Correlation of Hardness with MFFT And CPVC of Latex/Ceramic Coatings

Ming Lei, Lorraine F. Francis,† and L.E. Scriven—University of Minnesota*

Hardness, porosity, and microstructure of film-forming in polyvinyl acetate/alumina coatings from aqueous suspensions were investigated with a minimum film formation temperature (MFFT) bar, Vickers hardness tester, and scanning electron microscopy (SEM). The hardness of opaque composite coatings (alumina:latex = 1:2 by volume) increased abruptly at the MFFT of the latex, suggesting that the alumina particles did not change the latex film formation behavior and that the hardness measurement is an alterative to the optical criterion. Studies of coatings from latex particles that were smaller or larger than a common size of ceramic particles indicated that the composition of maximum hardness, called critical Vickers hardness concentration (CVHC), matched conventional critical pigment volume concentration (CPVC). More efficient polymer binding in the coatings from the smaller latex gave them higher peak hardness and CPVC.

INTRODUCTION

The incorporation of ceramic particles into latex coatings can impart or improve properties, thereby broadening the applications of the resulting coatings. For instance, clay or alumina particles enhance smoothness, brightness, and ink receptivity in paper coatings,[1] while titania particles opacify latex paints.[2] In the processing of composite coatings, the microstructure is developed during drying. Latex particles can consolidate, deform, and coalesce into a continuous, dense film,[3,4] while ceramic particles do not. When drying a coating of ceramic particles, the particles pack together, but they do not deform and the dried coating is porous and weak. In a composite coating, deforming latex particles can bind the ceramic particles together, and if enough polymer is present (i.e., the ceramic content is low enough), the composite can become dense as the polymer fills in the spaces between the ceramic. Therefore, the deformation behavior of the latex that leads to "film formation" and coalescence, and the amount of the ceramic relative to the polymer are two important factors in the microstructure development of composite coatings.

Few studies have addressed the change called film formation and the degree of polymer coalescence in composite coatings. In coatings of latex alone, three main stages of forming a continuous polymer coating have been identified: consolidation, deformation (better termed compaction), and coalescence.[3,4] Lepoutre et al.[5] showed that in coatings made of clay and latex, the latex does not simply fill in the spaces between the clay particles. At low volume fractions the added latex prevents the collapse of the network formed by the clay particles and the amount of latex needed to create what they called a dense coating is twice that needed to fill the porespace of a collapsed network, i.e., of a compacted layer of clay particles. The time required for film formation was found to be roughly independent of pigment volume concentration and particle size.[6] Using cryogenic scanning electron microscopy (cryo-SEM), Sheehan et al.[7] studied the deposition and adsorption of carboxylated latex particles on the surfaces of calcium carbonate particles. They found that the extent of carboxylation affects particle deformation and spreading on calcium carbonate surfaces. Granier and Sartre[8] observed that spreading latex particles above polymer T_g can be promoted by increasing the density of acrylic acid groups on their surfaces. However, the effect of both clay and ceramic particles on the state of latex par-

*Department of Chemical Engineering & Materials Science, 421 Washington Ave., SE, Minneapolis, MN 55455-0132.
†Author to whom correspondence should be sent.

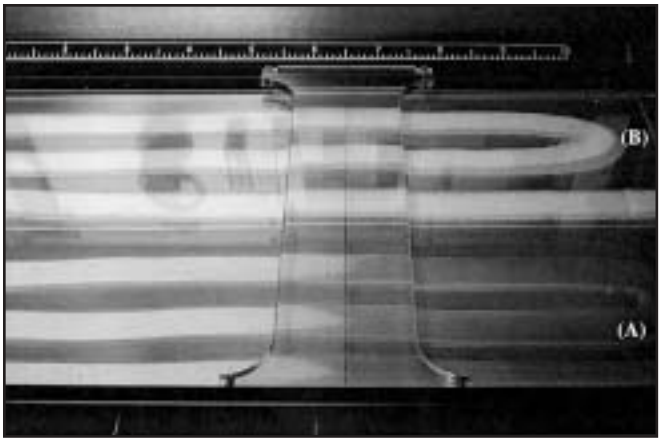

Figure 1—Films on an MFFT bar with a temperature gradient (the scale numbers correspond to drying temperatures). (A) Latex. At lower temperatures than MFFT (left), the films are opaque; at higher temperatures (right), transparent films are formed. (B) Latex/Alumina (33 vol% Al_2O_3) coating. There is no transition point in all the temperature range.

ticles called "formed film" is still uncertain. In the first part of this article, minimum film formation temperature (MFFT), above which a continuous film forms from latex, was correlated with Vickers hardness change. The effect of alumina particles on latex film formation was investigated by means of Vickers hardness tester and an MFFT bar. Low voltage SEM was also employed to examine the microstructures before and after film forming.

Hardness can also relate to the critical pigment volume concentration (CPVC) of composite coatings. Although the ceramic particles in this research are not intended to serve as pigments, the traditional concept of CPVC is appropriate for interpreting the microstructure and properties of coatings. Different mixing ratios of ceramic and latex, which serve as binders, produce a series of composite coatings with different microstructures, ranging from porous, mostly ceramic coatings to dense, mostly polymer coatings. The properties of the coating, in turn, depend on the microstructure. From above to below CPVC, most properties of composite coatings undergo a significant change. This change has been ascribed to the onset of air-filled porespace, or "voids," in coatings.[9] At this critical concentration, there is just adequate binder to fill all the space between the ceramic particles in the completely solidified coating, and those particles are consolidated, or packed, as in a random dense packing. At the CPVC, there are usually dramatic changes in coating properties, such as density,[10] tensile strength,[11] porosity,[12] and gloss,[9] which can be used to determine the CPVC value. Vickers hardness measurement, being a simple and nearly nondestructive test, provides a new method to determine the CPVC value. It can even be correlated with yield stress,[13,14] which is an important property of coatings. Above the CPVC, there is an insufficient amount of binder to fill in all the interstitial voids between ceramic particles and the coating is porous. However, mechanical strength may decrease due to the presence of connected porespace or even isolated pores[15] as well as insufficient adhesion between particles.

In the second part of this article, microscopy is employed to correlate CPVC and Vickers hardness change. An investigation of two systems, large ceramic particles with small latex particles and small ceramic particles with large latex particles, provides a case study of the attainment of porosity and strength in composite coatings. Their microstructures and mechanical strength, characterized by hardness, are compared to aid in obtaining a porous coating with adequate mechanical strength.

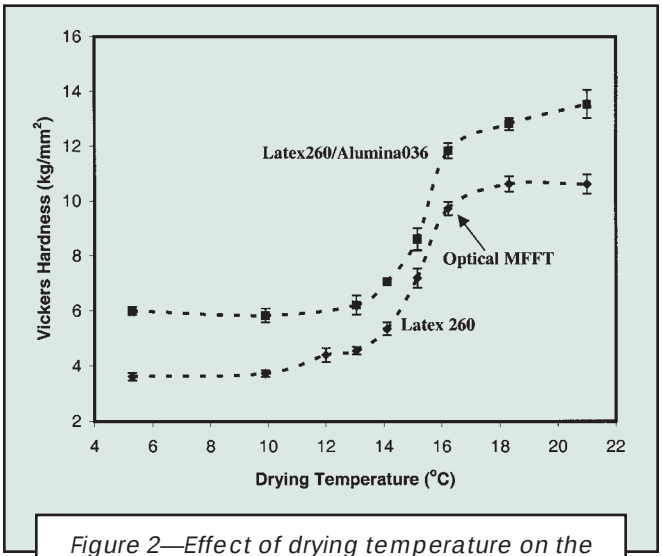

Figure 2—Effect of drying temperature on the hardness of Latex260 and Latex260/Alumina036 (33 vol% Al_2O_3) coatings. Hardness measurements taken on coatings dried on a temperature gradient bar.

EXPERIMENTAL

Materials

Two polyvinyl acetate (PVAc) latex starting materials were used in this work. Vinac XX-210 (Air Products & Chemicals Co., Allentown, PA) is a polydisperse latex stabilized with polyvinyl alcohol (PVA); the volume average particle size, Dv, is 2.60 μm and number average size, Dn is 1.11 μm, as determined by a particle analyzer (Coulter LS230, Coulter Corp., Miami, FL). Polydispersity index of this latex, Dv/Dn, is 2.34. The solids content of the aqueous-based latex is 55 wt% and the polymer T_g is 35°C. The second latex, Vinac 884 (Air Products), is also polydisperse with a volume average particle size of 0.19 μm and polydispersity index of 1.07; the particles are stabilized by an anionic surfactant. The solids content of the aqueous suspension is 51 wt% and the polymer T_g is 33°C. In this article, Vinac XX-210 and Vinac 884 are referred to as Latex260 and Latex019, designations that highlight the particle size.

Two alumina (α-Al_2O_3) powders were used. APA 8AF and APA-0.5 (Condea Vista Co., Houston, TX) have

volume-average particle sizes of 1.0 and 0.36 µm and polydispersity indexes of 3.30 and 3.19, respectively. APA 8AF and APA-0.5 are referred to here as Alumina100 and Alumina036. Sodium polymethacrylate (DARVAN7; R.T. Vanderbilt Co., Norwalk, CT) was used as the dispersing agent in alumina suspensions.

Suspension Preparation

Aqueous suspensions containing latex and alumina were prepared in a two-step procedure. First, the alumina powders were dispersed at 50 wt% solids in distilled water. The polyacrylate dispersant was added (1 wt% relative to the alumina) and the suspension was stirred by a spinning magnetic bar for four hours. Sodium polyacrylate ionized in the suspension, adsorbed onto the surface of alumina particles, and produced electrosteric repulsion to give a good dispersion.[16] Second, a calculated amount of latex suspension was added to the dispersion as it was stirred, and the mixture was stirred for one additional hour. Composite suspensions were prepared with various volume percentages of alumina relative to the total solids volume. For example, a suspension containing 39.5 g of the aqueous alumina suspension and 20.5 g of Latex260 yielded a suspension with a solids content of 33 vol% alumina and 67 vol% latex. The volume percents were calculated by taking the density of alumina to be 3.98 g/cm^3 [17] and that of polyvinyl acetate to be 1.12 g/cm^3 (as measured).

Coating Preparation for MFFT Measurement

A Rhopoint™ minimum film temperature tester (model MFFT-60 from Rhopoint Instrumentation Ltd., UK) was used to produce a temperature gradient during the drying of pure and composite coatings. The MFFT bar is a nickel-plated copper platen. In use, the bar is covered with a glass plate that serves as the substrate. Dry air flows over its surface, from cool end to warm end, to maintain a low and uniform humidity. A steady temperature gradient is established over the bar; the temperature range chosen was 5° to 23°C over a scaled length of 34.5 cm. Every position on the substrate corresponds to a drying temperature that can be determined from the gradient. According to the ASTM D 2354-98 standard,[18] suspensions are generally cast, or coated, on the glass substrate by a 75 µm cube applicator. The MFFT is taken as the temperature (position on the bar) at which, after two hours of drying, the latex coating changes in appearance from milky at lower temperature to clear at higher temperature; that is, at and above the transition temperature the coating has formed a microstructure in which the pores are too small to appreciably scatter light. In coatings that contain ceramic particles, optical clarity cannot be used to assess film formation.

Coatings of Latex260 and Latex260/Alumina036 (33 vol% alumina) were prepared by casting aqueous suspensions onto the temperature gradient bar and their MFFTs were assessed by the optical method when the latex alone was used, or by hardness testing (see below). Coatings prepared with the recommended 75 µm cube applicator were too thin for hardness testing. Therefore, drawdown by a doctor blade with a gap of 150 µm was used to apply suspensions in order to prepare coatings that were 40-50 µm thick after they were dried. The drying time of the suspensions was observed to be about 15 - 20 min and hardness was measured after two hours.

Coating Preparation for CPVC Measurement

Composite suspensions of Latex260/Alumina100 and Latex019/Alumina100 were prepared and cast on-

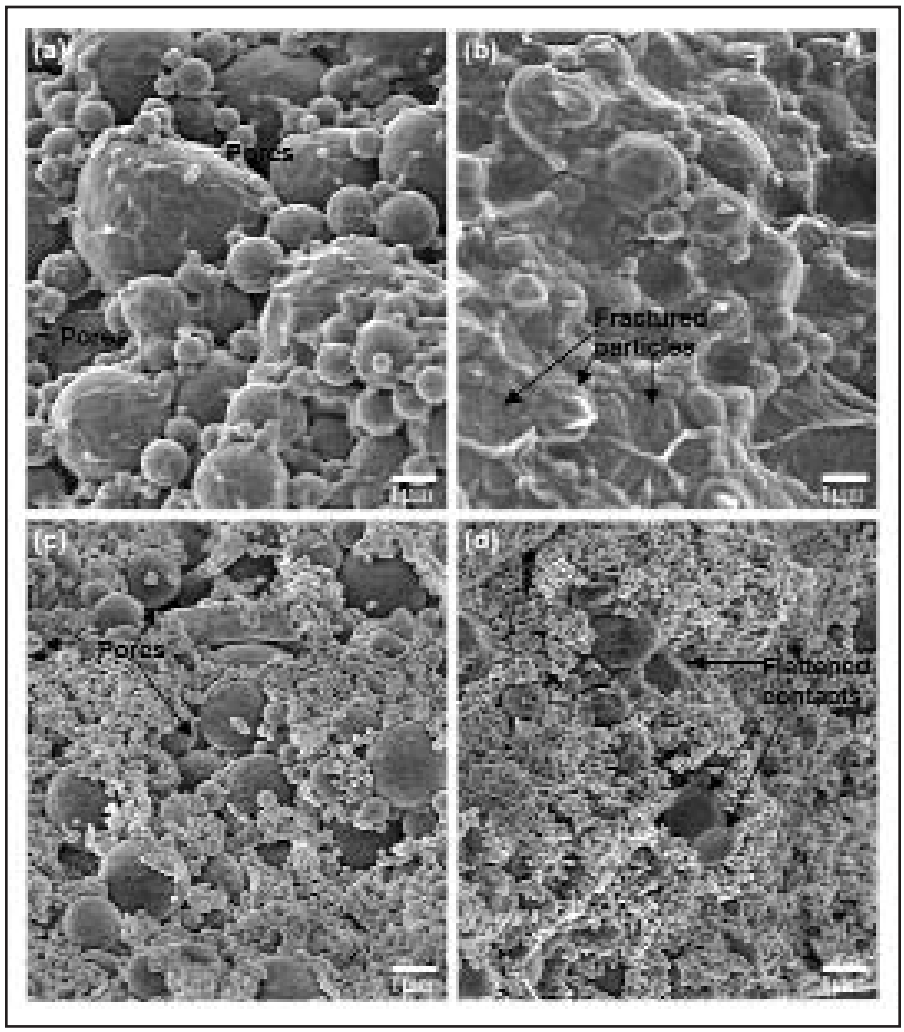

Figure 3—Freeze-fractured cross-section SEM images of (a) Latex-260 dried at 6.6°C, (b) Latex260 dried at 21.9°C, (c) Latex260/Alumina036 coatings dried at 6.7°C, and (d) Latex260/Alumina036 coatings dried at 21.8°C.

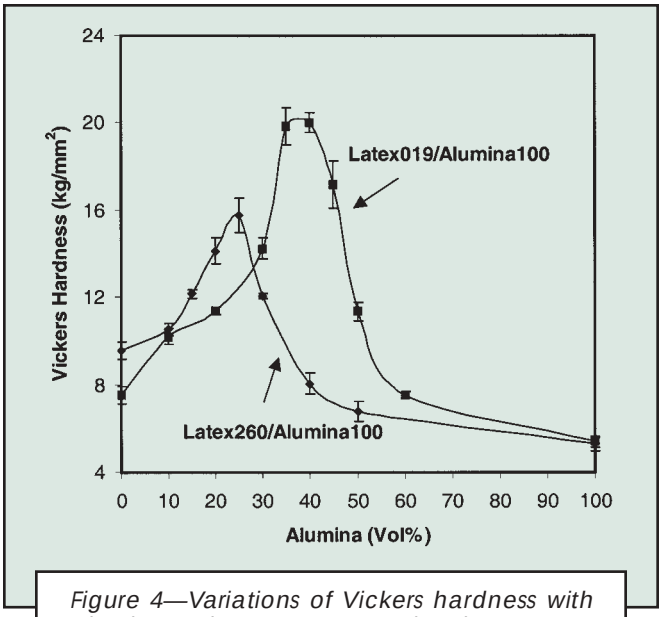

Figure 4—Variations of Vickers hardness with alumina volume concentration in two systems: Latex019/Alumina100 and Latex260/Alumina100.

to glass substrates. In each system, coatings were prepared with a range of contents from 100 vol% latex to 100 vol% alumina. CPVC of the coatings was determined by hardness testing and by SEM characterization. Coatings on glass substrates were prepared by manual drawdown of a doctor blade, followed by drying at 50°C. In these experiments, thick coatings were again needed for hardness testing. Deposition of a single thick layer, however, resulted in a nonuniform coating with alumina particles segregated to the lower half of the coating, presumably due to sedimentation during drying. To avoid this problem, a thinner coating of 10 to 20 μm was first cast with the blade coater and dried at 50°C. After five minutes at 50°C, the layer was dried enough that another layer could be applied on top of it without visibly disturbing it. Four more similar layers were applied and dried one by one to attain a final composite coating that was 100 to 200 μm thick. The final coating was annealed at 50°C for two hours. SEM images showed no obvious layering or interlayer interfaces inside the coatings.

Hardness Measurement

The Vickers hardness values of coatings were determined with a hardness tester (model DM-400 from Leco Corp., St. Joseph, MI) at ambient laboratory conditions (22° to 25°C). The diamond indenter used was a square-based pyramid with an apex angle of 136°. The load (P) was chosen to be 50 g, as described below. The holding time was chosen to be 15 sec. The diagonals (d) of indentation squares were observed and measured under an optical microscope at 40×. At high alumina concentration, the surfaces of the coatings scattered a lot of light and the edges of the indentation squares were difficult to locate. Therefore, about 2 nm of platinum was sputter-coated on the surface before indentation to increase contrast.[19] Comparison of indentation areas before and after Pt sputtering on coatings of low alumina concentrations demonstrated that the extremely thin metal coating had no discernible effect on the hardness results. According to the geometry of the indenter, the Vickers hardness (H_v) was calculated by the following equation[17]:

$$H_v = \frac{\text{Load}}{\text{Area}} = \frac{P}{d^2 / 2\sin(136^\circ/2)} = 1.854\frac{P}{d^2} \quad (1)$$

The units of the Vickers hardness number are kg/mm^2.

To find the proper load for hardness testing, the hardness numbers of Latex260 coatings dried at room temperature were measured under different loads. The load must be large enough to make an indent with easily measured dimension, but not so high that the harder glass substrate influences the hardness value. When the load is too high, the deformation zone beneath the indenter reaches the substrate or, in the extreme, the indenter penetrates the substrate. Thin coatings are particularly susceptible to producing an artificially high hardness value because of the substrate being close beneath. For example, the apparent hardness of a 15 μm-thick coating was influenced by the substrate effect at loads greater than 50 g. In the case of a somewhat thicker coating (~50 μm), the hardness numbers were nearly constant as the load was raised from 25 to 100 g and within the statistical range, 10.6 ± 0.4 $kg/\mu m^2$, of the value measured at a 50 g load. In addition, the hardness number of a thicker film (~150 μm) determined at 50 g load also fell within the statistical range, confirming that the mean of that range is representative of the bulk hardness. Therefore, a 50 g load was used to determine the hardness values of all the coatings.

Microstructure Characterization

Composite coating microstructures were characterized by SEM. Cross-sectional samples were prepared by immersing coated substrates into liquid nitrogen for 5 min and fracturing them. All samples were sputter-coated with 3 nm platinum and examined with an S-900 FE-SEM (Hitachi Corp., Pleasanton, CA) at the low voltage of 3 kV.

RESULTS AND DISCUSSION

MFFT Measurement

Figure 1 is an image of a Latex260 coating and a Latex260/Alumina036 composite coating with 33 vol% alumina dried on the temperature gradient bar after two hours of drying with the drying temperature rising from left to right. At low drying temperatures, the Latex260 coating is opaque due to scattering from the pores in the coating. At these temperatures, the latex particles do not deform and coalesce. At the progressively higher drying temperatures along the bar, the particles deform and compact more and more during drying and the pores concomitantly shrink in size; they may even be eliminated. As explained previously, the MFFT of the Latex260 coating is defined as the temper-

ature at which the coating becomes transparent to the naked eye, i.e., the pores have shrunk to sizes less than the wavelength of visible light. The MFFT of Latex260 is 16.2 ± 0.3°C, which is well below 35°C, the T_g of this latex. The reason the MFFT is so much lower than the T_g may be due to the plasticizing effect of water and the presence of small latex particles.[20] In contrast, the Latex260 / Alumina036 composite coating is opaque at all the drying temperatures the bar provides. Alumina particles have a higher refractive index than the latex particles and, therefore, scatter light regardless of the extent to which the latex particles in the coating have deformed and compacted, thereby shrinking the pores. If the microstructural change correlates with the MFFT, then hardness measurements may make it possible to locate the invisible MFFT in composite coatings.

The hardness of coatings dried on the temperature gradient bar is shown in *Figure* 2. The hardness of Latex260 is fairly constant at low temperatures (< 13°C), but then rises steadily from 4.6 kg / mm^2 at 13.0°C to 9.7 kg / mm^2 at 16.2°C, suggesting a microstructural change in this temperature range. At low drying temperatures, the coating is porous and deforms substantially under the 50 g load to produce a large indentation and a low hardness number. *Figure* 3a shows the microstructure of a porous Latex260 coating dried at a low temperature. At successively higher drying temperatures, the particles deform and compact more and more, with the porosity diminishing correspondingly. As the particles flatten increasingly against one another, they are likely to adhere more strongly owing to van der Waals attractions and hydrogen bonds between polyvinyl alcohol molecules present at the latex surfaces. There is a possibility that polymer chains of adjacent particles interdiffuse and even entangle, which is called coalescence. Denser, more strongly bonded coatings deform less during indentation and therefore have a higher hardness. At the optical MFFT, 16.2°C, the coating appears to be transparent, indicating that the pore size is smaller than the wavelength of visible light. *Figure* 3b shows the microstructure of a Latex260 coating dried above the MFFT. As emphasized above, the onset of visual clarity does not necessarily indicate the disappearance of porespace, but only the decrease in its internal diameters below the light-scattering limit. Therefore, hardness can still increase a little at higher temperatures as coalescence proceeds across particle-particle interfaces and remnant pores disappear. The hardness of the coating dried at 19°C is the same as that of the coating dried at 21.9°C, indicating that coalescence is substantially complete or that the pores are already gone at 19°C, or both. The MFFT by hardness measurements therefore lies between 16.2° and 19°C. Interestingly, little coalescence, i.e., interdiffusion and entanglement, occurred in a Latex260 coating dried at 21°C for two hours because the coating could be redispersed in water. This indicates that while the latex compacted enough that the remaining porespace could not scatter much light, there had been no appreciable welding by interdiffusion and entanglement. A similar observation of redispersion of a coating that had dried above the MFFT was made by Ming.[21] The presence of PVA stabilizer decreases the extent of coalescence, as observed by electron microscopy.[22]

The relationship between hardness and drying temperatures of the Latex260 / Alumina036 composite coating is similar. The alumina particles are much harder than the latex. (The hardness of dense polycrystalline alumina is ~20 GPa or 2×10^9 kg / mm^2 [23]) Hence, the presence of these less deformable particles should increase the coating hardness. In coatings dried at low

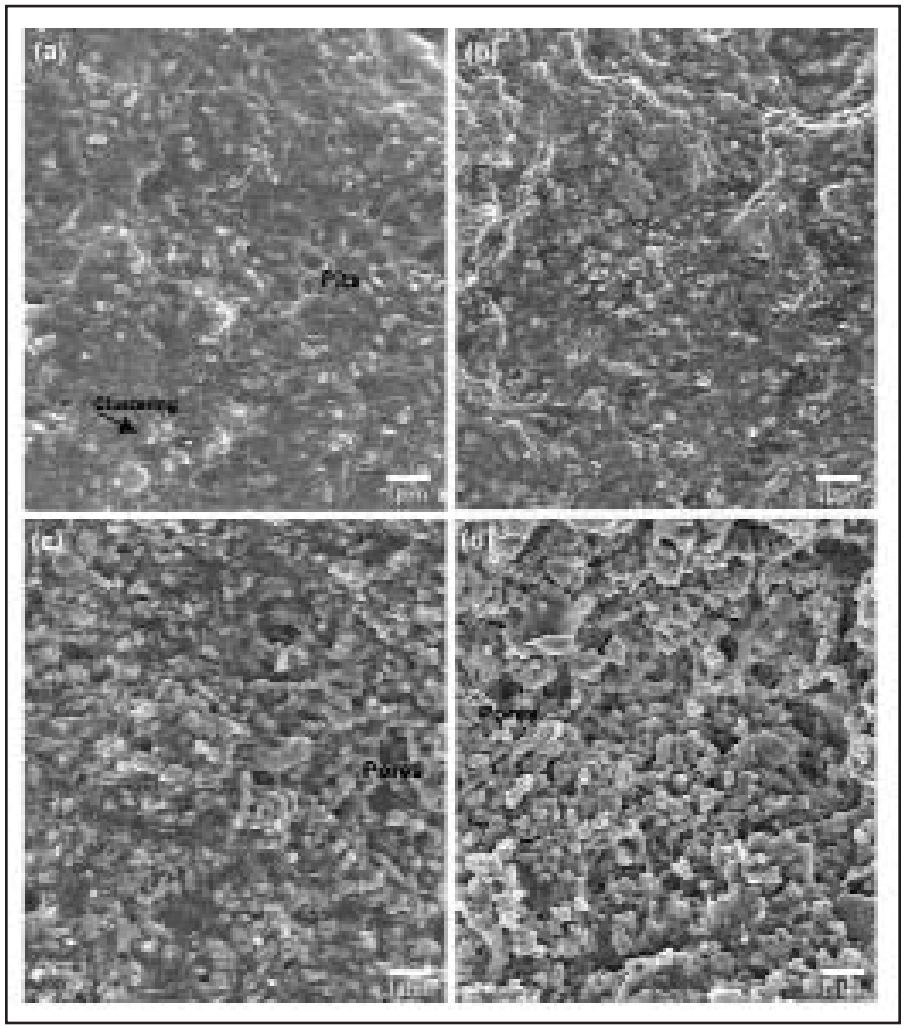

Figure 5—Freeze-fractured cross-section SEM images of Latex019/ Alumina100 coatings with alumina concentration of (a) 20, (b) 35, (c) 40, and (d) 50 vol%.

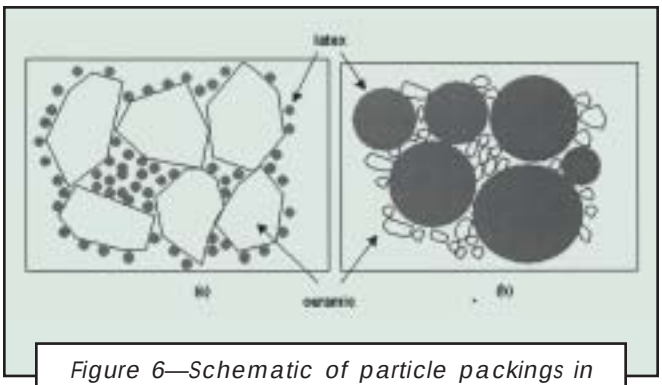

Figure 6—Schematic of particle packings in (a) large ceramic particles/small latex particles and (b) small ceramic particles / large latex particles.

temperatures, the latex and alumina particles are well consolidated, i.e., packed together (*Figure* 3c), but the spherical latex particles appear to be undeformed. As in the pure latex coatings, the porous structure and the relatively weak adhesion between particles lead to a low hardness relative to coatings dried at higher temperatures. The low hardness does not change much up to the transition temperature; above that temperature the hardness is substantially larger. Like Latex260 alone, this transition from low to high hardness occurs between 13° and 16°C. The microstructure of a composite coating dried at 21.8°C reveals the deformation of latex particles (*Figure* 3d). Flattened contacts are apparent on the fracture surface, indicating that adjacent latex particles deformed against each other. Some of the latex particles appear to have deformed so much that they may even have coalesced. They partly fill the void space between the alumina particles; however, at this composite composition porosity persists (i.e., the particle volume concentration exceeds the CPVC, as shown in *Figures* 3c and 3d). Hardness continues to increase with the drying temperature above the transition range, presumably because the composite is made denser by latex deforming and filling more of the space, providing greater binding of the alumina particles.

The similarity of the two curves indicates that, at each temperature, the latex particles deform in the same way in the presence of alumina particles as in their absence. In both cases, the hardness increases because the particles presumably become more strongly bonded and the porosity certainly decreases. Deformation of latex particles increases the contact area not only between neighboring latex particles but also between latex and ceramic particles. In addition, the polymer may penetrate into the porespace within agglomerates of ceramic particles and thereby decrease the porosity. There is no indication that alumina particles enhance or inhibit the latex particles' deformation in this composite coating. The evidence is that the latex particles are mainly deformed by direct action of liquid surface tension and the capillary pressure from curved liquid menisci during the drying process.[24,25] Apparently, the adhesion forces between PVAc and alumina are insufficiently strong enough to dominate the latex deformation and change the latex film formation behavior appreciably.

CPVC Measurement

A series of hardness values of composite coatings with different alumina volume concentrations is shown in *Figure* 4. Two coatings were investigated, one of smaller latex particles with ceramic particles (Latex019/Alumina100), and the other of larger latex particles with ceramic particles (Latex260/Alumina100). The drying temperature was 50°C, well above both the MFFT and the T_g of the latex polymer. Both sets of data show that hardness increases with the alumina content up to a certain point and then it falls as more alumina is added. The alumina volume concentration at which the hardness passes through a maximum is here called the critical Vickers hardness concentration (CVHC).

Correlation of CVHC with CPVC

The hardness of the Latex019/Alumina100 coatings increases with alumina content to a peak between 35 and 40 vol% alumina. Beyond the peak, the hardness decreases abruptly to the lowest hardness number of pure alumina coatings, 5.3 kg/mm^2. The reason for this behavior can be deduced from cross-sectional micrographs of coatings with various alumina contents, as seen in *Figure* 5. At the low alumina concentration of 20 vol% (*Figure* 5a), a dense film with few voids is formed. Ceramic particles are distributed throughout the polymer matrix. In the image, some pits and shallow cavities are apparent. These features can be attributed to the plucking out of alumina particles from the opposite fracture surface. When an alumina content is low enough for a nearly pore-free microstructure to form, the addition of the harder ceramic particles increases the hardness of the coating because the alumina particles pack together more closely and are not separated much by an intervening polymer. When the alumina concentration reaches 35 vol%, near the CVHC (*Figure* 5b), some of the alumina particles appear to contact each other. Nevertheless, the polymer still fills the interstices between the alumina particles, so that the amount of air-filled porosity is slight. At the alumina concentration of 40 vol%, slightly above the range of CVHC (*Figure* 5c), there is not enough polymer to fill the interstices, so that there are air-filled pores, which weaken the coating. Therefore, the presence of these pores makes the coating more susceptible to deformation under the indenter and results in a lower hardness. With still higher concentration of alumina, the porosity climbs (*Figure* 5d) and the hardness falls. Presumably, the lower the amount of polymer, the weaker the alumina particles are bound together. At the extreme, a coating of alumina particles alone, i.e., a layer of consolidated particles without binder, has a low hardness, 5.3 kg/mm^2. This is many orders of magnitude lower than the hardness of dense polycrystalline alumina because the porosity is high, the packing is irregular, and the contacts lack tensile strength and are weak in shear, though they can support local compressive stress up to a breaking strength.

The images of microstructure in *Figure* 5 support this rationale of the correlation of the CVHC determined by the hardness method with the CPVC. The hardness reaches its maximum when the volume fraction of poly-

mer binder in the coating is sufficient enough to completely fill the voids between the ceramic particles. Estimating CPVC from hardness measurements in this way has some advantages: it is quick, relatively accurate, almost nondestructive, and easier than conventional methods that require coatings to be stripped from their substrates. Moreover, hardness is in itself a useful property, for it is an indicator of the mechanical performance of a coating.

Comparison of the Two Systems

Similar variations in the hardness with ceramic concentration were found in the Latex260/Alumina100 system, as shown in *Figure* 4. However, in this system, the CVHC is lower, about 25 vol%. The difference can be attributed to the lower binding efficiency of latex particles that, on average, are larger than the alumina particles. As illustrated in *Figure* 6, at a given volume of polymer, small latex particles form more contact area with large ceramic particles, thereby promoting binding between the ceramic particles. However, when latex particles are large the smaller ceramic particles tend to locate in the interstices, or pore bodies, between latex particles, and this tends to promote the formation of pores between ceramic particles. Further, large polymer particles cannot easily penetrate into the porespace in the ceramic agglomerates. These results are consistent with those of del Rio and Rudin[26] who showed that the CPVC drops as the latex size is increased in paint formulations prepared with the same pigment.

Cross-sectional images of Latex260/Alumina100 coatings support this idea. At a low ceramic concentration of 10 vol% (*Figure* 7a), the latex is well consolidated and contains small clusters of smaller ceramic particles; there may be some pores in the clusters. Hence, the local CPVC[27] which is due to local concentration fluctuations may be surpassed even at this low concentration, but in the coating as a whole no large pores have formed. With the addition of more alumina particles, the latex still forms a continuous connected matrix in which agglomerates of particles are embedded (*Figure* 7b). The amount of air-filled porosity is still small; so the addition of the harder ceramic particles continues to increase coating hardness. At the nominal critical point of 25 vol%, a few larger pores appear (*Figure* 7c). Here, the CPVC is reached on a more global level, i.e., the sample average or film level, and the peak hardness occurs. At the ceramic concentration of 30 vol% (*Figure* 7d), the agglomerates are larger and more pores appear. Although the polymer appears to penetrate a little into the ceramic aggregates,

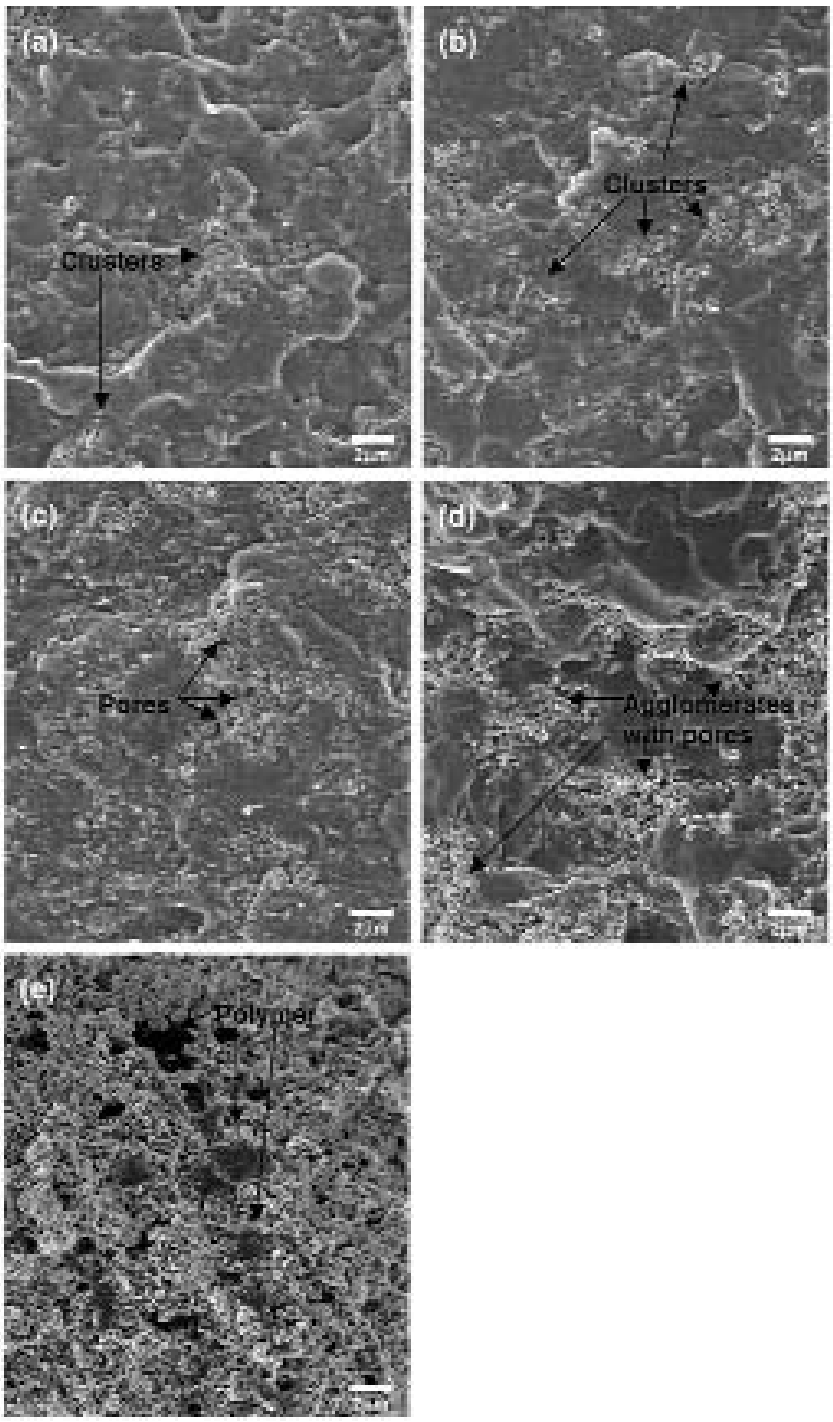

Figure 7—Freeze-fractured cross-section SEM images of Latex-260/ Alumina100 coatings with alumina concentration of (a) 10%, (b) 20%, (c) 25%, (d) 30%, and (e) 50 vol %.

the air-filled porespace within the agglomerates is difficult to fill. In the absence of the binder, ceramic particles within the agglomerates are weakly bonded together. Therefore, hardness decreases significantly. When ceramic concentration reaches 50 vol% (*Figure* 7e), the polymer phase appears more discontinuous and its ability to bind ceramic particles evidently is greatly reduced. The coating hardness approachs that of ceramic particles alone.

SUMMARY

A Vickers hardness test was combined with the MFFT test on a temperature gradient bar to characterize the deformation, compaction, and binding behavior of PVAc latex particles in latex/alumina composite coatings. Changes in microstructure with drying temperature were documented by SEM and linked to both hardness and appearance changes. In latex coatings from which alumina was absent, an abrupt increase in hardness was found to correlate with the MFFT determined by the onset of optical clarity as the drying temperature was increased. A latex/ceramic composite coating with 33 vol% alumina was also dried at a continuous progression of temperatures on a temperature gradient bar. Although the MFFT of the composite coating was invisible, the results of a Vickers hardness test and SEM images of its microstructures revealed that the presence of alumina particles did not change the latex film formation behavior from that of pure latex coatings.

The hardness of latex/alumina composite coatings dried above their MFFT was measured as a function of alumina content. The hardness passed through a maximum at a certain ceramic volume concentration, here named the critical Vickers hardness concentration (CVHC). By means of scanning electron microscopy, the CVHC was shown to be virtually the same as the traditional critical pigment volume concentration (CPVC). At a slightly higher volume concentration of alumina particles, air-filled pores were present in the coating and the hardness decreased abruptly as the concentration was increased further. The hardness method provided a simple and fast way to estimate CPVC values. Two series of composite coatings with different latex particle sizes were compared. Latex particles smaller than the ceramic particles allowed for more contact between particles and yielded a better binding efficiency. Latex particles larger than the ceramic particles left the latter able to aggregate in the interstices between latex particles. It was difficult for large polymer particles to bind the smaller, agglomerated ceramic particles together, resulting in ceramic particle packings containing the air. Therefore, composite coatings with larger latex particles had a lower peak hardness and CPVC value due to the poor binding efficiency.

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References

(1) Patel, M. and Tripathy, D.K., "Improvement in Pigment Coating Performance with Synthetic Binders and Different Pigments," *IPPTA*, 8, 31 (1996).
(2) Steig, F.B., "Titanium Dioxide, or Is It?," JOURNAL OF COATINGS TECHNOLOGY, *43*, No. 561, 36 (1971).
(3) Steward, P.A., Hearn, J., and Wilkinson, M.C., "An Overview of Polymer Latex Film Formation and Properties," *Adv. Colloid Interface Sci.*, 86, 195 (2000).
(4) Keddie, J.L., "Film Formation of Latex," *Mater. Sci. Eng.*, R: Reports, R21, 101 (1997).
(5) Lepoutre, P., "The Consolidation of a Paper Coating," *Pulp & Paper Canada*, 80, T58-61, 98 (1979).
(6) Gate, L.F. and Preston, J.S., "The Specular Reflection and Surface Structure of Emulsion Paint Films," *Sur. Coat. Int.*, 78, 321 (1995).
(7) Sheehan, J.G., Takamura, K., Davis, H.T., and Scriven, L.E, "Microstructure Development in Particulate Coatings Examined with High-Resolution Cryogenic Scanning Electron Microscopy," *TAPPI J.*, 76, No. 12, 93 (1993).
(8) Granier, V. and Sartre, A., "Ordering and Adhesion of Latex Particles on Model Inorganic Surfaces," *Langmuir*, 11, 2179 (1995).
(9) Asbeck, W.K. and Van Loo, M., "Critical Pigment Volume Relationships," *Ind. Eng. Chem.*, 41, 1470 (1949).
(10) Stieg, F.B., "Density Method for Determining the CPVC of Flat Latex Paints," JOURNAL OF COATINGS TECHNOLOGY, *55*, No. 696, 111 (1983).
(11) Toussaint, A., "Influence of Pigmentation on the Mechanical Properties of Paint Films," *Prog. Org. Coat*., 2, 237 (1973/1974).
(12) Rasenberg, C.J.F.M. and Huisman, H.F., "Measurement of the Critical Pigment Volume Concentration by Means of Mercury Porosimetry," *Prog. Org. Coat.*, 13, 223 (1985).
(13) Tabor, D., *The Hardness of Metals*, Clarendon Press, Oxford, 1951.
(14) Suwanprateeb, J., "Calcium Carbonate Filled Polyethylene: Correlation of Hardness and Yield Stress," *Composites, Part A: Applied Science and Manufacturing*, 31, 353 (2000).
(15) Duttagupta, S.P., Chen, X.L., Jenekhe, S.A., and Fauchet, P.M., "Microhardness of Porous Silicon Films and Composites," *Solid State Commun.*, 101, 33 (1997).
(16) Cesarano, J. III, Aksay, I.A., and Bleier A., "Stability of Aqueous Al_2O_3 Suspensions with Poly(methacrylic acid) Polyelectrolyte," *J. Am. Ceram. Soc.*, 71, 250 (1988).
(17) Callister, W.D. Jr., *Materials Science and Engineering: An Introduction*, 5th Ed., John Wiley & Sons, Inc., New York, 2000.
(18) ASTM D 2354-98, "Standard Test Method for Minimum Film Formation Temperature (MFFT) of Emulsion Vehicles." ASTM International, West Conshohocken, PA (1998)
(19) Grodzinski, P., "Elastic and Plastic Hardness of Hard Materials," *Nature*, 169, 925 (1952).
(20) Vandezande, G.A., and Rudin, A., "Film Formation of Vinyl Acrylic Latexes: Effects of Surfactant Type, Water, and Latex Particle Size," JOURNAL OF COATINGS TECHNOLOGY, *68*, No. 860, 63 (1996).
(21) Ming, Y., "Microstructure Development in Polymer Latex Coatings," Ph.D. Thesis, University of Minnesota, 1996. Published by University Microfilms International, Ann Arbor, MI.
(22) Cote, W.A. Jr., Day, A.C., Wilkes, G.W., and Marchessault, R.H., "Particle Packing in Latex Films," *J. Colloid and Interface Sci.*, 27, No. 1, 32 (1968).
(23) Krell, A., "Vickers Hardness and Microfracture of Single and Polycrystalline Aluminum Oxide," *Kristall und Technik*, 15, No. 12, 1467 (1980).
(24) Lin, F. and Meier, D.J., "A Study of Latex Film Formation by Atomic Force Microscopy. I. A Comparison of Wet and Dry Conditions," *Langmuir*, 11, 2726 (1995).
(25) Pekurovsky, L.A. and Scriven, L.E., "Capillary Forces and Stress Development in Drying Latex Coating," *Polym. Mater. Sci. Eng.*, 81, 177 (1999).
(26) del Rio, G. and Rudin, A., "Latex Particle Size and CPVC," *Prog. Org. Coat*., 28, 259 (1996).
(27) Bierwagen, G., Fishman, R., Storsved, T., and Johnson, J., "Recent Studies of Particle Packing in Organic Coatings," *Prog. Org. Coat*., 35, 1 (1999).