# Sintering of Latex Particles in Pigmented Coatings. II. Influence of the Latex Particle Size

B. ALINCE and P. LEPOUTRE, *Pulp and Paper Research Institute of Canada, Pointe Claire, Quebec, Canada H9R 3J9*

## Synopsis

The light-scattering coefficient $S$ of coatings formulated from a mixture of an inorganic pigment and polystyrene latex particles may be enhanced significantly when the dry coating is heated in order to cause sintering of the polystyrene spheres. The relative increase in $S$ depends on the size and the amount of the latex particles and the type of the inorganic pigment. Of the latexes examined (0.5, 0.2, 0.1, and 0.03 $\mu$m in diameter) the 0.2$\mu$m latex is the most effective in blends with platelike delaminated clay. The coatings based on spherelike precipitated calcium carbonate are less responsive to the heat treatment. The gloss of the clay–latex coatings is not significantly altered by the heat treatment up to 20 pph of latex; the gloss of the calcium carbonate coatings generally decreases upon heating.

## INTRODUCTION

In part I of this series[1] it was reported that when a pigmented latex coating was dried below the filming temperature of the latex and was subsequently heated above this temperature, a considerable increase in opacity was observed and the coating acquired strength. The opacity enhancement was explained by a change in the void structure. The sintering of the latex particles that occurred during the thermal treatment led to the formation of larger voids, more efficient in scattering the light. The effect was more striking when the pigment was platelike delaminated clay rather than spherelike precipitated calcium carbonate.

Here attention is paid to the influence of the size of the latex particles on the changes in optical properties brought about by the sintering of the latex.

It has been shown elsewhere[2] that the porosity and optical properties of binder-free coatings formulated from a mixture of inorganic pigment and polystyrene spheres differ considerably depending on the size and the amount of the polystyrene particles as well as the shape of the inorganic pigment. It is expected that upon sintering of the latex particles, the size and distribution of the optically active air voids will vary with the structure of the composite prior to the heat treatment.

## EXPERIMENTAL

Coatings were prepared from mixtures of aqueous suspensions of inorganic pigment and polystyrene latex particles applied with a metering rod on a polyester film. The inorganic pigments used were delaminated clay (Alphaplate, Anglo-American Clays) and precipitated calcium carbonate (Albagloss, Pfizer) dispersed at 60% solid. The latexes (Lytron 2501, 2203, 2101, and 604, Monsanto)

of particle size 0.5, 0.2, 0.1, and 0.03 $\mu$m, respectively, were added in increasing amount to either clay or $CaCO_3$ dispersions. Prior to admixing, the latexes were treated with 5% (on latex solids) poly(vinyl alcohol) in order to improve the cohesion of the coatings.

The coatings were dried at room temperature and subsequently exposed for 5 min to 150°C in an oven to cause sintering of the polystyrene spheres.

Compositions are expressed as weight parts of latex per 100 parts of inorganic pigments. In the graphs the curves are constructed from experimental data obtained on samples containing 5, 10, 20, 30, 40, and 50 pph latex.

The light-scattering coefficient was calculated from reflectance measurements (Spectronic 505) against black and white backgrounds using the Kubelka–Munk theory corrected for the polyester film.[3] Gloss was determined at 75°, on a Hunter glossmeter. Nitrogen surface area was measured by a dynamic gas chromatography method. Porosity was determined from the amount of the oil held by the coating.[4]

## RESULTS AND DISCUSSION

### Light Scattering

The apparent paradox that the scattering power of the mixtures of clay and latex particles increased when the polymeric spheres became optically ineffective upon forming a transparent film has been explained by the formation of a more effective void structure.[1] In Figure 1 the cross sections of fractured coatings illustrate the development of larger voids when the individual latex particles disappear and form a film. Obviously, the size and the distribution of the resulting voids will depend on the mutual accommodation of the two solid compounds prior the heat treatment. Thus, the coating can be described as a solid matrix containing microvoids.

Because the refractive indices of both solids are similar (clay = 1.56, polystyrene = 1.59), the scattering occurs on the solid–air interface and the voids are the actual scattering species. The optical theory, applied to a system consisting of voids dispersed in a solid, shows that for each wavelength there is an optimum void size at which the scattering of light is maximum. Experimental measurements[5] on model coatings prepared from a variety of polystyrene latex particles confirmed the theoretical prediction[6,7] that the optimum void size is in the vicinity of 0.2 $\mu$m in diameter when the refractive index of the solid is about 1.6.

The scattering efficiency of a coating will therefore depend on the void size distribution and when it is expressed per unit mass of coating (as is conventionally done in paper coatings), obviously also on the number of voids per unit mass of the coating, i.e., the total air–solid interface available for scattering. Since the specific scattering coefficient is a function of both void size and void volume, it is conceivable that a coating containing less effective but more numerous voids may be as effective as a coating having more effective but less numerous voids.
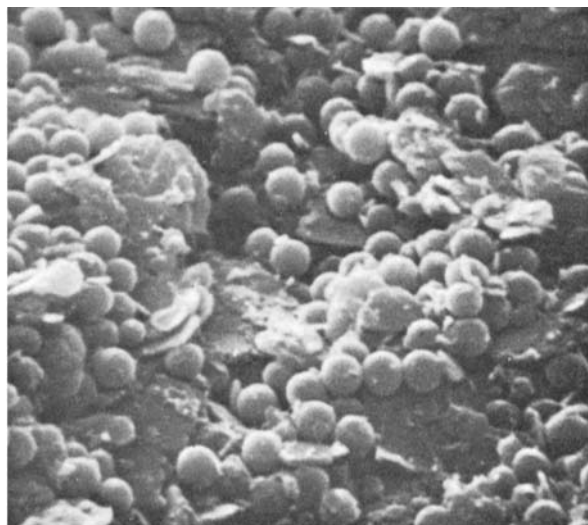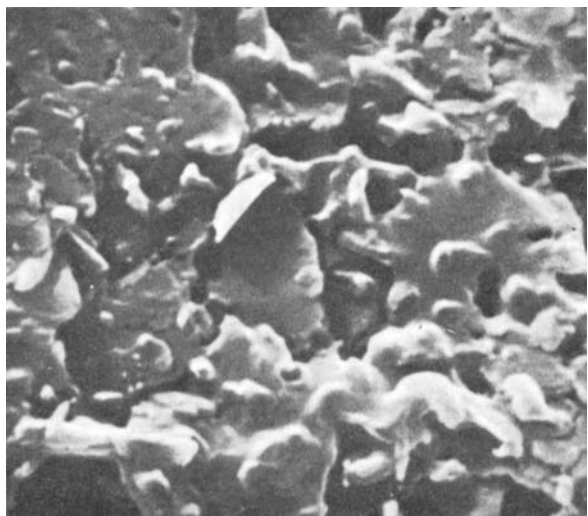
Fig. 1. Development of voids within a coating formulated from delaminated clay and 50 pph polystyrene latex particles 0.5 $\mu$m in diameter. SEM cross section of the fractured coating dried at 20°C (A) and then heated at 150°C for 5 min (B).

## Clay–Latex

The variation of the light scattering coefficient $S$ (cm$^2$/g) at 458 nm, expressed in units of reciprocal mass per area, is shown in Figure 2 as a function of latex content for the four latexes examined. The dashed lines represent data for coatings dried at room temperature[2]; the full lines are constructed from data obtained upon heating at 150°C for 5 min to cause sintering of the latex particles. Except for the blends with 0.5 $\mu$m latex particles, the scattering efficiency is enhanced and there is an obvious dependence on the size and the amount of the latex present.

The most dramatic effect in $S$ upon heating is observed with the 0.2-$\mu$m latex
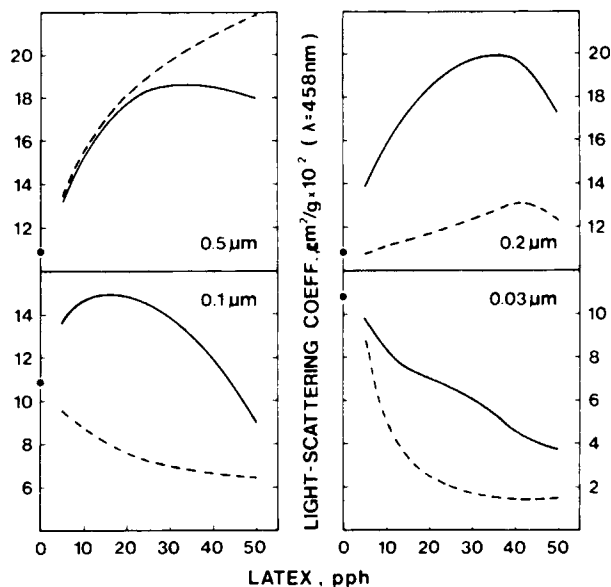
Fig. 2. Variation in light scattering coefficient $S$ (cm$^2$/g) at 458 nm of clay coatings blended with increasing amount of polystyrene latex particles 0.5, 0.2, 0.1, and 0.03 $\mu$m in diameter. Broken lines—coatings dried at 20°C; solid lines—dry coatings heated at 150°C for 5 min.

particles. As seen in Figure 2, $S$ gradually increases with latex addition up to 40 pph. An increase in the average void size toward the optimum size is apparently responsible for the improved light scattering. It was shown in part I[1] that the average spherical void diameter of a clay coating containing a nonfilming latex of 0.2 $\mu$m particle size increased from 0.14 to 0.21 $\mu$m upon heating above the film-forming temperature of the latex. The drop in $S$ above 40 pph latex content was explained by a concurrent drop in the void content of the coating during the sintering of the latex particles.

Coatings formulated with 0.1-$\mu$m latex particles show a considerable improvement up to 20 pph. Although at this content the relative increase in $S$ from 750 to 1500 cm$^2$/g is the largest among all the compositions investigated here, the absolute values remain below those obtained with the 0.2- and 0.5-$\mu$m latex particles. The coatings containing the 0.03-$\mu$m latex particles are optically inferior. The very small spheres may fill effectively the available space among the clay particles thus producing a densely packed structure. The porosity of such unheated mixtures was found to decrease considerably with the latex content,[2] and the obvious result is a structure composed of very small voids. Upon

TABLE I
Characteristics of a Coating: 50 Parts 0.5-$\mu$m Latex/100 Parts Clay

|  | Dried at 20°C | Heated at 150°C |
| --- | --- | --- |
| Void volume $V$, cm$^3$/g[a] | 0.383 | 0.368 |
| Internal surface area $A$, m$^2$/g[b] | 10.3 | 6.2 |
| Equiv. void diameter, $d$, $\mu$m[c] | 0.22 | 0.36 |

[a] Oil impregnation technique.[4]
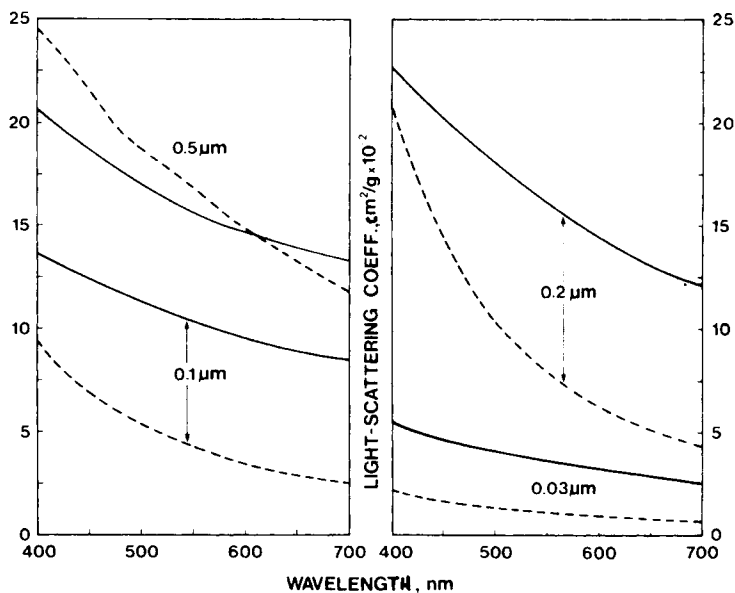[b] Nitrogen adsorption.
[c] $d = 6\ V/A$.

Fig. 3. Variation of light scattering coefficient $S$ (cm$^2$/g) with wavelength of clay coatings blended with 40 pph polystyrene latex particles 0.5, 0.2, 0.1, and 0.03 $\mu$m in diameter. Broken lines—coatings dried at 20°C; solid lines–dry coatings heated at 150°C for 5 min.

heating, the voids may increase in size but still remain far below the optimum size.

In the case of blends with the 0.5-$\mu$m latex particles (a size that is very effective in unheated coatings), the heat treatment does not result in a change of $S$ up to 20 pph addition. This suggests that upon heating the void structure remains equally effective. Above 20 pph latex, the observed decrease in $S$ upon heating is likely due to development of less favorable void structure. The data in Table I indicate that in the unheated sample containing 50 pph latex the average spherical void diameter of 0.22 $\mu$m is close to the optimum size, but upon heating it increases to 0.36 $\mu$m. In addition, there is also a decrease in the internal specific surface area (that can be related to the scattering interface) and a slight decrease in the void volume.

The general assumption here is that the average void size of the investigated coatings increases when exposed to a temperature at which sintering of the latex particles occurs. When the average void size of the unheated sample is below the optimum size, the light-scattering efficiency upon heating will be enhanced as seen in case of 0.2, 0.1, and 0.03-$\mu$m latex particles. Alternatively, the average void size may increase beyond the optimum as in the case of 50 pph 0.5-$\mu$m latex particles (Table I), and then the light scattering efficiency decreases. In addition, a simultaneous change in the specific void volume may, of course, affect the resulting scattering efficiency.

TABLE II
Change in $S_{400}/S_{700}$ Due to Heating of Coatings: 40 Parts Latex/100 Parts Clay

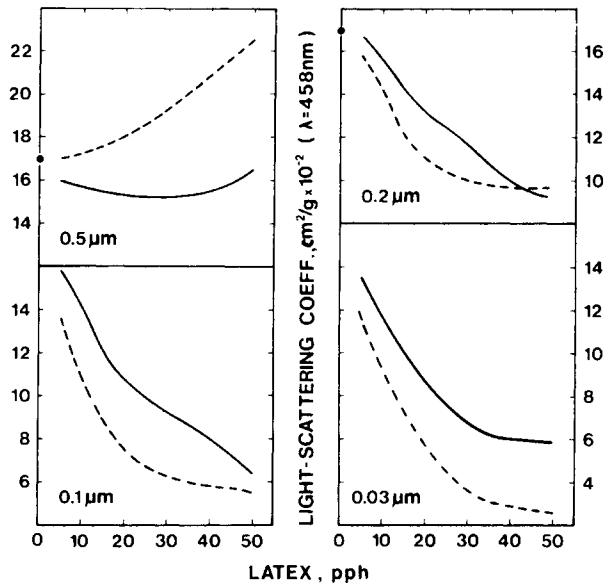| Latex particle $d$, $\mu$m | 0.03 | 0.1 | 0.2 | 0.5 |
|---|---|---|---|---|
| Dried at 20°C | 3.33 | 3.54 | 5.19 | 2.08 |
| Heated at 150°C | 2.08 | 1.59 | 1.90 | 1.58 |

Fig. 4. Variation in light-scattering coefficient $S$ (cm²/g) at 458 nm of CaCO₃ coatings blended with increasing amount of polystyrene latex particles 0.5, 0.2, 0.1, and 0.03 μm in diameter. Broken lines—coatings dried at 20°C; solid lines—dry coatings heated at 150°C for 5 min.

The redistribution of voids toward a larger average size upon heating can be substantiated by examining the variation of $S$ with wavelength λ. As an example, Figure 3 shows the variation of $S$ with wavelength for samples containing 40 pph latex. The broken lines are for samples dried at room temperature; the full lines are for the same samples after heating. The argument here is based on the relation between the wavelength λ and the optimum void size, that is, the smaller voids are relatively more effective at shorter λ, and vice versa.[3] The ratio
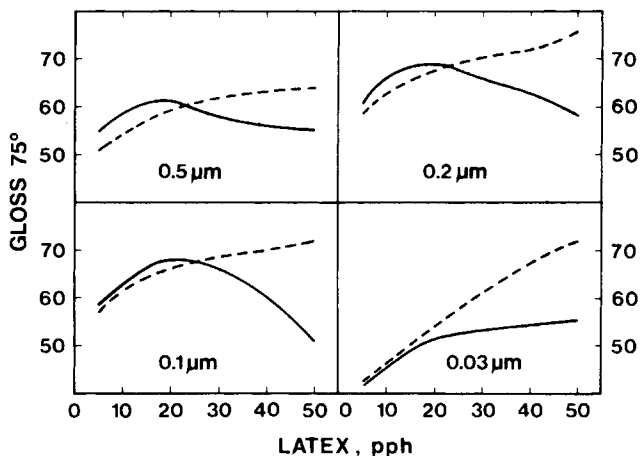


Fig. 5. Gloss (75°) of clay coatings blended with increasing amount of polystyrene latex particles 0.5, 0.2, 0.1, and 0.03 μm in diameter. Broken lines—coatings dried at 20°C; solid lines—dry coatings heated at 150°C for 5 min.
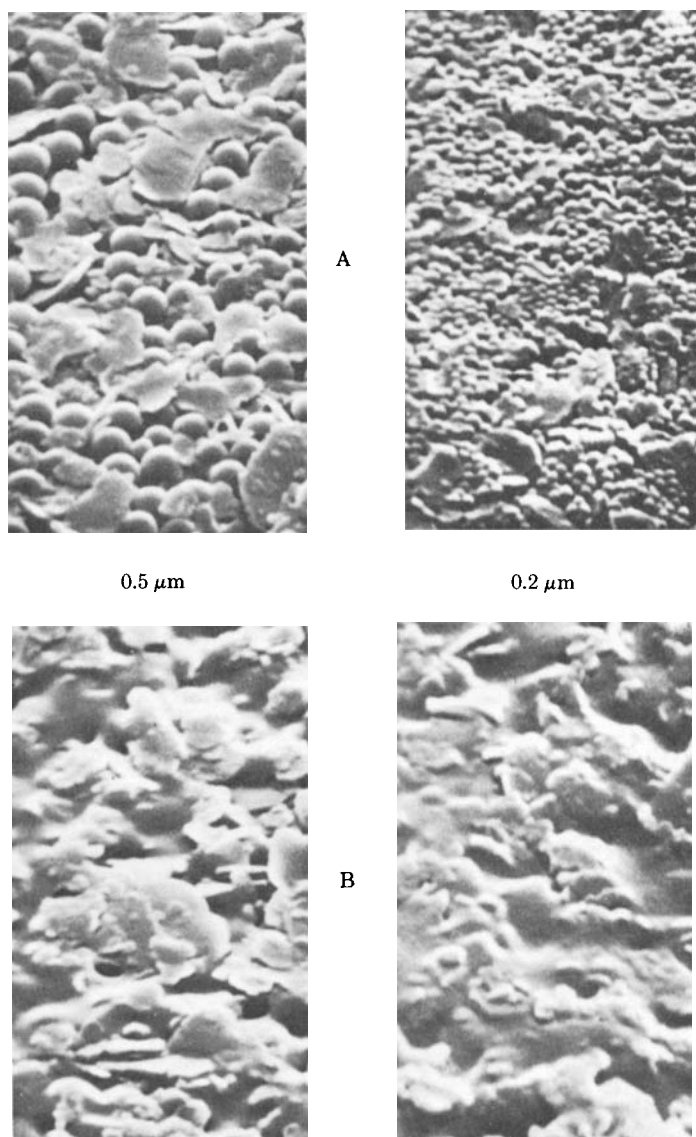
Fig. 6. Surface of clay coatings containing 50 pph polystyrene latex particles 0.5 and 0.2 $\mu$m in diameter dried at 20°C (A) and then heated at 150°C for 5 min (B).

of $S$ at 400 nm to $S$ at 700 nm may then provide, to some extent, an indication of the relative contribution of different voids to the total scattering. Thus, if the $S_{400}/S_{700}$ decreases upon heating, this is interpreted as a redistribution of the void structure toward a larger void size. In Table II, the $S_{400}/S_{700}$ of coatings containing 40 pph latex is shown to decrease in all cases. The most pronounced change is noticed on the coating formulated with the 0.2-$\mu$m latex particles.

Examination of Figure 3 also reveals that the curve for the heated sample containing the 0.2-$\mu$m latex becomes similar to the curve of the unheated sample containing the 0.5-$\mu$m latex particles. This indicates that the effective void structures of both coatings are similar.

## $CaCO_3$–Latex

Coatings formulated from a mixture of precipitated calcium carbonate and polystyrene latex particles do not respond to the heat treatment in the same way as the clay coatings. In Figure 4 the light-scattering coefficient is shown as a function of latex content. With the exception of the 0.5-$\mu$m latex particles, some improvement of $S$ takes place, but all the values remain below that of the pure $CaCO_3$. The results show that, overall, these blends do not offer the same advantage as those with clay. Because of the difference in the shape of the two inorganic pigments, a different packing arrangement can be expected. The platelike clay particles apparently do not mix well with the polystyrene spheres and tend to form a more open structure in their presence.[2] Such structure offers a better opportunity to form effective voids when latex spheres are transformed into a film. On the other hand, the mutual accommodation of the spherelike precipitated $CaCO_3$ and the polymeric spheres results in a higher packing density. When the polymeric spheres occupy the interstices between the $CaCO_3$ particles, the void volume fraction decreases progressively with increasing addition of the polystyrene latex.[2] The size of voids that may form upon heating is then likely restricted within such a closely packed system.

## Gloss

### Clay–Latex

Figure 5 illustrates the effect of heat treatment on the gloss of clay coatings containing latex particles of different sizes. The dashed lines represent coatings dried at room temperature; the solid lines are data obtained after the sintering stage. At lower levels of latex addition the gloss upon heating remains unchanged
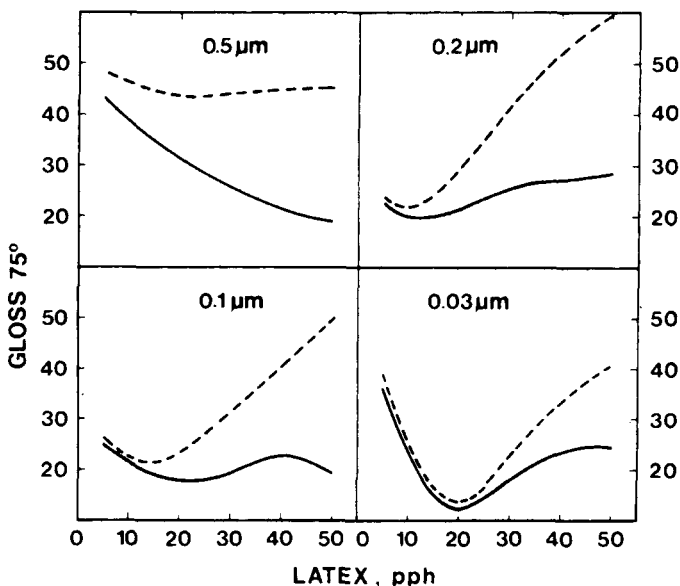


Fig. 7. Gloss (75°) of $CaCO_3$ coatings blended with increasing amount of polystyrene latex particles 0.5, 0.2, 0.1, and 0.03 $\mu$m in diameter. Broken lines—coatings dried at 20°C; solid lines—dry coatings heated at 150°C for 5 min.
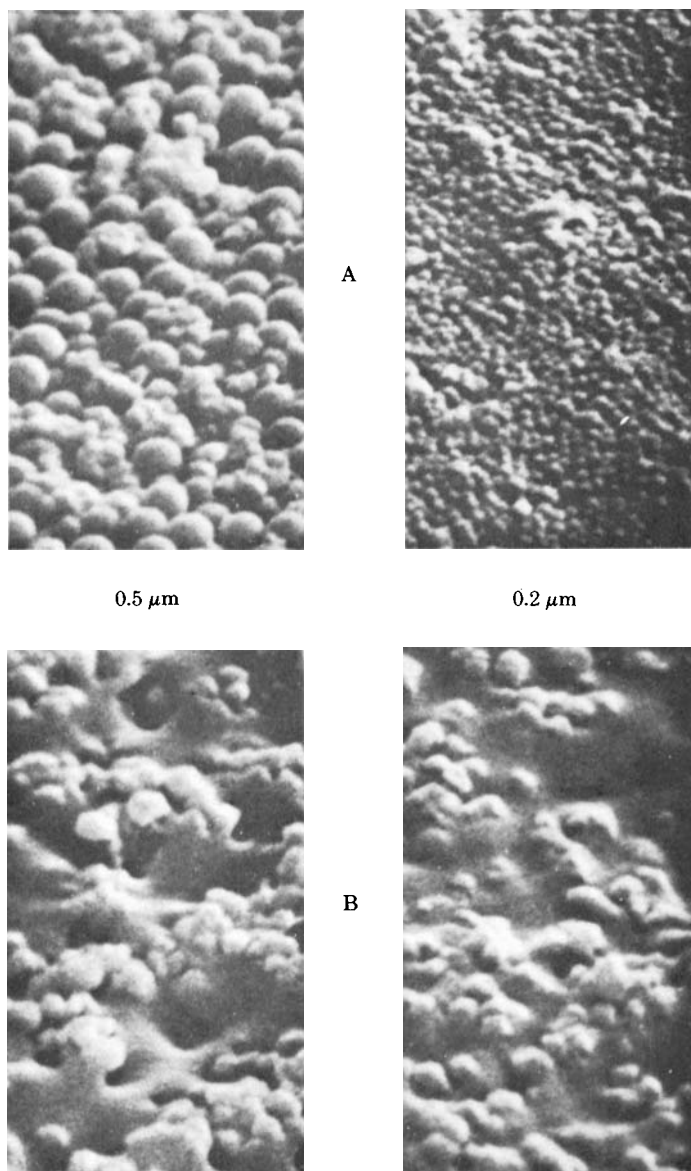
0.5 μm                                    0.2 μm

Fig. 8. Surface of CaCO₃ coatings containing 50 pph polystyrene latex particles 0.5 and 0.2 μm in diameter dried at 20°C (A) and then heated at 150°C for 5 min (B).

and even may increase, while at higher latex content a drop in gloss is observed.

The change in gloss likely reflects the change in the surface morphology of the coating. A direct observation of electron microscopy reveals the difference in the surface roughness upon heat treatment. In Figure 6 are shown the surfaces of clay coatings blended with 50 pph of 0.5- and 0.2-μm latex before and after the heat treatment. When the latex particles are transformed into a film, the surface becomes rugged and consequently the gloss decreases.

*CaCO₃–Latex*

The change in gloss development upon heating follows qualitatively a trend similar to coatings based on clay. As shown in Figure 7, the difference in gloss before and after heating increases with increasing latex content. It is obvious from the micrographs in Figure 8 that when the latex particles form a film, the underlying inorganic pigment affects the surface smoothness considerably.

## CONCLUSIONS

The improvement in the light-scattering coefficient of pigmented latex coatings, dried below the latex filming temperature and subsequently heated above this temperature, depends on the size and number of the latex particles and the shape of the inorganic pigment. In blends with delaminated clay, latex particles 0.2 $\mu$m in diameter produce the largest increase in light scattering upon heating. The blends based on precipitated calcium carbonate are far less responsive, and the light scattering remains below that of the pure inorganic pigment.

Polystyrene latexes (called plastic pigments) are increasingly used in paper coatings in combination with clay or $CaCO_3$ because of their low specific gravity and the higher gloss they confer to the coating. This work suggests that added benefits would be derived by subjecting such coatings to a heat treatment designed to cause sintering of the latex particles.

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