

Measuring binder migration with ultraviolet analysis

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By combining a controlled drying method and ultraviolet surface analysis, binder migration tendencies can be studied.

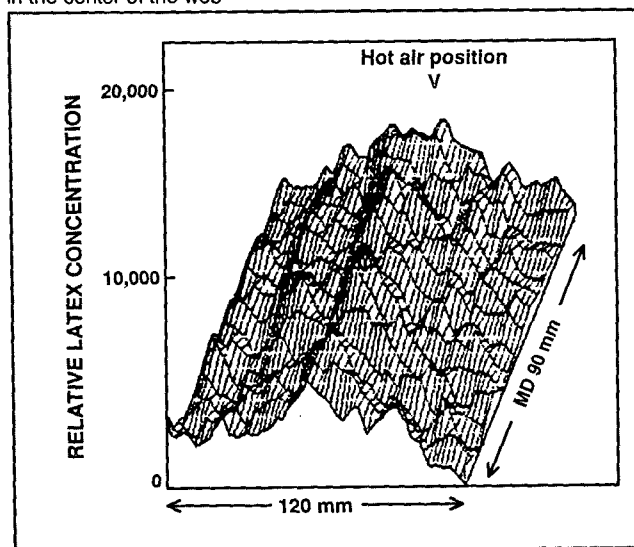
In earlier publications (1, 2) the basics of ultraviolet analysis have been explained. The technique is based on shining a light beam of controllable size and wavelength onto the surface of the coated paper sample and using three wavelengths to determine the absorption, which is related quantitatively to the amount of styrene at the surface. By moving the sample under the light beam, a map of the surface concentration can be generated by using a computer for the data reduction. Although the technique is capable of demonstrating the uniformity of latex concentration at the surface, other information is needed to correlate such data directly to the causes of migration of the binder. With that in mind, some successful techniques will be described that determine the tendencies of the latex to migrate.

Experimental design

Since this paper reports on a large body of individual projects, it is not possible to describe all of the procedures in a simple manner. However, most of the techniques and procedures used will be summarized. Special techniques related to this method of analysis which will be referred to later in the paper will be italicized.

All coatings were made with the pigment portion being 100% No. 2 clay and 15 pph binder, unless indicated otherwise. Coatings were applied between 60% and 63% solids. Coatings applied to Mylar were applied with a drawdown bar. Coatings applied to paper were applied using a puddle-type blade applicator and a Keagan coater. The drying on the Keagan coater was accomplished by a *strip drying technique* using a hot-air gun with a flared tip aligned in the direction of the web travel so that a strip of the coating would be dried more quickly than the rest of the coating. The gun delivered a low-velocity stream of air at approximately 200°C and was positioned roughly 1 cm from the sheet surface. The speed of the coater was about 3 m/min, meaning that the air-dried section was dry in about a second, but the rest required up to several seconds to dry. Even without additional heating, the

1. Wide scan plot of coating showing polystyrene pigment migration in the center of the web



coating outside the area of the hot-air strip was dry within the less than 2 m distance of travel in the coater, probably due to the hot air flowing laterally across the web surface after impinging on the strip zone.

Previous papers (1, 2) described the basics of ultraviolet analysis as developed using the area mapping technique. An alternate technique, referred to as the *line mode*, is available. This technique analyzes a strip of the surface, which is adjustable in width (0.4–6 mm) and comprises 63 incremental readings of 1 mm each, so that a line roughly 1 mm × 63 mm is tested.

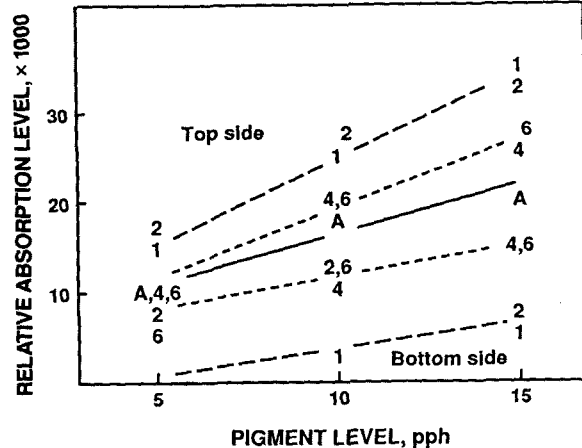
Another new method was developed for this study: the *wide scan*. For the analysis of the paper coated on the Keagan coater and dried with the strip drying technique, the area of migration was found to be wider in some cases than the 60-mm × 63-mm area of the normal area mapping technique. That program was therefore modified to cover a 120-mm × 90-mm area, using a 1.2-mm × 5-mm light beam and sample area of 2 mm × 6 mm. An example of the three-dimensional plot obtained is shown in Fig. 1. These plots give qualitative information on the degree and uniformity of migration and are valuable in that respect. However, the comparison of different plots to determine

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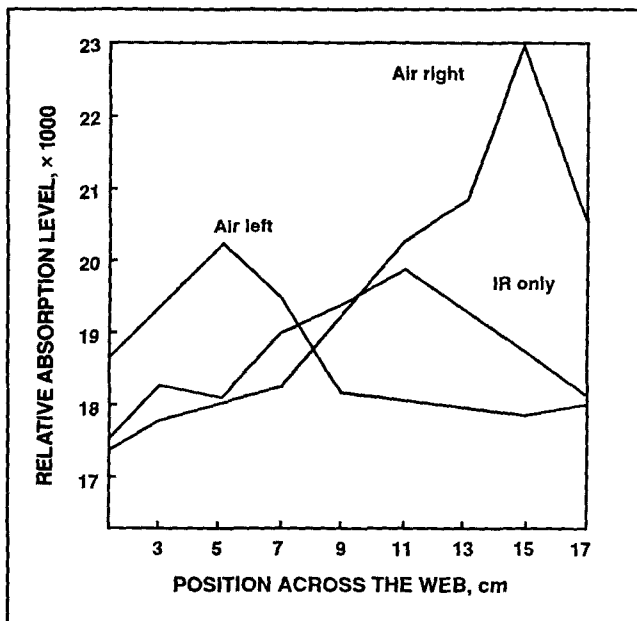
1. Relationship between pigment size and migration

Particle size, μm	pph	Surface absorption, per 1000			
		Top	Bottom	Δ	Avg.
0.1	5	37	20	17	29
	10	46	21	25	34
	15	53	25	28	39
0.2	5	38	24	14	31
	10	46	21	25	34
	15	53	25	28	39
0.4	5	34	22	12	28
	10	40	30	10	35
	15	45	36	9	41
0.6	5	34	23	11	29
	10	40	31	9	36
	15	46	36	10	41

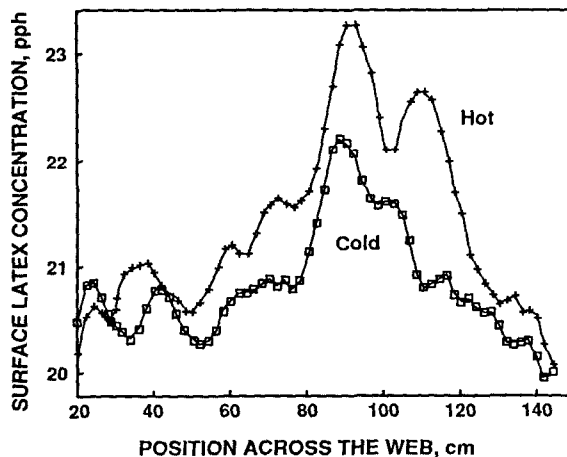
2. Relationship between particle size of pigment and top and bottom concentration. Particle size: 1=0.1, 2=0.2, 4=0.4, 6=0.6, A=average.



3. The effect of drying conditions on binder migration



4. The effect of hot and cold air on binder migration



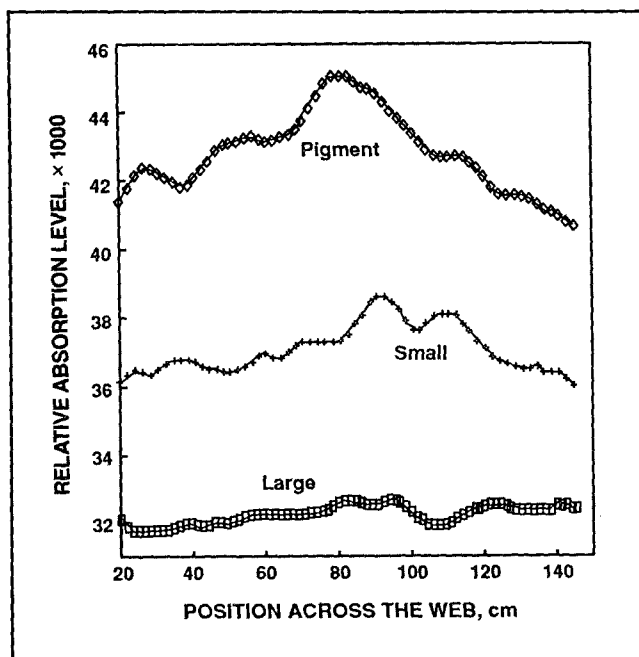
quantitative differences in migration requires that value judgments be made. The plot in Fig. 1 is made up of a series of 16 scans across the machine direction, each containing 63 data points. By using a spreadsheet program, all 16 scans can be combined to obtain a single, average concentration, or *composite line* (of the type shown in Fig. 4), which allows more direct comparisons to be made.

Results and discussion

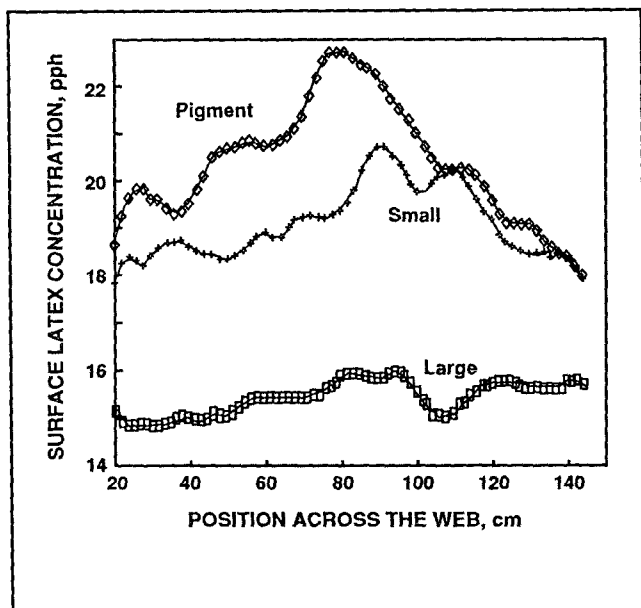
Polystyrene pigment studies

In an effort to study the effect of particle size on migration, a project was designed using model systems (3). Coatings were prepared using mixtures of No. 2 clay and polystyrene pigment with no binder added. The coatings were applied to Mylar film and dried with a hot-air gun at temperatures ranging from 150°C to 300°C. The pigment concentration at the surface was measured and then the coating was peeled off with tape to allow the bottom side (the side dried in contact with the Mylar) to be measured.

5. Absorption characteristics of two binders and a pigment



6. Migration tendencies of two binders and a pigment



Both measurements were made using the line mode technique. Since there was little difference between the different temperatures used, all data were averaged together and are presented in Table I.

The pigment concentrations at the top were consistently higher than at the bottom, and the differences between the top and bottom (Δ) are higher for the smaller-particle-size pigment. At and above $0.4\text{-}\mu\text{m}$ particle size, very little tendency towards migration is seen. The average of the concentration at the top and bottom was computed, and those values were subjected to regression analysis to

attempt to produce a calibration curve to determine the actual concentration at the surface. A fairly good curve was obtained with an intercept of 23,500 and slope of 1088.

When this pigment correction factor was applied to the data, the concentration of pigment at the surface is seen in Fig. 2 to be as high as 10 pph higher than the formula value. The data clearly show the ability of small particles to migrate to the free surface during drying, but the failure of the temperature to have any noticeable effect is not in keeping with prior beliefs. I propose in this case that the polystyrene spheres were moving with the water and were unaffected by the drying temperature.

The significance of the particle size can be related to the size of the pores in the drying pigment system, with the implication being that the larger spheres were restricted in movement, but the spheres below $0.4\text{ }\mu\text{m}$ were small enough to pass through the pigment structure. The temperature might be expected to become a factor if the latex spheres changed their mobility as the temperature changed.

Evaluation of drying methods on migration

In an effort to develop a technique to simulate binder migration by hot-air drying, the strip drying technique described earlier was devised. Coatings containing a styrene butadiene of $1200\text{-}\text{\AA}$ particle size were made and dried with the strip method. The resulting paper was analyzed using the line mode measuring lines in the machine direction every 2 cm across the width of the web (4). Data obtained by this method are presented in Fig. 3 to show that the hot air could cause a binder to migrate to the surface and that the migration did indeed follow the location of the hot air strip as it was moved from side to side. The binder was also seen to migrate to the surface when the infrared (IR) was used alone (4).

The evaluation was improved through the development of the wide scan and condensed line techniques to produce the evaluation of the effect of dryer temperature shown in Fig. 4. The same coating was run with the air gun blowing hot and cold (room temperature) air, and both caused the binder to migrate, although the hot air did cause more migration than the cold air.

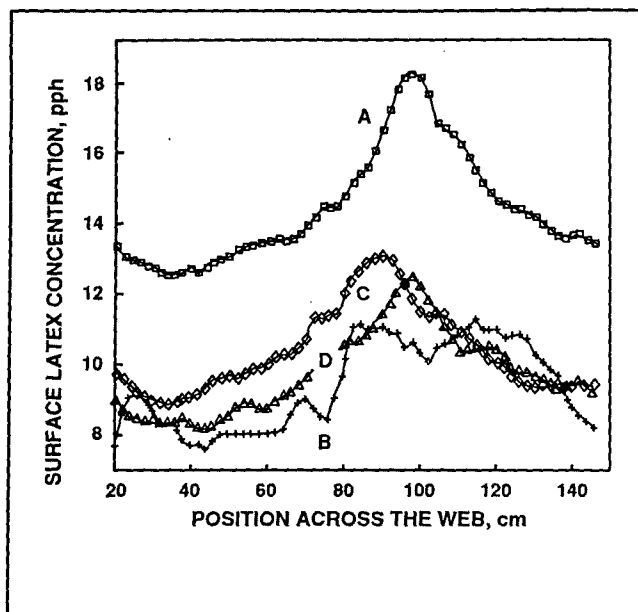
The relative absorption values are used in Fig. 3, and surface latex concentration is used in Fig. 4. These values have been converted to the latex concentration using a linear relationship originally developed by Fujiwara (1). The numbers used in Fig. 3 are nearly equal to the actual latex concentration. This data is more in keeping with previous beliefs that hotter air causes a faster movement to the free surface and therefore more migration.

Having thus demonstrated the ability of the technique to measure hot-air-induced migration, the evaluation shifted to attempts to measure the effects of latex properties on migration.

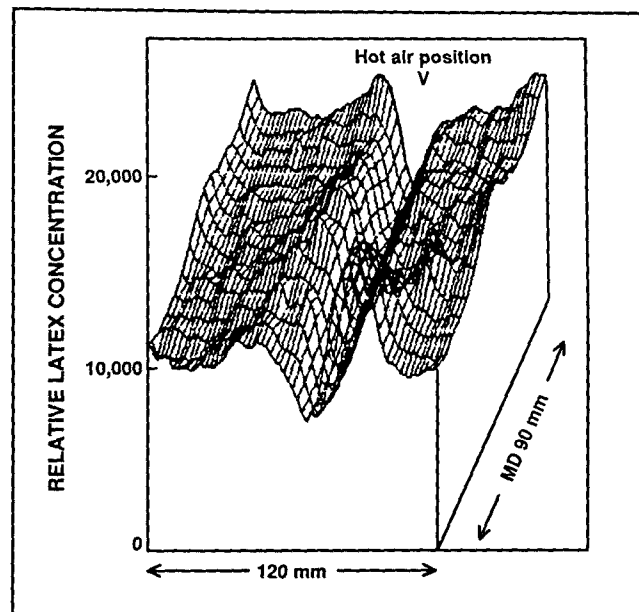
Comparison of pigment to binder

A series of three coatings were prepared, two of which contained different particle size (1200 and $1700\text{ }\text{\AA}$) styrene-butadiene binders at 15 pph and one containing a mixture of the $0.1\text{-}\mu\text{m}$ pigment at 10 pph and 5 pph of the larger binder. These coatings were prepared with No. 2 clay as the pigment and applied to a lightly sized free sheet using the strip drying technique. The data in Fig. 5 show the

7. Glass transition data: A = 39°, B = 23°, C = 18°, D = 11°



8. Extreme drying condition leading to reduced binder level under the hot air



relative level of absorption of the pigment to be higher than either of the two binders, but since the curves are at different levels it is difficult to determine exactly how much relative migration has taken place.

An attempt was made to develop a calibration curve for the binders by applying the coatings to Mylar and allowing them to dry at room temperature, thinking that little or no migration would occur. Unfortunately, the differences between the top and bottom concentrations were remarkably different for the small-particle-size latex, indicating considerable migration even at room temperature.

This situation leads to a problem in determining a calibration curve for a binder that migrates. By using the average between the top and bottom, an intercept of 20,000 and slope of 900 were obtained. These values were then applied to the data and the results plotted in Fig. 6. The data show the difference in migration tendencies of the two binders, but the mixture of binder and pigment leaves the pigment-containing curve slightly in error since the binder and the pigment both contribute to the shape and height of the curve. Since the large binder is not seen to migrate much, we can assume that a constant 5 pph should be subtracted from the curve, leaving between 14 pph and 18 pph of pigment at the surface. Since only 10 pph were in the formula, this indicates considerable movement of the pigment during drying. These data confirm the belief that the particle size of the latex is important to the degree of migration and that binders migrate less than pigments. Since one of the differences between pigments and binders is the glass transition temperature, these data indicate it may be important.

Evaluation of the glass transition temperature

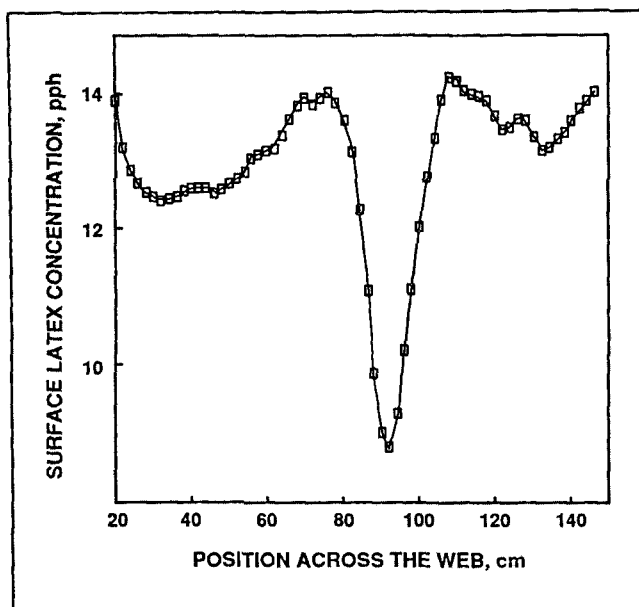
To evaluate the glass transition temperature (T_g) a series of styrene acrylic polymers were obtained with roughly equivalent particle sizes (68–80 Å) and T_g s ranging from 11°C to 39°C. Since the smaller particle size seemed to favor migration, we felt that the use of these extremely

small latexes would eliminate the effect of size from the evaluation. These coatings were prepared with 15 pph total binder and applied using the strip drying method. The surface concentration was again measured with the wide scan mapping technique, and those data reduced to a composite line. The relative absorption data were then converted to binder level using the previously determined calibration factors. The comparison shown in Fig. 7 partially confirms the importance of T_g in that the degree of migration is greatest for the highest T_g binder, but there is no correlation for the remainder of the binders. The binder with the T_g of 38 also was a better pigment than binder since it gave a low pick resistance and high gloss. In a comparison of coatings containing these five emulsions, the pick resistance of A was less than 30 cm/s, and the other emulsions ranged from 60 cm/s to 100 cm/s IGT pick resistance using a medium-viscosity test oil, Westvaco disc, and 35 Kgf pressure. The gloss of A was around 70 when the others were between 50 and 60 on lightly supercalendered samples.

The relative amount of migration of these extremely small binders was not as great as would be expected when compared to the larger latexes shown in Fig. 4, whose T_g s were also in the 10–20°C range. In fact, since the measured surface concentration was less than the formula level, there is the implication that the binder was actually penetrating into the basestock more than migrating to the surface, and that the hot air was helping to set the coating and prevent excessive penetration. If this is the case, then a flatter curve could mean that the binder migrated uniformly into the base, and a high center that the hot air stopped the binder from moving. This interpretation of the results would rely on the binder having an opposite response to the drying; that is, it would stop movement rather than cause it. If the binder is also being drawn to the surface at the same time, the results are too complex to interpret.

Although some confirmation of the importance of T_g was

9. Composite line representation of extreme drying condition



found, the complication created by the penetration and possible interference from other binder properties leaves that conclusion uncertain. It was previously proposed that a higher T_g will mean that the binder will be less "sticky" during drying and therefore more able to migrate. Since T_g can be changed by several different methods and is actually a measure of the relative hardness or tendency of a dry film to flow under shear and not of "stickiness," we should not be surprised by the failure of this parameter to correlate. The situation is further complicated by the variety of methods that can be used to change T_g .

Evaluation of acid level

Another factor that is often expected to influence binder migration is the degree of carboxylation, or the acid level. A series of styrene-butadiene binders was obtained with differing acid levels but with similar other properties. These latex emulsions were evaluated in a manner similar to the samples above, but the data failed to show any relationship between the acid level and tendency toward migration (5).

Theoretically, it would be expected that the higher acid level would cause more association between the binder and the pigment, or an increase in viscosity and reduced mobility of the binder, and thereby reduced migration tendencies. Unfortunately, the data failed to support this theory, or any other relationship between migration and acid level. Again the difficulty seems to be in the fact that the latex samples were of varying composition, and other parameters besides the acid level may have been changed at the same time.

Relationship between binder migration and ink wipe tests

During the analysis of different binders, a particular run was made with the hot-air gun so close to the paper that the paper was lightly scorched in the regions where coating was not being applied. In this extreme condition, the small-

particle styrene-butadiene latex used in the earlier data produced a dramatically different migration pattern (Fig. 8), which shows a deep valley in the binder concentration level directly under the hot air area.

The initial interpretation led to many theories including the possibility that the binder had been "blown away" or into the basestock by a high-velocity jet. When the data are reduced to the composite curve form and the calibration factor used to convert to the surface latex concentration, Fig. 9 shows that the actual binder level at the surface is less than the formula value in the trough area, and at or below in the rest of the area. It is possible that in this case the binder was penetrating into the base and that the hot air increased its mobility, helping it go. However, this conclusion is not fully compatible with the earlier data showing that the same binder is also drawn to the free surface by hot air. This seems to be a case where another mechanism should be proposed.

It has been proposed by Lepoutre (6) that rapid drying can cause the structure to remain bulky due to the failure of the binder to condense. If the coating is dried too rapidly, the structure may be formed at a low-solids, bulky structure and it may be set before the latex forms a film. The film-forming phase should normally contribute to shrinkage of the packed structure.

Scanning electron micrographs (SEMs) of the surface in the two areas, in the bottom of the trough and at the edge, are shown in Figs. 10 and 11. They demonstrate the more open structure of the low-latex area and show the filling in of the smaller pores by binder in the binder-rich area. This evidence supports the theory that rapid drying causes the more open structure.

The same samples were subjected to K&N and Croda ink rub tests, leaving each ink on for 2 min. The K&N ink failed to indicate any perceptible difference in the surface, while the Croda ink did follow the level of binder concentration a bit more. The low level of response to the combined effects of migration and pore structure was remarkable. Accordingly, the conclusion must be made that each ink is not sensitive to binder migration alone, but to a complex set of parameters, of which pore structure and latex concentration at the surface are only two factors. A further conclusion can be added that the K&N was shown to be particularly insensitive to either factor.

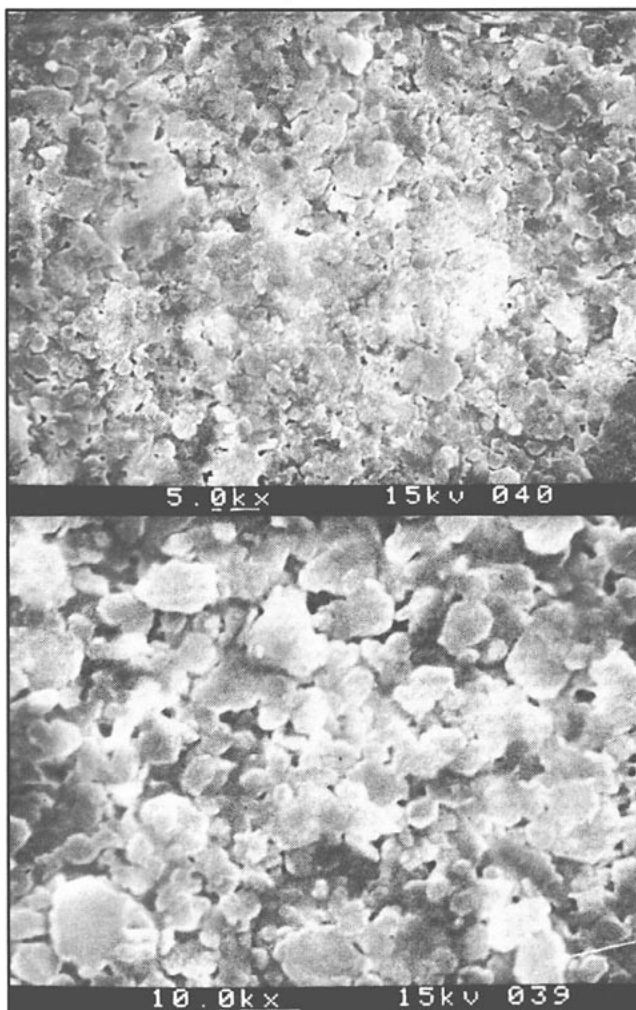
Conclusions

By combining a controlled drying method and ultraviolet surface analysis, binder migration tendencies can be studied. Migration to the surface has been shown to be induced by blowing cold as well as hot air on the surface, although hot air did cause more migration. IR drying without air assistance was also shown to cause a small amount of migration.

Other cases were demonstrated where the binder was assumed to be penetrating into the base more than migrating to the surface, and the hot air reduced this penetration tendency. In one special case, the data were interpreted to indicate that the hot air caused a more open pigment structure due to the rapid setting of the coating layer.

The relative importance of different latex properties can be observed in carefully controlled experiments, but the

10. SEMs of latex-rich coating surface next to valley



11. SEMs of latex-poor coating surface in valley



difficulty in obtaining latex samples in which only one variable was changed prevented the formation of sweeping conclusions on the basis of data contained in this report. However, there are indications that binders with smaller particle size or higher T_g values should be expected to migrate the most, but other factors can cause conflicting results.

The effect of the degree of carboxylation could not be determined.

Finally, the inability of the K&N ink wipe to measure migration and partial success with the Croda ink wipe were demonstrated. The ink wipe methods are sensitive to the structure of the coating as well as the relative concentrations of ingredients at the surface. □

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