

Adhesion of latex particles on inorganic surfaces

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ABSTRACT: *Dried synthetic latex with mineral pigments influences cohesion and adhesion of paper coating binders. Interfaces within the dried latex layer control ink and water penetration during printing. This work uses Atomic Force Microscopy to study the ordering and adhesion of latex particles on model inorganic surfaces as a function of latex parameters, drying conditions, and the chemical nature of the surface. An acid-base concept provides information about the influence of polymer particle spreading.*

KEYWORDS: *Adhesion, bibliographies, inorganic compounds, latex, microscopy, parameters, particles, spreading, surface properties.*

Synthetic latexes are aqueous dispersions of polymeric microspheres which find wide use as binders in paper coating (1). Color coatings are dispersions of mineral pigments in these latexes with thickeners. The synthetic latexes must provide the necessary rheology for the color coatings and develop the required binding strength after drying of the dispersion.

After the coating process, dehydration of the dispersion occurs to form a composite layer. Figure 1 shows the mixture of mineral pigments within a coating color before drying (A) and their confinement within the porous structure after

drying (B). One may consider the composite layer as a porous mineral structure which results from the way the pigments and latex particles settle (2). Latex particles partially or totally cover the surface of the pores of the porous structure.

During the printing process, the porosity as well as the interfaces within the layer control the penetration of ink and water into the coating (3). This coating surface contains both pigment and polymer particles. The most important interfaces at this point are the ones with polymer, since mineral surfaces do not react with ink solvent.

The adhesion of latex particles on the pigment also governs the coating cohesion and adhesion (4).

It is rather obvious, therefore, that the first step to an understanding of the properties of a coating should focus on the ordering and adhesion of latex particles within that coating.

Film formation studies

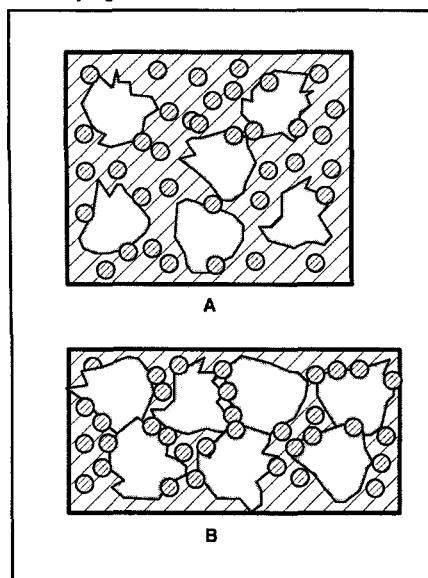
Earlier investigators have studied the formation and structure of a continuous film from latex (5-12). To summarize their work, the structure results from coalescence of particles provided that forces produced during water evaporation are strong enough to overcome both coulombic repulsion forces of the charged particles and particle rigidity.

In contrast, the spreading and the ordering of latex particles on an inorganic surface after water evaporation are poorly investigated fields of research (13), because the measurements are very difficult to perform at this minute scale with conventional techniques such as contact angle analysis and electron microscopy. Conventional electron microscopy has provided an examination of the final stage of latex film formation (14, 15). In addition, high-resolution cryogenic SEM has provided an examination of latex particles near the pigment surface (16, 17).

In this work, we investigate the wetting of model inorganic surfaces

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1. Mineral pigments in a coating before and after drying



by latex particles using a recent surface science technique: Atomic Force Microscopy (AFM) (18). This technique allows imaging of insulating surfaces and description of surface relief at the nanometer scale. In some cases, it is even possible to go as low as the atomic level without destroying the surface.

Upon dehydration of coating colors, latex particles encounter mineral pigments. This introduces the following questions:

- What happens to the latex particles during this process?
- Is there flocculation or aggregation of latex particles?
- Are the particles deformed or not?

Latex is a viscoelastic material. It is somewhere between a dispersion of a solid and an emulsion which contains droplets of oil in water. **Figure 2** shows the different possible structures for latex particles at various stages in a coating. A indicates the flocculation and formation of aggregates of dozens of particles between mineral pigments. In this case, packets of polymer particles bind the pigments. B shows another possible structure. Although the particles may

have some degree of deformation here, they have good dispersion on the mineral pigments and preserve their own identity. C depicts the particle spreading slowly to form a continuous polymeric film on the pigments. Obviously the ordering and spreading of latex particles will depend on latex characteristics, the chemical nature of the inorganic surface, and drying conditions.

Experimental work

Our work used AFM to study the ordering and spreading of latex particles as a function of various experimental parameters. The results provided information for the mechanisms governing particle spreading and adhesion.

Latex

Table I shows the four aqueous dispersions of polymer latex particles used in this study. The particles are spherical droplets comprising a hydrophobic polymer core surrounded by a hydrophilic layer. The core contains a random copolymer of varying amounts of styrene (S) and butyl acrylate (BA). The glass transition temperature of these copolymers is between 5°C and 41°C. At room temperature, copolymers A, B, and C are viscoelastic, amorphous materials. Copolymer D is a glassy material at room temperature. A thin hydrophilic layer made of acrylic acid (AA) sequences copolymerized with the core polymer surrounds the core of each latex particle. The amount of AA sequences expressed in arbitrary units ranges from 1 to 9. Latex A has a medium acid content, latex B has a low acid content, and latexes C and D have a high acid content. Because the AA groups have neutralization at pH 8.0, they have a charge and generate long-range repulsions between particles. This stabilizes the dispersion.

Figure 3 is a transmission electron microscopy photo of a dilute dispersion of latex A in water spread on

a Collodion membrane, dried, and placed on a grid in the electron microscope. The marker bar represents 100 nm.

After their synthesis, the dispersions underwent purification in an ultrafiltration cell. The average particle diameter measured by electron microscopy was between 100 nm and 125 nm. The corresponding size distribution is very narrow.

Mineral substrates

The study used three chemically different mineral substrates: silicon wafers covered by a thin layer of silica (called silica substrate in the following text), mica sheets, and calcium carbonate crystals. Mica is an aluminosilicate similar to clay, but it has a different crystalline structure. We chose it over clay because it was impossible to obtain clay samples of 5 mm x 5 mm dimensions with very smooth surfaces having roughness less than 5 nm.

Principle of AFM

Figure 4 shows schematically the commercial AFM which we used. It operates by scanning a surface with a sharp tip mounted on a cantilever. The tip is triangular. The angle at the end of the probe tip is about 30°. These experiments used a 25 µm x-y scanner which allowed imaging of relatively large fields.

The AFM head includes a focused laser beam which reflects off the upper apex surface of a gold-coated silicon nitride triangular cantilever to a two-element photodiode detector. The triangular cantilevers were 200 µm long with a spring constant of 0.12 N/m. The optical beam detection allows for precise measurement less than 1 nm in the vertical direction or z axis of deflections by the cantilever and the attached probe tip. The sample stage mounting includes an x, y, and z piezoelectric single tube scanner which provides the precise x and y raster movement of the sample.

The image processing system converts the variation in voltage signals

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from the photodetector and z-piezo as a function of probe position into a three-dimensional image.

It is possible to operate the microscope in two modes. In the constant force mode, the applied force remains constant by using an integral feedback loop. The vertical movement of the tip describes the surface relief. In the constant height mode, the distance between the tip and the surface remains constant. The apparatus measures the force, F , between the tip and the surface.

AFM imaging

This work recorded AFM images using the constant force mode.

Measuring particle profiles in AFM experiments provides quantitative information on particle spreading on a substrate. Consequently, the roughness of mineral substrates (defined as the maximum displacement) must be smaller than the polymer particle diameter. The silica substrates as received had very smooth surfaces with a roughness less than 1 nm. On the contrary, it was necessary to cleave the calcium carbonate crystals and the mica sheets to obtain very smooth surfaces with roughness less than 3 nm. **Figure 5** shows a 2000 nm x 2000 nm AFM constant-force image of a cleaved calcium carbonate crystal. The vertical scale is height in nm.

We prepared samples by placing a 1- μ L droplet of a diluted latex solution onto a substrate. The mass concentration of the initial diluted latex solution was 0.2×10^{-3} , because this corresponds to the same approximate substrate surface coverage as mineral pigments in typical offset coatings. This is approximately 10 parts of latex per 100 parts of pigment.

After drying at room temperature, the samples underwent direct imaging in air. For some experiments, the samples had annealing in an oven at different temperatures before AFM imaging.

Results

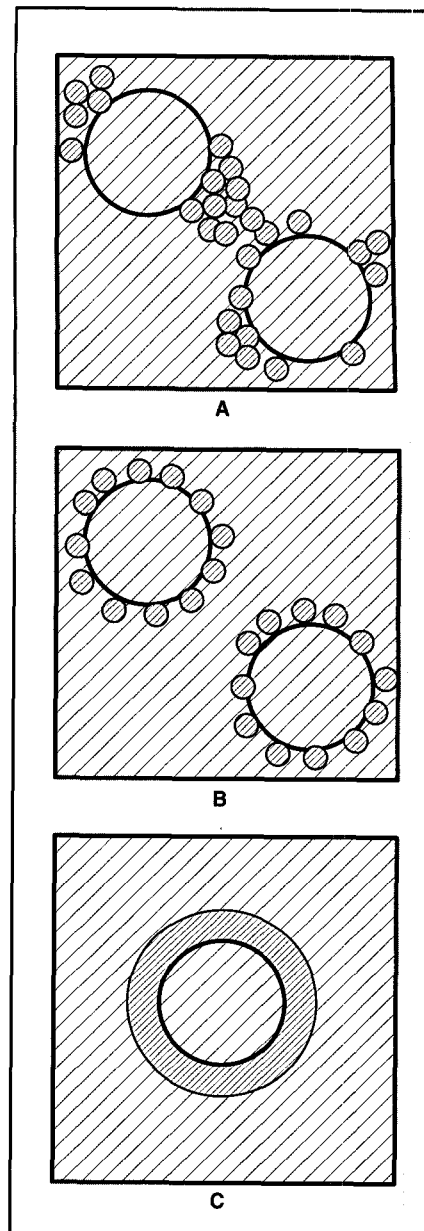
Ordering of polymer particles

Figure 6 shows a typical AFM image obtained with latex A on a calcium carbonate crystal. The vertical scale again is height in nm. This image reveals the ordering of polymer particles after water evaporation. The particles have rather good dispersion on the crystal. At this particular solution concentration, they do not cover the whole crystal surface. The substrate surface wetted by a 1- μ L droplet of the diluted latex solution is about 16 mm². This induces a surface coverage of 12.5 ng of latex per mm². It is possible to express this calculated surface coverage in terms of latex ratio in a coating color. Using a specific surface area of 7 m²/g for mineral pigments, the latex concentration of 12.5 ng/mm² is the same as in a coating color containing 9 parts of latex per 100 parts of pigment. The AFM experimental conditions therefore correspond to industrial pigment surface coverages.

Obviously, when the latex solution concentration increases, the substrate surface coverage increases to provide complete coverage at high latex concentrations. A rough calculation without considering latex particle spreading shows that a monolayer of latex particles covers pigment surfaces when the latex level in a coating is about 40 parts per 100 parts of pigment.

Figure 7 shows an AFM image obtained with a concentrated latex A solution on a calcium carbonate crystal. For this experiment, the mass concentration of the latex solution was 1.0×10^{-3} . In terms of surface coverage, this corresponds to a coating color containing 45 parts of latex per 100 parts of pigment. This image shows that a latex film covers the whole crystal surface as one would expect. In addition, there are no aggregates. The most striking feature is the strong periodicity in particle packing. This is consistent with local face-centered cubic (FCC) structure

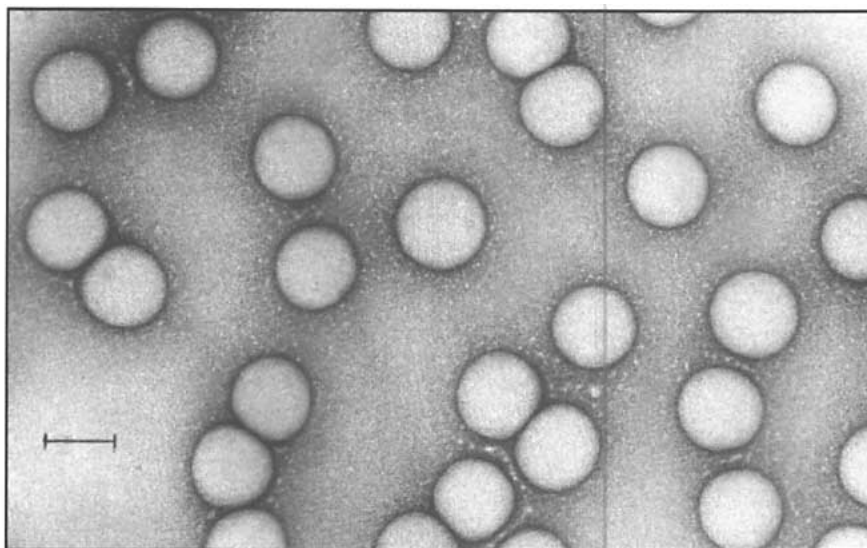
2. Possible structures for latex particles in a coating



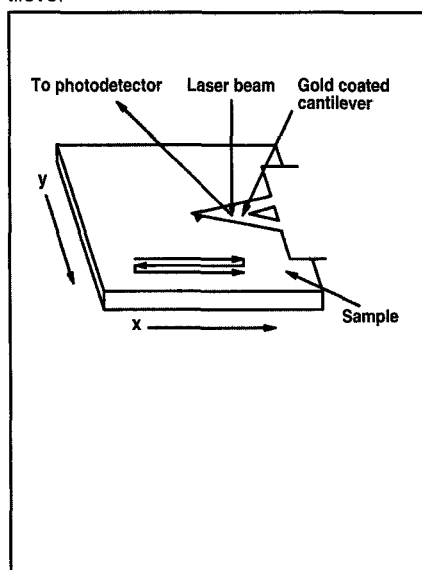
which induces the well known foam structure. Our observations agree with AFM results dealing with the surface structure of poly (butyl methacrylate) latex film (19, 20). It appears that, during preparation of latex films by casting onto a substrate, there is formation of monolayers of latex particles which show long-range periodic order consistent with FCC packing.

The AFM image of Fig. 6 shows that only a few particles come into contact with other particles. This

3. Transmission electron microscopy photograph of a dilute dispersion of latex A in water



4. Schematic diagram of AFM showing cantilever



means that the latex on drying does not flocculate to form aggregates of dozens of particles. In addition, as the solution evaporates from the surface, the capillary force pulls only a few spheres together.

Latexes B, C, and D as well as the silica and mica substrates exhibited the same results concerning particle ordering. This indicates that our observations are not dependent on latex or substrate characteristics. With the AFM technique, we can only ana-

lyze a two-dimensional system—the substrate surface. The coating is a three-dimensional system. We do not know if it is possible to extrapolate results in two dimensions directly to three dimensions without correction. Nevertheless, we can consider the surface of the pores as a two-dimensional system. Returning to the different possible structures for latex particles shown in Fig. 2, we can affirm that the first one, A, is not realistic. Packets of polymer particles can not bind mineral pigments in the coating, since AFM observations do not indicate any flocculation or aggregation during the drying process.

Consequently, we propose a coating structure indicated by the schematic view in Fig. 8. This shows latex particles with rather good dispersion on mineral pigments and no flocculation or aggregation during water evaporation. At this point, however, we do not know if particles deform or not or if they can form a continuous polymeric film on pigments. Only a few particles are in contact with other particles.

Adhesion and spreading

An image processing system can record polymer particle profiles to

give some information on particle dimensions. Figure 9 shows a typical particle profile for latex A on a calcium carbonate crystal. It is an AFM image of Fig. 2. The analysis of particle profiles allows determination of their diameter and height. The analysis of ten profiles gives 260 ± 10 nm average diameter (distance from A to A in the figure) and 30 ± 2 nm average height (distance from B to B in the figure). This result indicates that latex A particles spread on the crystal surface. With the AFM technique, we can therefore quantify the spreading.

It is possible to compare particle dimensions obtained from AFM images using different latexes and substrates. Such a comparison shows that some latex and substrate characteristics are critical for particle spreading and adhesion.

Effect of polymer Tg

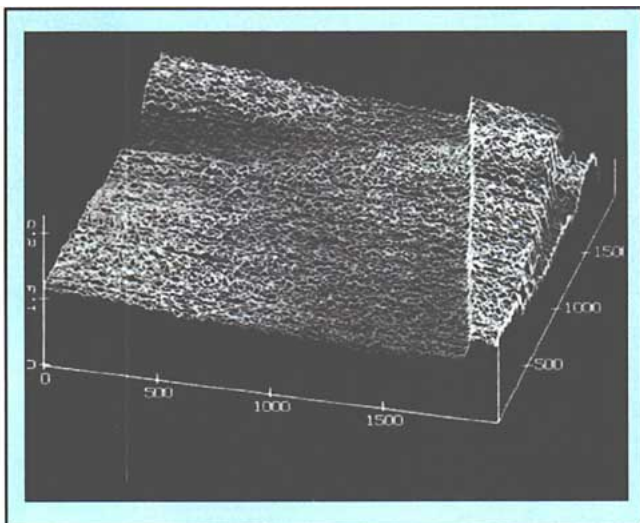
During AFM imaging of a calcium carbonate crystal covered with latex D particles, we observed that the probe tip tends to move the particles slowly in the fast or x scanning direction until the resistance of the particles is sufficient to cause a deflection of the tip. A of Fig. 10 shows the AFM constant-force image of latex D particles on a calcium carbonate crystal after water evaporation at room temperature. There were five scans before imaging. The probe tip brought the particles which were initially well dispersed on the crystal surface into contact.

Latex D particles have weak adhesion to the crystal surface, since the tip can move them. We are not able to measure their adhesion level, however, because we have no quantitative measure for the forces exerted locally by the tip on latex particles. These forces may depend on tip geometry as well as instrumental parameters.

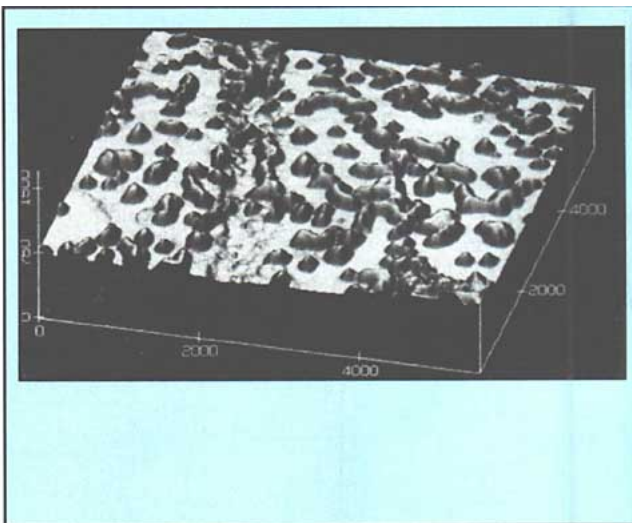
We found that the tip interaction decreases with increasing full-scale scanning range. It is possible to image particles without the tip disturbing them, but only at the cost of lower

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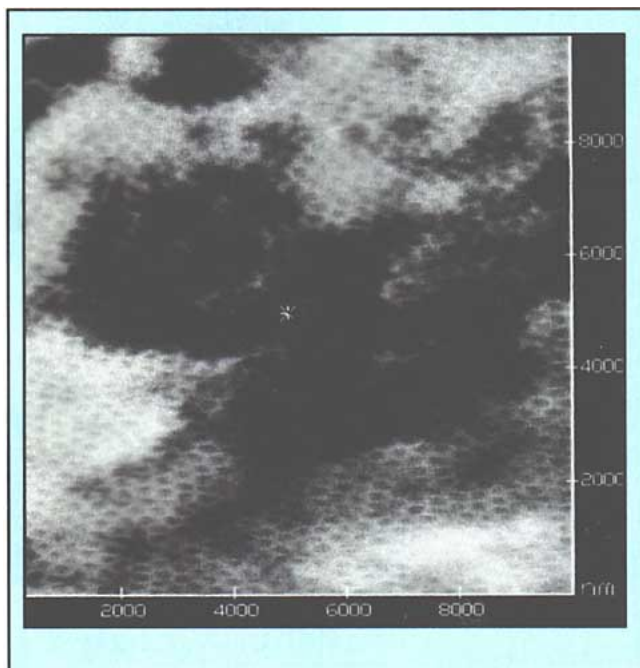
5. A 2000 nm x 2000 nm AFM constant-force image of a cleaved calcium carbonate crystal



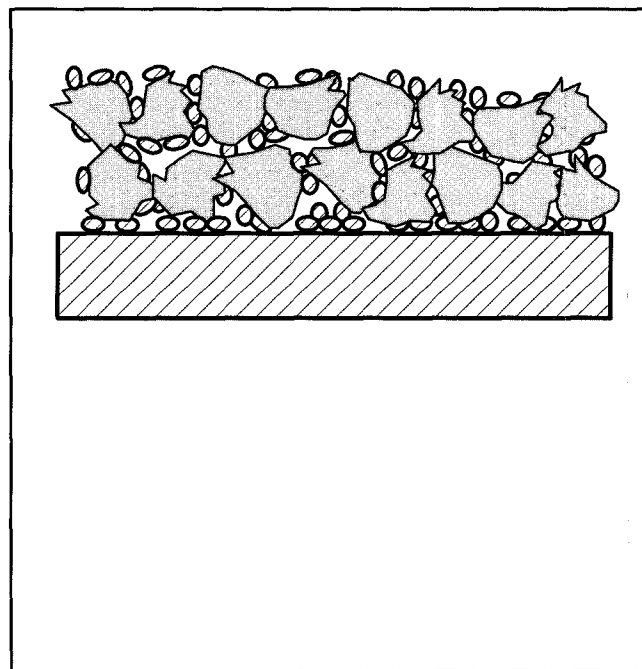
6. A 5000 nm x 5000 nm AFM constant-force image of latex A deposited on a calcium carbonate crystal after water evaporation



7. A 10,000 nm x 10,000 nm AFM constant-force image of latex A film prepared by casting onto a calcium carbonate crystal



8. Schematic view of proposed coating structure



resolution. The increased x and y scanning velocities at the higher scan size may contribute to this phenomenon. Our attempts to image latex particles over a 1000-nm full-scale range resulted in the significant particle distortions of A in Fig. 10, although we used minimum force to image the crystal.

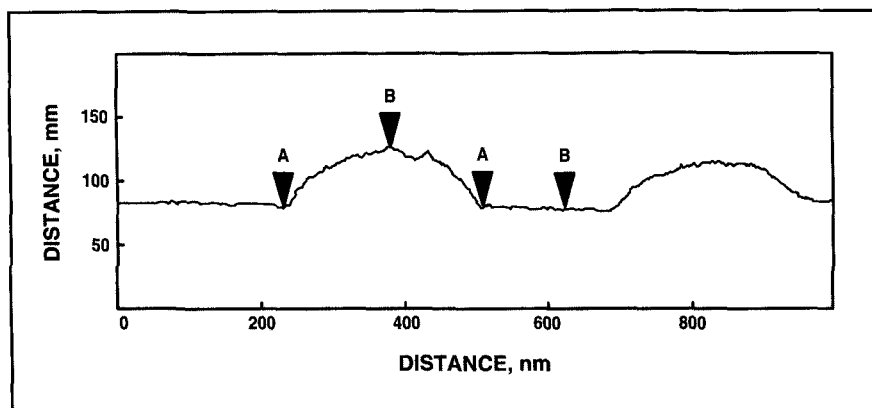
The analysis of the particle profiles gives 112 ± 6 nm average par-

ticle height. This value is very close to the initial latex particle diameter of 100 nm measured by electron microscopy. Latex D particles remain spherical. Latex A particles did not remain in that shape. During water evaporation, capillary forces do not cause any spreading of latex D particles. It is difficult to determine latex D particle diameter. The tip moves the particles during the scanning due to their weak adhesion to

the crystal surface, which induces an error in the measured value.

After annealing of sample at 80°C for 30 min, we noticed a sudden spreading of the particles. The probe tip was no longer able to move them, as B of Fig. 10 indicates. The average particle diameter was 250 nm. This sudden spreading is not due to capillary forces, since the sample experienced drying before annealing.

9. A typical particle profile obtained with the image processing system for latex A on a calcium carbonate crystal



I. Features of the synthesized latex particles

Latex	Core composition, ^a weight %	Particle diameter, ^b nm	T _g , °C	Amount of AA groups, ^c arbitrary units
A	S: 40 BA: 60	120	5	6.6
B	S: 40 BA: 60	120	5	1
C	S: 40 BA: 60	125	5	9
D	S: 60 BA: 40	100	41	9.3

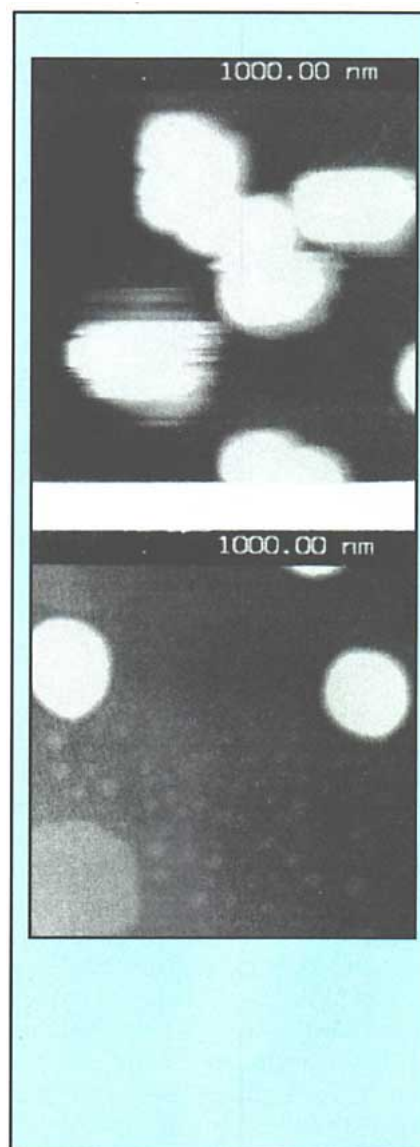
^aParticle core is a random copolymer of styrene and butyl acrylate
^bParticle diameters measured according to pictures from transmission electron microscopy
^cAmount of acrylic acid sequences which are copolymerized with the core polymers to form the hydrophilic membrane as expressed in arbitrary units.

Placing a droplet of latex D solution on a calcium carbonate crystal and drying for 3 min at 80°C instead of room temperature results in particles which the probe tip does not move. The measured diameter is also 250 nm. Particle spreading is therefore the same after drying at room temperature followed by annealing at 80°C as after drying at 80°C only.

Figure 11 depicts the profiles of latex D particles as a function of the thermal treatment of the sample. By comparing the profiles for the three types of experiments, we can state

that capillary forces do not govern particle spreading, although these forces are the “drive” for the formation of a continuous film from latex (5, 6). This spreading phenomenon is because the annealing temperature was higher than the latex T_g. Above its T_g, the polymer is in a rubbery state. The molecular chain mobility greatly increases compared to the glassy state below the T_g. Capillary forces do not govern the fact that latex particles can spread. The latex “mechanical properties” control this phenomenon. In other

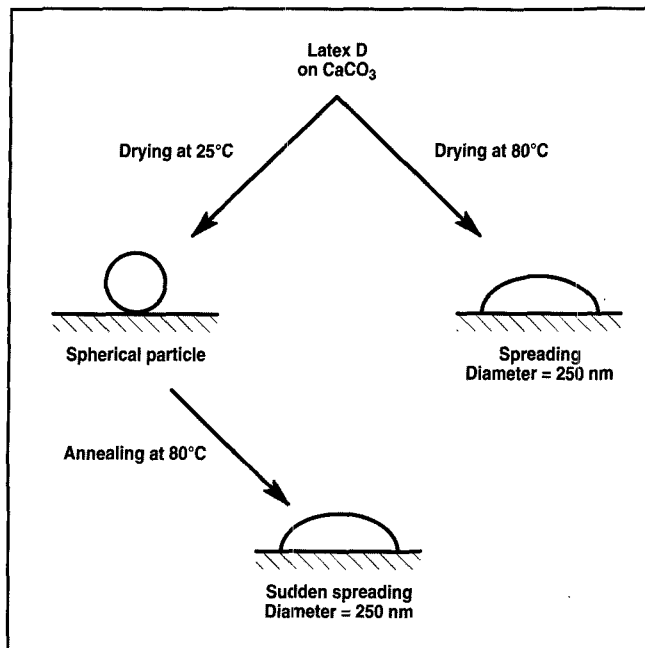
10. 1000 nm x 1000 nm AFM constant-force images of latex D particles on a calcium carbonate crystal



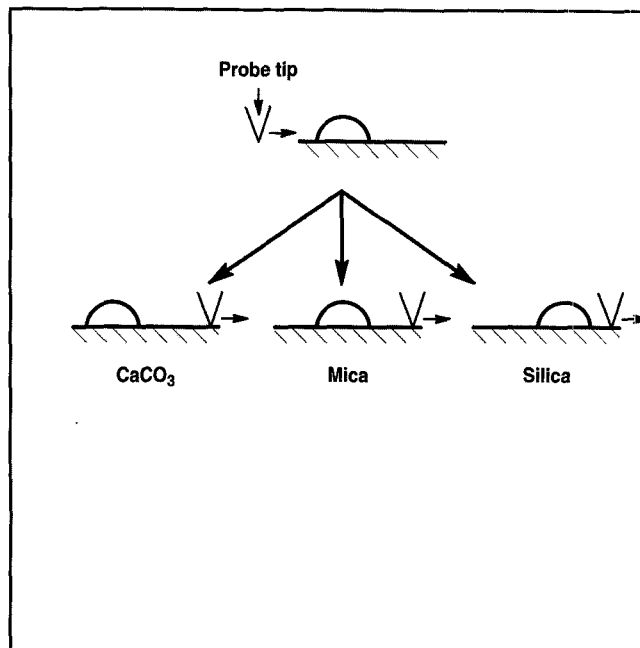
words, a particle can spread on a surface only if the chain mobility is high enough. This condition occurs for latex A at room temperature. Above the T_g, spreading occurs. The spreading ratio certainly depends on latex and surface characteristics.

After water evaporation at a temperature higher than polymer T_g (room temperature for latex A and 80°C for latex D), we annealed the samples at different temperatures to determine if further annealing can modify the spreading observed above polymer T_g. The analysis of

11. Profiles of latex D particles as a function of thermal treatment



12. Profiles of latex particles on different surfaces after one scan with the AFM probe tip



the particle profiles shows that the latex A particle diameter remains equal to 260 nm even with annealing up to 140°C. Sample annealing does not modify the spreading. The same result occurred with latex D. Above 80°C, the particle diameter remains equal to 250 nm even after annealing for 12 h at 140°C. Above polymer T_g , there is a sudden spreading which sample annealing can not modify, even if the temperature is such that the cores are in a liquid state. Polymer particles cannot form a continuous polymeric film on pigments, and the structure proposed in C of Fig. 2 for latex particles within the coating is not realistic. The wettability of the substrate by latex particles is really only a case of partial wetting—the particle contact angle is not zero.

Substrate influence

All the experiments in this section used latex A. With this latex, the final particle spreading occurs after water evaporation at room temperature. No further annealing is necessary.

Figure 12 shows the results from the three different substrates indi-

cating the influence of the chemical nature of the substrate on particle adhesion. With calcium carbonate, the particles remain fixed on the surface. Using a mica substrate, the tip can slowly move the particles during scanning. The tip can easily move the particles during scanning in the case of a silica substrate. When the full-scale scan range is 1000 nm, the particle shift induced by the tip is about 500 nm per scan.

Our results show that latex adhesion to the surface depends on the chemical nature of the surface. Adhesion is strong with calcium carbonate, weak with silica, and intermediate with mica. Again, it is not possible to characterize the adhesion level by a number, because we have no quantitative measure for the forces exerted by the tip on latex particles. It is possible nevertheless to quantify latex adhesion to different substrates by using the particle shift induced by the tip. It is impossible, however, to determine a difference between the adhesion level of two latexes on a calcium carbonate substrate, since there is no particle shift.

Particle diameter is difficult to determine on mica and silica substrates. The tip moves the polymer particles during scanning due to their weak adhesion to the substrate. This induces a significant error in the measured value.

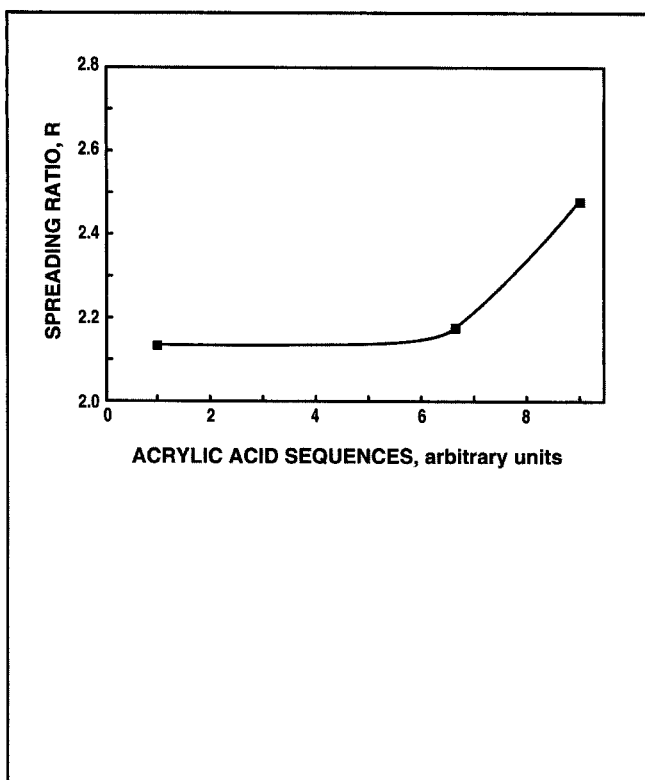
Effect of acid level

We studied the effect of the amount of latex acid on particle spreading using a calcium carbonate substrate with latexes A, B, and C. The dispersions underwent purification in an ultrafiltration cell after their synthesis. Consequently, there was no acid in the water phase, and all the acidic functionality came from the latex itself.

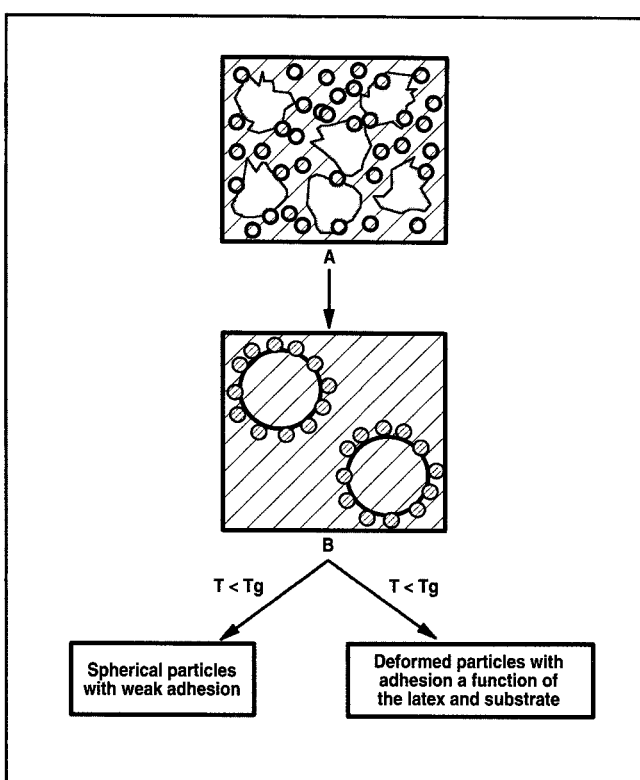
In all the experiments, the final spreading occurred after sample drying at room temperature with the particles fixed on the substrate, i.e., no tip-induced movement during scanning.

The average particle diameters measured by AFM were 260 nm, 255 nm, and 310 nm for latexes A, B, and C respectively. Since the initial particle diameters in the dispersion are different for these three latexes,

13. Variation of the spreading ratio on a calcium carbonate substrate as a function of the amount of acrylic acid copolymerized with the core polymers to form the hydrophilic membranes



14. Transformations of latex particles upon drying



however, it is difficult to compare the different diameter values obtained by AFM. So we have defined a "spreading ratio," R , which is equal to the particle diameter measured by AFM after spreading on the substrate divided by the initial diameter in the latex dispersion. By determining the values for R , it is possible to compare results obtained with latexes of different initial particle diameters.

The R values are 2.17, 2.13, and 2.48 for latexes A, B, and C respectively. Figure 13 shows the variation of R as a function of the amount of acrylic acid sequences copolymerized with the core polymers. When the latex acid content as expressed in arbitrary units increases from 1 to 7, there is only a small increase of the spreading ratio. Above an acid content of 7, the increase of the spreading ratio is much greater. This indicates that the spreading ratio depends on the thickness of the hydrophilic membrane of the particle.

Discussion

We have examined the ordering and adhesion of latex particles on a mineral surface and proposed a coating structure. The particle adhesion and spreading depend on the characteristics of the latex and the substrate. Figure 14 summarizes the results. A indicates the initial dispersion of the particles among mineral pigments in the coating color. After drying at room temperature, B shows the composite layer which forms. Most of the particles in it have good dispersion within the coating. Some of them are in contact with other particles as in Fig. 8. We do not know if these particles conserve their own identity or there is coalescence.

We know that latex films from particles with membranes made of copolymerized acid sequences have foam structures (11). This is the case for all the latexes used in this work. Polymer interdiffusion only occurs after annealing at very high tem-

peratures. We do not know, however, if the substrate affects coalescence. When one casts the latex on a mineral substrate, there might be modification of the particle surface energy. The membranes might break up which would allow coalescence and interdiffusion of the core polymers. The AFM images in Fig. 7 have shown that a substrate covered by a monolayer of latex particles has the same particle packing as for thick latex films. There is no coalescence for a carboxylated latex. Consequently, one may deduce the transformation of particles in contact with neighboring particles from studies of latex film formation. We can therefore affirm that there is no coalescence of particles which are in contact with neighboring particles in the coating.

The particles isolated on the substrate surface may contain some deformation depending on the polymer glass transition as seen in C of Fig. 14. If the drying or annealing tem-

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perature is below the Tg of the core polymer, the particles remain spherical with weak adhesion to the substrate. In contrast, D of Fig. 14 shows that a coating dried or annealed at a temperature above polymer Tg has deformed particles. These particles cannot form a continuous polymeric film on pigments, and their adhesion depends on the chemical nature of the substrate. It is strong with calcium carbonate and weak with silica. Latex particles do not interact in the same way with calcium carbonate, silica, and mica. This behavior agrees with nuclear magnetic resonance (NMR) experiments (21, 22) which have shown that the degree of interaction between a styrene-butadiene latex and a pigment is higher for calcium carbonate than for clay.

In recent years, there has been increasing awareness of the importance of acid-base interactions in adhesion primarily as a result of the pioneering work of Fowkes (23, 24). One can consider latex particles whose core polymers have a surrounding hydrophilic layer formed by copolymerized acrylic acid sequences as acidic surfaces. According to the acid-base theory the latex adhesion to a substrate will therefore be stronger, if the pigment is a basic surface. For mineral products, the acidic or basic nature of the surface derives from the isoelectric point of the surface (IEPS) (25). This is the pH value of suspensions of the pigments in water at which the surface charge is zero, i.e., the number of positive charges equals the number of negative charges and the zeta potential is zero. A low IEPS value indicates an acidic surface and a high IEPS value indicates a basic surface.

The IEPS values are 2, 6, and 9.6 for silica, mica, and calcium carbonate, respectively. The silica surface is an acidic surface, the calcium carbonate surface is a basic surface, and the mica surface is intermediate between the two. Latex adhesion to the substrate therefore increases with the basic nature of the mineral surface. This proves that acid-base

interactions between polymer particles and the substrate control latex adhesion. To obtain good adhesion with an acidic surface like silica, there should be a covering of the latex particles with a basic layer.

The acid-base interactions can also explain the observed influence of latex acid content on particle spreading. With a basic surface like calcium carbonate, the spreading ratio increases with latex acid content as Fig. 13 indicated. When the polymer chain mobility is high enough to allow particle spreading (a condition which occurs above the polymer Tg), modifying the acid-base interactions between latex particles and the surface can control the spreading ratio.

The results obtained in this study are useful to establish connections between the structure of a coating and its properties:

- The particle spreading ratio increases with latex acid content. This means that the contact surface as well as the adhesion between polymer particles and mineral pigments within the coating increases with a high acid content latex. This also improves the coating cohesion.
- The adhesion of latex particles depends on the chemical nature of the substrate. Specific interactions between polymer particles and pigments might explain to a certain extent the influence of the pigment (clay or calcium carbonate) on coating properties.
- Clay, an aluminosilicate like mica, contains plates. The crystalline structures and the physical and chemical properties of faces and edges are different. In particular, the IEPS value is not the same for faces and edges. The IEPS value is about 7.5 for the edge surface, and it is equal to 6 for the face surface. This means that latex adhesion to clay is higher on edges than on faces. Consequently, the in-plane strength for clay coatings

must be higher than the z-direction strength observed experimentally (21, 22).

- Compared to calcium carbonate, however, the clay surface is less basic. Latex adhesion to the pigment is therefore stronger with calcium carbonate than with clay. This means that calcium carbonate gives a higher strength than clay in a dry picking resistance test of coating layers (22). Obviously, acid-base interactions cannot explain all the observed differences. It is necessary to consider other parameters such as pigment shape.
- The results on particle spreading might help to understand the printing process. The porosity and the interfaces within the layer control the penetration of ink and water in the coating. By adjusting the specific interactions between the polymer particles and the mineral surface, one could control the particle spreading and therefore the extent of polymer to air interfaces within the coating.

Our AFM results show that acid-base interactions between latex particles and the surface control the particle spreading ratio at temperatures above Tg. This work used styrene-butyl acrylate latexes. We did not study the influence of the chemical nature of monomers. For a given mineral substrate, acid-base interactions only depend on latex acid content. We therefore think that the same results would occur with styrene-butadiene latex particles surrounded by membranes made of acid sequences. With the AFM technique, we can quantify the particle adhesion and spreading. Our results used a model system containing latex on a mineral substrate. The question of whether some components of coating colors such as dispersing agents and cobinders have an influence on latex particle spreading and adhesion remains for answer and is currently under investigation.

Conclusion

This study shows that AFM can investigate the ordering and adhesion of latex particles on an inorganic surface at the particle scale. After drying, there is a monolayer of rather well dispersed particles on the surface. In particular, there is no flocculation or aggregation.

Above polymer T_g , there is a sudden and partial spreading of the surface governed by the polymer chain mobility and not by capillary forces. Acid-base interactions between latex particles and the surface control the particle adhesion and spreading ratio. Increasing the latex acid content can improve particle spreading. ■

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