

# Stability and Film Properties of Tung Oil Modified Soybean Alkyd Emulsion

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**ABSTRACT:** A series of tung oil modified soybean alkyd emulsions are prepared by an inversion emulsified technique. In these alkyd resins, the tung oil contents are about 0, 12.5, and 25.0 wt % (based on the total oil). Using IGEPAL CO-630 as the surfactant, a very stable alkyd emulsion can be obtained. With the increase of the tung oil contents in alkyd emulsions, the initial droplet sizes of the emulsions increase dramatically. Aging under 50°C can eliminate the difference in droplet sizes; the final droplet sizes of the emulsions are about 50 nm. The alkyd resins also have good hydrolytic stability. The tung oil contents in the alkyd resins also strongly influences the film properties; suitable tung oil content improves the film gloss. An atomic force microscopy investigation shows that the film from the alkyd emulsion is more water sensitive; after a 50-h deionized water immersion, the film surface appears to have a lot of dents. This indicates that the film surface may be very rich in surfactant species. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1698–1706, 2000

**Key words:** alkyd emulsions; soybean oil; tung oil; monoglyceride; alkyd resin; atomic force microscopy

## INTRODUCTION

Emulsion polymerization is an important method to disperse polymers in water. A lot of monomers, such as styrene, alkyl (methyl)acrylate, vinyl acetate, and so on, can be used in emulsion polymerization; the product is usually called latex. Latexes with different particle sizes and properties can be prepared by different polymerization processes, such as conventional emulsion polymerization,<sup>1,2</sup> dispersion polymerization,<sup>3</sup> mini-emulsion polymerization,<sup>4</sup> soapless emulsion polymerization,<sup>5</sup> macroemulsion polymerization,<sup>6</sup> and so on. Now the emulsion polymerization pro-

cess has become the most widely used polymerization technique in industry, especially in the coatings field. Because latex is a heterogeneous system and the polymer is highly dispersed in water, it usually needs the help of a film forming agent to form a good film. Because the film usually does not cure, the film properties are sometimes unsatisfactory for use. In order to improve the film properties, some functional monomers were introduced into the polymerization system.<sup>7,8</sup> These functional monomers can supply crosslinked points in dry film. But the improvements were usually limited and the price of the latex increased. Under this condition, alkyd resins were again sought as a dispersed phase in the emulsion.

The alkyd emulsions were prepared by a postemulsified process (i.e., the alkyd resin were dispersed in water as fine droplets). A crucial

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factor for acquiring good colloidal stability is that small droplets are obtained in the emulsification process.<sup>9</sup> The choice of surfactants here is critical. For a nonionic surfactant, it is essential to consider the hydrophilic-lipophilic balance (HLB) values of the surfactants. These should be selected based on the polarity of the resin to be emulsified (e.g., the hydroxyl value, oil length, and acid number) and other parameters, such as the degree of the neutralization and emulsified temperature. An increased degree of neutralization has been shown to increase the HLB value of the nonionic surfactants whereas it is decreased by increasing temperature. Addition of ionic surfactants, particularly anionic surfactants, has been found to raise the temperature stability of emulsions. A suitable surfactant simplifies the formation of the droplets during emulsification and afterward stabilizes them against flocculation and coalescence.<sup>10,11</sup> A good surfactant fulfills these requirements even at low concentrations. The neutralizing agents and the emulsified temperature also influence the emulsion properties. The presence of both neutralizing agents and surfactants leads to a further decrease of the interfacial tension and reduces the droplet size.

Emulsions are always an unstable system in a thermodynamic sense. Their stability is not a matter of equilibrium but a question of kinetics. The possible pathways of the destabilization of an emulsion may have two steps. The first step is the so-called flocculation of the droplets; this means that they coagulate but retain their individuality. This process can be monitored by the laser scattering method. We use this method to monitor the changes of the emulsion. The second step is the ruptures occurring in the protective layer around the droplets, in which case they begin to coalesce to larger drops. This process is irreversible. Ongoing coalescence ultimately leads to a complete phase separation of the emulsion.

For alkyd emulsions, another problem is the hydrolytic stability of alkyd resins. As is known, alkyd resins are polyesters and are consequently susceptible to hydrolysis reactions in water. The hydrolysis of the ester groups can be catalyzed by either acidic or alkaline conditions and usually shows a minimum rate at pH 7. Because of the hydrolysis, the molecular weight of the alkyd decreases and the acid value increases. Also, the produced carboxylic acid groups decrease the emulsion pH and accelerate it if the emulsion was initially acidic. The reduced molecular weight affects the film properties of the emulsion-based

coating (most noticeably the film hardness), while the changes of acid value and pH may affect the stability and drying properties. Apart from the pH and temperature, the hydrolytic resistance of an alkyd emulsion depends on the alkyd's chemical composition.<sup>12</sup> For example, alkyds produced with isophthalic acid (IPA) as the dibasic acid are more hydrolytically stable than those prepared from orthophthalic acid.

We adopted a postemulsified method and inversion technique: the emulsifier was first mixed with the resin and then the water was added into the mixture at an evaluated temperature to obtain an oil and water (O/W) emulsion to prepare the alkyd emulsions. The storage stability of the emulsions, the resin hydrolytic stability, and the film properties were studied. At the same time, the film morphology when immersed in deionized water was directly observed by atomic force microscopy (AFM).

## EXPERIMENTAL

### Materials

Soybean oil was supplied by Cargill Company (technical oil, iodine number =  $\sim 137$ ; percent by weight of the fatty acid content was 12.0% palmitic, 4.3% stearic, 23.1% oleic, 53.5% linoelic, and 7.1% linolenic). Tung oil (ca. 80% ester of eleostearic acid and ca. 20% ester of linolenic, 9,12-linoleic, oleic, steric, and palmitic acids), trimethylolpropane (TMP), 2-butoxyethanol, *n,n*-dimethyl ethanolamine, toluene, 2-propanol, and 0.1N potassium hydroxide solution in methanol were purchased from Aldrich Chemical Company. Purified IPA was supplied by AMCO Company. Fascat 4100 (butylstannic acid) was supplied by Elf Autochem Company. IGEPAL CO-630 [nonyl phenoxy, poly(ethyleneoxy)ethanol, branched;  $(C_2H_4O)_n C_{15}H_{24}O$ ,  $n = 9-10$ ] was supplied by Rhone-Poulenc. Hydrocure® II 5% cobalt, Hydrochem® 5% calcium, and Hydrochem® 12% zirconium were supplied by the OM Group Inc. Exkin® #2 (methylethyl ketoxime) was supplied by Huls Company. BYK® 301 (a solution of a polyether modified dimethylpolysiloxane copolymer) was supplied by BYK Chemie.

### Synthesis of Alkyd Resins

One hundred forty-six grams of soybean oil and tung oil (varying the feed weight ratio, see Table I) and 67 g of TMP were charged to a 500-mL

three-necked round-bottom flask equipped with a total condenser, a water separator, an agitator, an inert gas sparge that lead the N<sub>2</sub> below the level of the liquid, and a thermometer. The reaction mixture was heated to 204°C under an N<sub>2</sub> atmosphere; 0.11 g of the Fascat® 4100 catalyst was added. Heating was continued until a temperature of 250°C was reached (about 15 min). After the temperature reached 250°C, the reaction was continued and monitored by withdrawing a 1-mL sample from the flask every 15 min and adding the sample to 3 mL of methanol to check its solubility. After about 1 h at 250°C the 1-mL sample was completely soluble in 3 mL of methanol, indicating that the alcoholysis reaction was approaching equilibrium. After the heating was stopped and the temperature dropped to 180°C, 100 g of IPA was charged to the reaction flask. Then the reaction mixture was heated again until a temperature of 250°C was reached (about 25 min). This temperature was maintained and the water was separated under the N<sub>2</sub> atmosphere by the water separator. When the reaction system was clear (about 2.5 h), a 1-g sample was taken from the reaction flask every 15 min and then dissolved in 100 mL of neutral solvent mixture (equal parts by volume of isopropyl alcohol and toluene) immediately. The sample was titrated with 0.1N KOH methanol solution to trace the acid value until it reached about 20. The reaction was stopped and a clear light yellow high viscosity resin was obtained.

### Preparation of Alkyd Emulsion

*n,n*-Dimethyl ethanolamine (1 mol per equivalent of carboxyl groups) and 20 g of 2-butoxyethanol were added to 100 g of warm (70°C) alkyd resin in a wide-mouth glass container equipped with an addition funnel and a high speed air-driven stirrer with a turbine propeller. Deionized water (about 50 wt % of the final total weight) was metered into the glass container over 1 h under high speed stirring. The mixture in the glass container became a high viscosity white opaque liquid at first. As more water was added, the viscosity of the mixture decreased. After the water addition was complete, the stirring was continued for 1 h. The product was a colorless, low viscosity, milky alkyd emulsion with solids of about 40 wt %.

### Storage Stability Test

Samples of alkyd emulsions were left in 125-mL wide-mouth glass bottles and stored in a 50°C

oven. After storage, a 0.2-g sample of the emulsion was weighed and dispersed in 10 g of deionized water in a glass vial with a magnetic stir bar and stirred for about 15 min. After the emulsion was dispersed completely, the droplet size was immediately measured with the laser diffraction instrument.

### Hydrolytic Stability Test

Samples of alkyd emulsions were stored in a 50°C oven or ambient temperature. After storage, a 3–4 g sample of the alkyd emulsion was accurately weighed and dissolved in 100 mL of a solvent mixture (equal parts by volume of isopropyl alcohol and toluene) in a 250-mL Erlenmeyer flask with a magnetic stir bar. After the alkyd emulsion was completely dissolved, it was titrated with 0.1N KOH in methanol to measure the acid value.

### Preparation of Emulsion Samples for Applying Film

A portion of the alkyd emulsion was charged into a wide-mouth glass container equipped with a high speed air-driven stirrer with a turbine propeller. Then 3 wt % of Hydrocure® II 5% cobalt, 3 wt % of Hydrochem® 5% calcium, 1.25 wt % of Hydrochem® 12% zirconium, 0.45 wt % of Exkin® #2, and 0.75 wt % of BYK® 301 (all percentages based on the weight of the resin) were added. Stirring was continued for about 15 min; a brown liquid was obtained.

Films were applied on 0.32 × 3 × 6 in. R-36-P phosphate dull matte steel panels (Q-Panel Company). The panels were baked at 120°C for 1 h in a forced air oven or kept at ambient temperature for 7 days and then tested. The thickness of the dry films was 20–30 μm.

### Direct Observation of Influence of 50°C Deionized Water on Film Surface

Some small applied film panels (1 × 1 cm), which were baked at 120°C for 1 h, were immersed in 50°C deionized water (in an oven); then they were gently dried with a nitrogen flow, and the film topography was immediately mapped by AFM.

### Characterization Methods

The droplet sizes of the emulsions were measured with a laser diffraction instrument (Microtac series 9200). The AFM images were obtained with a Nanoscope III scanning force microscope manu-

**Table I Synthesis, Formulation, and Properties of Alkyd Resins**

	Parts by Weight (g)		
	R1	R2	R3
<b>Materials</b>			
Soybean oil	146.4	127.2	109.3
Tung oil	0 (0%) <sup>a</sup>	18.0 (12.5%)	36.4 (25%)
TMP	67.2	66.6	67.1
IPA	100.4	100.2	99.9
<b>Resin properties</b>			
Appearance	Clear	Clear	Clear
NVM (%)	100	100	100
Acid value	17.9	19.8	23.8
Oil length (%)	50	50	50

<sup>a</sup> The weight percent is based on the total oil.

factured by Digital Instruments (Santa Barbara, CA). A J scanner and a V-shaped traditional silicon nitride cantilever (with a length of 100  $\mu\text{m}$ , a spring constant of 0.58 N/m, and a silicon nitride sharpened tip) were used. The scan rate was 2.001 Hz.

The acid value and nonvolatile weight percentage (NVW%) were measured using ASTM D-1639 and ASTM D-2369, respectively. All pH measurements were done using a Fisher Account model 925 pH meter. The film thickness was measured with a DeFelsko Mikrotest magnetic film thickness gauge. The gloss was measured with BYK Microgloss glossmeter. The pencil hardness was measured according to ASTM D-3363-92a. The impact resistance was measured using a Gardner impact tester having a maximum impact of 1.84 m kg (160 in. lb).

## RESULTS AND DISCUSSION

### Preparation and Properties of Alkyd Emulsions

Three alkyd resins (R1, R2, and R3) containing different ratios of soybean oil and tung oil were synthesized by condensation polymerization of IPA and monoglyceride, which was prepared by alcoholysis from TMP, soybean oil, and tung oil. The formulations and properties are summarized in Table I. The table shows that in all three formulations the synthesis, excess hydroxyl group, and soybean oil and tung oil were the same, but the tung oil contents were different; they were 0, 12.5, and 25 wt % for R1, R2, and R3, respectively.

All the resins were clear and possessed high viscosity. Their acid values were 17.9, 19.8, and 23.8 for R1, R2, and R3, respectively. The alkyd resins had the same oil length. The oil lengths of the alkyd resins were about 50 as calculated from the following equation:

oil length

$$= \frac{\text{weight of soybean oil and tung oil in monoglyceride}}{\text{weight of alkyd - water evolved in synthesis}} \times 100$$

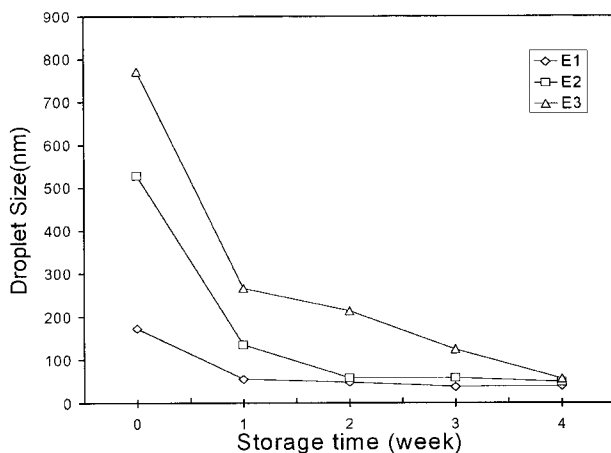
Three alkyd emulsions, E1, E2, and E3, were prepared from R1, R2, and R3, respectively. The formulations and properties are listed in Table II. The emulsifier was IGEPAL CO-630. The emulsions had a similar appearance (milky) and pH value, but the initial droplet sizes were quite different. With increasing tung oil content, the initial droplet size increased from 172 to 771 nm. An increase of the tung oil content in the alkyd increased the viscosity of the alkyd resin a lot. In order to make the emulsion have a similar viscosity, E3 had to have more water added than E1 and E2; so, E3 (33 wt %) had lower solid content than those of E1 (43.2 wt %) and E2 (42.3 wt %).

The emulsions (E1, E2, and E3) were left in an oven at 50°C for 4 weeks in order to study the emulsion stability. Their droplet sizes were mea-

**Table II Formulation and Properties for Alkyd Emulsion**

	Weight Percentage (wt %)		
	E1	E2	E3
<b>Materials</b>			
R <sub>x</sub>	34.9	40.70	28.0
IGEPAL CO-630	3.15	3.25	2.30
2-Butoxyethanol	7.90	8.04	5.75
1-Pentanol	0.37	0.40	0.31
N,N-Dimethylethanolamine	1.17	1.36	1.07
Deionized water	47.97	49.49	61.68
<b>Emulsion properties</b>			
Appearance	Milky	Milky	Milky
Droplet size (nm)	172	527	771
NVM (%)	43.2	42.3	33.0
pH	7.62	7.64	7.71

<sup>a</sup> The variable *x* denotes 1, 2, and 3, respectively.

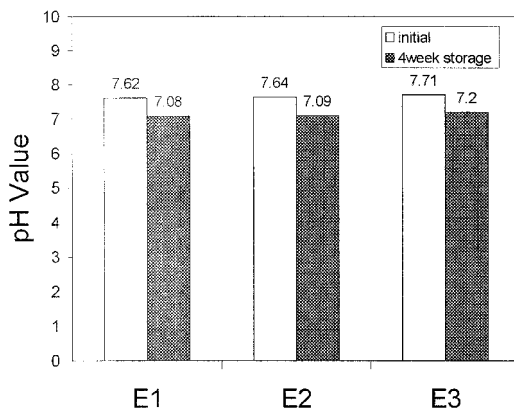


**Figure 1** The influence of 50°C storage on the droplet sizes (nm) of E1, E2, and E3.

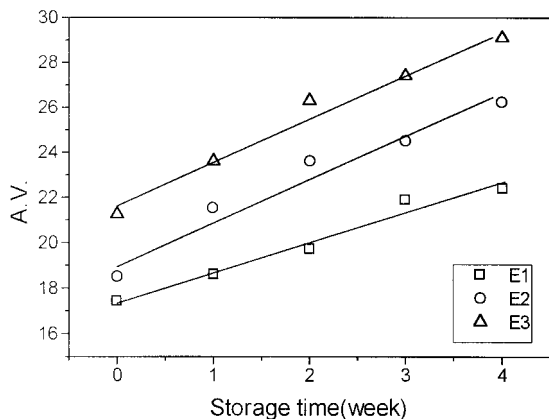
sured each week. The results are shown in Figure 1. The figure shows that all samples were very stable under 50°C storage; none were broken after 4 weeks of evaluated temperature storage. The emulsions had very different droplet sizes before they were put in the oven; however, after being stored in the oven at 50°C, all the droplet sizes were substantially reduced and became very close to each other. They were about 40–56 nm after 4 weeks of oven storage. The emulsion appearances also changed from milky to translucent and finally to almost transparent. The pH value also had a little change. The initial pH was 7.6–7.7; after 4 weeks at 50°C storage, the pH value dropped to 7.1–7.2 (see Fig. 2).

Alkyd emulsions are mostly used in air-dry paints and lacquers, but the alkyds that are used are usually long oil alkyds; such resins are suitable for emulsification because their viscosities are relatively low. There is also an emerging interest in emulsification of medium and short oil alkyds; because these kinds of alkyds have relatively high viscosity, the emulsification process is more difficult. However, at low temperature and atmospheric pressure, we prepared the emulsion and fine droplet sizes were obtained; but the initial droplet size of the emulsion strongly depended on the resin's viscosity, surfactant content, and surfactant type. We tried some surfactants, such as GAFAC RE-610 [ $C_9H_{19}C_6H_4O(C_2H_4O)_9PO_4H_2$ , anionic, Rhone-Poulenc], IGEPAL CA-887 [ $C_8H_{17}C_6H_4O(C_2H_4O)_{30}H$ , nonionic, Rhone-Poulenc], Witflow 928 (organic polymer blend, Witico), IGEPAL CO-630, and so forth, and found that IGEPAL CO-630 and Witflow 928 were suitable for the alkyd. The IGEPAL

CO-630 is much more effective for the alkyd system, so it was selected as a emulsifier for this alkyd system. Three emulsions (E1, E2, and E3) were prepared using the IGEPAL CO-630 and resins R1, R2, and R3. The emulsions had very different initial droplet sizes; this may be due to their very different alkyd viscosity. With the increase of the tung oil content in the alkyd resins, the viscosity of the alkyds increased dramatically; this may be related to the conjugated double bonds of the tung oil. These double bonds are active under the reaction condition. With the increase of the tung oil content from 0 to 12.5 and then to 25.0 wt %, the viscosity of the monoglycerides increased from 370 to 600 and then to 880 cP (Brookfield Viscometer, model DV-II, at 25°C). This suggests that some conjugated double bonds of tung oil reacted with each other under the reaction condition. The difference of the initial droplet size can be eliminated in 50°C oven storage. After some time storage (aging) in an oven above room temperature (50°C), the droplet sizes of the emulsions gradually decreased; the final droplet size had a similar small value, so the droplet size was stable for further storage. We consider these results as relating to the emulsion system not reaching the equilibrium condition at the beginning; the higher the viscosity of the resin, the further away from the equilibrium of the emulsion. This result also indicates that the emulsion system is very stable. If it is an unstable emulsion system, the emulsion will break under the evaluated temperature storage for a couple of weeks. The stability of the emulsions might originate from two aspects: one is that the surfactant has suitable HLB, which can match the alkyd resin; the other aspect might relate to the salted



**Figure 2** The influence of 50°C 4-week storage on the pH value of E1, E2, and E3.

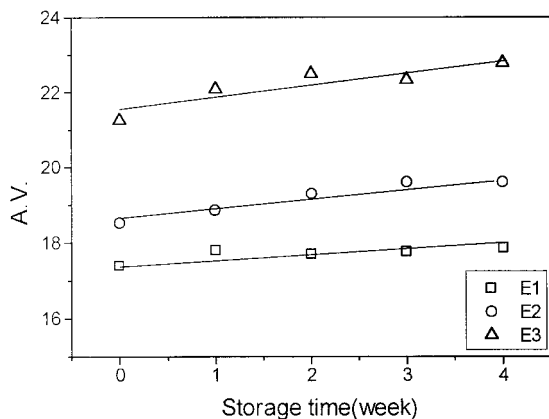


**Figure 3** The influence of 50°C storage on the acid values (mg KOH/g resin) of E1, E2, and E3.

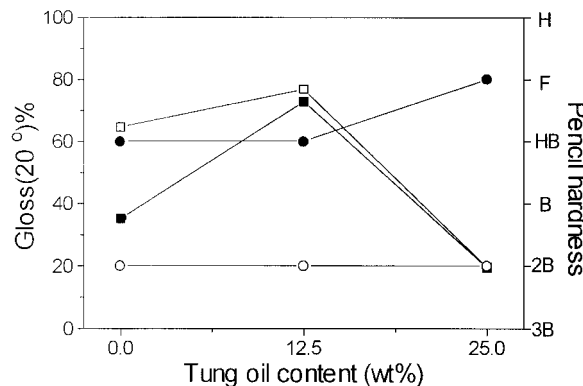
carboxylic acid in the resin. This group is more hydrophilic; it also can help disperse the alkyd chain in the water.

Figures 3 and 4 are the hydrolysis data of E1, E2, and E3 in a 50°C oven and ambient temperature storage. They show that the alkyds with or without tung oil only have a little difference in their hydrolysis rates; the alkyd resin without tung oil has a little lower hydrolysis rate than those resins containing tung oil. After 4 weeks of oven storage at 50°C, the acid values increased to about 34%. The results of the hydrolysis data of E1, E2, and E3 under room temperature storage had trends very similar to those under 50°C storage. After 4 weeks at room temperature storage, the increase of the acid values were about 6%.

Compared with the resin dispersion based on a commercial alkyd resin, Kelsol 3906-B2G-75



**Figure 4** The influence of room temperature storage on the acid values (g KOH/g resin) of E1, E2, and E3.



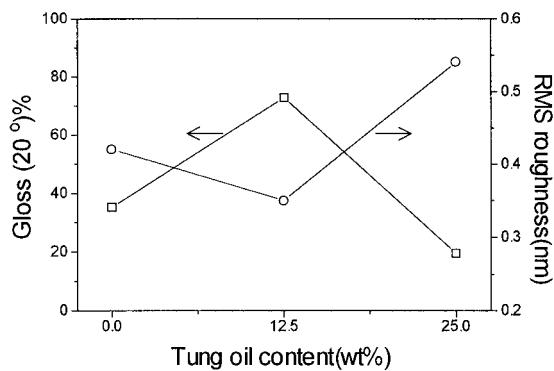
**Figure 5** The influence of the tung oil content on the (□) air dried or (■) baked film gloss (20°) and (○) air dried or (●) baked pencil hardness.

(KRD), the percent changes of the acid value for 4-week aging at room temperature or for 50°C storage of E1, E2, and E3 was lower than that of KRD. The percent changes of the acid values of E1, E2, and E3 were about 6% at room temperature and about 34% under 50°C storage for 4 weeks; meanwhile, the percent change of KRD was about 18% at room temperature and about 44% under 50°C storage.

### Film Properties of Alkyd Emulsion

The alkyd resin films were prepared by the emulsions (E1–E3) containing some dryers and assisting agents. All films had good adhesion (5B) and impact resistance (160/160 in. lb). As seen in Figure 5, the increase of tung oil in the alkyd resins caused the film gloss to increase at first and then decrease. The films were not cured very well after air drying for 7 days; their pencil hardnesses were about 2B; the influence of the tung oil content was not obvious. After baking at 120°C for 1 h, the pencil hardness increased from HB to F with the increasing tung oil content. The above results indicate that a suitable addition of tung oil in the alkyd resin may improve the film properties, but adding too much more tung oil in the alkyd resin may result in synthesis difficulty and poor film properties, such as low gloss, yellowing, film shrinkage, and so on.

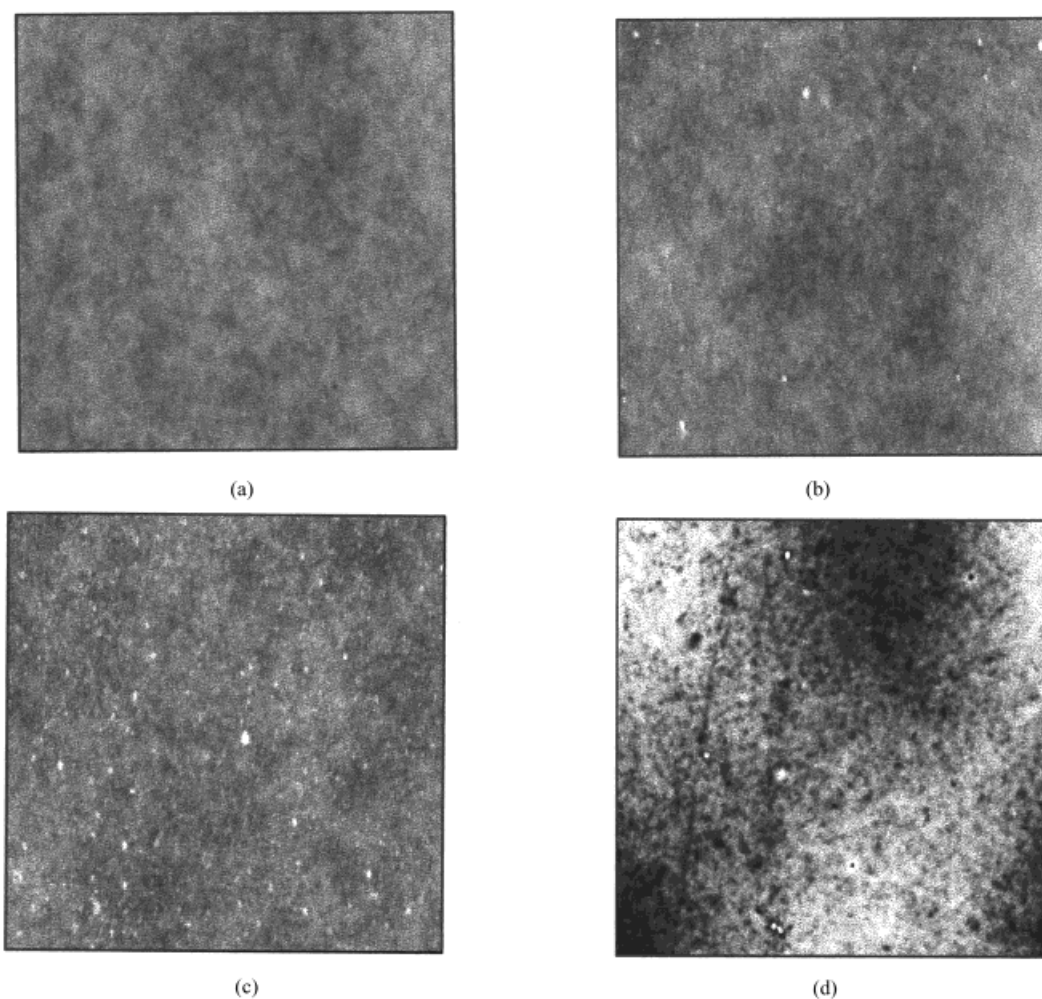
The influence of the tung oil content on the film properties was also studied by AFM. As is known, AFM, or its more general version scanning force microscopy, has played a major role in characterizing surfaces of conducting and nonconducting samples. The direct measure of the force acting between the tip and sample with a well-charac-



**Figure 6** The influence of the tung oil content on the film gloss (20°) and RMS roughness (nm).

terized cantilever produces high resolution images of the surface structure. Recently, AFM was used a real space analytical tool and was successfully exploited in the polymer surface structure.<sup>13-15</sup> The AFM images showed that all film surfaces were very smooth, but a roughness analysis still showed the films had different roughnesses. The films' root mean square (RMS) roughness had a trend that was the trend of the film gloss: the higher gloss sample had a lower RMS roughness (see Fig. 6). The film containing 12.5 wt % tung oil (based the total oil) had the lowest RMS roughness. This result fit the gloss result very well.

From above results we can find that adding a suitable amount of tung oil in the alkyd can obviously improve the film gloss. This may relate to the



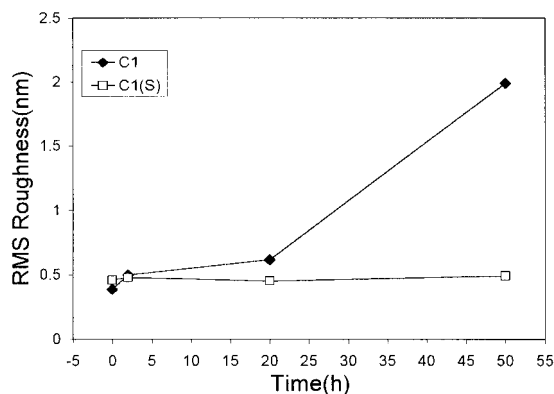
**Figure 7** The influence of 50°C water immersion on the surface morphology of the C1 film after 120°C baking for 1 h ( $10 \times 10 \mu\text{m}$ ). The films were immersed for (a) 0, (b) 2, (c) 20, and (d) 50 h.

unsaturated bond density. As we know, a high-level unsaturated bond improves the film gloss. However, a further increasing of tung oil in the alkyd will cause some problems, such as film shrinkage and high viscosity of the resin; all these influence the properties of the final film properties, especially the gloss of the alkyd film. Theoretically, the increase of tung oil content will improve the pencil hardness of the film because of the increase of the crosslink density, but the experimental result did not show this. This may have been due to the existence of the surfactant in the film, which will offset the improvement of the pencil hardness of the film.

### Direct Observation of Influence of 50°C Deionized Water on Alkyd Film Surface

Several articles<sup>16–18</sup> mentioned that the emulsions generally are slower in drying and exhibit somewhat impaired film properties. The dried film is usually softer and more water sensitive than the film obtained from same resin formulated in an organic solvent. The water-sensitive property may be due to the surfactant in the film. However, so far direct observation of the changes of the film surface morphology effected by water have not been reported. We sought to observe the influence of 50°C deionized water on the baked films of C1 (tung oil content = 0 wt %) and C1(S) (same formulation as C1, but the water was replaced by toluene and no surfactant). Figure 7 (a–d) contains the height images of C1 films, which were immersed in 50°C water for 0, 2, 20, and 50 h, respectively. The morphology of the film surface was already changed a little after water immersion for 2 h; the morphology changed more after 20-h water immersion. After 50-h water immersion, the surface of the film appeared to have a lot of dents, and the film surface was much rougher than the original film (Fig. 7). The results of the C1(S) were much different from the results of C1 after 50-h immersion; the image of the C1(S) film did not show any evidence that the film surface had been changed after 50-h water immersion. This impression was confirmed by the surface roughness (see Fig. 8). The RMS roughness of C1(S) did not change much even after 50-h water immersion, but the RMS roughness of C1 showed considerable change under the same treatment condition.

Torstensson and coworkers<sup>19</sup> reported that the surface of a dried lacquer film applied on glass may consist of 50% surfactant, even if the total surfactant concentration in the formulation is as low as 1 wt % as determined by electron spectroscopy for



**Figure 8** The relationship between the RMS roughness and the time of deionized water immersion of C1 and C1(S).

chemical analysis. If the same case existed in our films, the dried films from the emulsion would be very sensitive to water treatment, even if the film had cured completely. Figure 8 shows that the film from the emulsion was much more water sensitive than the film from solvent-based alkyd. We considered that the rougher surface of the film might be due to the surfactant migration from the surface of the alkyd film to the water.

## CONCLUSIONS

Tung oil modified soybean alkyd emulsions were prepared using IGEPAL CO-630 as the surfactant. The alkyd emulsions had very good stability. The tung oil contents in the alkyd resins strongly influenced the film properties: a suitable tung oil content improves the film properties (such as gloss, etc.). The AFM investigation showed that the coating film was more water sensitive and indicated that the coating surface may be very rich in surfactant species.

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