A simple method for measuring immobilization using the surface gloss technique

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This method is useful for measuring the effect of coating solids and binder ratio on coating dehydration and immobilization.

Dehydration and immobilization are important processes in the consolidation of pigmented paper coatings. Although many methods for measuring these processes have been reported (*1*, *2*), the lack of an acceptable method is one of the recognized gaps in paper coating technology.

Baumeister and Kraft (*3*) assumed that liquid flow in immobilized coating can be represented by the Hagen-Poiseulle equation. They extrapolated the dehydration velocity line back to one second to get immobilization solids. Reinbold and Ullrich (*4*) described a method using a glass rod to stir coating on a glass plate. The coating is considered to be immobilized when it separates from the glass plate and sticks to the glass rod. Engstrom and Rigdahl (*5*) studied the consolidation of a coating by scraping the coating from the web on a pilot coater. Whalen-Shaw (*6*) and Baumeister (*7*) described the method of using a plot of solids and viscosity to determine the point of viscosity immobilization. This does not necessarily represent immobilization of the solid phase of the coating.

Lee (*8*) described the method of using a plot of relative viscosity and solids volume fraction data to obtain the close packing volume fraction based on the Mooney equation. Close packing volume is considered to be the immobilization solids. Beck, Goossens, Rahlwes and Wallpott (*9*) described a method where a sharp reduction in the gloss of a coating applied on a ceramic plate is considered the point at which the coating is immobilized. This is based on the method described by Lepoutre (*10*). Two pressure filtration methods were reported by Reinbold and Ullrich (*4*) and Beck, Goossens, Rahlwes, and Wallpott (*9*).

The fact that many test methods have been reported is evidence that the development of a universally accepted method is very difficult. The purpose of this work is to develop and evaluate a method that is simple, quick, reproducible, and more representative of actual coating consolidation than the methods reported.

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The experiment

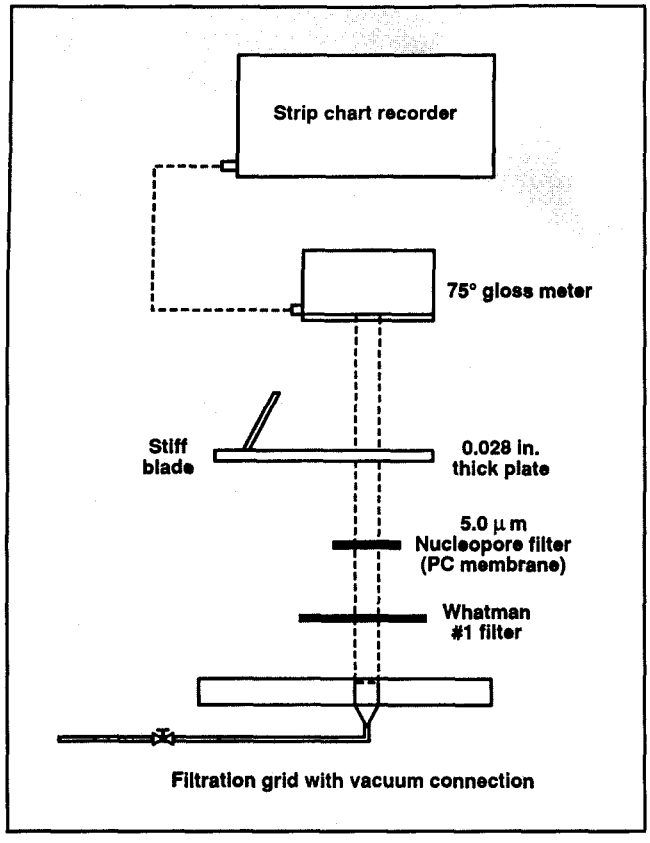
Test method and procedure

The test measures dehydration and immobilization using the surface gloss technique described by Lepoutre (*10*, *11*). The method involves the measurement of gloss as a function of time for a thin layer of coating applied over a Nucleopore filter and under vacuum. Contrary to the work of Lepoutre, who used film, we chose a smooth uniform substrate that was porous, in order to approximate a paper substrate. Immobilization solids (GIMS) and time to immobilization (TIMS) are determined at the point when the gloss drops sharply. Dehydration rates are obtained by measuring solids of the thin layer of coating at predetermined time increments.

The immobilization point is not necessarily a single point in time or in the structure developing during consolidation. It may be influenced by drying rate, coating component distribution, and the differential porosity of the raw stock. Thus a method to compare the immobilization characteristics of a coating will be for a specific set of conditions. Effects such as formulation solids should be evaluated relative to a control.

Figure 1 presents a diagram showing the parts of the immobilization tester. The immobilization tester has a circular grid of 2.5 cm^2 connected to a constant 22.5-in. Hg vacuum. A Whatman No. 1 filter paper was first placed over the grid, and a Nucleopore filter (PC membrane) of 5.0 μm pore diameter was placed over the Whatman filter paper through which the vacuum was applied to the coating. (This combination was found to give the most uniform water removal across the open area over which coating was applied. Nucleopore filters of 5 μm were chosen for two reasons: first, because this pore size reflects a mean pore size often found in paper coating raw stock; and second, because this size provided a reasonable time frame for the measurement.) A metallic plate with a circular area

1. Immobilization tester



I. Summary of experimental studies to evaluate test method

A. Coating solids: 56%, 59%, 62%
Binder Ratios:
CMC-Latex, 1/12
Protein-Latex, 2/11
Starch-Latex, 3/10
*CMC-Latex, 1/12

*CMC-Latex with constant liquid phase viscosity equal to the liquid phase viscosity of the 62% solids regular system

B. Binder ratios @ 60% solids

CMC	*Latex*	*Protein*	*Latex*	*Starch*	*Latex*
0.5	12.5	1.0	12.0	2.0	11.0
1.5	11.5	1.5	11.5	4.0	9.0
2.0	11.0	3.0	10.0	5.0	8.0

C. Test performed
1. Time to reach gloss immobilization (TIMS)
2. Gloss immobilization solids (GIMS)
3. Solids vs. time
4. S.D. Warren water retention

D. Materials used

Clay: #1 coating grade
89.5-91.0 brightness
92% finer than 2 μm
0.55 μm mean particle size diameter
13 m^2/g surface area

Latex: Carboxylated styrene-butadiene latex
0.175 mean particle size
8-10 degree glass transition temperature
60/40 styrene/butadiene
Low acid modification

Protein: Anionic carboxylated soy protein
205,000 nondissociated average mol. wt.
-60 net negative charge (moles COO-/100 kg)
High degree of hydrolysis

Starch: Hydroxyethylated cornstarch
1.45-1.65 E.O. substitution
Low viscosity grade

CMC: Industrial grade
90,000 average molecular weight
Salt content less than 0.5%
0.7 degree of substitution

III. Effect of coating solids and binder ratio on HC/C, LPHCCV and SVF

Variable	*Increasing coating solids*	*Increasing hydrocolloid level in total binder*
HC/C	No change	Increase
LPHCC	Increase	Increase
SVF	Increase	No change

of 2.5 cm^2 and thickness of 0.028 in. was placed over the circular grid on the immobilization tester. A 75° glossmeter was then placed over the coating to monitor gloss of the wet coating layer as it lost water through the filters. The glossmeter was modified to directly plot gloss vs. time on a strip chart recorder. The speed of the recorder was set at 2 min/in., and the glossmeter was calibrated with a standard before each experiment.

The coating was poured on the plate and scraped over the grid area with a stiff blade to give a coating layer with a uniform thickness of 0.028 in. The glossmeter was immediately placed over the coating and the recorder started. The time between coating application and starting the recorder was maintained at 8-10 s. The time at which gloss began to decrease rapidly was taken as immobilization of the coating. The vacuum was immediately released at this point, and the wet coating was carefully removed for solids determination by weight difference with oven drying. Dehydration rates were obtained by simply taking solids measurements at increasing predetermined time increments.

Experiment design

Three traditional coating systems were used in this study to evaluate the test method. They were:

1. Clay-CMC-Latex
2. Clay-Protein-Latex
3. Clay-Starch-Latex.

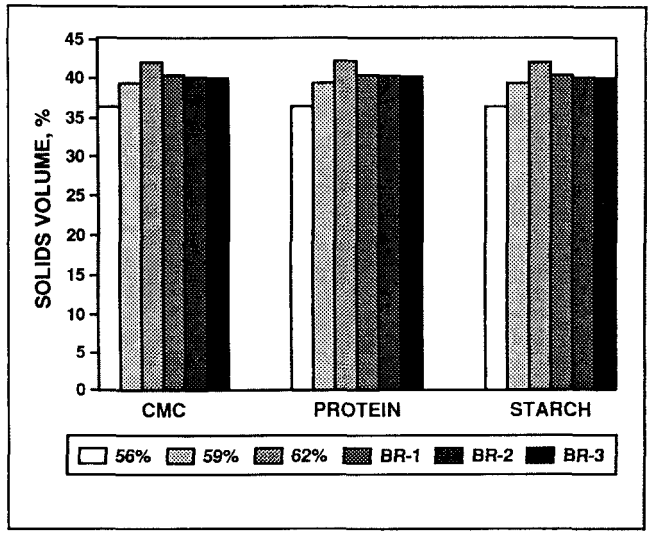
Experimental studies were performed with the formulations to determine the effect of coating solids and binder ratio on coating dehydration and immobilization. A summary of information about the studies is contained in **Table I.**

II. Percent variation for S. D. Warren method and gloss immobilization method

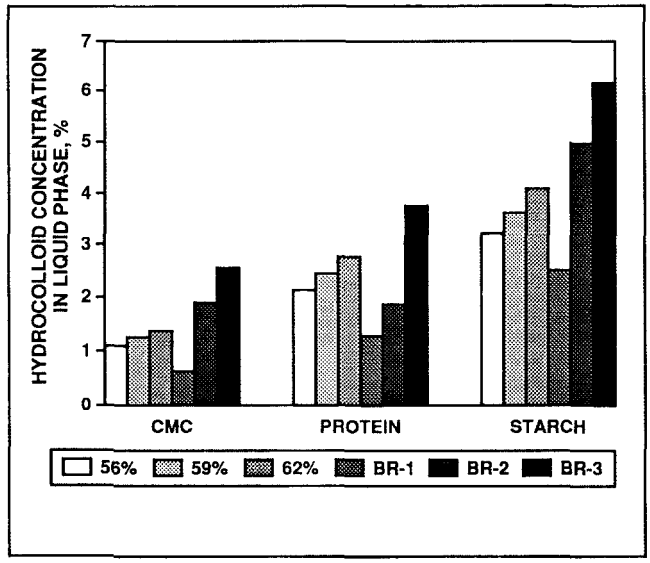
Formulation	S. D. Warren method	Time to reach gloss immobili-zation	Solids at gloss immobili-zation
1 CMC/12 latex - 56%	8.20	7.69	0.48
1 CMC/12 latex - 59%	6.32	2.60	0.24
1 CMC/12 latex - 62%	5.49	4.47	0.97
2 protein/11 latex - 56%	4.86	9.39	0.06
2 protein/11 latex - 59%	6.27	8.85	1.40
2 protein/11 latex - 62%	3.16	6.54	0.67
3 starch/10 latex - 56%	6.31	8.99	0.90
3 starch/10 latex - 59%	6.94	7.12	0.25
3 starch/10 latex - 62%	7.42	8.69	0.06
0.5 CMC/12.5 latex	7.31	4.06	0.11
1.5 CMC/11.5 latex	5.55	3.04	0.28
2.0 CMC/11.0 latex	4.43	6.33	0.24
1.0 protein/12.0 latex	4.24	4.46	0.34
1.5 protein/11.5 latex	3.64	7.25	0.21
3.0 protein/10.0 latex	5.26	5.80	0.20
2.0 starch/11.0 latex	3.06	4.93	0.56
4.0 starch/9.0 latex	4.05	3.17	0.26
5.0 starch/8.0 latex	5.22	3.20	0.37
*1 CMC/12 latex - 56%	6.73	5.77	0.13
*1 CMC/12 latex - 59%	8.94	3.81	0.54
*1 CMC/12 latex - 62%	2.97	4.37	0.15
Average % variation	5.54	6.00	0.41

*CMC Coatings with constant liquid phase viscosity.

2. Change in percent solids volume with coating solids and binder ratio



3. Change in hydrocolloid concentration with coating solids and binder ratio



Results and discussion

Test method

Time to gloss immobilization (TIMS), gloss immobilization solids (GIMS) and dehydration rates were determined for each formulation in the coating solids and binder ratio studies. An average of three measurements was obtained for each formulation for TIMS, GIMS and dehydration measurements. Percent variations for S. D. Warren and gloss immobilization methods are presented in **Table II.**

The test proved to be a simple, relatively quick, and reproducible method for static water retention and immobilization solids measurement. The procedure is a sequence of steps that are simple and easy to perform. About one hour is required for three measurements of GIMS and TIMS for a coating. Removal of the coating from the filter membrane and solids determination with the oven proved to be the more difficult and time-consuming part of the test. Steps are being taken to improve the test by automating the instrument and using an IR detector to directly read and record solids. Time required for the test can be reduced by application of less coating using a thinner plate. The application method can be improved by motorized operation of scraping the coating over the circular opening in the plate.

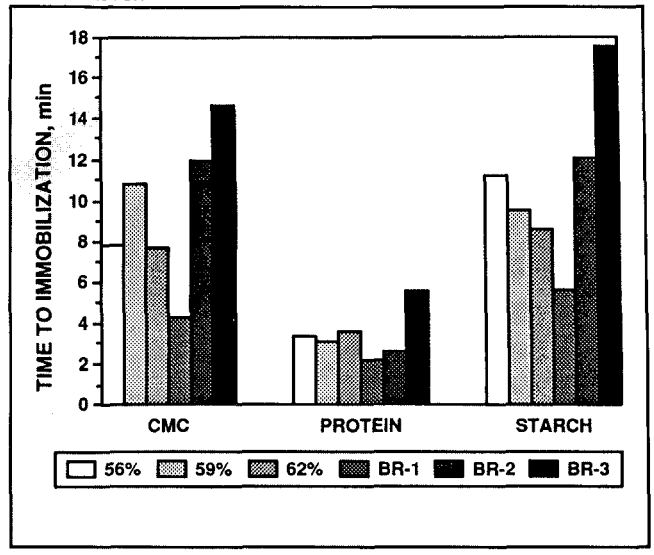
Reproducibility of the test is good. The percent variations for solids measurements (GIMS and dehydration) were 0.1-1.4%. For TIMS measurements, the percent variations were comparable to the S. D. Warren water retention test (3-9%) as well as that reported by Sandas (*12*). Reproducibility in the time to immobilization (TIMS) measurements is expected to improve further with an automated unit because of consistent application of coating through a motorized scraping mechanism.

IV. Effect of coating solids and binder ratio on liquid phase viscosity

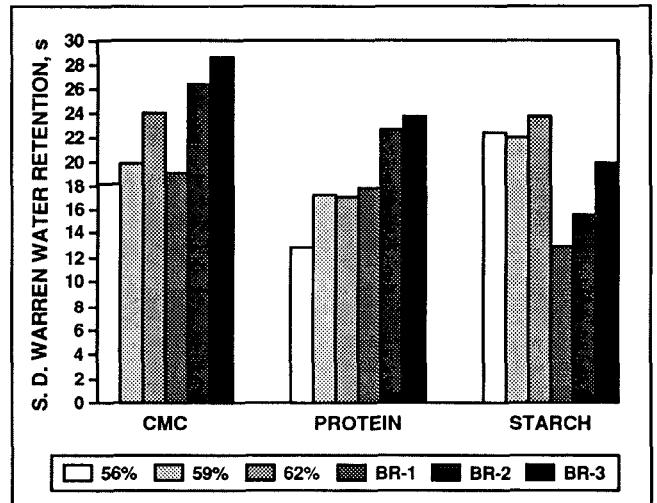
Formulation	*Liquid phase viscosity at 10 rpm, cps*
1 CMC/12 latex - 56%	50
1 CMC/12 latex - 59%	135
1 CMC/12 latex - 62%	210
2 protein/11 latex - 56%	10
2 protein/11 latex - 59%	12
2 protein/11 latex - 62%	23
3 starch/10 latex - 56%	18
3 starch/10 latex - 59%	27
3 starch/10 latex - 62%	35
0.5 CMC/12.5 latex	67
1.5 CMC/11.5 latex	280
2.0 CMC/11.0 latex	375
1.0 protein/12.0 latex	12
1.5 protein/11.5 latex	15
3.0 protein/10.0 latex	27
2.0 starch/11.0 latex	24
4.0 starch/9.0 latex	68
5.0 starch/8.0 latex	93
*1 CMC/12 latex - 56%	228
*1 CMC/12 latex - 59%	218
*1 CMC/12 latex - 62%	225

*CMC coatings with constant liquid phase viscosity.

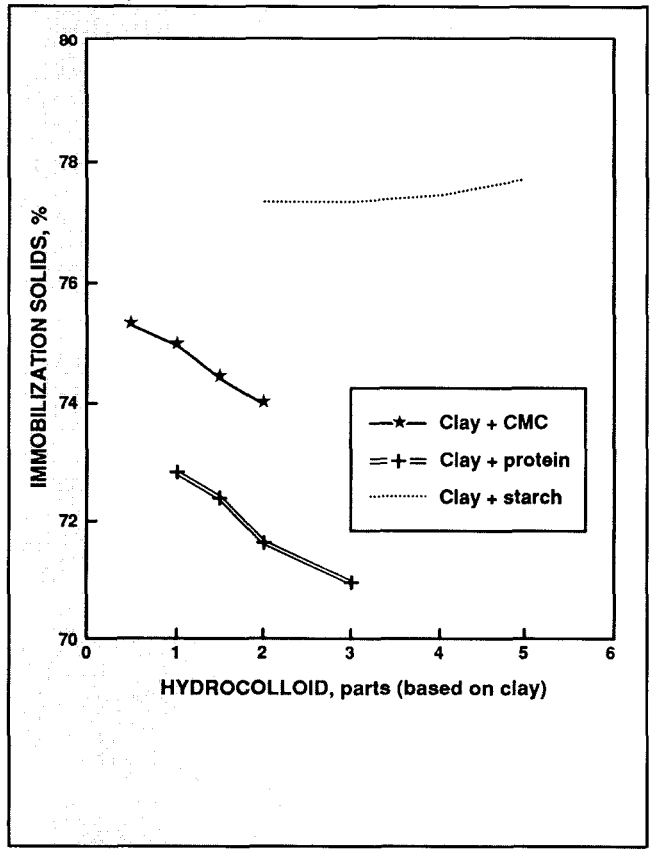
4. Effect of coating solids and binder ratio on time to reach immobilization



5. Effect of coating solids and binder ratio on S. D. Warren water retention



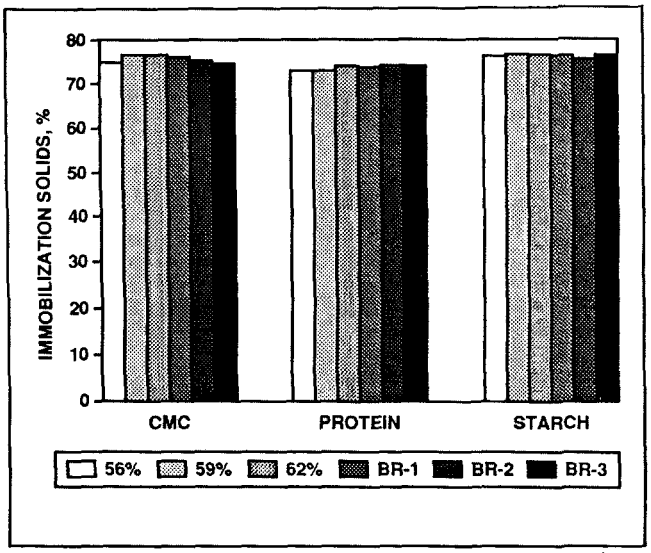
6. Effect of hydrocolloids on immobilization solids



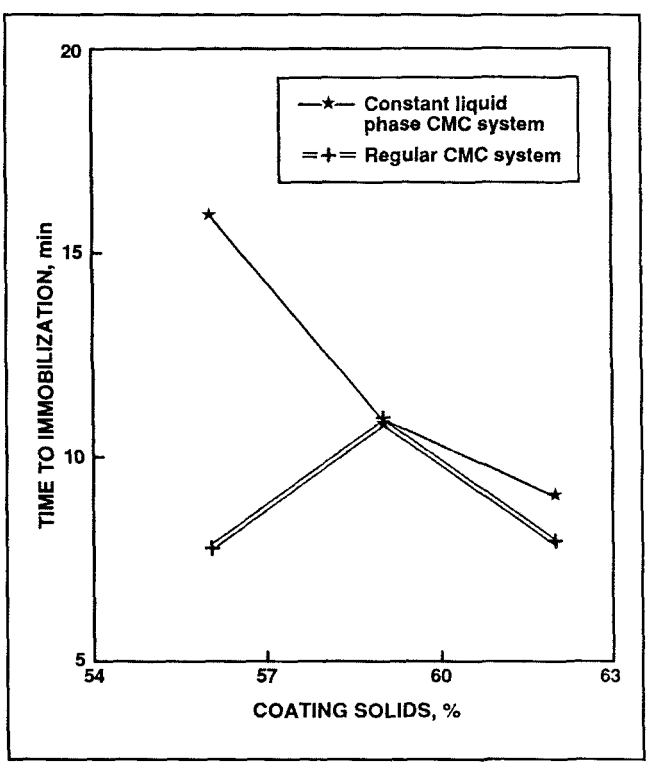
Variables associated with coating solids and binder ratio

Before we proceed further, it should be pointed out that the study was designed to determine the effect of coating solids and binder ratio on TIMS, GIMS, and dehydration of three coating systems having a total binder content of 13 parts based on clay. Three variables were identified as associated with the changes in coating solids and binder ratio. They are:

7. Effect of coating solids and binder ratio on immobilization solids



8. Effect of liquid-phase viscosity on time to immobilization



1. Hydrocolloid to clay ratio (HC/C)
2. Hydrocolloid concentration in the liquid phase (LPHCC)
3. Solids volume fraction (SVF).

The qualitative changes in these variables with changing coating solids and binder ratio are summarized in **Table III.**

It is instructive to analyze the effects of coating solids and binder ratio in terms of hydrocolloid/clay ratio (HC/C), liquid-phase hydrocolloid concentration (LPHCC), and solids volume fraction (SVF) of the coating. **Figures 2 and 3** present the changes in percent solids volume and hydrocolloid concentration in the liquid phase (LPHCC), respectively. This experimental design helps us to understand the effect of these three factors separately.

Effect of coating solids and binder ratio on liquid-phase viscosity

Table IV summarizes the effect of coating solids and binder ratio on liquid-phase viscosity. At equal concentration, the liquid-phase viscosity of three systems can be rated as CMC > starch > protein. Liquid-phase viscosity gives an indication of the relative ability of water soluble polymers to impart water retention to coating colors. However, other factors such as pigment-binder interaction, coating solids, etc., also have a pronounced effect on the resultant water retention.

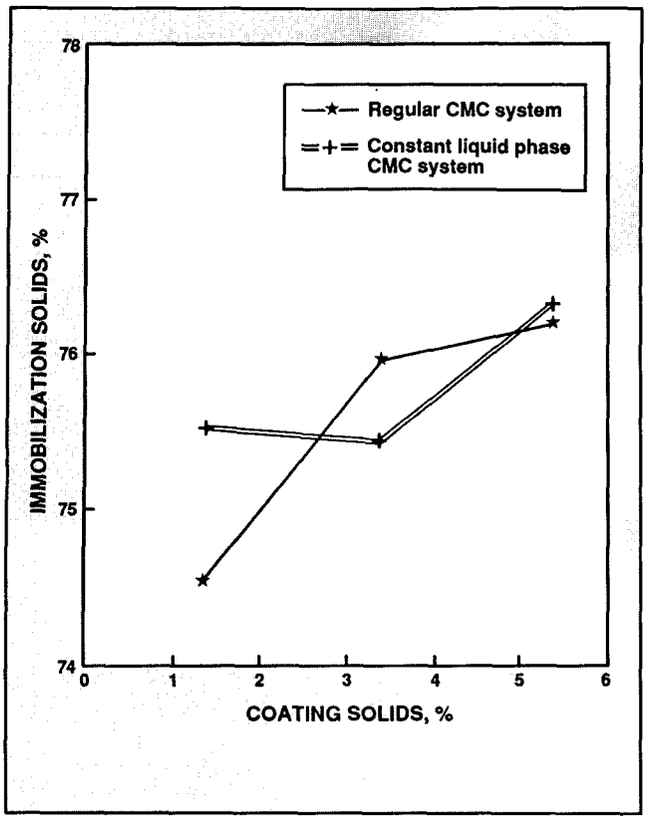
Effect of coating solids and binder ratio on TIMS and dehydration

It has been reported that solids volume fraction (SVF) and binder composition (HC/C) have an effect on immobilization, dehydration, and rheological properties of coating formulations (*13–15*). **Figures 4 and 5** show the effect of solids and binder ratio on TIMS and S. D. Warren (SDW) water retention, respectively. As expected, both TIMS and SDW showed an increase with increasing levels of hydrocolloid. However, at equal hydrocolloid concentration, the two tests did not rate the three systems in the same order with regard to the water holding capacity (TIMS-CMC > Starch > Protein; SDW-CMC > Protein > Starch). With increasing coating solids, SDW showed increased water-holding capacity for all three systems, while TIMS did not show any consistent trend except in the starch system.

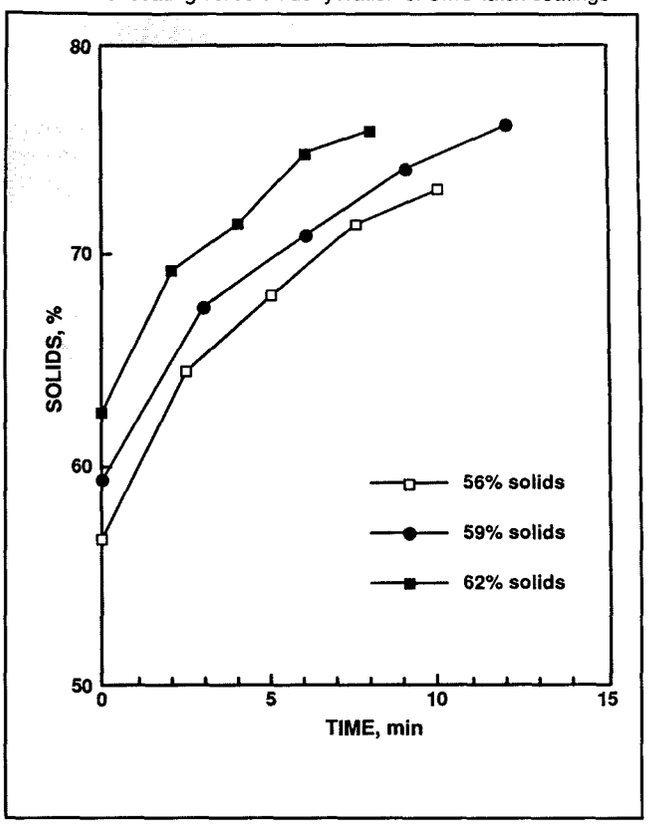
Gautam *et al.* (*16*) have reported that the water retention of a coating color is influenced by type and amount of wet structure and the liquid-phase viscosity. Our results suggest that increased SVF with coating solids caused changes in wet structure as well as liquid-phase viscosity. If the immobilization solids level does not change with increasing coating solids, higher coating solids simply means less water to be removed to get to immobilization solids level.

Therefore, time to immobilization (TIMS) should decrease with increasing coating solids. It is quite evident in the starch system and CMC system (with constant liquid phase) where increase in coating solids showed a decrease in TIMS but no significant change in liquid-phase viscosity and small changes in GIMS. A comparison of TIMS and liquid-phase viscosity of protein and starch systems (Table IV and Fig. 4) in the coating solids study indicates the importance of wet structure in the water-holding capacity of a coating color. Large differences in TIMS of starch and protein systems with increasing coating solids (liquid-phase viscosity is not significantly different) are probably due to difference in wet structure (*16, 17*). Because of greater packing, starch coatings offer higher resistance to liquid flow through the pigment/binder structure and therefore dehydrate much slower than protein coatings.

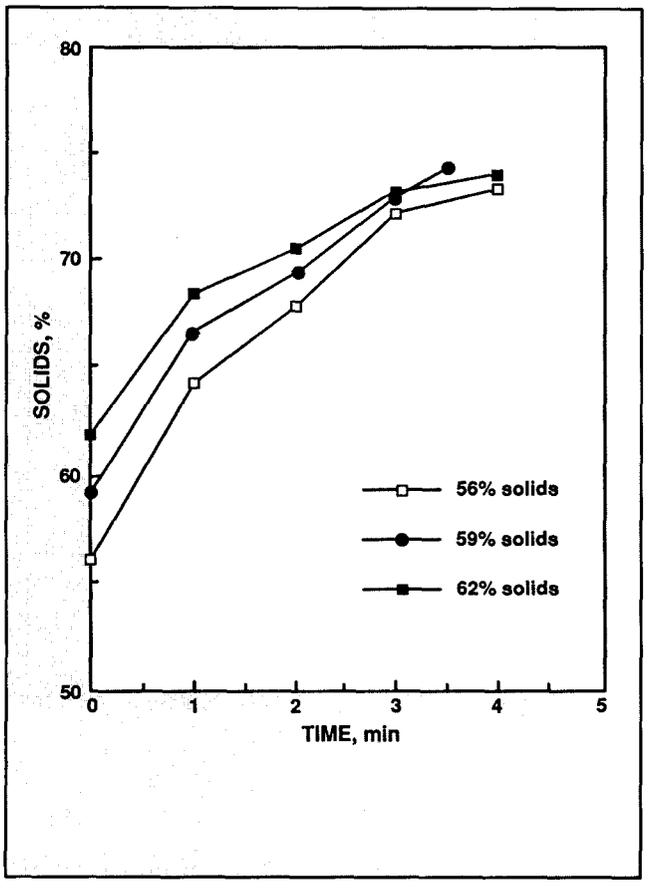
9. Immobilization solids—constant liquid phase vs. regular system



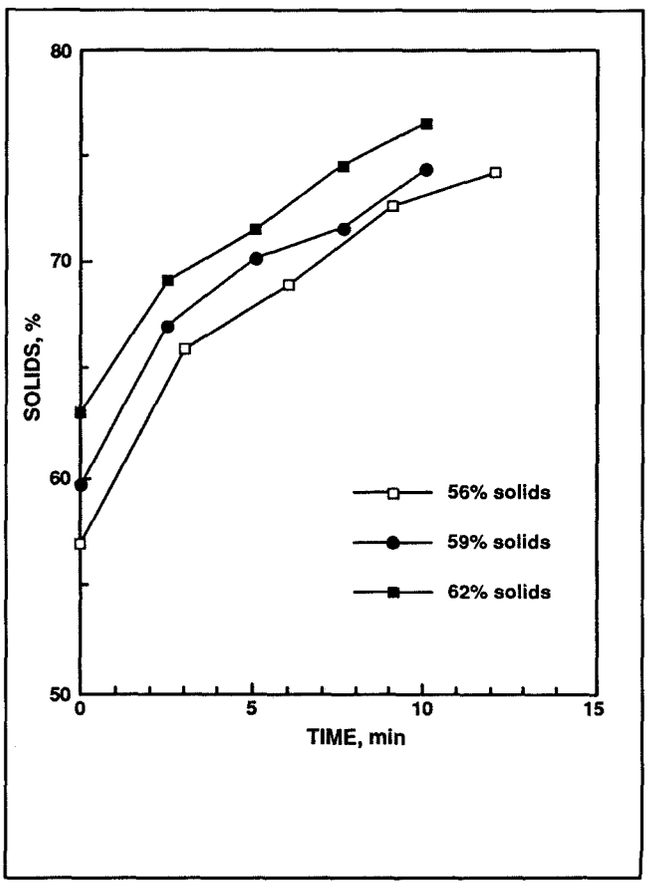
10. Effect of coating solids on dehydration of CMC-latex coatings



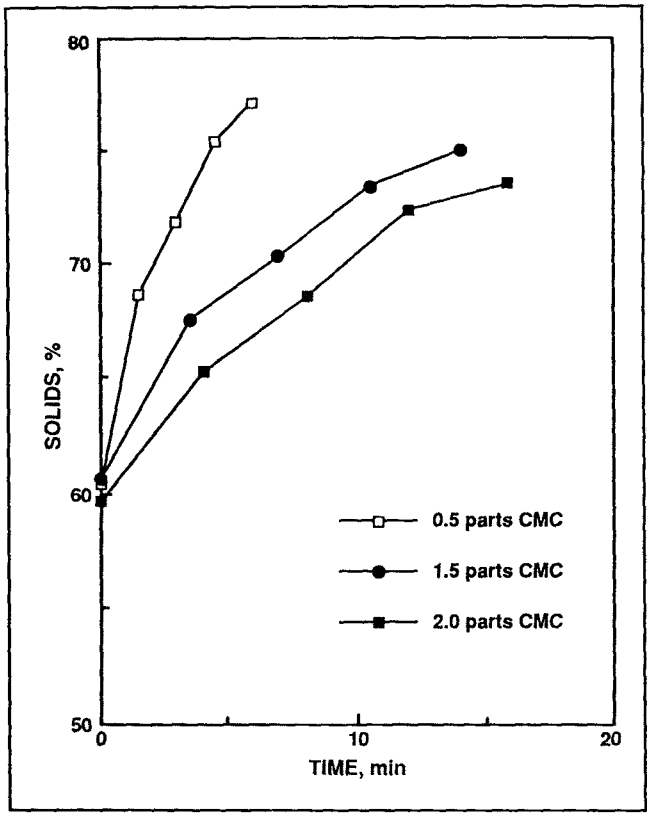
11. Effect of coating solids on dehydration of protein-latex coatings



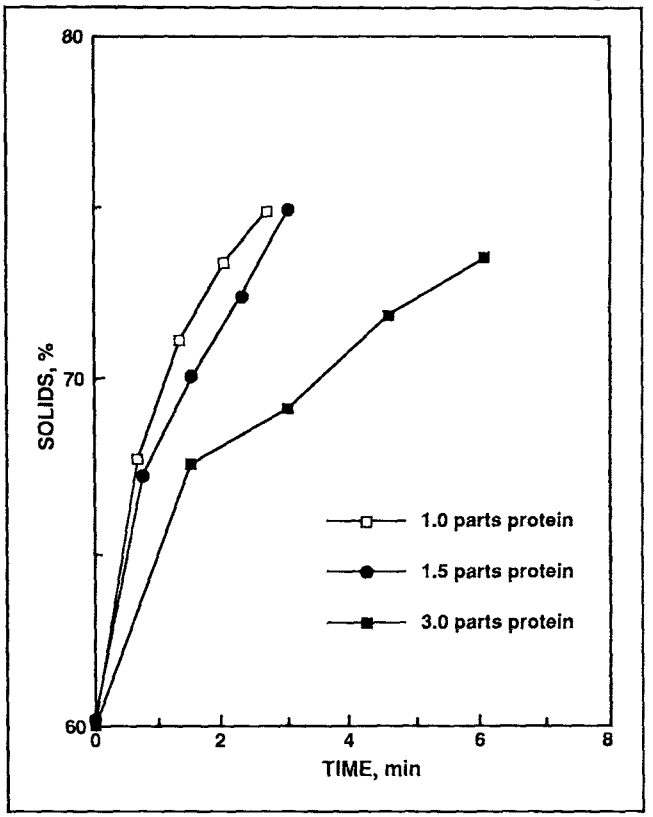
12. Effect of coating solids on dehydration of starch-latex coatings



13. Effect of binder ratio on dehydration of CMC-latex coatings



14. Effect of binder ratio on dehydration of protein-latex coatings



Effect of solids and binder ratio on immobilization solids (GIMS)

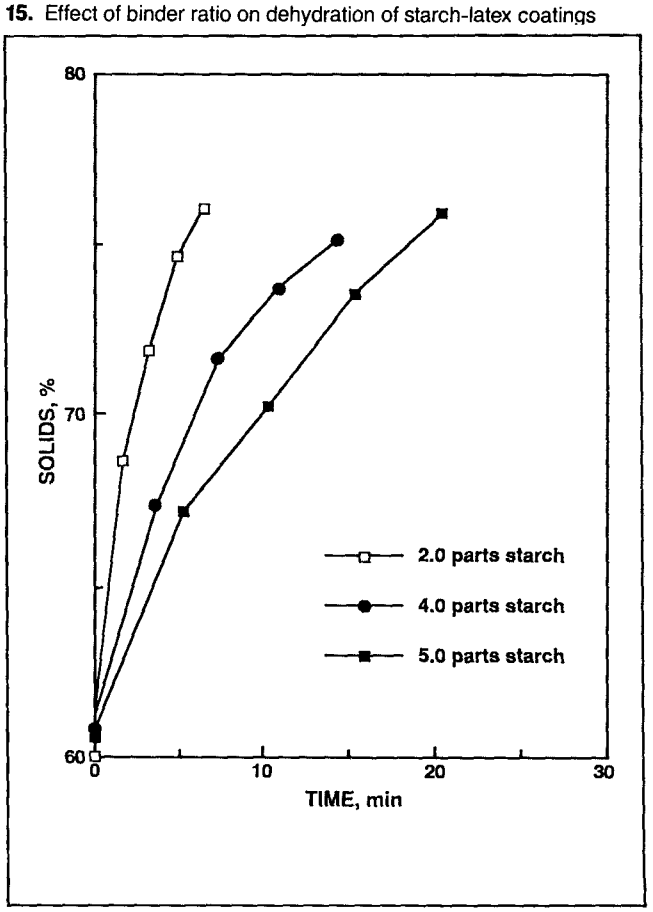
Immobilization solids of a coating reflect the state of dispersion of various components in the coating formulation (*6*, *16*). It is generally believed that the basic structure of a coating is established by the natural binders. **Figure 6** shows the effect of increasing levels of hydrocolloids on the GIMS of a coating. The protein system had the lowest GIMS, followed by CMC, and starch had the highest. These results are in agreement with those reported (*6*, *16*, *18*).

Figure 7 shows the effect of solids and binder ratio on the GIMS of the three coating systems. The starch system immobilized at a higher solids level as compared to protein and CMC. The GIMS of increasing coating solids caused a small increase in GIMS, with the maximum change observed in the CMC system. This suggests that the increased solids volume fraction caused smaller and more dense structures in the CMC system. Increasing levels of hydrocolloids did not cause any large change in the GIMS of latex containing coatings (compare Figs. 6 and 7). This suggests that the latex particles occupy the void spaces of clay structures created by the addition of hydrocolloid.

Constant liquid-phase viscosity

To determine the effect of liquid-phase viscosity on water-holding characteristics of a coating color, we measured TIMS and SDW of three CMC-latex coatings at three solids levels (56%, 59%, 62%) but with the same liquid-phase viscosity. The liquid-phase viscosity was held the same (equal to that of 62% CMC-latex coating) for the three levels of solids by manipulating the molecular weight of CMC.

15. Effect of binder ratio on dehydration of starch-latex coatings



Figures 8 and 9 show the TIMS and GIMS results for CMC coatings with the same liquid-phase viscosity. The greater level of higher molecular weight CMC at 56% solids increased the GIMS slightly. Increasing solids volume fraction with constant liquid-phase viscosity showed a sharp decrease in TIMS. Since the GIMS was not affected much by solids volume fraction in this case, a decrease in GIMS simply means that less water is to be removed to get to GIMS. Comparison of these data with that of regular CMC coatings suggest that water retention of CMC coatings is a complex function of wet structure and liquid-phase viscosity.

Dehydration characteristics

Figures 10-15 show the solids versus time curves for various coatings. These data simply support the time to reach immobilization results. Protein coatings dehydrate faster than CMC and starch coatings. Higher liquid-phase hydrocolloid concentration (LPHCC) with increasing hydrocolloid in binder reduced dehydration rate. Increasing solids volume fraction did not show a consistent effect on dehydration rates.

Conclusions

The following conclusions are made from the results of the study:

1. The gloss immobilization test method proved to be a simple and quick procedure for measuring immobilization solids, time to immobilization, and dehydration rates for common coating formulations of CMC/latex, protein/latex, and starch/latex binder systems.
2. Reproducibility of the test method is good, with a percent variation range of 0.1-1.4% for GIMS and 3.0-9.8% for TIMS.
3. The method can be used to evaluate the effect of coating solids and various interactive and noninteractive binders on the immobilization solids and water-holding characteristics of a coating color.
4. The water-holding characteristics of three common coating systems are controlled by the type and amount of hydrocolloid, which greatly influences the wet structure and liquid-phase viscosity. Protein coatings, because of lower liquid-phase viscosity and more open structure, dehydrate faster. Starch coatings dehydrate slower as compared to protein coatings because of tighter structure.
5. Coating solids showed no relationship to dehydration of CMC/latex and protein/latex systems. Immobilization solids of these two systems increased with increasing coating solids. Increased coating solids result in lower TIMS if liquid-phase viscosity and wet structure are not affected significantly.
6. Protein caused considerable structuring of clay followed by CMC. Starch coatings immobilized at a higher solids level as compared to CMC and protein coatings.□

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