II indicate that the imbibition of a sol under a given set of conditions is reproducible with an expected deviation of about 5 per cent from the average. The differences observed when the concentration or dispersion conditions were varied were much greater than this.

TABLE II

IMBIBITION RATES FOR DIFFERENT SOLS OF THE SAME MATERIAL MEASURED UNDER SIMILAR CONDITIONS

<table>
<thead>
<tr>
<th>Material</th>
<th>Rate of rise in manometer, cm./hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Starch B</td>
<td>0.670</td>
</tr>
<tr>
<td></td>
<td>0.694</td>
</tr>
<tr>
<td></td>
<td>0.710</td>
</tr>
<tr>
<td></td>
<td>0.690</td>
</tr>
<tr>
<td></td>
<td>0.706</td>
</tr>
<tr>
<td>15% Polyvinyl alcohol</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>0.97</td>
</tr>
</tbody>
</table>
Variation of Imbibition with Concentration of Sol

The imbibition of a given type of starch increases with concentration until the sol is too thick to flow. This relationship is shown in Figure 6. It is quite possible that high solids gels still have a great affinity for water, but the rate of imbibition falls since the solution does not flow as readily. Whether or not high solids sols have great imbibing capacity does not affect the determination of relative starch imbibition, since sols can be compared at concentrations at which they are fluid.

Factors Affecting Imbibition

Starch imbibition, as measured by the rate of flow through a membrane, seems to depend mainly on the type of starch and the degree of dispersion. Imbibition of a given starch increases until the material is completely dispersed and then remains relatively constant. The amount of water used to dilute the starch to the desired solids content did not seem to affect the imbibition of the chlorinated starch tested. However, a minimum amount of dilution water was used. Dilutions were all made at 60° C. Starch agglomerates may remain if the dilution temperature is too low, and evaporation losses are considerable at the dispersion temperature. Ungelatinised starch showed a small imbibition, probably because of the osmotic pressure of the electrolytes present and the soluble starch particles. Ungelatinized Starch B was stirred in water, allowed to stand for 24 hours, and the supernatant liquor drawn off. This liquor, after centrifuging to remove solids, contained 5 per cent of the original solids on evaporation.
FIGURE 6
Variation of Inhibition of Starch B with Concentration
Sodium hydroxide and hydrochloric acid were used to adjust the pH but did not greatly affect imbibition, although the acid starch imbibed somewhat less. The ash content of the starches tested did not correlate with imbibition, indicating that imbibition does not depend primarily on presence of electrolytes. Lower testing temperatures give lower imbibitions as shown by a test on polyvinyl alcohol. It was also noted that bubbles in the fittings have little effect on imbibition, although an attempt was made to eliminate them before making each measurement. The imbibition was only two per cent high when the bubbles in the fittings were left during the measurement of a 20 per cent solution of Starch B. Data concerning these factors are given in Table III.

IMBIBITION OF CLAY AND STARCH

Imbibition of Clay

Clay slips cause considerable flow of water through the membrane of the imbibition meter. However, this seems to be due to the electrolyte added as a dispersing agent. A 30 per cent slip was the most concentrated Clay C slip that was fluid without the addition of a dispersing agent. This slip showed no apparent imbibition, although similar slips fluxed with increasing amounts of dispersing agents showed increasing imbibition. Sixty per cent slips showed greater imbibition than 30 per cent slips, but not as much as might be expected from the amount of electrolyte added. The rate of flow into a high solids slip may be reduced by a slow diffusion rate.
TABLE III

INFLUENCE OF VARIOUS FACTORS ON IMBIBITION

<table>
<thead>
<tr>
<th>Imbibing Sol</th>
<th>Conditions</th>
<th>Imbibition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Starch B</td>
<td>Normal, dispersed 10 min. at 92° C., 21 g. water added, pH 8.3.</td>
<td>68.3</td>
</tr>
<tr>
<td>20% Starch B</td>
<td>Low dilution, 3.9 g. water required to adjust solids content</td>
<td>68.3</td>
</tr>
<tr>
<td>20% Starch B</td>
<td>High dilution, 53 g. water required to adjust solids content</td>
<td>65.9</td>
</tr>
<tr>
<td>20% Starch B</td>
<td>Ungelatinized</td>
<td>10.3</td>
</tr>
<tr>
<td>20% Starch B</td>
<td>Low temp. dispersion, dispersed 10 min. at 82° C.</td>
<td>53.5</td>
</tr>
<tr>
<td>20% Starch B</td>
<td>Long dispersion time, dispersed 20 min. at 92° C.</td>
<td>71.2</td>
</tr>
<tr>
<td>20% Starch B</td>
<td>High pH (pH 10.4)</td>
<td>70.6</td>
</tr>
<tr>
<td>20% Starch B</td>
<td>Low pH (pH 3.5)</td>
<td>60.4</td>
</tr>
<tr>
<td>15% PVA</td>
<td>Normal, meter maintained at 27° C.</td>
<td>100.0</td>
</tr>
<tr>
<td>15% PVA</td>
<td>Low temp., meter maintained at 18° C.</td>
<td>85.1</td>
</tr>
<tr>
<td>10% Starch A</td>
<td>Ash content 1.59%</td>
<td>17.8</td>
</tr>
<tr>
<td>10% Starch B</td>
<td>Ash content 2.84%</td>
<td>26.7</td>
</tr>
<tr>
<td>10% Starch C</td>
<td>Ash content 1.91%</td>
<td>41.0</td>
</tr>
<tr>
<td>10% Starch Y</td>
<td>Ash content 0.16%</td>
<td>19.8</td>
</tr>
<tr>
<td>10% Starch Z</td>
<td>Ash content 0.16%</td>
<td>18.8</td>
</tr>
</tbody>
</table>
If the hydrous nature of the clay were a major factor in
imbibition by clay slips, one would expect a clay with a smaller sedi-
mentation volume to show less imbibition with a given amount of electrolyte
than a more hydrous clay. When 60 per cent slips of Clays B and C were
tested with 0.5 and 1.0 per cent dispersing agent, Clay B had the greater
imbibition with 0.5 per cent, whereas Clay C had the greater imbibition
with 1.0 per cent. This observation was not investigated further, since
it was felt that the dispersing agent played the major part in clay
imbibition, but it may have been due in part to experimental error (no
duplicate runs were made) and in part to viscosity effects. Data ob-
tained for the imbibition of clays with varying amounts of dispersing
agents are given in Figure 7.

Imbibition of Starch

The starches used were compared at 10 per cent concentration.
All were fluid at this solids content. Only the two low viscosity
chlorinated starches were fluid enough to be definitely free of the
viscosity effects shown in Figure 6 at 20 per cent concentration.
The relative imbibition of these starches is shown in Figure 8.

DISTRIBUTION OF WATER BETWEEN
STARCH AND CLAY IN MIXTURES

Starch-clay coating mixtures seem to consist of clay particles
suspended in a starch sol. This is indicated by the relative imbibition
of starch and clay, since the most hydrous clay investigated showed no
imbibing power without a dispersing agent and all starches tested showed
appreciable imbibition. This concept is also reasonable in view of
viscosity tests and spreading tests on raw stock reported later.
FIGURE 7

Apparent Inhibition of Oxy
with Various Amounts of Dispersing Agents
FIGURE 8
Relative Inhibition of Stenone
Other writers (5, 6) have mentioned that the distribution of water between starch and clay may have an important effect on the viscosity of the mixture. This suggests the picture of starch and clay competing as hydrophilic colloids for the water present in the system. However, no appreciable changes in viscosity were noted when mixtures of the same composition were compounded from dilute clay and concentrated starch, or from concentrated clay and dilute starch. There was also but little variation in the viscosity with time after mixing, although such a variation might be expected as equilibrium was approached, if one component took water from an almost equally hydrophilic component.

### TABLE IV

<table>
<thead>
<tr>
<th>Components mixed for color</th>
<th>Time after mixing, hrs.</th>
<th>Area in sq. cm. on:</th>
<th>Glass Coated sheet</th>
<th>Raw stock</th>
<th>Kraft stock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch B, Clay C, %</td>
<td>0, 4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>125.6 84.5</td>
<td>63.9</td>
<td>38.7</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>119.8 82.3</td>
<td>61.1</td>
<td>37.9</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>127.7 81.8</td>
<td>64.5</td>
<td>40.3</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td></td>
<td>123.0 84.3</td>
<td>64.8</td>
<td>38.1</td>
<td></td>
</tr>
</tbody>
</table>

Table IV gives the high shear spreading areas of 50 per cent colors at 60 centimeters per second roll speed. Starch sols and clay slips were prepared and allowed to stand in covered jars for one hour. The components were mixed by stirring for two minutes with a spatula and then run at once on the high shear plane. One reading was taken on glass and on each of the papers, and the sequence repeated till three readings checked to within three per cent. There was no regular variation.
in the values obtained for successive readings. For example, successive readings for a 20-70 per cent mixture at zero time were: 39.8, 41.2, and 39.8 for kraft; and 64.8, 65.0, and 63.8 for raw stock. Data were obtained in the same manner after the mixture had stood in a covered jar for 4 1/2 hours. The material was stirred with a spatula for one minute after 4 hours and for another minute just before the viscosity was measured.

The low shear viscosity of the mixtures reported in Table IV is shown in Figure 9. It will be noted that there is little variation in viscosity with time, but some variation between colors. It is thought that the somewhat lower viscosity at both high and low shear of the 20 per cent starch mixture was due to a more complete dispersion of the starch at low solids, giving a lower viscosity starch sol. If the difference were due to a difference in initial water distribution, the two mixtures should reach the same equilibrium point on standing. When similar mixtures were allowed to stand for 24 hours with several periods of stirring with a variable speed stirrer, the mixture containing 20 per cent starch remained more fluid than the one containing 35 per cent starch. It was noted that the viscosity of each mixture decreased slightly after each period of mechanical stirring. This was probably due to disintegration of a gel structure which was built up during the standing period.

Apparently starch has such a great affinity for water that when the two are mixed, it instantaneously forms a sol with almost all the water in the clay slip. This affinity was demonstrated by pouring
FIGURE 9

Variation in Love's candle viscosity of 50 percent solids mixtures with time and initial distribution of water

○ 3/4 hours after mixing components
○ 5 hours after mixing components

30° Starch B
70° Clay C

35° Starch B
70° Clay C
a thick 70 per cent slip of Clay C into a weighing bottle and carefully pouring a 20 per cent Starch B sol on top of it so that the surface was not disturbed. After 72 hours, the starch was poured off, leaving a solid mass of clay, which was dried at 105° C. Tests on the clay cake showed that the starch had penetrated the clay surface a short distance and had also gone down the sides and over the bottom of the weighing bottle.

Seventy per cent Clay C slips were covered with water or 20 per cent Starch B to see if the solid mass of clay was due to aging and sedimentation or to the removal of water and dispersing agent by the starch. After 48 hours an uncovered slip in a stoppered bottle was still fluid and had a 70.0 per cent solids content. The slip covered with water was still fluid and showed a solids content of 69.3 per cent. The clay covered with starch was quite solid and had a 71.8 per cent solids content. The increased solids content indicated that the starch removed more water from the clay than the water of solvation it took up when it penetrated the slip. It also seems logical that some of the dispersing agent diffused into the starch layer and was held there, since the material was much thicker than a normal 71.8 per cent clay slip dispersed with 0.5 per cent quadraflos. All solids measurements were made by pouring off the water on starch covering the slip and determining the moisture loss on drying to constant weight at 105° C.

This dehydrating tendency was also noted with polyvinyl alcohol. A standard 15 per cent solution of polyvinyl alcohol was poured over 70 per cent slips of Clays A, B, and C. It will be noted from Table V
that the solids content after contact with polyvinyl alcohol is in
the same order as the clay sedimentation volumes. Clay C is the
most hydrous and retained a higher percentage of its water. Clay A
settled during the 48 hours as indicated by the solids content of the
blank.

**TABLE V**

**DEHYDRATION OF 70 PER CENT CLAY SLIPS BY**
**15 PER CENT POLYVINYL ALCOHOL**

<table>
<thead>
<tr>
<th>Type clay</th>
<th>Solids after standing 48 hours, %</th>
<th>Solids after contact with PVA for 48 hours, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>73.3</td>
<td>77.1</td>
</tr>
<tr>
<td>B</td>
<td>70.2</td>
<td>74.0</td>
</tr>
<tr>
<td>C</td>
<td>70.2</td>
<td>71.4</td>
</tr>
</tbody>
</table>

**INFLUENCE OF HYDROUS CLAYS IN COATING**

It is known that the hydrous nature of clay is of great
importance in coating operations, yet inhibition studies indicate that
the starch is solvated by practically all the water present in the sys-
tem. This does not preclude the possibility that water may be adsorbed
by the clay or held in its pores, but it is thought that this must be
a very small amount. Hydrous clays generally give more viscous colors
than nonhydrous clays for the same amount of dispersing agent and solids
content. This may be explained by assuming that hydrous clays have a
greater affinity for the starch sol and immobilize it. However, hydrous
clays may well influence the migration of the adhesive into the sheet
by forming an impervious filter cake, rather than by retaining more water.
This is indicated by the filtration experiments reported in Table VI.

<table>
<thead>
<tr>
<th>Clay Type Weight, g.</th>
<th>Composition of mixture 10% Starch Weight, g.</th>
<th>Other Component</th>
<th>Volume of filtrate, ml.</th>
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</thead>
<tbody>
<tr>
<td>C 30</td>
<td>-</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>B 30</td>
<td>-</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>A 30</td>
<td>-</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>A 27</td>
<td>-</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>-</td>
<td>B 45</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>-</td>
<td>Y 45</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>C 30</td>
<td>B 45</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>B 30</td>
<td>B 45</td>
<td>-</td>
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</tr>
<tr>
<td>A 30</td>
<td>B 45</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>A 30</td>
<td>Y 45</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>C 30</td>
<td>-</td>
<td>0.15 g. Quadraflos</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Table VI shows that there is a great variation in filtration rates for different combinations of clay, starch, and dispersing agent. To find the fundamental causes of these differences would be beyond the scope of the present investigation. Such a study might well include investigations as to the effect of particle shape, particle size, particle size distribution, exchangeable base content, and other factors generally considered to contribute to hydration as measured by sedimentation volume. These filtrations were very approximate, but similar experiments with a known vacuum or other constant force on the mixture might be found to correlate very well with certain characteristics of costing raw stock, since the adhesive migrates from the coating color into
the raw stock in a manner similar to the passage of the fluid from these mixtures into and through the filter paper. A more precise filtering method for clays is described by Harman and Parmelee (13).

The filtration rates given in Table VI follow the hydration of clays as measured by sedimentation volume. Hydrous clays do not permit water to flow as readily as nonhydrous clays. The addition of a dispersing agent to a clay increases the sedimentation volume and decreases the rate of filtration of a clay slip. Starch added to the clay also greatly decreases the filtration rate. This is probably due to two factors. The more viscous starch does not flow through the pores of the filter as readily as water, and it also acts as a protective colloid to better disperse the clay. The slowing of the rate by starch does not seem to be due to viscosity increase alone, since starches of the same concentration as those in the clay mixtures flowed quite freely. Conditions of dilution also affect the rate of flow of starch. Six milliliters of a 10 per cent starch Y sol passed through the filter in one hour. When a 20 per cent sol of the same starch was diluted to 10 per cent with water at room temperature, none would flow through in one hour, while only a few drops went through when the 20 per cent sol was diluted to 10 per cent with water at 60° C. All filtrations were run with the sols at room temperature (27° C.). The sols which were diluted at temperatures lower than the dispersion temperature did not seem to be completely dispersed at the lower concentration, even with prolonged agitation with a variable speed stirrer. When the solution was filtered, the high solids flocs seemed to form a layer which prevented the flow of the rest of the solution.
Slow filtration rates of hydrous clays could possibly be caused by the particles packing together to mechanically form an impervious layer, or by the ability of hydrous clay to hold its fluid against the force of gravity. It was noted that hydrous clays gave clear filtrates, while the filtrates from nonhydrous clay were cloudy. The addition of dispersing agent to hydrous clay gave a very cloudy filtrate. This indicates that the slowing of the rate of filtration is not entirely due to mechanical packing of clay particles at the paper surface, since the slow-filtering clay with dispersing agent permitted clay to pass through the paper. A more probable explanation is that hydrous clays form a gelatinous layer at the paper surface through which the suspending medium can pass with difficulty, but which retains the clay particles. The addition of a dispersing agent disperses the agglomerates into smaller particles which have relatively more hydration. This forms an even more gelatinous layer, but the distance between particles is greater than the particle size; therefore, the material that does pass through contains more clay particles. It will be noted that the addition of 10 per cent of hydrous bentonite to a free flowing Clay A slip caused a great reduction in the rate of flow. This could well be accounted for by the formation of a gelatinous bentonite layer which hindered the flow. These possibilities are shown schematically in Figure 10.

The concept of hydrous clays preventing the flow of suspending medium into the sheet seems to agree quite well with observations in machine coating. A hydrous clay will tend to make the color flake because enough adhesive cannot migrate into the sheet, whereas nonhydrous clays may cause dusting because too much adhesive goes into the sheet. It has
also been noted that, when two coats are to be applied to a sheet, the second coat will flake off if the first coat contains too hydrous a pigment. The formation of a clay layer next to the sheet can be demonstrated by dropping a blotter on the surface of a high solids clay slip. The fluid will be drawn into the blotter and, when the blotter is removed, a layer of compacted clay will adhere to the underside.

MIGRATION OF ADHESIVE INTO RAW STOCK

A starch-clay coating is anchored to the sheet by starch which migrates from the coating mixture into the sheet. The effect of hydrous clay on the flow of adhesive has already been discussed. A slack sized raw stock does not extract water alone from the coating mixture, but the starch migrates with the water to the limit of penetration. This was demonstrated by dipping the end of a blotter strip in a starch sol and allowing the fluid to climb the blotter as it does a wick. After marking the furthest rise, the blotter was allowed to dry and a drop of iodine solution was placed at the "high water" mark. A sharp line coinciding with the "high water" mark was noted in the iodine drop, indicating that the starch iodide complex was formed as far up the blotter as the fluid had climbed. Similar results were obtained when the fluid in a dilute coating color was allowed to climb to an iodine spot on a blotter, and when starch was allowed to climb to a spot on a slack sized raw stock. This indicates that starch penetrates the sheet with water, and does not lag behind the water, as can be observed when iodine or dyes are allowed to climb a blotter.
FIGURE 10
Possible Effect of Hydration and Dispersing Agent on Sheet Penetration from Coating Mixtures

Hydrated clay.
With dispersing agent.
Liquid goes through easily.
Clay goes through with difficulty.

Hydrated clay.
No dispersing agent.
Liquid goes through with difficulty.
Clay goes through with great difficulty.

Hydrated clay.
With no clay.
Liquid goes through with great difficulty.
Clay goes through relatively easily.
Rowland (14) attributes this migration of starch to the fact that both starch and cellulose have a negative charge, so that the starch is not attracted but is repelled by the capillary walls. He has demonstrated that, when the pores of the sheet become sufficiently charged with positive materials, such as alum or aluminia, the starch is attracted to the capillary walls and further penetration is arrested, although water in the sol will continue to penetrate the sheet.

Hard sized raw stock could not be tested for starch penetration since neither water nor starch sol would climb the sheet far enough to be tested. However, tests on blotters soaked in approximately ten per cent alum solutions indicated that starch traveled up the sheet with water. Blotter strips were soaked in alum, dried, dipped in a dilute Starch B sol, dried, and tested with iodine solution. It was further noted that the blotter strips were hard sized where the starch sol had penetrated. Strips dipped in starch or alum alone were unsized. The results of the above experiments indicate that the amount of alum used in sizing raw stocks is probably insufficient to give the capillaries a sufficiently positive charge to prevent starch from migrating into the sheet with the water.

An attempt was made to correlate the penetration of a starch-clay coating color, as measured by the relative high shear spreading area of the mixture on glass and raw stock, with standard sheet characteristics. Two series were run, one on very dissimilar sheets and one on a series of similar raw stocks taken from the production of a single mill. Results are shown in Tables VII and VIII. A 50 per cent color consisting of 20 per cent Starch B on Clay C dispersed with 0.5 per cent Quadrafos
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Glass</td>
<td>116.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coated</td>
<td>81.5</td>
<td>0.699</td>
<td>68.9</td>
<td>0.0040</td>
<td>510</td>
<td>1260</td>
<td>25</td>
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<tr>
<td>Bond</td>
<td>67.3</td>
<td>0.578</td>
<td>43.7</td>
<td>0.0035</td>
<td>29</td>
<td>151</td>
<td>18</td>
</tr>
<tr>
<td>Glassine</td>
<td>60.6</td>
<td>0.521</td>
<td>20.5</td>
<td>0.0015</td>
<td>24</td>
<td>1660</td>
<td>19</td>
</tr>
<tr>
<td>Raw stock</td>
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<td>30.9</td>
<td>0.0030</td>
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<td>39</td>
<td>35</td>
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<tr>
<td>Kraft</td>
<td>37.8</td>
<td>0.325</td>
<td>41.9</td>
<td>0.0039</td>
<td>4</td>
<td>23</td>
<td>48</td>
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<tr>
<td>Blotter</td>
<td>25.5</td>
<td>0.219</td>
<td>163.0</td>
<td>0.0208</td>
<td>2</td>
<td>10</td>
<td>3</td>
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</table>
### TABLE VIII
COMPARISON OF HIGH SHEAR SPREADING AREAS OF 50 PER CENT COLOR ON SIMILAR RAW STOCKS

<table>
<thead>
<tr>
<th></th>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Raw stock A</td>
<td>69.6</td>
<td>0.534</td>
<td>38.7</td>
<td>0.0038</td>
<td>64</td>
<td>75</td>
<td>59</td>
</tr>
<tr>
<td>Raw stock B</td>
<td>65.5</td>
<td>0.502</td>
<td>32.2</td>
<td>0.0037</td>
<td>37</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>Raw stock C</td>
<td>65.2</td>
<td>0.499</td>
<td>31.3</td>
<td>0.0030</td>
<td>64</td>
<td>91</td>
<td>31</td>
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<tr>
<td>Raw stock D</td>
<td>63.3</td>
<td>0.485</td>
<td>37.1</td>
<td>0.0036</td>
<td>63</td>
<td>54</td>
<td>40</td>
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<tr>
<td>Raw stock E</td>
<td>50.2</td>
<td>0.385</td>
<td>36.2</td>
<td>0.0044</td>
<td>16</td>
<td>36</td>
<td>6</td>
</tr>
<tr>
<td>Raw stock F</td>
<td>48.9</td>
<td>0.374</td>
<td>37.8</td>
<td>0.0048</td>
<td>17</td>
<td>36</td>
<td>17</td>
</tr>
</tbody>
</table>
was used. The dissimilar sheets were tested five hours after 54 per cent clay and 35 per cent starch were mixed, whereas the similar sheets were tested three hours after 70 per cent clay and 20 per cent starch were mixed. Areas were obtained at 60 centimeters per second roll speed, and all tests were made on the same side of the sheet.

It will be seen that the area to which a coating mixture will spread varies greatly, even on similar types of paper. However, none of the standard sheet properties measured predict how the coating will penetrate the sheet. Size, porosity, and smoothness all probably affect sheet receptivity. It is known that the caliper of the paper influences this means of measuring penetration. Both a kraft sheet and a raw stock gave areas about 8 per cent low when the caliper was doubled by placing two sheets on the plane instead of one. However, when comparing papers of similar thickness, this error is probably small.

The fluorescence size test placed the similar papers in about the same groups as the spreading ratio test, but this ranking did not hold for dissimilar sheets. The dissimilar papers gave spreading ratios which correlated more closely with smoothness. It seems logical to believe that penetration is dependent on a combination of factors. Spreading ratio on the raw stocks seemed to agree fairly well with a wettability test developed by Knight (15). Indexes for Knight's dye penetration were 0.61 (the least penetration) for Sheet D, 0.67 for Sheet A, 0.80 for Sheet C, 0.85 for Sheet B, 1.04 for Sheet E, and 1.11 for Sheet F. Except for Sheet D, there was close agreement between dye penetration and spreading ratio.
An attempt was made to determine the effect of various starches and clays on sheet penetration from the area to which the component or color would spread on raw stock. It was noted that the more viscous materials seemed to give higher spreading ratios, regardless of the mixture used. Values for the spreading ratio on raw stock 2 for colors with various starch dispersion temperatures, amounts and types of dispersing agent, and initial water concentration in the components are given in Table IX and Figure 11. Spreading ratios are also given for various starch sols and clay slips. It can be seen that water penetrated the sheet from a clay slip much more easily than did the starch from a coating color. Also, thick starch from a color sol did not penetrate as rapidly as fluid starch. This is reasonable, since viscous solutions should be harder to force into the capillaries of the sheet. The spreading ratio of a starch sol seems to agree quite closely with that of a color of the same viscosity, indicating that, under instantaneous high shear action, the clay plays a minor role in spreading. The color from Clay A is an exception to this. It is believed that a high spreading ratio was obtained with this clay because it was very dilatant and the lesser shear between the roll and raw stock permitted it to spread relatively more on raw stock than on glass. Similar data were obtained for coated and kraft sheets, and in each case the value for the color from Clay A was greater than that of starch sols or colors of the same viscosity. The approximate variation of spreading ratio with viscosity for starches and colors on raw stock 2, kraft, and coated sheets is shown in Figure 12.

The amount of dispersing agent used undoubtedly affects the
### TABLE IX

<table>
<thead>
<tr>
<th>Percentage solids</th>
<th>Type clay</th>
<th>Type starch</th>
<th>Area on glass, sq. cm.</th>
<th>Area on raw stock, sq. cm.</th>
<th>High Shear Spreading Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>C</td>
<td>B</td>
<td>120</td>
<td>65.5</td>
<td>.545</td>
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<td>50</td>
<td>C</td>
<td>B</td>
<td>116</td>
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<td>C</td>
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<td>B</td>
<td>20.9</td>
<td>8.6</td>
<td>.411</td>
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</table>
FIGURE 11

Variation in Mud, Clay Sinking Ratio of Coating Mixture with Viscosity as Indicated by Area on Glass

- ○ Color from clay C
- ● Color from clay B
- □ Color from clay A
- ○ Starch
- □ Clay B slip
- ○ Clay A slip

Axes: Area on glass (cm²)
transfer of adhesive into the sheet. Filtration experiments show how greatly the addition of dispersing agent affects the flow through a filter paper, and one would expect different agents and different amounts of agent to affect the penetration rate. This was borne out by blotter freeness tests made on a series of Clay C slips with various amounts of dispersing agent. This test measures the rate at which water will penetrate a blotter laid on the surface of the slip. It could not be applied to coating colors since it took too long for the fluid to penetrate the blotter.

Figures 13 and 14 and Table X show the penetration times for various Clay C slips for both an undisturbed surface and a fresh surface. It was found that great differences in penetration time were obtained when the slip surface was allowed to stand before dropping the blotter on it. A skin seemed to form on the high solids–low dispersing agent slips which greatly increased the time of penetration. This was particularly apparent when soda ash was used as a dispersing agent. On the other hand, very low solids slips with little dispersing agent would tend to settle out and give faster penetration than a freshly suspended slip since the surface solids content was abnormally low.

To account for these phenomena, two values were obtained for each slip; one immediately after stirring the mixture, and the other after allowing the slip to stand 5 minutes. Figures 13 and 14 indicate that, for a hydrous clay, the water retention of a slip increases with increasing amounts of dispersing agent and then falls off. The percentage dispersing agent required for maximum water retention is greater for low solids slips than for high solids slips. There is much less difference
### TABLE X

**BLOTTER FREENESS OF CLAY C SLIPS**

<table>
<thead>
<tr>
<th>Solids content, %</th>
<th>Quadrafo, %</th>
<th>Freeness of undisturbed surface, sec.</th>
<th>Freeness of disturbed surface, sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.3</td>
<td>330</td>
<td>93</td>
</tr>
<tr>
<td>70</td>
<td>0.5</td>
<td>230</td>
<td>112</td>
</tr>
<tr>
<td>70</td>
<td>0.75</td>
<td>156</td>
<td>122</td>
</tr>
<tr>
<td>70</td>
<td>1.0</td>
<td>136</td>
<td>106</td>
</tr>
<tr>
<td>70</td>
<td>1.5</td>
<td>105</td>
<td>88</td>
</tr>
<tr>
<td>70</td>
<td>2.0</td>
<td>157</td>
<td>87</td>
</tr>
<tr>
<td>60</td>
<td>0.3</td>
<td>95</td>
<td>60</td>
</tr>
<tr>
<td>60</td>
<td>0.5</td>
<td>125</td>
<td>82</td>
</tr>
<tr>
<td>60</td>
<td>0.75</td>
<td>107</td>
<td>82</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>83</td>
<td>73</td>
</tr>
<tr>
<td>60</td>
<td>1.5</td>
<td>62</td>
<td>51</td>
</tr>
<tr>
<td>60</td>
<td>2.0</td>
<td>42</td>
<td>41</td>
</tr>
<tr>
<td>50</td>
<td>0.3</td>
<td>51</td>
<td>40</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>67</td>
<td>54</td>
</tr>
<tr>
<td>50</td>
<td>0.75</td>
<td>70</td>
<td>61</td>
</tr>
<tr>
<td>50</td>
<td>1.0</td>
<td>69</td>
<td>63</td>
</tr>
<tr>
<td>50</td>
<td>1.5</td>
<td>55</td>
<td>46</td>
</tr>
<tr>
<td>50</td>
<td>2.0</td>
<td>34</td>
<td>31</td>
</tr>
<tr>
<td>30</td>
<td>0.3</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
<td>21</td>
<td>29</td>
</tr>
<tr>
<td>30</td>
<td>0.75</td>
<td>21</td>
<td>33</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>39</td>
<td>40</td>
</tr>
<tr>
<td>30</td>
<td>1.5</td>
<td>46</td>
<td>41</td>
</tr>
<tr>
<td>30</td>
<td>2.0</td>
<td>32</td>
<td>31</td>
</tr>
</tbody>
</table>
FIGURE 13
Effect of Freezing of Clay C
with Different Amounts of Dissolved Salt (Test made on Fresh Surface)
FIGURE 14
Blotter Freeness of Clay C slips with Different Amounts of Dispersing Agent (Test made after 5 minutes standing)
in penetration time between a disturbed surface and an undisturbed surface with an excess of dispersing agent than with a small amount of dispersing agent. Different clays and dispersing agents give greatly different penetration times. For example, 70 per cent Clay A with 0.5 per cent Quadrafos had a penetration time of 25 seconds on a fresh surface as compared with 112 seconds for a similar Clay C slip. When 0.5 per cent soda ash was used to disperse 30 per cent Clay C, the freeness for a fresh surface was 9 seconds, whereas 0.5 per cent Quadrafos with the same clay gave 29 seconds.

Erratic results were obtained with the blotter freeness test when it was applied to starch sols. The starches used had to be diluted to 10 per cent concentration to obtain a reasonable time of penetration. The amount of dilution, temperature of dilution, time after dispersion and, probably, other factors combined to give a wide variation in time for a given starch sol. Since these tests were applied to materials prepared for other purposes, no attempt was made to evaluate the causes of the variation. However, the series of tests made on a 10 per cent Starch Y sol shown in Table XI indicates the magnitude of the differences.
### TABLE XI
VARIATION IN BLOTTER FREEMESS WITH TIME
AND DILUTION CONDITIONS

<table>
<thead>
<tr>
<th>Material</th>
<th>BLOTTER FREEMESS, sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>10% Starch Y sol</strong></td>
<td></td>
</tr>
<tr>
<td>Immediately after cooling to 27° C.</td>
<td>15</td>
</tr>
<tr>
<td>After 150 minutes at 27° C.</td>
<td>33</td>
</tr>
<tr>
<td><strong>10% Starch Y sol diluted from 20% sol at 60° C.</strong></td>
<td></td>
</tr>
<tr>
<td>Immediately after cooling to 27° C.</td>
<td>120</td>
</tr>
<tr>
<td>After 150 minutes at 27° C.</td>
<td>210</td>
</tr>
<tr>
<td><strong>10% Starch Y sol diluted from 20% sol at 27° C.</strong></td>
<td></td>
</tr>
<tr>
<td>Immediately after cooling to 27° C.</td>
<td>300</td>
</tr>
<tr>
<td>After 150 minutes at 27° C.</td>
<td>600</td>
</tr>
<tr>
<td>Heated to 70° C. and cooled to 27° C.</td>
<td>140</td>
</tr>
</tbody>
</table>

Blotter freeness readings are fairly reproducible for materials giving low values, but the end point is hard to estimate for values over 100 seconds. Not only does the dye change color slowly, but there is a possibility of water vapor changing the TAPPI indicator. An example of the reproducibility of the test on a given clay is successive readings of 83, 81, 74, and 81 seconds. On the other hand, successive readings on a 10 per cent Starch Y sol varied from 240 to 420 seconds. Normal variation in clay blotter freeness was about five per cent from the mean.

**VISCOSITY OF COLORS AND THEIR COMPONENTS**

In the course of this investigation several observations were made concerning the viscosity of colors and their components at high and low rates of shear. All viscosities in a series were measured at the same time interval (usually 4 to 5 hours) after the preparation of
the starch and clay, since the viscosity of starch mixtures changes on standing. Color components were mixed to make the color one hour after they were prepared.

It was immediately apparent that a color viscosity could not be predicted accurately from the viscosity of its components, although high viscosity components generally gave a high viscosity color. High and low shear viscosities of some coating mixtures and their components are shown in Figure 15. At both high and low rates of shear, the viscosity of a 50 per cent solids color from Starch B and Clay C was intermediate the viscosities of its components. The low shear viscosity of a 60 per cent solids color was higher than that of either component, whereas its high shear viscosity was lower than that of either component. This is attributed to the false body effect of the starch which seemed to control viscosity at low rates of shear but which was dissipated by the action of the high shear roll. The 60 per cent solids color maintained its form, as does whipped cream, at low rates of shear but could not resist high shearing action. Thus, starch seems to have a great effect on low shear viscosity, whereas the clay, which may be dilatant or thixotropic, has a relatively greater influence on high shear viscosity. Slips of hydrous clay without dispersing agent also exhibited considerable false body, but it disappeared on the addition of dispersing agent.

The great difficulty in predicting high shear color viscosity from the low shear viscosity of its components can be seen from Figure 15. On the other hand, Figures 16 and 17 show a rough correlation between the high and low shear viscosities obtained for various coating mixtures.
Although both methods generally rank colors in the same order, it can be seen that the relative values differ, and even the ranking varies with the cup speed of the low shear viscometer. Even though one would expect the action of high shearing machine coating rolls to vary somewhat from that of a given high shear viscometer, it seems reasonable that a high shear viscometer would better predict the suitability of a color for such use than a low shear viscometer.

A series of 60 per cent solids colors was prepared to determine whether the imbibing power of starch would be reflected in the viscosity of the color. Similar colors were made by combining Clay C with Starch C (90 per cent imbibition at 20 per cent solids), Starch B dispersed at 92° C. (68 per cent imbibition at 20 per cent solids), Starch B dispersed at 80° C. (54 per cent imbibition at 20 per cent solids), and Starch Z (19 per cent imbibition at 10 per cent solids). The viscosity of these mixtures is given in Figure 18. Imbibition apparently does not affect color viscosity. For example, the low imbibing dextrinized Starch Z has a very high sol viscosity, but relatively low color viscosity; the somewhat higher imbibing Starch B dispersed at 80° C. has a lower sol viscosity and higher color viscosity than Starch Z; and the high imbibing Starch C is lower in both sol and color viscosity. The type and viscosity of the starch seem to control color viscosity when it is used with a given clay. The color viscosity of the chlorinated starch series was in the same order as the sol viscosity. This increase in color viscosity with sol viscosity was found to be true with all series of similar starches tested. Figure 18 shows that the viscosities of colors from chlorinated
FIGURE 16
Viscosity of 2% Solids Containing Mixtures
(1 cm. cylinder used for Macaulay viscosity)

(1) 50 clay C, 10 starch B, 30 water
(2) 60 clay C, 10 starch B, 20 water
(3) 50 clay B, 10 starch B, 40 water
(4) 50 clay C, 8 starch B, 42 water
FIGURE 17
Viscosity of 50% Solids Coating Mixtures
(2 cm. cylinder used for Wackenroder viscosity)

Color Composition
(1) Clay C, starch A
(2) Clay C, starch B (80°C.)
(3) Clay C, starch B
(4) Clay C, starch Z
(5) Clay F, starch B
FIGURE 18

Viscosity of 60\% Coating Mixtures and Components
(1 cm. cylinder used for Mackichael viscosity)

(1) 70\% clay C
(2) 35\% starch C
(3) 35\% starch B
(4) 35\% starch Z (80°C)
(5) 35\% starch Z

--- Component viscosity
--- Viscosity of color from clay C and designated starches

Mackichael cup speed, r.p.m.
Roll speed, cm./sec.

MacKichael viscosity, degrees
Film thickness, microns
starches were ranked in the same order at both high and low rates of shear, but the dextrinized Starch Z had a relatively lower low shear viscosity. It ranked below Starch B dispersed at 92° C, at low rates of shear and above it at high rates of shear. This is attributed to the lack of false body found in colors from dextrinized starches.

When Clays B and C were used with the same starch to make 50 per cent solids mixtures, it was found that the lower viscosity clay gave a lower viscosity mixture at both high and low rates of shear. Again, the difficulty of predicting the viscosity of the mixture from the viscosity of the components was apparent. The low shear viscosity of a mixture of Starch B and Clay C was intermediate that of the two components, whereas the viscosity of a mixture of Starch B and Clay B was higher than that of either component. This is shown in Figure 19. Clay A, the least hydrous clay used, gave a lower low shear viscosity and a higher high shear viscosity than the other two clays, both for the 70 per cent slip and 50 per cent solids color. This was because Clay A was extremely dilatant and the effect was not apparent except at very high rates of shear. Excluding the effect of dilatancy and thixotropy, the more hydrous clays seem to give greater high and low shear viscosity. Of course, a dilatant clay would be expected to give an abnormally high shear viscosity, whereas a thixotropic clay, such as bentonite would give an abnormally low high shear viscosity.

ROLE OF DISPERSING AGENT IN COLOR VISCOSITY

It is generally known that the viscosity of a clay slip or starch-clay mixture decreases as more dispersing agent is added, until
FIGURE 19
Viscosity of 70% solids Coating mixtures from 4 different Clays

(1) 70% starch B
(2) 70% clay C
(3) 70% clay D
(4) 70% clay A

--- Viscosity of component
--- Viscosity of coating
--- Coating values for 50% solids component

Top limit to measure
a minimum viscosity is reached. The addition of more dispersing agent beyond this amount causes a viscosity increase. Certain dispersing agents, such as sodium silicate, are known to give minimum viscosity over a very small concentration range, whereas others, such as the higher phosphates, give a minimum viscosity over a wide concentration range. Quadrafos, which was used as the dispersing agent for this investigation, is one of the higher phosphates with the formula Na₅P₃O₁₀.

Brown (16) observed that different amounts of dispersing agent were required to obtain minimum low shear viscosity when combining different types of starches with the same clay. He concluded that there must be some combination between the starch and the dispersing agent, so that more dispersing agent is required for minimum viscosity if the starch has a greater affinity for the agent.

The modifying influence of starch on the amount of dispersing agent required for minimum viscosity was also noted in this investigation. The usual 70 per cent Clay C slip, fluxed with 0.5 per cent Quadrafos, had a high shear film thickness of about 105 microns at 60 centimeters per second roll speed. Increasing the dispersing agent to 1.5 and 2.0 per cent greatly increased the viscosity, whereas decreasing the dispersing agent to 0.3 per cent gave a lower viscosity. This indicates that the minimum viscosity for the slip would be obtained with less than 0.5 per cent Quadrafos. However, the minimum viscosity of a series of colors made from the same clay was obtained with more than 0.5 per cent agent. The additional dispersing agent required was apparently taken up by the starch.
TABLE XII

VISCOOSITY OF CLAY C AND COATING MIXTURES FROM CLAY C WITH VARIOUS AMOUNTS OF DISPERISING AGENT

<table>
<thead>
<tr>
<th>Material</th>
<th>Per cent Quadraxon on clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>70% Clay C</td>
<td></td>
</tr>
<tr>
<td>High shear film thickness at 60 cm./sec., microns</td>
<td>* 87 105 - 140 *</td>
</tr>
<tr>
<td>MacMichael viscosity at 25 r.p.m., degrees</td>
<td>* 54 102 - * *</td>
</tr>
<tr>
<td>50% color (Clay C-Starch B)</td>
<td></td>
</tr>
<tr>
<td>High shear film thickness at 60 cm./sec., microns</td>
<td>12 2 - 10.0 9.65 9.35 9.65</td>
</tr>
<tr>
<td>MacMichael viscosity at 25 r.p.m., degrees</td>
<td>* - 41 33 36 49</td>
</tr>
</tbody>
</table>

*Viscosity too high to measure

Table XII shows the great differences in viscosity for large amounts of dispersing agent for clay slips, but not for colors; apparently, this is because the solids content of the colors was lower and the amount of dispersing agent was not as critical at lower solids contents. The dispersing action of the starch may also help to stabilise the color viscosity. Arnold (6) found that, for the clay slips he investigated, the amount of dispersing agent required for minimum viscosity increased with increasing clay concentration. With starch present, apparently more dispersing agent is required for minimum viscosity, even at lower solids concentration, because allowance must be made for some of the agent to combine with starch. The low shear viscosity of a 50 per cent color prepared without dispersing agent was too high to measure since the color exhibited a great deal of false body, but the high shear viscosity was only slightly greater than that of a normal color.
A small difference was noted in the mixture when the dispersing agent was added to the starch instead of to the clay. The low shear viscosity was 62 degrees at 25 r.p.m. and the film thickness was 10.6 microns. Normal values for a 50 per cent solids color with the same components were 54 degrees for low shear and 10.0 microns for high shear. Although the differences may not be significant, it is quite possible that a different equilibrium is established when the starch has the first opportunity to combine with the dispersing agent than when the agent is first used to flux the clay.
SUMMARY

The distribution of water between starch and clay in mixtures was investigated in an attempt to explain how clays of varying hydration affected the viscosity and raw stock penetration of coating colors. Techniques were developed and adapted which show that, even though clays may vary in hydration, the starch is solvated by almost all the water present in the system. It has been indicated that hydrous clays probably increase color viscosity by binding a greater amount of starch sol than nonhydrous clays. It is further indicated that hydrous clays form a gelatinous layer between the coating and raw stock, thus inhibiting the penetration of the adhesive into the sheet. Incidental observations have been made on the effects of dispersing agents and the viscosity of starch-clay mixtures and their components. The complex nature of paper coating makes it likely that the data obtained in this work would apply only when integrated with numerous other variables in commercial coating problems. It is thought that the techniques and results described, however, should be applicable to an investigation of the influence of coating materials used or available.
CONCLUSIONS

1. A meter has been developed which measures the relative water imbibing power of various starches.

2. The imbibition of water by starch is primarily due to the solvation of the hydrophilic colloidal particles.

3. The apparent imbibition of water by fluxed clay slips is primarily due to the electrolyte used as the dispersing agent.

4. The rate of imbibition of water by a given type of starch increases with concentration until the sol becomes very viscous, after which it apparently decreases with increasing concentration. It is believed that the imbibition rate decrease at high solids is due to the limitations of the imbibition meter, and that there is a direct relationship between concentration and affinity for water at all concentrations.

5. The imbibition of water by a given type of starch increases with the degree of dispersion until the material gives a maximum imbibition on complete dispersion.

6. Starch solvates itself with almost all the water present in the system when starch and clay are mixed.

7. The viscosity of a given starch-clay mixture is approximately the same regardless of which component contained the bulk of the water before mixing.

8. A starch sol in contact with a clay slip will penetrate into the slip, partially dehydrate the clay, and cause the slip to become
less fluid. The increase in viscosity of the mixture is probably due to a migration of water and dispersing agent to the starch, as well as to the presence of starch.

9. Hydrous clays may influence the viscosity of coating mixtures by retaining more of a layer of starch sol than do nonhydrous clays.

10. Hydrous clays may influence the coating operation by forming a gelatinous layer next to the raw stock which inhibits the migration of the adhesive into the sheet.

11. Starch penetrates into the raw stock at the same rate as the water in which it is suspended and does not lag behind, as do dyes.

12. The penetration of adhesive into raw stock, as measured by the relative high shear spreading area on glass and paper, does not correlate with standard sheet characteristics, such as smoothness, porosity, degree of sizing.

13. Starch from viscous coating mixtures penetrates a given sheet less than that from more fluid mixtures.

14. The viscosity of a coating mixture cannot be predicted reliably from the viscosity of its components.

15. Starch seems to influence greatly the low shear viscosity of starch-clay mixtures, giving abnormally high viscosity values at low rates of shear, whereas clay exerts relatively greater influence at high rates of shear.
16. High shear viscosities of a series of similar colors cannot be predicted accurately from low shear measurements, although fairly accurate predictions can be made as to the relative order of viscosity.

17. Imbibition of water by starch does not directly affect color viscosity.

18. More dispersing agent is required to obtain minimum viscosity for a given amount of clay when starch is present in the mixture. It is probable that starch combines with some of the dispersing agent and decreases the amount available to the clay.
APPENDIX

A. PROCEDURE FOR DISPERSING CLAY

1. A 250-ml. beaker and a spatula were weighed to the nearest 0.1 gram.

2. The dispersing agent was weighed to the nearest 0.1 milligram and dissolved in a small amount of distilled water. (It was found desirable to prepare fresh dispersing agent for each test since quadrafos (Na₂F₅O₁₃), the dispersing agent used in most of the work, hydrolyzes in solution.)

3. The amount of clay required to make 200 grams of suspension was placed in the beaker and mixed with about 80 per cent of the distilled water required.

4. The dispersing agent was added and mixed into the slip with a spatula. Traces of agent in the dissolving container were washed into the slip with distilled water.

5. The beaker containing the slip and spatula was placed on a balance and the remainder of the water required to adjust the solids content was added.

6. The slip was mixed thoroughly with the spatula and passed through a 60-mesh screen.

B. PROCEDURE FOR DISPERSING STARCH

1. A 250-ml. beaker, thermometer, and propeller from a variable-speed stirrer were weighed to the nearest 0.1 gram.

2. The required weight of starch (oven-dry basis) for 200 grams of sol was added to the beaker.

3. Enough distilled water was added to bring the total weight of the mixture to approximately 200 grams.

4. The beaker was placed in a steam bath and slowly raised over a period of about 10 minutes to 92° C. The mixture was agitated with a variable-speed stirrer during the time it was on the steam bath.

5. The temperature was maintained at 92 ± 1° C. for 10 minutes.

6. The steam bath was drained, and the sol allowed to cool in air to 60° C.
7. The beaker, thermometer, and propeller were placed on a balance and enough water added to bring the total sol weight to 200 grams. This replaced the water lost by evaporation.

8. The sol was cooled, with stirring, in a water bath to room temperature (27° C.).

C. PROCEDURE FOR DISPERSING STANDARD POLYVINYL ALCOHOL

1. A 250-ml. beaker, thermometer, and propeller from a variable speed stirrer were weighed to the nearest 0.1 gram.

2. Thirty grams of DuPont Elvanol 70-A-05 (oven-dry basis) were added to the beaker.

3. One hundred and seventy milliliters of distilled water were added to the beaker, and the mixture stirred at room temperature with a variable-speed stirrer until the material was wet. This required at least 5 minutes at high speed.

4. The beaker was placed in a steam bath and slowly raised over a period of about 10 minutes to 85° C. The mixture was agitated with a variable-speed stirrer during the time it was on the steam bath.

5. The temperature was maintained at 85 ± 1° C. for 5 minutes.

6. The steam bath was drained, and the sol allowed to cool in air to 60° C.

7. The beaker, thermometer, and propeller were placed on a balance and enough water added to bring the total sol weight to 200 grams. This replaced the water lost by evaporation.

8. The sol was cooled, with stirring, in a water bath to room temperature (27° C.)
LITERATURE CITED


