New laboratory test to characterize immobilization and dewatering of paper coating colors

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ABSTRACT

A novel laboratory test characterizes the immobilization and water retention of paper coating colors. A modified commercial rheometer measures the transient viscosity during dewatering. A fiber optical reflection near infrared spectroscopy device integrated into the rheometer gap determines the loss of water in a thin layer at the paper to coating color interface. With this technique, the characterization of dewatering of coating colors uses conditions closer to the manufacturing process than previously used laboratory tests. Using a thin coating color layer and a shear stress and pressure gradient, the color dewaters directly into the base paper. Examples show prediction of runnability, and the loss of water of coating colors during processing are better with the new technique than with other laboratory tests. The instrument has easy handling and can adapt to many commercial rotational rheometers for the immobilization measurements. It is therefore useful for optimization of coating color formulations and quality control.

Application:

Measuring the immobilization kinetics of paper coating colors under dynamic conditions can improve their runnability.

RUNNABILITY OF PAPER COATING colors and the final product properties of a coated paper depend strongly on dewatering of the color into the base paper during application. Dewatering increases the solids content of the color with concomitant drastic changes in rheological properties *(1)*. Considerable effort occurs on adjustment of the water retention properties of paper coating colors by proper selection of their ingredients especially the co-binders, thickeners, or both. Consequently, many laboratory tests are available to characterize dewatering before conducting expensive and time-consuming pilot coater or machine trials. Conductivity measurements *(2, 3)*, ultrasound velocity *(4)*, and attenuation *(5)* measurements of paper in contact with a coating color and an optical technique requiring the addition of a water soluble dye to the color *(6)* have use to characterize the water retention properties of paper coating colors. In all these tests, the thickness of the applied coating layer is much higher than in a typical coating process. In addition, the sample does not undergo the pressure or shear conditions similar to those in a commercial process.

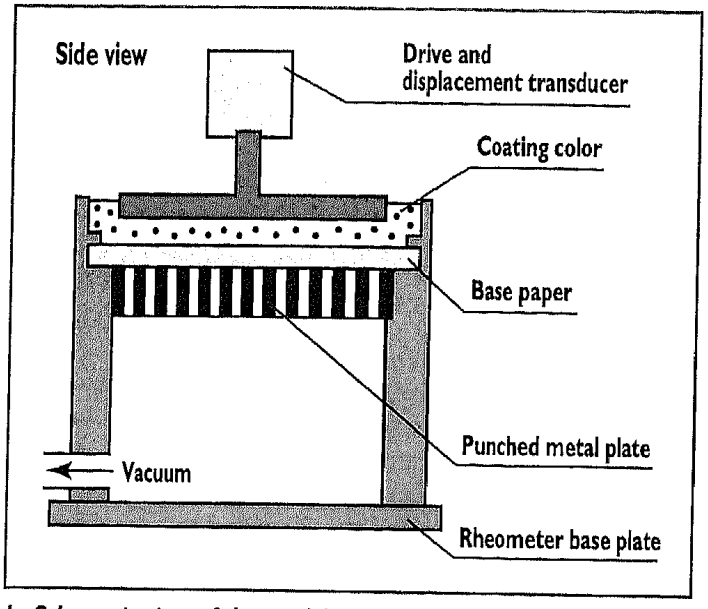
With the film splitting technique *(7)*, raw paper contacts a coating layer similar to that in the actual process. This uses an appropriate pressure but no shear during the dewatering. Gloss measurements *(8, 9)* during drainage of the liquid phase of the coating color into a ceramic plate also have frequent use. Such tests do not consider the influence of raw paper on dewatering. The pressure filtration technique of Sandas *et al. (10)* also uses a coating layer much thicker than normal use and does not apply shear. The fluid phase also penetrates through a filter and therefore screens the influence of the base paper below. A filtration test introduced by Ramthun *et al. (11)* includes application of shear during dewatering. The dewatering coating layer is not well defined but very much thicker than in the actual coating process. Loss of water is determined gravimetrically from the amount of water penetrating through the base paper. This implies that the coating color dewaters into a completely wetted paper that is far from the actual situation in a commercial process.

This paper presents a new laboratory test that allows simultaneous determination of the immobilization and the increase of solids content of paper coating colors during dewatering into a base paper. The thickness of the coating layer is such that it is near that of coating processes. This ensures that the base paper is not completely wetted. The technique can resolve differences between different coating colors with sufficient accuracy. The color experiences a pressure gradient and a shear field. Variation of these external parameters allows study of their effect on the immobilization properties and estimation of the behavior under process conditions. The immobilization kinetics is characterized viscometrically. The loss of water is determined from near infrared spectroscopy using a fiber optical device.

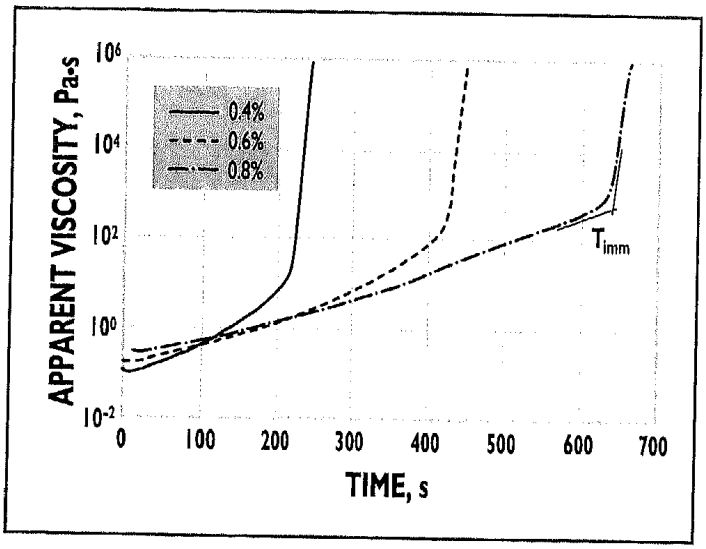
DESCRIPTION

Immobilization measurement

Measuring the increase of viscosity during dewatering of a thin coating color layer into a sheet of base paper uses a commercial controlled stress rotational rheometer equipped with plate-plate geometry as **Fig. 1** shows *(12)*. A cylindrical metal tube with a punched metal plate on top mounts



1. Schematic view of the modified rheometer



2. Typical viscosity vs. time curves obtained during dewatering of coating color MT at three different concentrations of synthetic thickener

Gap width/coating layer thickness, h, µm	Shear stress, τ, Pa	Δp*, pa
50–2,000	0.1–1,500	0–80,000

* Pressure difference between coating layer and back side of the base paper

I. Technical specifications of the modified immobilization rheometer

to the base plate of a rheometer. The punched plate supports an appropriate sheet of base paper that acts as the lower part of the rheometer gap. The coating color is placed into the rheometer gap. Application of a vacuum to the back side of the paper forces the liquid phase to penetrate into the base paper. Simultaneously, a constant shear stress is applied to the upper plate of the rheometer. The viscosity of the coating color is determined from the resulting angular velocity or shear rate. The increase of viscosity with time characterizes the kinetics of immobilization determined by the water retention properties of the particular coating color and the structural rearrangements during the dewatering process.

Varying the gap width, applied vacuum, and shear stress can simulate different processing conditions. **Table I** summarizes the specifications for the vacuum, range of accessible shear stresses, and layer thickness of the coating color.

To keep the coating layer in contact with the upper plate even during the loss of liquid phase, a surplus of fluid from a reservoir is applied to the base paper surrounding the gap. As Fig. 1 shows, this surplus of fluid is held by an appropriately shaped ring that simultaneously pinches the base paper. The mobile fluid from the reservoir flows partly into the gap to compensate for the loss of material due to the dewatering and to keep the coating layer in contact with the upper plate of the rheometer. The outer part of the gap is therefore always at a lower solids content than the center part. Due to these inhomogeneities, the measured viscosities are apparent or relative values. The viscosity nevertheless increases with time. The measurement stops when the upper limit of the measuring range is reached, i.e., when the coating color is immobilized.

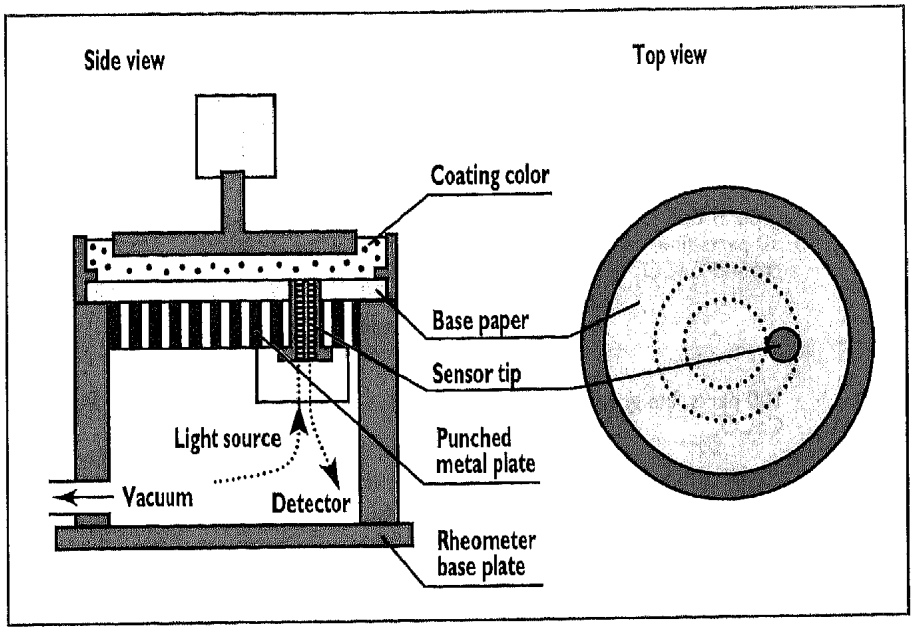
The center part of the sample is a solid filter cake containing about 15%–20% water. **Figure 2** shows typical viscosity vs. time curves. These semi-log plots exhibit a characteristic shape with a linear increase at short times and a sharp upward curvature when reaching the immobilization point. For convenience, the time when an apparent viscosity of 10^6 Pa•s occurs is the immobilization time, T_{imm}, of a particular coating color on a specific base paper under given external conditions of layer thickness, shear stress, and applied vacuum. Alternatively, determination of T_{imm} could use the intersection of the tangents to the two branches of the viscosity vs. time curve as Fig. 2 shows.

Spectroscopic determination of water

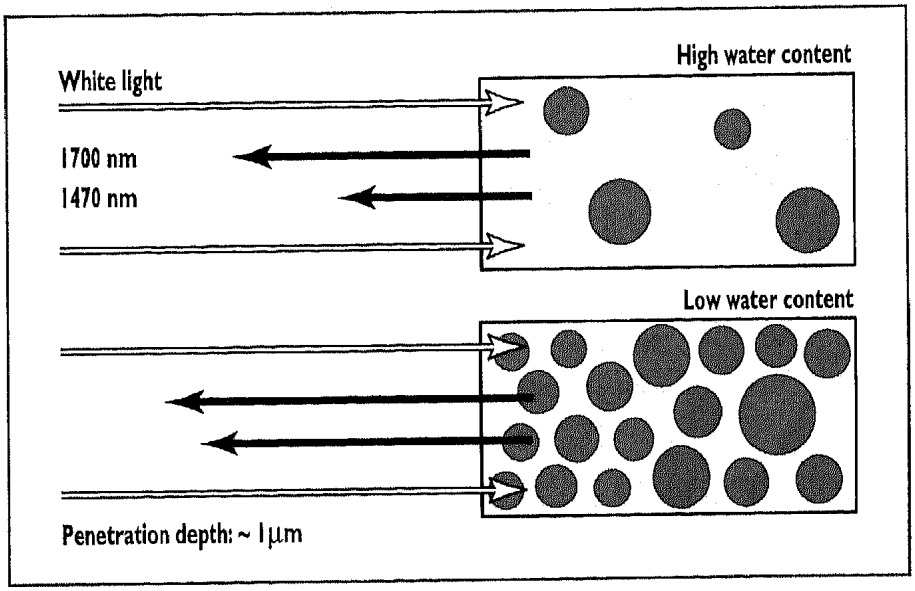
The correlation between viscosity and solids strongly depends on the recipe of the coating color. A separate calibration would be necessary for each color to calculate the increase of solids during dewatering from the increase of the viscosity signal. Such a calibration would also be difficult to establish for our instrument due to the inhomogeneity of the sample in the rheometer gap. We have therefore integrated a fiber optical light scattering device into the punched support plate of our modified rheometer to determine the amount of water in the sample as a function of dewatering time.

Young *et al. (13)* have used a similar near infrared spectroscopic technique to determine the water or moisture content at the coating color surface during drying in air. In our device, the sensor tip mounts parallel and almost in the plane with the paper as **Fig. 3** shows. A circular hole of appropriate size is punched into the sheet of paper to couple the light directly into the sample. The area of the sensor tip of 4-mm diameter is small compared with the area of the rheometer gap of 40-mm diameter. The sample volume above the sensor is exchanged on a circular line due to the applied shear as Fig. 3 shows. One can therefore assume that the presence of the sensor does not significantly influence dewatering. The measured loss of water is representative for the entire color in the rheometer gap.

The following briefly describes the operating principle of the optical device of **Fig. 4** using reflection spectroscopy *(14)*. Technical details are available elsewhere *(15)*. The light of a broad band halogen lamp is coupled into the sample via glass fibers. The back scattered light is collected by a parallel bunch of fibers connected to a near infrared detector. Penetration depth of the near infrared light waves into the coating color is typically about a few μm. The dewatering of a thin coating layer adjacent to the paper surface is therefore characterized by this method. Intensity of the 1470 nm absorption band (second harmonic of the OH oscillation) determines the water content. The signal is corrected for the diffuse back scattering of the sample without water by a simultaneous measurement of the intensity at a wavelength where no absorption by water occurs. Intensity of the light source at the selected wavelengths is also controlled to eliminate signal fluctuations due to drift of the halogen lamp. The corrected intensity signal is calibrated using a series of samples with similar composition but different, well-defined solids contents.



3. Schematic view of the modified rheometer including the fiber optical device



4. Schematic illustration of water content determination for paper coating colors using fiber optical near infrared reflection spectroscopy

RESULTS AND DISCUSSION

Coating color composition

Table II summarizes the essential features of all the coating color recipes used in this study.

Immobilization kinetics

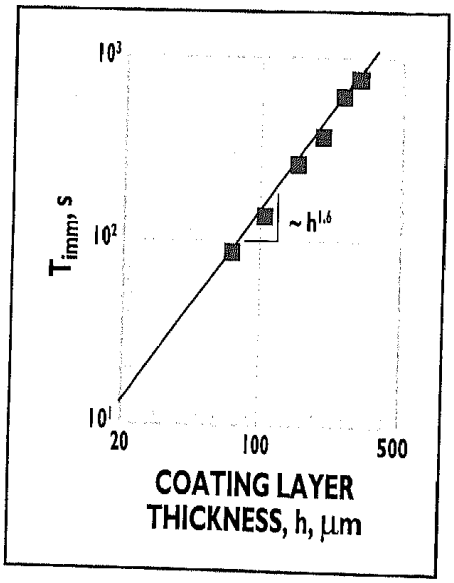
Effects of coating layer thickness and pressure gradient. The purpose of the new device is not a perfect simulation of the technical coating process on a laboratory scale. Instead, the device tries to capture the essential features of the coating process to distinguish between the immobilization and dewatering properties of different coating colors. The effect of the external parameters, sample thickness, h, and pressure gradient, Δp, will be discussed first.

As expected, the immobilization time increases with increasing layer thickness and decreasing pressure difference. **Figure 5** shows the

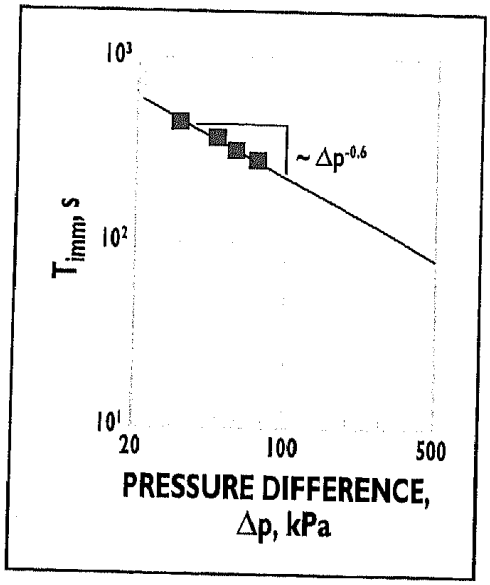
Label	Pigment	Binder	Thickener/Co-binder	Solids, %
PG	70 parts talc 30 parts fine English clay	Alkali swellable rotogravure binder		58
MT	70 parts coarse ground $CaCO_3$ 30 parts fine ground $CaCO_3$	XSB	x[1] parts CMC (medium thickening, η = 400 mpa•s in 4% aqueous solution) or synthetic thickener (acrylic ester/acrylic acid copolymer	62
PC	100 parts fine ground $CaCO_3$	XSB	Synthetic co-binder	70
C	80 parts fine ground $CaCO_3$ 20 parts fine English clay	XSB	Synthetic co-binder	70
SC	100 parts coarse ground $CaCO_3$	XSB	0.5 parts synthetic thickener (acrylic ester/acrylic acid copolymer	80.5[2]

1 Table 3 gives various thickener concentrations.
2 Starting with a solids of 80.5%, a concentration series was made by dilution with water.

II. Composition of coating colors



5. Immobilization time vs. gap height with 50 kPa pressure gradient and 300 Pa shear stress at the rim for coating color PG using wood-free base paper of 70 g/m²



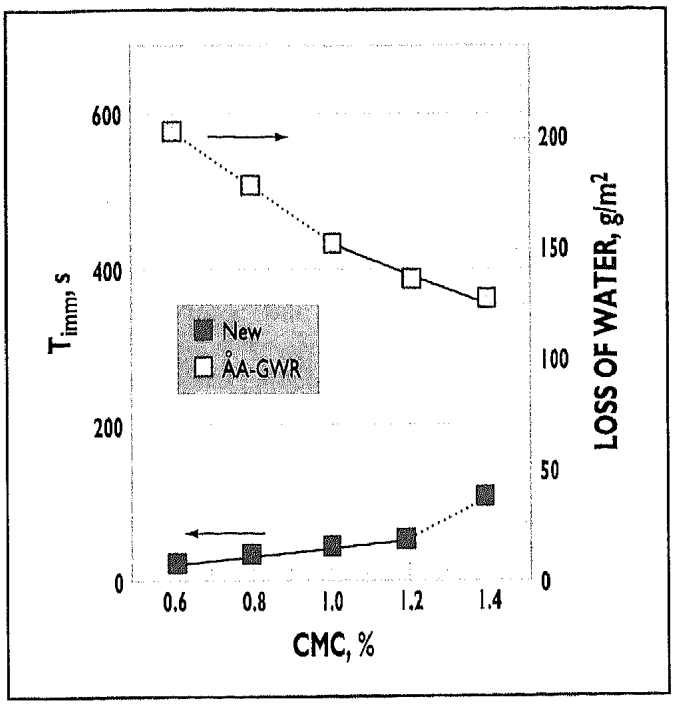
6. Immobilization time vs. pressure gradient with 20 µm gap height and 300 Pa shear stress at the rim for coating color PG using wood-free base paper of 70 g/m²

change of T_{imm} with coating layer thickness, h, i.e., gap width, for coating color PG. Testing of the color used a wood-free base paper. See figure caption for applied τ and Δp. The slope of the straight line fit to the data indicates that T_{imm} increases with h according to $T_{imm} \propto h^{1.6}$. For the same coating color and base paper combination, Fig. 6 shows that Timm decreases with increasing pressure gradient as $T_{imm} \propto p^{-0.6}$. Similar results occurred for other coating color and base paper systems. Extrapolating to typical conditions in the coating process (Δp = 800 kPa, h = 20 µm) gives immobilization times of a few seconds or less. This seems reasonable under process conditions.

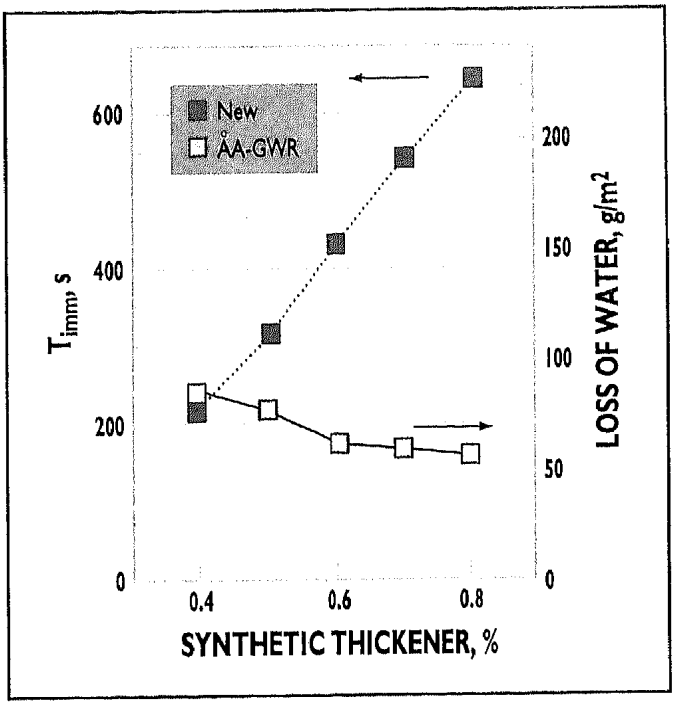
The results show that the coating layer thickness especially requires careful consideration. It must be close to that in the coating process to avoid changing the dewatering mechanism. In particular, a complete wetting of the base paper must be avoided because this could change the driving force of dewatering. The layer thickness must be sufficiently high to resolve differences between different coating color formulations with sufficient accuracy. This is the "slow motion" effect. The gap height should also be sufficiently high to allow for reasonable and reproducible viscosity measurements. This is at least ten times the pigment particle size.

Correlation to machine trials. This section presents an example showing that the method correlates very well with machine trials. Under certain conditions, its sensitivity is much higher than that of the popular ÅA-GWR test. A coating color, MT, uses two different thickeners, carboxymethylcellulose (CMC) and a synthetic acrylic ester/acrylic acid copolymer thickener. The water retention of this recipe is poor due to the coarsely ground $CaCO_3$ used as pigment. As a result, streaks frequently occur in the coated paper.

Machine trials used a short dwell coater in an on-line coating process to study the performance of coating color MT at various concentrations of CMC and synthetic thickener. A significant increase of solids content in the coating color circuit occurred with CMC at any concentration. The problem was reduced step-by-step by replacing the CMC with an increasing amount of synthetic thickener. After 17 h of nonstop coating for example, the solids content in the circuit increased from 52% to 59% when the color used 1% CMC. It increased from 51% to only 54% when using 0.6% synthetic thickener.



7. Immobilization time for coating color MT at various CMC concentrations using the new technique compared with water retention measurements with the ÅA-GWR test



8. Immobilization time for coating color MT at various synthetic thickener concentrations using the new technique compared with water retention measurements with the ÅA-GWR test

	CMC					Synthetic thickener				
Thickener content, %	0.6	0.8	1.0	1.2	1.4	0.4	0.5	0.6	0.7	0.8
T_{imm}[1], s	22	32	42	52	103	222	317	428	540	640
Loss of water[2], gm²	206	180	155	139	126	87	77	63	60	57

1 Dewatering conditions: Model base paper, nitrocellulose filter (pore size 5 µm), τ = 100 pa, h = 200 µm, Δp = 70 kPa, and T = °C.
2 Gradek test: Pressure = 50 kPa, time = 60 s, and dewatering through a polycarbonate filter.

III. Immobilization time and water retention of color MT for various concentrations of CMC and synthetic thickener

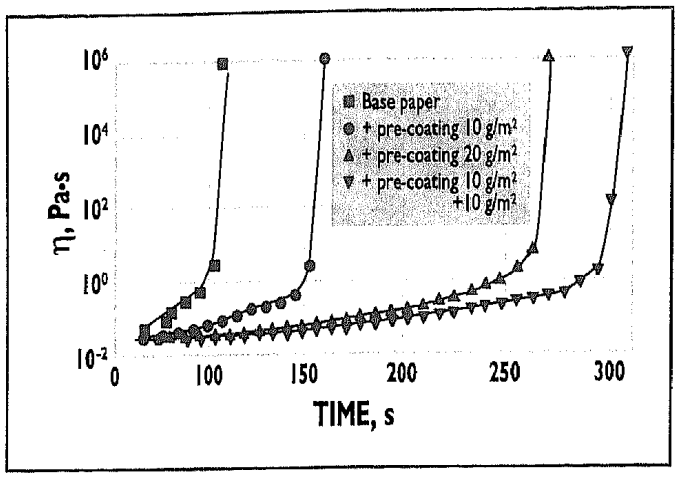
Our new technique predicts these runnability properties very well. **Figure 7** shows that the immobilization time is low at any CMC concentration, but **Fig. 8** shows that it rapidly increases with increasing amounts of synthetic thickener in the formulation.

We have compared the immobilization times, T_{imm}, determined with our new technique to the water retention data obtained from the popular ÅA-GWR test *(10)*. Figures 7 and 8 and **Table III** show the results. As expected, the immobilization time increases with decreasing loss of water as measured with the other device. Both methods yield different information. The water retention of the formulations with CMC is poor, but it increases rapidly with increasing amounts of CMC according to the other technique. The immobilization time hardly changes with CMC concentration. A strong increase in immobilization time occurs with increasing synthetic thickener concentration, but the loss of water according to the other test decreases only slightly in this case.

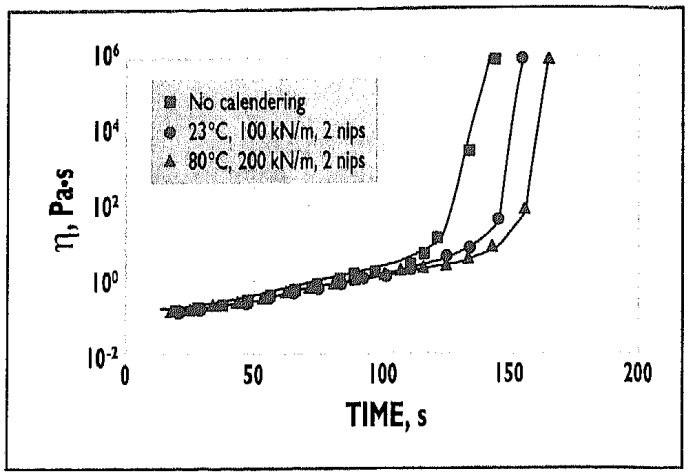
In both cases, the data from our new technique correlate much better to the results of the machine trials than the other data. The new technique is much more sensitive to dewatering characteristics of coating colors at high levels of water retention than the alternate test.

Effect of paper properties. To demonstrate the capabilities of the new technique, this section presents some examples examining the effect of base paper properties and applied shear on the immobilization kinetics of paper coating colors. **Figure 9** shows the immobilization kinetics of coating color PC on differently precoated and untreated base paper. Precoating used the same color PC. The immobilization time increases with increasing coating weight and is delayed if the pre-coating is applied in two layers instead of one layer with similar thickness or weight. Accordingly, a decreasing blade pressure was observed in corresponding high speed blade coating machine trials.

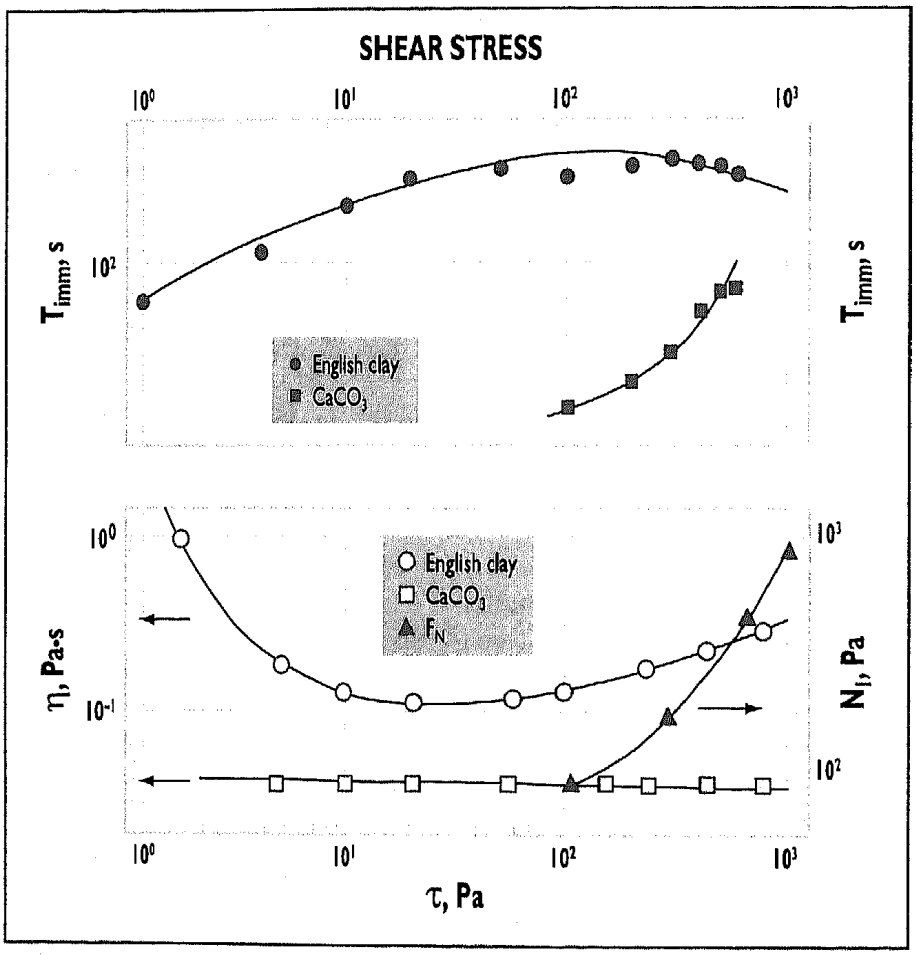
As **Fig. 10** shows, calendering can also reduce dewatering of the coating color. The immobilization time of color C increases with increasing calendering temperature and pressure. As expected, the effects are less pronounced at least in this coating color and base paper system than for precoating.



9. Effect of pre-coating on the immobilization kinetics of coating color PC with h = 0.1 mm, Δp = 50 kPa, τ = 300 Pa for wood-free base paper



10. Effect of calendering of the base paper on the immobilization kinetics of coating color C with h = 0.2 mm, Δp = 20 kPa, and τ = 300 Pa for wood-free base paper of 88 g/m²



11. T_{imm} vs. shear stress for slurries with initial solids of 68% for fine English clay and finely ground $CaCO_3$ with h = 0.3 mm and Δp = 20 kPa for model base paper using nitrocellulose filter (top); viscosity vs. shear stress for the same slurries in and first normal stress difference vs. shear stress for the same clay slurry (bottom).

Effect of applied shear stress. Investigation of the effect of external shear on immobilization used two well-dispersed pigment slurries (fine English clay and finely ground $CaCO_3$) without any additional binder or thickener. **Figure 11** plots T_{imm} vs. the applied, rim shear stress, τ **(top)** and shows the viscosity as a function of shear stress for the same samples **(bottom)**. For the clay slurry, corresponding data for the apparent first normal stress difference, $N_1 = 2 F_N/A$, are also plotted. F_N is the normal force acting perpendicular to the plane of shear, and A is the cross-sectional area of the sample gap. The occurrence of normal forces is typical for such shear-thickening coating colors *(16)*. No measurable normal forces have been detected for the Newtonian $CaCO_3$ slurry. T_{imm} is higher for the clay slurry than for the $CaCO_3$ slurry at any shear stress investigated. This is due to the stronger ability of the clay particles to trap water molecules in hydration layers around themselves. For both slurries, the immobilization time increases with increasing shear stress. This might be the result of an increased amount of water bound in hydration layers coming with an increase of free pigment particle surface by shear-induced breakup of aggregates. For the clay slurry, the increase of immobilization time with τ is less pronounced. Finally, T_{imm} decreases with increasing shear stress as shear thickening occurs. This can be understood at least qualitatively by assuming that the water is pushed from the coating layer by the strong normal forces that are the same order of magnitude as the applied shear stress.

These first results show that the novel technique really provides new insight into the mechanisms of dewatering that have not been available

previously. The shear induced dewatering of paper coating colors is a complex phenomenon governed by size, shape, and surface properties of the pigment particles and the interactions among themselves and with thickener molecules and (presumably less important) binder particles. This topic will receive further discussion in more detail in a future paper.

Spectroscopic characterization

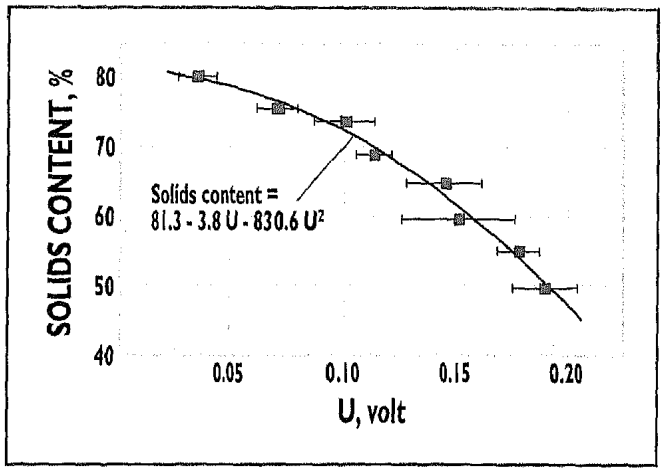
The near infrared signal from the fiber optical light scattering device described above has been calibrated for coating color SC. A series of samples with different solids levels resulted from dilution with water starting with a solids content of 80.5%. **Figure 12** is a plot of the relationship between the corrected output signal, U, of the detector and the solids content of these samples. A second order polynomial fits the data resulting in the following empirical relationship:

$$\text{Solids content} = 81.1 - 3.8\,U - 830.6\,U^2 \qquad (1)$$

Eq. 1 gives the solids content in % when the detector signal is in units of volt.

The calibration curve of Fig. 12 was obtained directly in our modified rheometer using static conditions. Investigations on the effect of shear on the near infrared are in progress. More specifically, the calibration given in Eq. 1 is only valid for coating color SC. Effects of coating color composition on this calibration function are therefore under current investigation. The pigment type and size should especially have some influence on the calibration constants.

Using the above calibration, the loss of water and the immobilization kinetics during dewatering have been determined for color SC. **Figure 13** presents the results using the indicated dewatering conditions. The solids content in a layer of a few µm adjacent to the paper surface increases gradually with time. It reaches its final value of 82% when T_{imm} occurs and the coating layer is completely immobile. This seems to contrast with the commonly accepted model *(9, 10, 12, 17-19)* of an immobile layer that forms at the paper to color interface immediately after dewatering starts whose height grows as dewatering proceeds. A reason for this apparent contradiction could be the different time scales of our experiment and the coating process. A concentration gradient within the coating layer may be equalized by diffusion of the liquid phase in our experiment. This may not be possible on the much shorter time scale of the coating process. Further investigations will be necessary to clarify this topic.

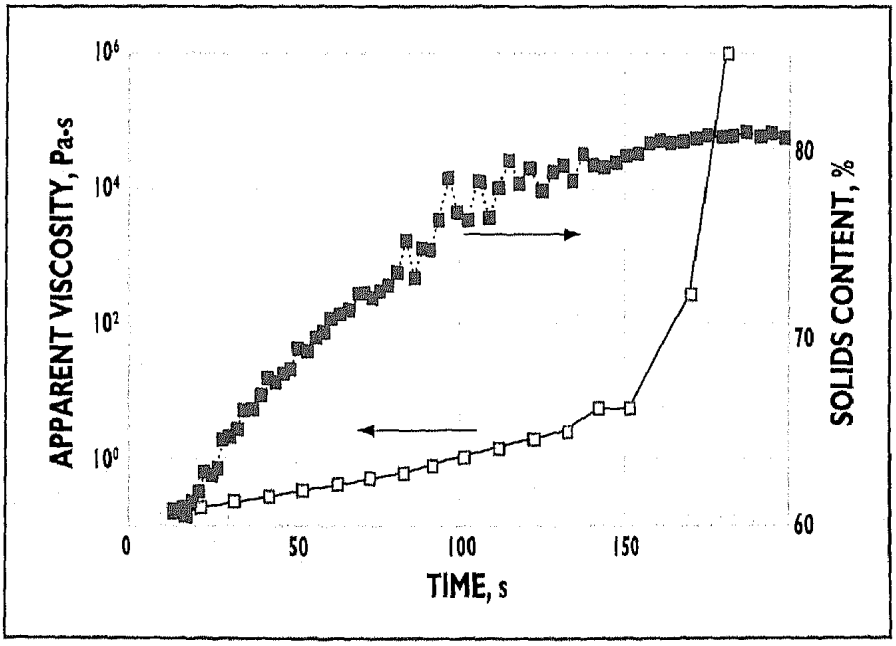


12. Correlation between the corrected output signal of the fiber optical light scattering device and the solids content for a concentration series of color SC

SUMMARY AND RECOMMENDATIONS

Our work has shown the following:

- A novel laboratory test characterizes the immobilization and water retention of paper coating colors using a modified commercial controlled stress rheometer. The immobilization kinetics are characterized by measuring the transient viscosity during dewatering.



13. Loss of water and immobilization kinetics during dewatering of color SC with initial solids content = 63% and dewatering conditions of τ = 100 Pa, h = 200 µm, and Δp = 70 kPa using model base paper with nitrocellulose filter of pore size 5 µm

A fiber optical reflection near infrared spectroscopy device is integrated into the rheometer gap to determine the loss of water simultaneously.

- With this technique, the dewatering of coating colors is characterized under conditions closer to the manufacturing process than with previously used laboratory tests. A thin coating color layer is used with a shear stress and a pressure gradient. The color can be dewatered into the base paper used in the coating process.
- Examples are presented where the runnability and the loss of water of the coating colors during processing are characterized better with the new technique than with other laboratory tests.
- The instrument is easy to handle and can adapt to many commercial rotational rheometers for immobilization measurements. This part of the technique is therefore useful for optimization of coating color formulations and quality control. The optional optical part is more sophisticated and should be used for fundamental research on dewatering mechanisms and processes at the current stage of development. **TJ**

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