Surface Structure of Latex Films, Varnishes, and Paint Films Studied with an Atomic Force Microscope

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The surface topographies of different latex films, varnishes, and white paint films were investigated with an atomic force microscope. Four different latexes, consisting of homogeneous and composite particles as well as mixtures of different particles, were studied. The atomic force microscope proved to be an appropriate tool to reveal the surface structure of the films under ambient conditions. One result was that the gloss of the paint film is strictly correlated to the surface roughness of the corresponding pure latex film. With the exception of one example, the study revealed that solvents needed to prepare a varnish tend to reduce the surface roughness.

INTRODUCTION

Decorative coatings based upon latex dispersions are becoming more and more important. The use of modern binders enables one to minimize the amount of volatile organic compounds (VOC) in a paint or varnish formulation. Binders based on latex dispersions consist of polymer particles dispersed in an aqueous medium often stabilized by surfactants to prevent flocculation. When cast onto a substrate, water evaporates and a continuous clear film forms.[1-7]

We studied the surface structure of latex dispersion films, varnishes, and white paint films with an atomic force microscope (AFM).[8] With the AFM, topographic images of surfaces can be obtained at high resolution. Imaging can be done in air without taking special care for a dust-free environment. No special preparation is needed, and the samples do not have to be exposed to vacuum. For this reason the AFM has been used to study latex dispersion films.[9-18]

To our knowledge this is the first systematic AFM study of varnishes and paints based on latex dispersions. The purpose of this study was: (1) to reveal the surface morphology at high resolution without dehydrating or coating the films; (2) to find correlations between the microscopic surface structure and macroscopic parameters like hardness or gloss; and (3) to find morphological characteristics which provide information about film formation.

Four different latex dispersion films and the corresponding coatings based on a paint and varnish formulation were studied. Homogeneous latex particles, composite particles, and mixtures of latexes were used as binders. Solvents, pigments, and wax emulsions were chosen as critical parameters which could influence the surface properties of the film. A solvent plus wax containing varnish and a solvent plus pigment containing paint were formulated with the four binders. Adding solvents to a binder facilitates the diffusion of polymer molecules between latex particles in the film. Wax increased the hydrophobicity of the film surface. For the formulation of a paint with a pigment volume concentration (PVC) much lower than the critical pigment volume concentration (CPVC), it is of interest to compare the influence of the binder and the pigment on the surface morphology.

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Four different types of binders were chosen: HOM represented a typical, conventional homogeneous acrylic dispersion recommended for gloss paints and varnishes. COM1 was a "core-shell" type composition latex with a low MFT but better blocking resistance than HOM.* MIX was a mixture of two homogeneous dispersions. These two dispersions contained the same kind of polymers but at different concentrations, which led to different glass transition temperatures

*High-blocking resistance means that two film surfaces pressed together could easily be separated again.

Table 1—Chemical Composition of the Latexes Used and Their T_g[a]

Sample	Composition	T_g of Comp. 1	T_g of Comp. 2
HOM	MMA/BuA	+18°C	—
COM1	Styrene/MMA/BuA	–10°C	+60°C
COM2	MMA/EHA/BuA	+18°C	+90°C
MIX	MMA/EHA/BuA	+18°C	+90°C

(a) Since HOM is composed of only one component, only one T_g is reported. In the case of COM1, COM2 and MIX both components contained the given polymers, but the ratios were different which led to different T_gs for the two components.

Table 2—Mean Film Formation Temperatures of the Particles Investigated, the Diameters by Dynamic Light Scattering, the NND Measured with the AFM, and the Roughnesses Measured with the AFM on Pure Polymer Films, Polymer Films Prepared with Solvent, Varnishes, and White Paint Films[a]

Sample	MFT °C	Diameter nm	NND nm	Roughness nm	Rougheness + Solvent nm	Roughness Varnish nm	Roughness Solvent nm
HOM	15	100	93	4.6	2.6	2.2	24
COM1	0	100	—	7.7	2.8	3.9	20
COM2	28	100	93	8.6	7.7	6.9	26
MIX	30	70	63	14	16	16	21

(a) For COM1 no NND could be determined because single particles could not unambiguously be identified.

(*Table* 1). For another sample, COM2, the same two dispersions were used. In this case, however, composite particles were formed. The film surfaces of COM2 and MIX were harder and more scratch resistant than the surfaces of HOM and COM1 films.

MATERIALS AND METHODS

Latex Film, Varnish, and Paint Film Preparation

Four different latex dispersions were used: HOM consisted of homogeneous particles. Relatively soft (COM1) and hard (COM2) composite particles were the basis for two other latex dispersions. Finally, a latex dispersion containing a 1:1 mixture of homogeneous soft and hard particles was studied (MIX).

The mean particle diameters were determined with dynamic light scattering as described in reference (19). The glass transition temperature (T_g), measured by differential scanning calorimetry (DIN 53765, temperature change 10 K/min), and the minimum film formation temperatures (MFT[20]), measured as described in reference (7), are given in *Tables* 1 and 2, respectively. The MFT could only be measured between 0 and 44°C. Gloss was measured by a glossmeter (Dr. Lange, Laborreflektormeter RL3) at an angle of 20° after seven days drying of the paint films.

Latexes were prepared from different compositions (*Table* 1) of 2-ethylhexylacrylate (EHA, T_g = –85°C), n-butyl acrylate (BuA, T_g = –54°C), methyl methacrylate (MMA, T_g = 105°C), and styrene (T_g = 100°C). Homogeneous latexes prepared in one step (HOM, both components of MIX) and composition particles prepared in two steps (COM1, COM2) according to Eckersely and Rudin[7] were investigated. In the case of COM1, COM2, and MIX, the two emulsions were mixed in a ratio of 1:1. The two emulsions of COM2 were the same as used for the two emulsions of MIX.

In the semicontinuous emulsion polymerization process, 10 wt% of the emulsion was used in a seed initial copolymerization. The emulsifier used was sodium tri-butylnonylphenol sulfonate at a concentration of 3 wt%.

A varnish was obtained by mixing 74.5 wt% latex dispersion (ca. 50% solid content), 3 wt% wax, 2.5 wt% methoxybutanol, 1 wt% 1,2 propandiol, 1 wt% Texanol™ (2,2,4-trimethyl-1,3-pentadiol-monoisobutyrate), 0.4 wt% polyurethane thickener (Tafigel PUR 40), 0.2 wt% preservative (Mergal K 10, benzisothiazolinone), 0.2 wt% wetting agent (AMP 90, 2-amino-2-methylpropanol), 0.2 wt% defoamer plus water.

The white paint contained 56 wt% latex dispersion, 21 wt% TiO_2 particles of approximately 300 nm diameter, 6.5 wt% propyleneglycol, 1.5 wt% methoxybutanol, 0.5 wt% Texanol™, 2 wt% thickener (Mowilith VDM 7000, associative acrylate thickener), 0.8 wt% dispersing agent (Lopon 890, polyacrylate), 0.3 wt% neutralization agent (ammonium), 0.2 wt% preservative (Mergal K 10), 0.2 wt% wetting agent (AMP 90), 0.2 wt% defoamer (Agitan 295) plus water. The PVC was about 20%.

Films, varnishes, and paint films were prepared by casting the dispersion onto microscope slides with a wet film thickness of 100 μm, leading to a thickness of the dry film of about 50 μm. Films were formed at 22-25°C.

Atomic Force Microscopy

After three hours to five days* the samples were imaged in air with a Nanoscope™ III (Digital Instruments, Santa Bar-

*We did not expect drastic changes of surface morphology in that time span.[15]

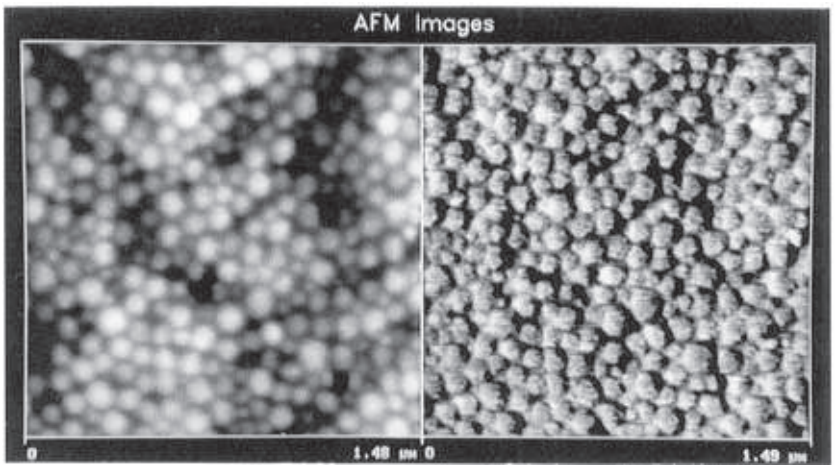

Figure 1—Surface of an HOM polymer film imaged simultaneously in height (left) and friction mode (right). The total z-range in the left image is 22 nm. For friction, only relative values are given.

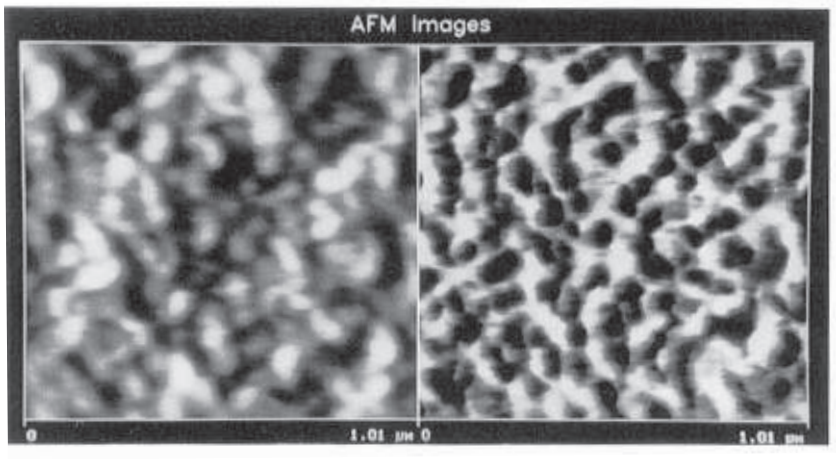

Figure 2—COM1 polymer film imaged in height (left) and friction mode (right). The total z-range in the left image is 20 nm.

bara, CA) in contact, constant force mode. We used silicon nitride cantilevers of 100 µm (spring constant 0.09 N/m) or 200 µm (spring constant 0.02 N/m) length with integrated sharpened tips (Olympus, Tokyo, Japan). The force between tip and sample was ≈10 nN. With the AFM, the topography and the friction between tip and sample could be recorded simultaneously. Typical radii of curvature of the tip were 5 nm, as specified by the manufacturer. With the same tips used here, we could image with almost atomic resolution on other samples. While scanning latex films often the resolution suddenly degraded. This was probably due to material being picked up by the tip, thus increasing its effective radius of curvature. Also the reverse—a sudden increase in resolution back to the original performance—was frequently observed. In this case the tip probably lost the material again.

To characterize films, the roughness (mean square deviation from the mean plane measured over 2×2 µm^2) and the peak-to-valley distance Δz (difference between the height measured on top of a particle and in interstitial regions) were measured. In addition, the nearest-neighbor-distance (NND) is reported. The mean NND was not measured directly. Instead, we counted the number of particles N within a certain area A. Assuming that the particles are closed packed the NND can be calculated from $\mathrm{NND} = \sqrt{A / N \sin 60^\circ}$. Hence, the nearest-neighbor-distance reported is directly a measure of the number of particles per unit area. If the particles are not closed packed, the NND reported might be slightly higher than the distance between two adjacent particles. The advantage of the method is that a large number of particles contributes and the statistical error is small.

In some cases we do not report Δz or the NND. Then we were not able to determine the parameters for two reasons: the particles were not clearly identifiable or the surface was too rough. In addition to mean values, we reported the standard deviation for single measurements. This reflects how much the result of a single measurement varied between different experiments; it is not the statistical error of the mean.

RESULTS AND DISCUSSION

Latex Films

In HOM films, individual particles were visible (*Figure* 1). Most of the originally spherical latex particles were deformed: their boundaries were not circular but deformed into polygons (mostly hexagons) and the peak-to-valley distance Δz was only 4.2 ± 2.2 nm. This is much lower than half the diameter of the particles, which one would expect for underformed particles. Also the roughness of 4.6 ± 1.0 nm was relatively low (*Table* 2).

With the AFM we measured an NND of 93 ± 1 nm compared to 100 nm measured by dynamic light scattering. With dynamic light scattering the hydrodynamic diameter of the particles was measured. The hydrodynamic diameter is larger than the actual particle diameter. Comparing results obtained with other particles using laser aerosol spectroscopy*[19] and dynamic light scattering, we estimated that the hydrodynamic diameter is 5-9 nm larger

*Laser aerosol spectroscopy could only be used reliably with particles having a diameter larger than 100 nm.

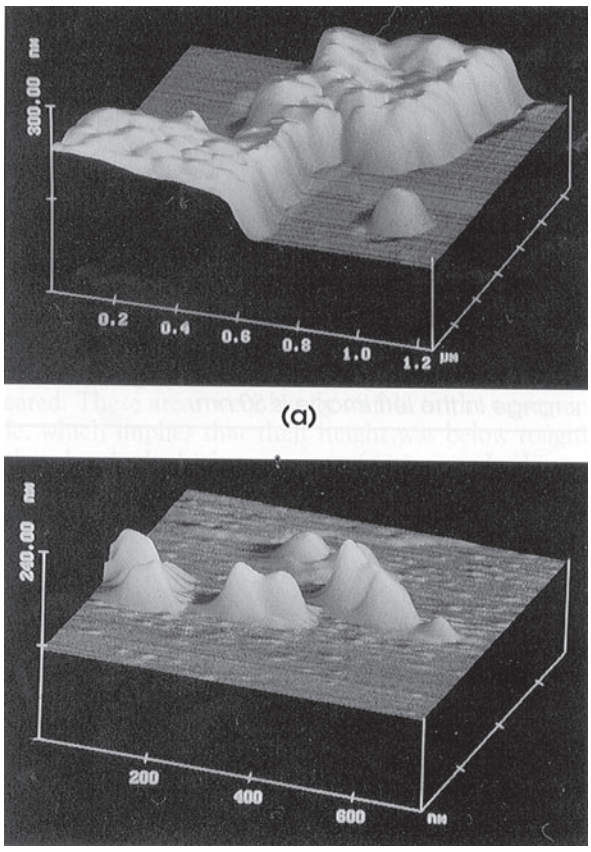

Figure 3—Single particles on a mica surface. a—HOM particles often formed large aggregates or lay isolated on the mica. b—COM1 particles tended to form pairs or rows.

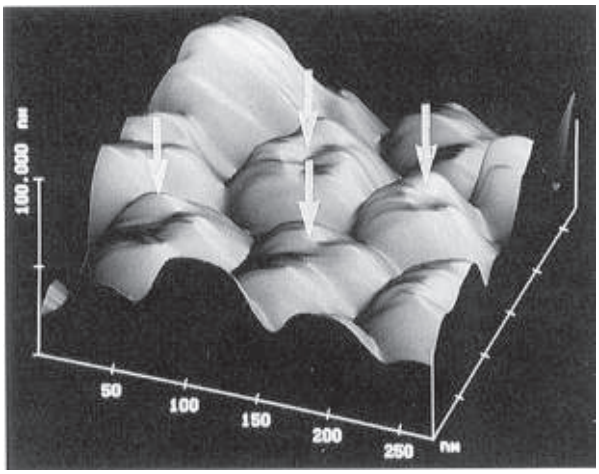

Figure 4—Typical doughnut-shape of particles in COM2 polymer film. The positions of four individual particles are indicated by arrows.

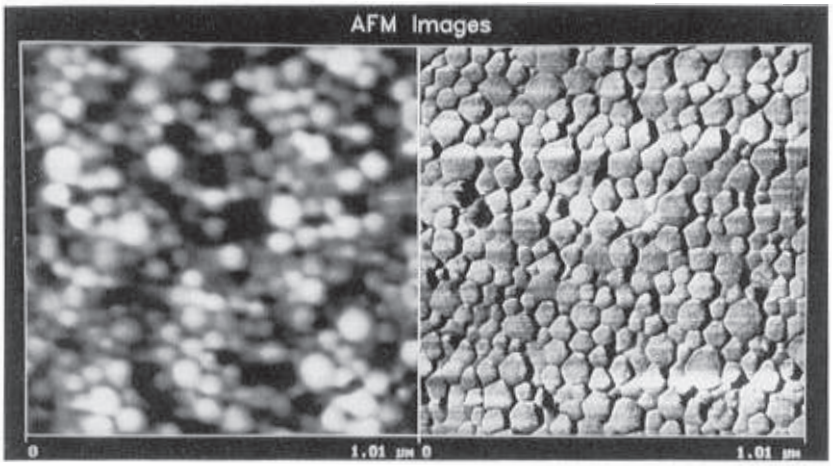

Figure 5—MIX polymer film imaged in height (left) and simultaneously in friction mode (right). The total z-range in the left image is 50 nm.

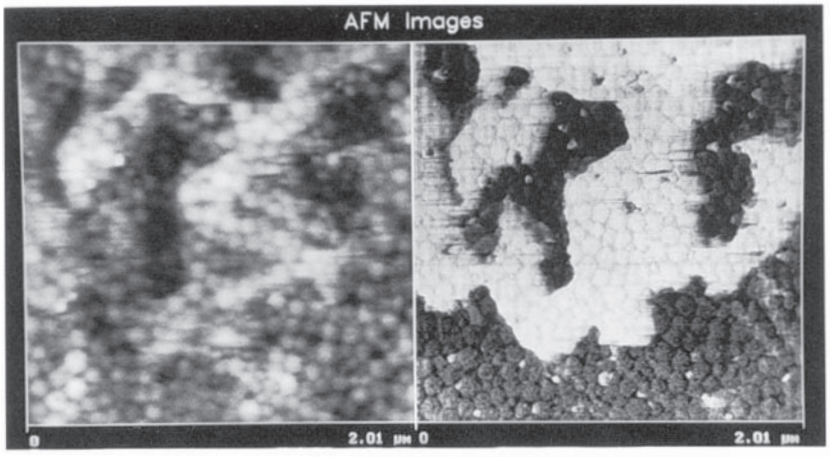

Figure 6—Varnish HOM imaged simultaneously in height (left) and friction mode (right). The total z-range in the left image is 13 nm.

than the real particle diameter. Hence, the NND is similar to the particle diameter.

For hard, undeformable spheres, one expects an NND equal to the particle diameter. Due to deformation of the particles, the NND is expected to decrease.[2,7,21,22] However, Goh et al.[11] found no decrease of the NND on the surface of latex films formed from poly(butyl methacrylate) particles above their MFT. They concluded that the particles deformed but did not interpenetrate. Butt and Gerharz[18] observed a decrease of the NND on layers which were formed 5-20°C below their MFT, on films formed above the MFT the NND was similar to the particle diameter. HOM was also formed above its MFT. Hence, it seems as if one can distinguish three regimes: in layers formed far below their MFT, the particles do not deform at all. Slightly below their MFT the particles deform, and the NND becomes smaller than the particle diameter. If the film is formed above the MFT the particles clearly deform, as indicated by the low Δz, but the NND is similar to the particle diameter again. In this case, film formation is probably better described by a viscous flow of the polymer rather than the deformation of an elastic sphere.

COM1 films (*Figure* 2) were, with a roughness of 7.7 ± 3.0 nm, slightly rougher than HOM films. Still a granular structure was visible, but individual particles could not unambiguously be identified. The reason is probably the lower MFT of COM1 films, and the more complex morphology of composite particles.

Particles in COM1 films showed a tendency to aggregate in pairs or rows. This can be seen in the friction mode (*Figure* 2, right). To investigate this aggregation more accurately, we diluted the latex dispersion $1{:}10^5$ in distilled water and 10 µl of the solution was pipetted onto a freshly cleaved mica surface and allowed to dry. A minor part of the mica surface was covered by a relatively densely packed monolayer of latex particles. Large areas, however, were almost free of latex particles. On these parts we often observed pairs or chains, sometimes small clusters of latex particles (*Figure* 3b). These pairs or chains were far less frequently observed in samples prepared with HOM in the same way (*Figure* 3a). On HOM samples either large clusters or single, isolated particles were imaged [also see reference (18)]. This indicates that the COM1 particles were not isotropic—either in their polymer composition or the surfactant distribution.

In COM2 films, individual particles were visible but the boundaries were indistinct. The shape of the particles was clearly no longer spherical. Often doughnut-shaped particles were observed in films (*Figure* 4). The NND of 93 ± 4 nm was about the same as the particle diameter (*Table* 2). However, in this case the NND is not very reliable. Due to the inhomogeneous shape of the particles they were difficult to count. In addition, the in-

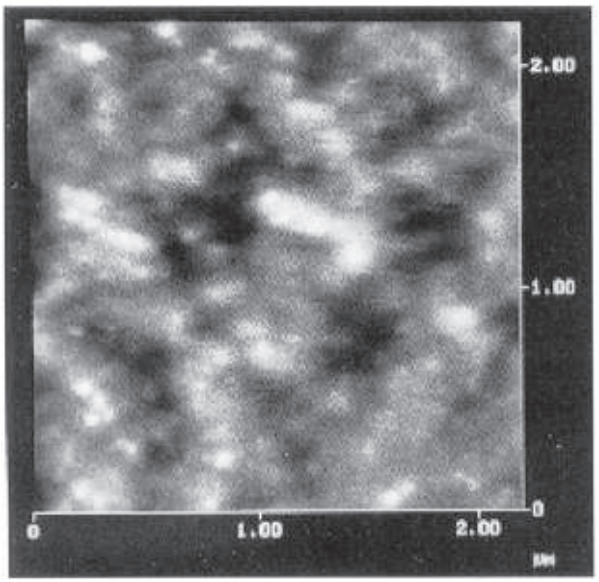

Figure 7—Top view of varnish COM1. The total z-range is 17 nm.

terpretation of the NND is not straightforward because it should depend on the relative orientations of adjacent particles.

MIX films had a high roughness of 13.6 ± 2.5 nm. In films, individual particles could be identified (*Figure* 5). The particles were deformed and had a polyhedral shape, which can be seen in the friction mode. An NND of 63 ± 3 nm was measured in agreement with the particle diameter (*Table* 2).

The high roughness of MIX films is difficult to understand. A possible explanation is that the soft particles (T_g = 18°C) acted as a glue. When casting the dispersion on a substrate, water evaporates and the concentration of particles increases. When a soft particle comes into contact with a hard particle, it adheres, deforms, and due to the large contact area binds strongly. Soft particles are not free to move on the surface of a hard particle. In contrast, when two hard particles come into contact they may adhere but they do not deform significantly and one particle is free to move on the surface of the other. If a pair of particles comes into contact with another particle, hard particles can rearrange. If soft particles are involved, this rearrangement is impossible or at least hindered. The hindered possibility to rearrange during the first stage of film formation may be the reason for the high roughness.

Films made from a dispersion which only contained particles with a polymer composition of the low T_g component had a small roughness of about 3 nm. This was expected, because when the temperature is above the T_g the polymer can diffuse. Though, according to our hypothesis the films might have been rough after the first stage of film formation, they become smoother due to polymer diffusion and viscous flow of the polymer.

Films COM2 and MIX were relatively hard and scratch resistant. This is understandable: in films COM2 the hard particle shell, made of the polymer of T_g = 90°C, is responsible for the mechanical stability. In MIX films the soft particles, after melting, probably fill the voids and gaps between hard particles. Hence, most macroscopic structures touching a MIX film first come into contact with the protruding hard particles. Only sharp structures, with radii of curvature much smaller than particle radii, have a chance to come into contact with the soft interstitial areas.

Varnishes

Two main ingredients are responsible for making a varnish instead of a polymer film: a solvent and wax. To determine the effects of these ingredients, we imaged (1) films prepared only with solvent without wax; (2) films prepared with solvent and wax (normal varnish); and (3) films prepared with solvent and an extra amount of wax.

The main effect of the solvent was a reduction of the surface roughness (*Table* 2). Solvent is known to reduce the MFT.[23-25] Hence, film formation and particle coalescence was probably more progressed in the presence of solvent. Accordingly, the peak-to-valley distance in HOM films was reduced from 4.2 nm to 2.7 ± 1.7 nm.

Films MIX were, however, an exception: the roughness slightly increased when adding solvent. This finding is in accordance with the proposed explanation for the high roughness of MIX polymer films: the soft particles hinder a rearrangement of the latex particles during the first stage of film formation. Hence, making the soft particles even more deformable might even increase their tendency to prevent this rearrangement.

The effect of wax was slightly different for the four polymer films. On HOM varnish surfaces area of few 100 nm extension appeared. These areas were barely visible in the topographic mode, which implies that their height was below roughly 2 nm, but they had a high contrast in friction mode (*Figure* 6). Since these layers did not appear on films prepared without wax, we think that the surface of the varnish was partly

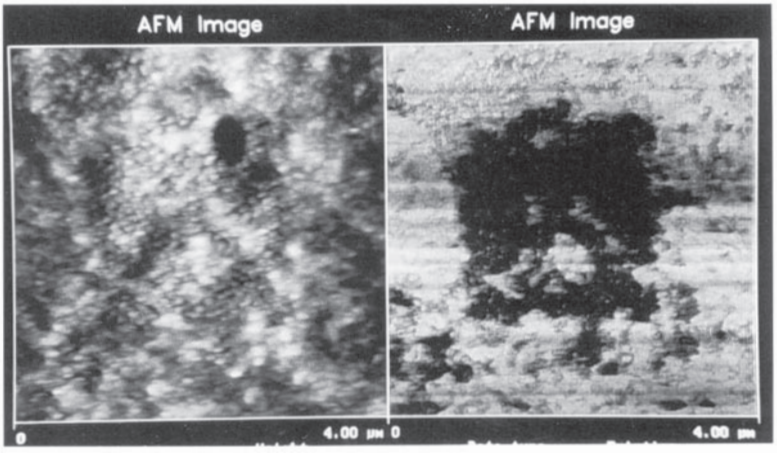

Figure 8—Top view of varnish COM1 prepared with an extra amount of wax imaged in height (left) and friction mode (right). The total z-range in the left image is 35 nm. The central square was scraped free of wax by scanning it several times with an increased force.

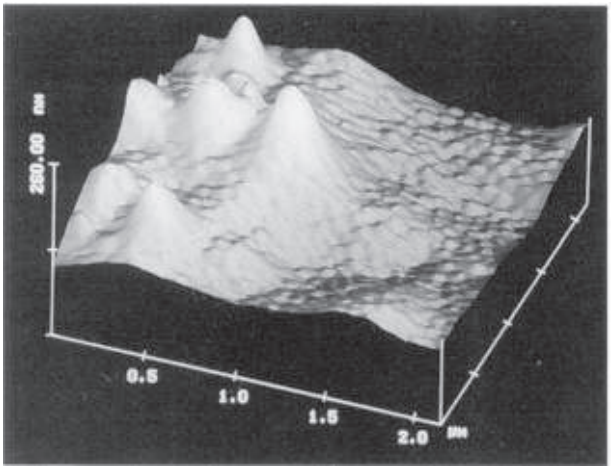

Figure 9—Surface plot of a white paint based on HOM.

covered by a thin layer of wax. It is also possible that the areas were formed by the surfactant which was squeezed out of the film during film formation. This was previously observed.[15,18] Then, however, one needs to assume that wax influences the behavior of the surfactant.

Images of varnish COM1 (*Figure* 7), and to a lesser degree COM2, looked hazy. This was probably due to a thin layer of homogeneously distributed wax because images of varnishes prepared without wax were clear. On varnishes COM1 prepared with an increased amount of wax, we were able to remove parts of the wax layer off the surface (*Figure* 8). This was accomplished by scanning that region several times with a relatively high force of about 30 nN.

A difference between preparations HOM on one side and COM1 and COM2 on the other side lay in the distribution of the wax layer: in HOM we observed patches of wax while COM1 and COM2 were homogeneously covered. We would like to mention, however, the possibility that varnishes HOM were also covered with a continuous layer and that the tip formed patches out of a homogeneous layer. Though this is unlikely, because the layers observed were stable, we cannot totally exclude that possibility.

On varnishes MIX the only wax effect we observed was in deepenings: they were often filled with a material, which had a smooth surface. This material was probably wax since it is not present in varnish prepared without wax. However, due to the high surface roughness, subtle effects might not have been visible.

White Paints

In paint films HOM, the TiO_2 particles were conspicuous (*Figure* 9). Even the boundaries of the TiO_2 particles were visible. Increasing the TiO_2 particle concentration also increased the number of large particles observed per area. As in the other paints the top parts of the TiO_2 particles protruded about 60 nm from the otherwise smooth polymer film. This increased the roughness of the surfaces of 20-25 nm. The TiO_2 particles imaged were smaller than their diameter. Hence, only the top protruded from the film, much like an iceberg in water.

In paints MIX and COM2 also the TiO_2 particles were visible, but, in contrast to paints HOM and COM1, the boundaries were indistinct (*Figure* 10). Images looked as if the TiO_2 particles were covered with a layer of latex particles. This indicates that the interaction between latex particles COM2 and MIX with TiO_2 particles is stronger than the interaction between HOM and COM1 latex particles and TiO_2 particles. The coverage of TiO_2 particles with latex particles might affect

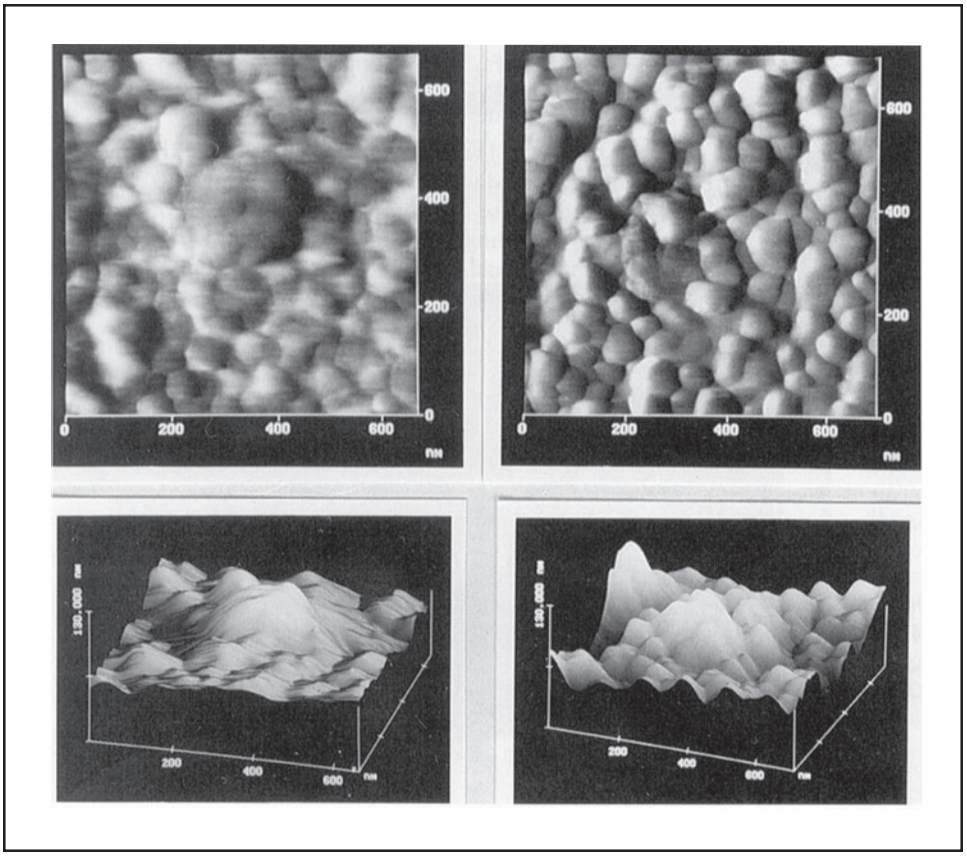

Figure 10—White paint COM1 (left) and MIX (right) imaged simultaneously in height (as surface plot) and friction mode (top view). In each case a TiO_2 particle is shown. In friction mode it can be seen that the TiO_2 particles of sample MIX are covered with latex particles. It is also visible that the surrounding latex film is rougher in MIX films than in COM1 films.

the macroscopic behavior (e.g., surface energy, hydrophobicity, hardness) of the paint film: when the TiO_2 particles are covered with latex, the latex dominates the properties of the paint film. Otherwise, the TiO_2 particles contribute to the surface characteristics.

CONCLUSION

The nearest-neighbor-distance between adjacent latex particles in films formed above the MFT is expected to be smaller than the particle diameter.[2,7,21,22] In contrast, in all films studied we found no significant decrease of the NND.

The roughness of latex films is correlated with the gloss of varnishes based upon these latexes: a low roughness led to high gloss and vice versa.

Films formed from a latex composed of a mixture of hard (T_g = 18°C) and soft (T_g = 90°C) particles showed a high roughness. A possible explanation is that the soft particles might hinder a rearrangement of the particles during the first stage of film formation.

Solvents needed to prepare a varnish tend to reduce the film roughness.

The interaction between latex and TiO_2 particles was different for the paint films studied. In some cases the TiO_2 particles were totally covered with latex particles, in other cases the bare, uncoated TiO_2 surface was observed.

ACKNOWLEDGMENTS

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