Dry Sintering of Latex Particles in Pigmented Coatings. I. Influence on Coating Structure and Properties

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Synopsis

When a clay–latex coating, dried below the minimum film-forming temperature (MFT) of the latex, was subsequently heated above the MFT, its opacity and brightness were considerably enhanced. The improvement in optical properties was optimum in the latex content range of 20–40 parts per 100 parts of clay. The sintering of the latex particles, brought about by the thermal treatment, increased the average size of the microvoids to a diameter that is optimum for the scattering of light, without significantly affecting the total void content. Data on light-scattering coefficient, porosity, gloss, brightness, and oil permeability are discussed and compared to those of conventional coatings, i.e., of coatings dried above the MFT of the latex. Similar improvements in optical properties were obtained when coalescence of the latex particles was induced by exposure to a solvent.

INTRODUCTION

Synthetic polymer latexes are used largely in paper coatings as binders or as pigments. When used as binders, the latexes—generally based on styrene/butadiene, vinylacetate, or acrylic polymers—are formulated so that they form a film under normal drying conditions; in fact, their minimum film-forming temperature (MFT) is usually below room temperature. Indeed, it is their ability to coalesce into a coherent film capable of bonding the pigment particles (predominantly clay) to themselves and to the paper substrate that provides the coating with the mechanical strength that is required in the subsequent printing and converting operations. While giving strength to the coating, these latexes adversely affect the optical properties of a pigmented paper coating in that the gloss and the light-scattering coefficient decrease with increasing binder level.

Synthetic polymer latexes are also used in paper coatings as pigments in combination with conventional inorganic pigments. They are called "plastic pigments." Here, however, the latex, usually based on polystyrene, does not form a film upon drying and the individual latex spheres remain intact and act as light-scattering sites. Their size is adjusted to provide maximum light scattering. This optimum diameter has been found experimentally to be in the range of 0.4 μm.[1] However, these non-film-forming latexes have no binding power and a binder must be added. This leads, of course, to a reduction in the light-scattering efficiency.
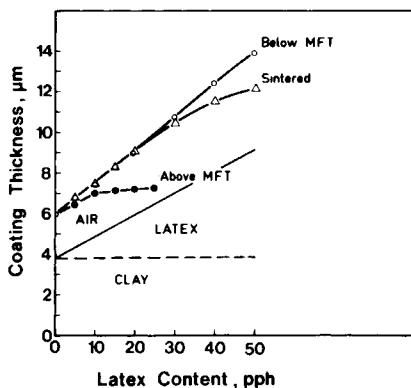
Fig. 1. Dimensions and compositions of clay coatings containing increasing amounts of latex as function of processing conditions.   All coatings contain 10 g/m² clay.

Since the size and shape of the plastic pigment have been optimized to provide maximum scattering, it seems logical that the patent literature would recommend that "it is critical that the temperature of the coating does not exceed the softening point of the plastic particles; otherwise, the particles will lose their discrete character of proper size and shape.   When this occurs, the opacity and brightness of the coated surface drop substantially."[2]   For the same reasons, it is recommended that contact with solvents for the polymer be avoided.

In view of this, we were quite surprised to observe a dramatic increase in the opacity of a clay–latex coating that was dried below the MFT of the latex and then subjected to a heat treatment that promoted coalescence, or sintering, of the discrete spherical particles; a similar effect was observed when the coalescence was induced by exposure to solvent vapors.

This article discusses the phenomenon and the changes that it creates in the structure and the properties of the coating.

EXPERIMENTAL

A mechanically delaminated clay (Alphaplate, Anglo-American Clays Co.) was dispersed in water at 60% solids.   Increasing amounts of a carboxylated 77/23 styrene/butadiene latex (particle size $\sim 0.2~\mu m$; MFT, 42°C) were then added. Coatings were cast on polyester films with a drawdown bar, and were dried, respectively, against a hot plate heated to 90°C (i.e., above the MFT of the latex), at room temperature (i.e., below the latex MFT), and at room temperature, followed by heating to 90°C in an oven for 10 min.   Then 75° gloss, light-scattering coefficient, brightness, void volume fraction, and oil permeability were measured according to the methods described in refs. 3 and 4.   In addition, the coatings were examined in the scanning electron microscope.   Nitrogen surface area was determined on some samples.

RESULTS AND DISCUSSION

Coating Dimension and Composition

Figure 1 represents the change in the thickness of coatings containing a constant mass of clay (10 g/m²), but increasing amounts of latex, as a function of the processing conditions. The thickness was computed from the knowledge of the composition (clay/latex ratio), the mass per unit area and the measured void volume fraction. Note the much larger void content of the coatings dried below MFT.

The typical two-slope curve normally found with conventional film-forming latexes and discussed elsewhere[3] is observed for the coatings dried at 90°C, but not for those dried below MFT. The vertical distance between the two curves represents the contribution of the coalescence of the latex to the structural collapse that results in a reduced void content when drying is done below the MFT.

After the heat treatment of the coatings dried at room temperature, little change in dimension is observed up to 30 parts latex per 100 parts of clay (pph). In other words, there is no collapse of the structure during this "dry" coalescence or sintering. That coalescence did occur during the heat treatment is readily verified by comparing Figures 2 and 3, scanning electron micrographs taken before and after the heat treatment of a coating containing 20 pph latex and dried at room temperature. Above 30 pph latex content, however, shrinkage of the coating thickness begins.

The large difference in structural collapse between the wet coalesced and sintered coatings is noteworthy. It is speculated that in the wet coalescence process, the liquid–water phase plays an important role in distributing the surface-tension-induced stresses throughout the coating structure and this leads to an overall shrinkage of the structure. In contrast, in the sintering process, only when there is enough latex present around the clay particles to form a continuum will the local stresses induced by the polymer–polymer and polymer–clay interfacial tensions be distributed evenly. This would seem to happen above 30 pph latex content according to Figure 1.
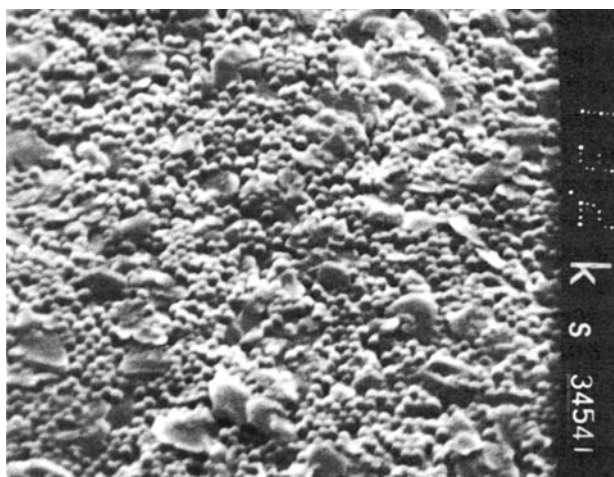

Fig. 2. Surface of coating containing 20 pph latex dried below latex MFT, before heat treatment (13,000×).
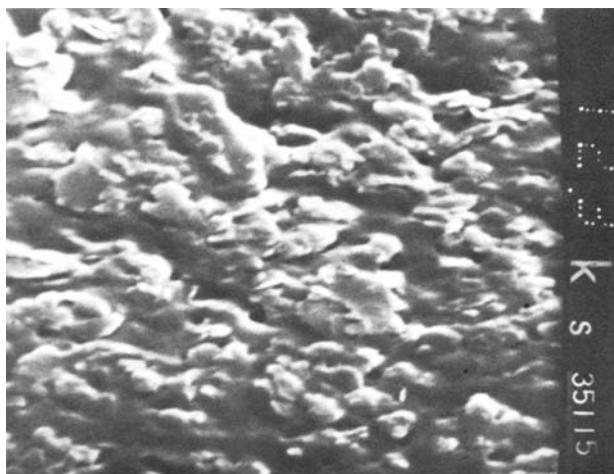
Fig. 3. Coating of Fig. 2 after heat treatment (13,000×).

Surface Morphology and Gloss

Figure 4 shows the 75° gloss of coatings containing increasing amounts of latex as a function of the processing conditions. The gloss of the coatings dried above the latex MFT decreased continuously with latex addition as is normally found on coatings formulated with conventional film-forming latexes.[3]

The gloss of the coatings dried below the latex MFT increased gradually with latex content. This is what is normally found with clay coatings containing 0.2-μm plastic pigments.[5] After heat treatment, a drop in gloss accompanies the sintering of the latex, very small at low latex content but greater as the latex content increases.

Examination of the surfaces of coatings containing 20 pph latex (Figs. 2, 3, and 5) shows that the gloss values reflect the difference in surface morphology. The coating dried at room temperature is very smooth (Fig. 2). After the heat treatment (Fig. 3), the latex particles have fused into a continuous film but the surface remains quite smooth. In contrast, the wet coalesced coating (Fig. 5) shows a rugged relief, the result of the structural collapse discussed earlier.
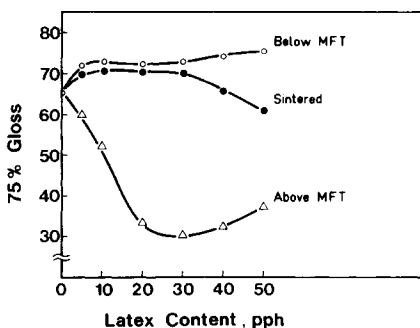

Fig. 4. 75° gloss of clay coatings containing increasing amounts of latex as function of processing conditions.
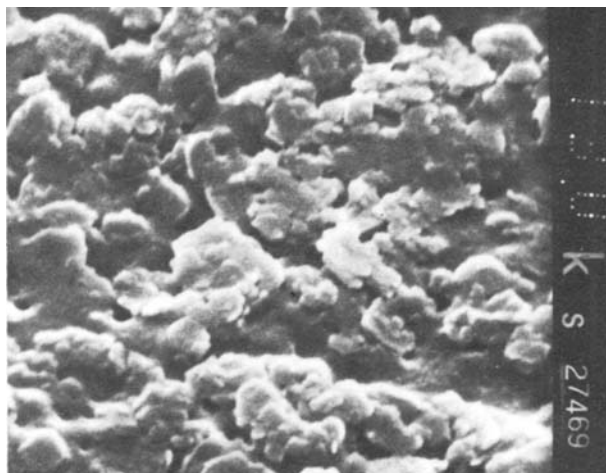
Fig. 5. Surface of clay coating containing 20 pph latex dried above latex MFT.
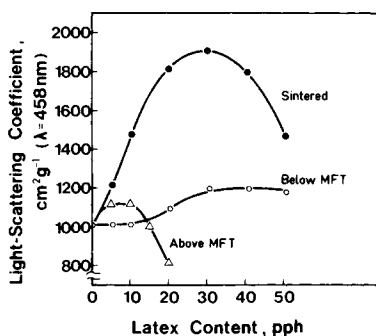

Fig. 6. Light-scattering coefficient of clay coatings containing increasing amounts of latex as function of processing conditions (λ = 458 nm).

Light Scattering

Figures 6 and 7 show the light-scattering coefficient at 458 and 548 nm of coatings containing increasing amounts of latex as a function of the processing conditions.

Again, the curve for the wet coalesced coatings—a maximum followed by a sharp decline—is typical of coatings formulated with a conventional film-forming
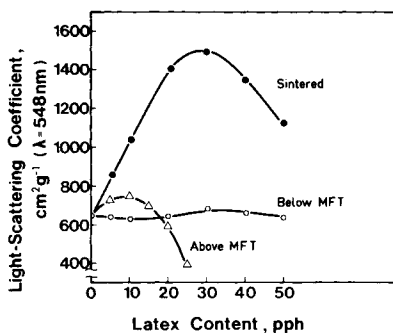

Fig. 7. Light-scattering coefficient of clay coatings containing increasing amounts of latex as function of processing conditions (λ = 548 nm).

latex.[3] Similarly, the values obtained for the coatings dried below the latex MFT
are typical of blends of clay and 0.2-μm plastic pigments.[5]

The large increase in the light-scattering coefficient following the heat treat-
ment is striking and certainly unexpected, particularly when one keeps in mind
that the opaque film of the pure latex dried at room temperature becomes
transparent upon heating.

If, as done traditionally, one looks at the pigment particles in a paper coating
as the sites for light scattering, then the opacity increase accompanying the
disappearance of the spherical particles becomes very difficult to explain. On
the other hand, if one considers the coating as a dispersion of air voids of various
shapes in a matrix of refractive index ~1.6 (formed by the clay and the polymeric
spheres), then an explanation is found.

In the uncoalesced coating, the voids are those found between the spheres and
between the spheres and the kaolin plates. An equivalent spherical diameter
(esd) may be calculated simply as 6 V/A, where V is the specific void volume,
cm^3/g, and A is the specific internal surface area, cm^2/g, measured by nitrogen
adsorption. For an uncoalesced coating containing 30 pph of latex (void volume
fraction, 0.36; surface area, 14 m^2/g), an esd of ~0.14 μm is obtained.

After the heat treatment, the nitrogen surface area dropped from 14.0 to 8.8
m^2/g with no change in void volume so that the esd of the average void increased
to 0.21 μm. According to the data given by Ross,[6] the calculated scattering
coefficient (λ = 560 nm) for spherical air bubbles dispersed in a resin of refractive
index 1.5 increases by a ratio of approximately 1.8 when the air-bubble diameter
increases from 0.14 to 0.21 μm. Figure 7 shows that the light-scattering coeffi-
cient (λ = 548 nm) increased from 700 to 1500 cm^2/g, a factor of 2.

From the polymer rheology viewpoint, the heat treatment has induced the
coalescence of the latex. From the optical viewpoint, the heat treatment has
induced the coalescence of the small air voids into larger size voids without af-
fecting their total volume. Figure 8 illustrates how this might happen.

Further support for this concept may be found in the dependence of the
light-scattering coefficient on the wavelength of light, see Table I. The heat
treatment is seen to increase the scattering by 150% at 700 nm and only by 24%
at 400 nm. This reflects a change in the distribution of scattering sizes towards
larger values.

Finally, the decline in the light-scattering curve above 30 pph corresponds to
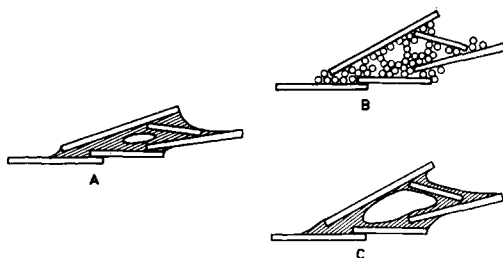the drop in the void volume fraction shown on Figure 1.

Fig. 8. Suggested representation of structural changes in coating produced by heat treatment:
(A) wet coalesced coating, (B) noncoalesced coating, (C) sintered coating.

TABLE I
Dependence of Light-Scattering Coefficient on Wavelength of Light

	Light-Scattering Coefficient, $cm^2\,g^{-1}$			
Wavelength, nm	400	500	600	700
Uncoalesced coating	1850	950	570	400
After heat treatment	2300	1800	1370	1000
Increase, %	24	89	140	150

Brightness

The brightness of a coating is a function of the ratio of the light-scattering to the light-absorption coefficients. Since the light absorption coefficient did not change with heat treatment, the brightness ($\lambda = 458$ nm) increased concurrently with the light-scattering coefficient after the heat treatment, as shown on Table II.

Oil Permeability

Figure 9 shows the time required for the absorption of a 1-μm thick film of oil into the coatings. Here again, the increase in absorption time with the latex content observed with the wet coalesced latex is in accordance with the results obtained with conventional film-forming latexes.[4] Similarly, the slow decrease in oil absorption time for the noncoalesced latex is typical of that measured on clay–plastic pigment coatings. However, it was unexpected that the sintering process would not change the absorption characteristics (except above 40 pph latex content). Presumably, the slowing-down effect of the closing of the small channels is offset by the accelerating effect of the increase in the average size of the pores.

Solvent Exposure

When a dry, uncoalesced clay coating containing 20 pph latex was exposed to benzene vapor, the scattering coefficient ($\lambda = 458$ nm) of the coating increased from 1100 to 1700 cm^2/g. Benzene, a swelling agent for the styrene/butadiene polymer, lowers its glass-transition temperature and promotes coalescence of the latex particles. This is then equivalent to a thermal treatment.

TABLE II
Brightness versus Processing Conditions

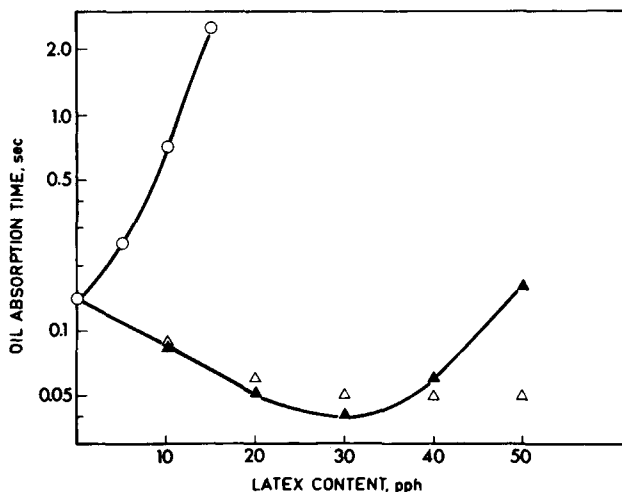| Latex content, pph	Brightness		
	"Wet" coalesced	Uncoalesced	Sintered
10	0.817	0.810	0.839
20	0.781	0.826	0.857
30	0.63	0.834	0.864
40	—	0.837	0.860

Fig. 9. Time required for absorption of 1-μm film of oil as function of processing conditions. Oil viscosity: 0.14 Pa sec at 20°C (see ref. 6 for test procedure). O, Wet coalescence; $\triangle$, uncoalesced; $\blacktriangle$, sintered. '

CONCLUSION

It has been shown that the structure and properties of a pigmented latex coating are quite different when the coalescence of the latex particles takes place after the drying stage, rather than concurrently with the drying.

The improvement in the optical properties (gloss, opacity, and brightness) are quite marked. The commercial applications are clear. Using this process (a patent covering this process has been filed), one may meet given optical specifications for a coated paper at a lower coat weight, or with a substrate of inferior optical properties.

The influence of the size of the latex particles on the opacifying effect will be discussed in Part II of this series.

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