# Drying of Alkyd Emulsion Paints

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*The drying and film formation of long oil alkyd emulsions was investigated with emphasis on loss of dry upon storage. The main reason for loss of dry was adsorption of the cobalt (drier) on pigment surfaces as a precipitated hydroxide. Titanium dioxides with alumina surface treatment and organic pigments were most detrimental to drying. Acrylate- and phosphate-based dispersants also deactivated the cobalt, presumably due to complexation and precipitation of the cobalt. Emulsions prepared with an emulsifiable cobalt drier containing 2,2′-bipyridyl (complexing agent for cobalt) showed the best resistance to loss of dry. Atomic force microscopy of films formed from the emulsions showed that the emulsifier migrated to the film surface which, when washed with water, leaves holes or pits in the film. The pits were arranged in a hexagonal pattern characteristic of Bénard cells, which form due to surface tension and/or temperature gradients generated in the film during evaporation of water.*

## INTRODUCTION

The development of alkyd emulsion-based coatings has resulted, like many other waterborne and powder coatings, from the harmful effects of organic solvents used in solventborne coatings on the environment and paint users.[1] The first generation of alkyd emulsion and waterborne paints in general were inferior to their solventborne counterparts, mainly due to changes in binder chemistry, high levels of surfactant, lack of additives, and inexperience of the formulators. This resulted in criticism of waterborne paints which, unfairly, still remains today. In fact, the myth that solventborne alkyds are "best" still exists despite the latest generation of alkyd emulsion paints having better performance properties.[2] This unfortunate history has contributed to solventborne alkyds still having a significant share of the total alkyd paint market, especially in the industrial sector where alkyds of shorter oil length are used. However, the even stricter legislation currently being introduced in some countries has meant that the use of solventborne coatings, high-solids coatings, and even some waterborne coatings (e.g., latex dispersion paints based on high $T_g$ latexes) is becoming very restricted. This trend towards zero volatile organic compound content, high performance coatings, especially for indoor application, favors paints based on alkyd resin emulsions.

To further increase the acceptance of alkyd emulsions in the industrial and do-it-yourself sectors, research on the drying properties of alkyd emulsions is required. Drying of alkyd resin based paints (solvent- and waterborne), which rely on autooxidation, usually have very good drying times shortly after they have been prepared, due to the addition of cobalt carboxylate driers which catalyze autooxidation. However, after a period of aging (6 to 24 months in the sealed can), the drying time often increases by several hours or the paints do not dry at all, which can be very annoying and expensive if the paint has already been applied to the substrate. Despite this experience being known to industrial users of alkyd paints and drier manufacturers, little research has been published in an effort to better understand this problem (for a brief review, see Bergenståhl et al.[3]). Drier manufacturers have developed driers to help prevent "loss of dry" upon storage. These driers contain a chelating agent, which help maintain the catalytic activity of the drier.[4] An even larger threat to the drying time and stability of alkyd paints comes from European health legislators taking steps to minimize or stop the usage of cobalt in paints. Hence, there is a clear need to under-

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stand the reasons for the loss of dry in current and future generations of alkyd emulsion paints.

Ongoing research on alkyd emulsion paints is following a similar route to that of latex dispersion paints. In addition to investigations on the drying properties of alkyd emulsions, research is also being carried out on the film formation of alkyd emulsions with the aim of reducing water sensitivity. Much of the work that has been carried out on latex dispersions can also be applied to alkyd emulsions. In this paper, results from a systematic investigation on the loss of dry upon storage of long oil alkyd emulsions are presented, along with some preliminary results from a study on the film formation of long oil alkyd emulsions.

## EXPERIMENTAL

### Materials

**Alkyd Resins**: A long oil alkyd resin based on pentaerythritol, isophthalic acid, and tall oil fatty acids was used for the investigation on the drying properties and loss of dry upon storage of alkyd resin emulsions. The oil length was 83%, and the acid value was between 6 and 9 mg KOH/g alkyd. For further reference in the text, this resin will be designated LO83. The alkyd resin used for the film formation study was based on pentaerythritol, phthalic anhydride, and tall oil fatty acids. Oil length was 70% and the acid value was between 5 and 10 mg KOH/g alkyd. For further reference in the text, this resin will be designated LO70.

**Emulsifiers**: Conventional surfactants were used for the emulsification of the alkyd resins. The LO83 resin was emulsified with a fatty alcohol ether sulphate ($C_{12}EO30\text{-}SO_4\text{-}Na_2$) used as a 32% active aqueous solution or a fatty alcohol ethoxylate ($C_{12}/C_{14}EO30$) used as a 65% active aqueous solution.

**Driers**: Cobalt (II) chloride hexahydrate, cobalt caprioate, cobalt neodecanoate, and a water emulsifiable cobalt drier were used for the surface drying time and loss of dry upon storage tests. The water emulsifiable cobalt drier consists of cobalt neodecanoate, surfactants, and 2,2′-bipyridyl in a mineral spirits carrier. Driers were supplied by OMG Europe GmbH, with the exception of cobalt chloride (Merck, pro analysi, 1.02539).

**Dispersants**: A wide range of dispersants were tested for their effects on the drying and loss of dry upon storage of the LO83 emulsions. Details of dispersants are given in the Results and Discussion section.

Table 1—Pigments Used for the Loss of Dry Upon Storage Tests

| Pigment | Type / Surface Treatment | Surface Area ($m^2g^{-1}$) |
|---|---|---|
| Red | Organic | 17 |
| Blue | Phthalocyanine | 36 |
| Black | Carbon black | 30 |
| Brown | Iron oxide | 9 |
| $TiO_2$ - 1 | 4.6% alumina, organic coating | 15 |
| $TiO_2$ - 2 | 1.9% silica, 5.5% alumina, organic coating | 17 |
| $TiO_2$ - 3 | 9.5% silica, 4.5% alumina | 30 |
| $TiO_2$ - 4 | 99.5% $TiO_2$ , no treatment | 8 |

**Pigments**: The pigments added to the LO83 long oil alkyd emulsions and tested for their effect on drying time and loss of dry are listed in *Table* 1. The titanium dioxide pigments were supplied by Tioxide Europe Ltd., England. The colored pigments were supplied by Jotun A/S, Norway.

**Other Reagents**: All other reagents and solutions were prepared from AR grade solids or solutions of KOH, HCl, $NH_4OH$, and NaCl. Double distilled water was used in all experiments.

### Methods

**Alkyd Resin Emulsification**:

*Driers added to alkyd prior to emulsification*: The drier was added directly to the LO83 alkyd resin. Cobalt concentration was typically 0.05% w/w per alkyd. If necessary, the drier/alkyd mixture was heated (under nitrogen) to aid dissolution/dispersion of the drier. An equal weight of water containing the emulsifier (pre-dissolved) was added. The mixture was stirred gently and the pH increased to ~7 with a 50% solution of KOH (4-5 drops required per 150 mL of alkyd/water mixture). The mixture was stirred (magnetic stirrer bar), heated to the emulsification temperature, usually between 50 and 60°C, and introduced into a high pressure homogenizer (Microfluidizer TM-120 from Microfluidics). Emulsification was carried out for a period equivalent to about three passes of the total sample through the homogenization cell (the length of time was dependent on sample volume, which usually was about 150 mL). The temperature was measured immediately after homogenization and droplet diameter, pH, and Brookfield viscosity within 24 hr.

Large batches of emulsions (up to 1.5 L) with either cobalt neodecanoate or cobalt caprioate were prepared for the work with the additives and pigments. The same batch of emulsion was used for all the tests.

*Driers post-added to emulsions (emulsifiable cobalt drier and cobalt chloride only)*: Large batches of emulsions were prepared as previously mentioned, but with alkyd, water, and emulsifier only. The emulsifiable cobalt drier or cobalt chloride were post-added to the emulsion with vigorous shaking from a vibrating test tube shaker (Vibrax). The cobalt chloride was added as a concentrated aqueous solution (volume <1 mL).

**Addition of Dispersants to LO83 Alkyd Emulsions**: Dispersants were post-added dropwise (as supplied) with shaking to small aliquots (~20 g) of emulsion. The emulsion was shaken vigorously for two minutes on a vibrating test tube shaker, transferred to a shaking or rotating table, and gently shaken for 24 hr before measuring the drying time. Dispersant concentration was 2.0% w/w per emulsion. Since no pigment was present, this concentration represents a large excess of free dispersant (non-adsorbed). In a real formulation, the free dispersant concentration would be much less, however, the aim of this work was to establish and exaggerate which dispersants cause loss of dry.

Table 2—Composition of Pigment/Alkyd Mixtures

| Pigment | Pigment (wt%) | Dispersant (wt%) | Alkyd (wt%) | Water (wt%) | Total Pigment Surface Area (m$^2$) |
|---|---|---|---|---|---|
| Red organic | 21.2 | 1.0 | 23.8 | ~52 | 180 |
| Blue organic | 10.0 | 1.0 | 23.8 | ~63 | 180 |
| Carbon black | 12.0 | 1.0 | 23.8 | ~61 | 180 |
| Brown iron oxide | 40.0 | 1.0 | 23.8 | ~33 | 180 |
| $TiO_2$ - 1 | 24.0 | 1.0 | 23.8 | ~49 | 180 |
| $TiO_2$ - 2 | 21.2 | 1.0 | 23.8 | ~52 | 180 |
| $TiO_2$ - 3 | 12.0 | 1.0 | 23.8 | ~61 | 180 |
| $TiO_2$ - 4 | 22.5 | 1.0 | 23.8 | ~51 | 90 |

Balance is emulsifier (1.2 wt%) and cobalt drier. Dispersant was an anionic block copolymer. Water concentration is approximate. Total sample weight was 50.0 g.

**ADDITION OF PIGMENTS TO LO83 ALKYD EMULSIONS**: Addition of the pigments to the alkyd emulsions was carried out in two steps. First the pigment was dispersed in dispersant solution using a Dispermat CV laboratory dissolver with either a dissolver impeller or bead milling accessory (plus ceramic beads), and second the alkyd emulsion was mixed in with the pigment slurry using the dissolver impeller at slow speed to avoid shear destabilization of the alkyd emulsion droplets (pre-checked by measuring droplet size distribution). Finally, the mixture was allowed to shake approximately 24 hr on a shaking or rotating table to ensure good mixing before measuring the drying time. The first step of producing a stable pigment dispersion was difficult and a trial and error approach was used to produce the best possible dispersion. For some pigments this was not possible and pigment flocculation resulted. All pigment/emulsion mixtures were shaken daily with a Vibrax test tube shaker to ensure good mixing and contact between the pigment, alkyd droplets, and solution. Particle size analysis indicated that some pigments were well dispersed, however, these pigments flocculated upon storage, suggesting that the dispersant concentration was too low. The instability of the pigment dispersions was mainly due to the choice of the experimental design which was optimized to allow comparison of the effects of the pigments on loss of dry. For example, optimization of dispersant concentration and correct solids level would have resulted in more stable dispersions.

The pigment concentration was chosen so that the total pigment surface area in the emulsion was the same for all pigments, hence, the potential adsorption surface area for cobalt was approximately the same (assuming the coverage of dispersant and any free emulsifier was the same). This approach was preferred over using a constant weight percent of pigment which would result in a wide range of adsorption surface areas and biased comparisons between the influence of pigments on loss of dry. The dispersant was an anionic block copolymer and the concentration was kept constant at 0.5 g per 180 m$^2$ of pigment. *Table* 2 summarizes the composition of the pigment/alkyd mixtures.

**STORAGE STABILITY AND LOSS OF DRY TESTS**: The drying time and pH of the emulsions were measured within 24 hr after preparation (fresh), and after approximately 7, 14, and 35 days of storage at 50°C. For emulsions containing additives and pigments, the fresh drying time was measured after the 24 hr mixing step (aged one day at room temperature). After 35 days, the droplet diameter was measured. All samples were stored in tightly sealed glass vials filled almost to the top. Before sealing the vial, nitrogen was blown over the sample. These steps were taken to decrease any possible uptake of airborne oxygen by the emulsion.

**BK DRYING TESTS**: Beck-Koller drying tests were carried out using a standard BK drying recorder from Mickle Laboratory Engineering Co. Before sampling the emulsions, they were shaken for two minutes with a vibrating test tube shaker. Films of wet film thickness 60 μm were applied to a glass plate using a six-holed film applicator and automated bar coater, which pushed the applicator along the glass plate at a uniform and controlled speed. Surface drying time was measured in a room thermostated at 23±1°C and 50% relative humidity (RH). Surface dry was taken as the time at which the needle started to lift out of the bulk film and skimmed along the surface leaving a faint and irregular trace. At this time, the surface was also finger touch dry. In some cases, it was difficult to determine the exact surface drying time, hence, times should be taken as approximates and at best to within ± 0.5 hr (30 min). To improve accuracy, all measurements and readings of surface drying times were carried out by the same person, and all samples were measured in duplicate and the times were averaged.

**EMULSION CHARACTERIZATION**: Emulsions were characterized in terms of droplet size, pH, and viscosity. Droplet size was measured using a Malvern MasterSizer MS20. This requires dilution of the emulsion (50 to 100 times) so that scattering of laser light is sufficient for signal detection but without saturation. Viscosity was measured using a Brookfield LVT viscometer at a speed of 30 rpm.

**FILM FORMATION STUDIES**: The alkyd emulsions were applied to cleaned glass cover slips using a 60 μm cube applicator, hence, after drying, the film thickness was ~30 μm. The films were dried in a controlled temperature and humidity room (23°C, 50% RH) under open cover to avoid contact with dust. After at least 24 hr drying, the cover slip was cut to size (about 10 × 10 mm) to allow it to fit in the atomic force microscope (AFM) sample chamber. AFM images of the dry alkyd film were obtained using a Digital Instruments Nanoscope IIIa multimode atomic force microscope in the "tapping" mode and under ambient conditions. Topography and phase images were obtained from three to five areas distributed over the film. The Z-height and XY scan size were varied for each area. A 20 × 20 μm scan size usually gave the most informative images. Washing of the dry film was carried out under a stream of water (from a water bottle). The film was rinsed with approximately 10-20 mL of water and blown dry with nitrogen. Images

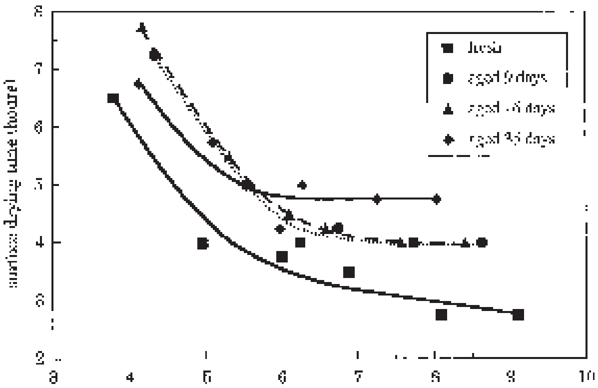

Figure 1—Effect of pH and aging at 50°C on loss of dry and surface drying time for emulsions prepared using LO83 alkyd resin, 5% $C_{12}EO30\text{-}SO_4\text{-}Na_2$ w/w per alkyd, and 0.05% Co as cobalt neodecanoate w/w per alkyd. The fresh pH was 6.89 and droplet diameter d(0.1) = 0.21, D(0.5) = 0.38, D(0.9) = 0.66 $\mu$m.

of the washed films were obtained at least 1.5 hr after washing.

## RESULTS AND DISCUSSION

### Drying Properties of Pure Alkyd Emulsions

**Effect of Emulsion pH**: Storage of alkyd emulsions often results in a steady decrease of the pH from about neutral down to about 4-5. This is due to the acid hydrolysis of ester linkages and formation of weak carboxylic acids. The pH decrease can be minimized by use of isophthalic acid instead of phthalic anhydride during the synthesis of the alkyd resin.[3] To simulate if any decrease in pH of the alkyd emulsion upon storage can influence drying time, the pH of the emulsions was deliberately adjusted over the pH range of 4 to 9. Since this is not the normal mechanism by which the pH is lowered, the results only show the potential effect of any decrease in pH due to resin hydrolysis. *Figures* 1 and 2 show the results for emulsions prepared using an anionic and a non-ionic surfactant. The emulsions were aged, and the pH changes monitored.

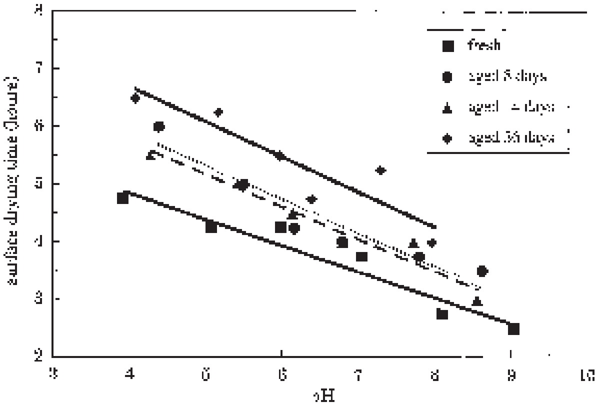

Figure 2— Effect of pH and aging at 50°C on loss of dry and surface drying time for emulsions prepared using LO83 alkyd resin, 5% $C_{12}/C_{14}EO30$ w/w per alkyd, and 0.05% Co as cobalt meodecanoate w/w per alkyd. The fresh pH was 7.05 and droplet diameter d(0.1) = 0.22, D(0.5) = 0.39, D(0.9) = 0.67 $\mu$m.

The results clearly show that an increase in pH causes a decrease in surface dry time. These results can be explained by the work of Östberg et al.[5] who showed that cobalt concentration in the alkyd droplets increases with pH. Their results indicated that higher cobalt concentrations in the alkyd phase decreased surface dry time.

The effect of aging on surface drying time was similar over the pH range investigated (pH 4 to 9). After 35 days of aging at 50°C, the surface dry time increased by approximately one and a half to two hours for both emulsifiers. This is not a significant increase and only slightly greater than the experimental error in surface dry time.

Comparison of the results for the two emulsifiers implies that the non-ionic surfactant gives better drying at increasing alkaline pH values. This is possibly due to differences in free cobalt concentrations in the water phase. Since the anionic surfactant contains $Na^+$ as counter ions to the $SO_4^{2-}$ group, it is postulated that they are replaced by $Co^{2+}$. This would lead to a higher cobalt concentration in the water phase as pH is increased due to the precipitation of $Co(OH)_2$. Precipitation of $Co(OH)_2$ from a 0.05% $Co^{2+}$ aqueous solution (0.008 mol $L^{-1}$) is expected to start at approximately pH 7.5 - 8.0.[6]

**Effect of Cobalt Form and Location**: For solventborne alkyd resins, the cobalt is usually added as a carboxylate salt with carbon number ranging from 6 to 18. In a waterborne system, the compatibility with water becomes a problem and, hence, self-emulsifiable cobalt carboxylates are used. These can be post-added to the emulsion and form small droplets in the water phase. The stability of the drier droplets was not investigated, but simple experiments in water showed that they would coalesce and phase separate upon standing for a few days. The separated phase could easily be re-emulsified. Since the location of the cobalt in the water phase and its state as small droplets may inhibit drying time, a series of tests were developed where different forms of cobalt were either added directly to the alkyd resin prior to emulsification or post-added to the emulsion. Results are shown in *Figures* 3 and 4.

*Figure* 3 shows the surface drying time and loss of dry for the emulsifiable cobalt drier, cobalt chloride, and cobalt neodecanoate, each added to the alkyd phase prior to emulsification (ensuring the maximum possible cobalt concentration in the alkyd droplets). The cobalt neodecanoate gave slightly faster drying times but showed some loss of dry. On average and considering the experimental error in drying times, the performance of the three driers was similar.

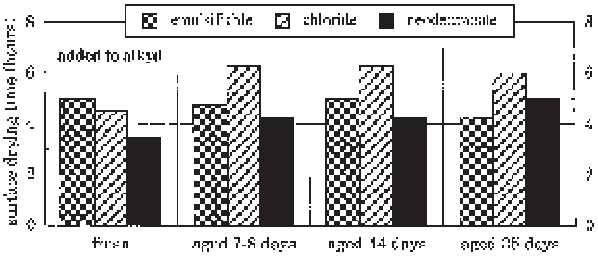

*Figure 3— Effect of aging at 50°C on loss of LO83 alkyd emulsions prepared using 5% $C_{12}EO30\text{-}SO_4\text{-}Na_2$ w/w per alkyd and containing either the emulsifiable cobalt drier, cobalt neodecanoate or cobalt chloride added to the alkyd resin prior to emulsification. The cobalt concentration was 0.05% w/w Co per alkyd.*

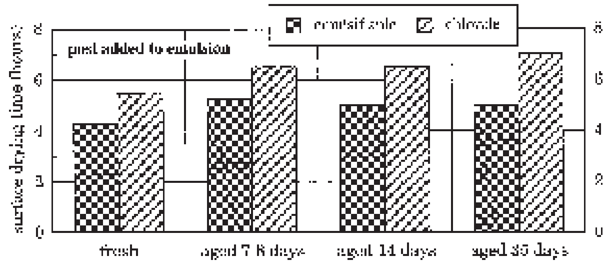

*Figure 4— Effect of aging at 50°C on loss of dry of LO83 alkyd emulsions prepared using 5% $C_{12}EO30\text{-}SO_4\text{-}Na_2$ w/w per alkyd and containing either the emulsifiable cobalt drier or cobalt chloride post-added to the emulsion. The cobalt concentration was 0.05% w/w Co per alkyd.*

The comparison in *Figure* 4 between the emulsifiable cobalt neodecanoate and cobalt chloride post-added to the emulsion (i.e., cobalt in water phase), where the cobalt neodecanoate exists as droplets stabilized by surfactant and the cobalt chloride exists as a dissolved salt solution, shows that the emulsifiable cobalt drier gave slightly faster drying times and less loss of dry. The difference of about one to two hours is not considered significant and was surprisingly small given that the cobalt chloride was expected to be relatively easily hydrolyzed and deactivated. There was no significant difference in drying time for cobalt added either to the alkyd prior to emulsification or post-added (compare *Figures* 3 and 4).

These results suggest that location or form of cobalt has no significant effect on drying time or on loss of dry. To confirm this possibility, some key questions must be answered. First, does the form of cobalt influence the distribution of cobalt between the alkyd and water phases? Second, how does homogenization influence cobalt distribution? If cobalt distribution is independent of cobalt form at fixed pH, and equilibrium is established very rapidly (<24 hr), then the results in *Figures* 3 and 4 are for the same and constant ratio of cobalt in alkyd to cobalt in water. It may also be that the cobalt adsorbs at the interface. Cobalt distribution and adsorption studies are necessary to answer these questions. It also remains to be tested if these results apply to rate of hardness development for other alkyd resins. Emulsions of medium or short oil alkyds may favor cobalt in the alkyd phase because cobalt in the water phase may not be able to diffuse into the viscous alkyd droplets during film formation.

OTHER VARIABLES: The effect of surfactant type and concentration was briefly investigated. Priority was given to obtaining a stable emulsion and optimizing the surfactant concentration at the sacrifice of drying time. Nonionic surfactants having long ethylene oxide (EO) chains used in excessive concentrations were detrimental to drying time. Crosslinkable anionic surfactants based on amide functionality gave good drying times but suffered from loss of dry. Anionic surfactants gave good drying and films, but the risk of some loss of dry upon storage increased.

The method of resin neutralization prior to emulsification was also investigated by comparing potassium hydroxide and ammonium hydroxide. Use of ammonium hydroxide showed an immediate effect and increased drying time by about one to three hours relative to potassium hydroxide. This was presumably due to the formation of the cobalt hexamine complex, which deactivated some of the cobalt.[3] The emulsifiable cobalt drier was least affected by the use of ammonium hydroxide.

Aging of the emulsions with a range of cobalt driers was extended beyond one month at 50°C, in an attempt to induce loss of dry in the pure alkyd emulsions. All emulsions suffered from loss of dry after about six months of storage at 50°C, and either had drying times greater than 12 hr or did not dry. Droplet stability of the emulsions was excellent with no change in droplet size distribution. The pH had decreased to approximately 5.0-5.5, suggesting that hydrolysis of the alkyd had occurred. The decrease in pH may explain the loss of dry, however, the stability of the cobalt drier after such prolonged aging must also be questioned.

## Drying Properties of Emulsions Containing Pigment Dispersants

The effects of six commonly used dispersing agents on surface drying time and loss of dry are shown in *Figures* 5 and 6. The first three dispersants (*Figure* 5, graphs 2-4 from the top) had very little effect on loss of dry and increased drying time slightly relative to the reference emulsion containing no dispersant (top graph in *Figure* 5). Film appearance was glossy, smooth, and transparent.

The effect of the second three dispersants (*Figure* 6) on drying time was already evident in the fresh emulsions (i.e., immediate deactivation of the cobalt). In the worst cases there was no surface dry and even after a few days the films were still tacky. The emulsifiable cobalt drier was the only drier which resisted complete deactivation, but still had surface drying times more than double the times for the reference emulsion containing no dispersant.

For the acrylate-based polymers with either sodium or ammonium as counter ions, a possible explanation for the deactivation of cobalt is exchange with the sodium or ammonium ions to form cobalt acrylates. Visual evidence that some form of reaction had taken place was the slight pink color of the emulsions and a cloudy dry film, suggesting that some type of precipitate had formed. For the ammonium form, there is the additional possibility of reaction with ammonium ions to form hexamine complexes.[3] This also explains the slightly better drying times for the sodium form.

In the case of the sodium hexametaphosphate (SHMP), there is most likely a reaction between the cobalt cations and polymeric phosphate anions to form a pseudo cobalt metaphosphate precipitate. This is consistent with the observation of a pink precipitate in the emulsions after seven days of storage and a cloudy dry film. Cobalt (II) phosphate is pink and has a solubility product of 2 × $10^{-35}$ and is insoluble in water, which supports formation of a pseudo cobalt metaphosphate precipitate.

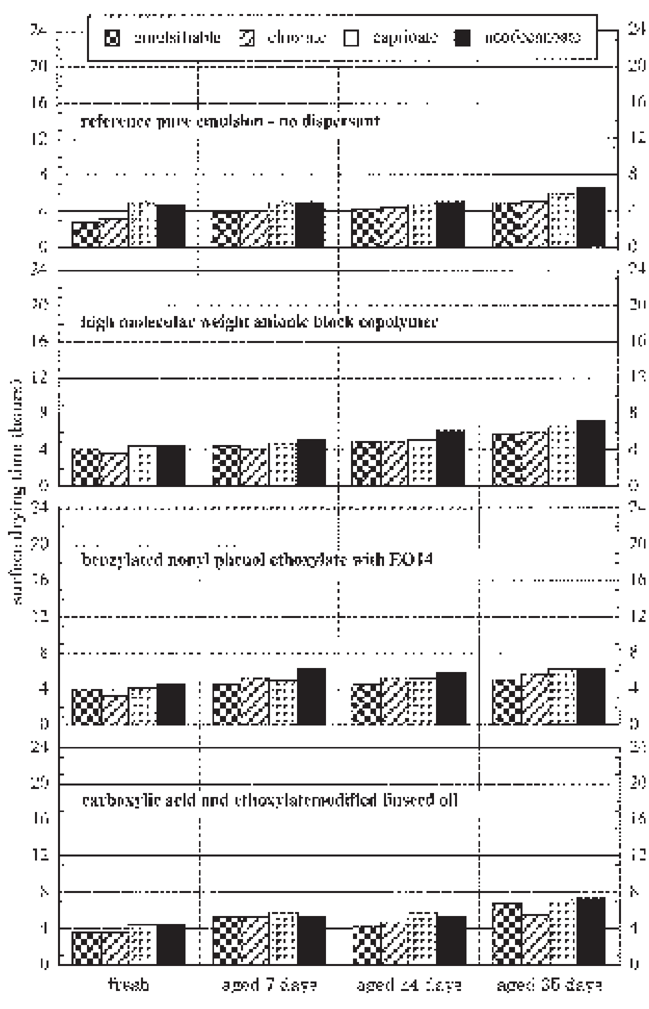

*Figure 5—Effect of dispersants on surface drying time and loss of dry after aging at 50°C of LO83 alkyd emulsions prepared using 5% $C_{12}$/$C_{14}$EO30 w/w per alkyd. The dispersant concentration was 2.0% w/w per emulsion. Emulsifiable cobalt drier and cobalt chloride used was 0.10% w/w Co per alkyd. Cobalt caprioate and neodecanoate was used at 0.05% w/w Co per alkyd.*

Since the free dispersant concentration in fully formulated alkyd emulsion paints should be much lower than 2.0% w/w per emulsion, the effect of dispersant may be significantly less dramatic than shown in *Figure* 6. However, based on the results shown, the commonly used acrylate- and phosphate-based dispersants should be carefully tested before using them in a final alkyd paint formulation. At the very least, the dispersant and pigment should be added to the emulsion before the drier to avoid high free dispersant concentrations and potential immediate deactivation of the cobalt drier. This means that the emulsifiable cobalt driers (or cobalt chloride), which can be post-added to the emulsions, should be used and added to the alkyd emulsion after the dispersant(s) and pigment(s).

Comparison between the cobalt forms shows that the emulsifiable cobalt drier and cobalt chloride gave shorter surface dry times. This cannot be interpreted as better resistance to deactivation since the cobalt concentration was double that used for the cobalt caprioate and

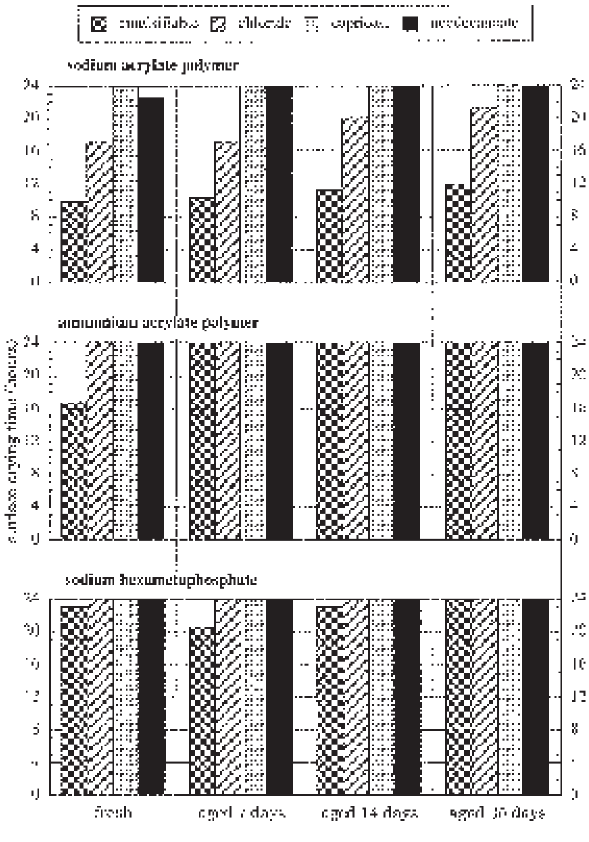

*Figure 6—Effect of dispersants on surface drying time and loss of dry after aging at 50°C of LO83 alkyd emulsion prepared using 5% $C_{12}$/$C_{14}$EO30 w/w per alkyd. Dispersant concentration 2.0% w/w per emulsion. Emulsifiable cobalt drier and cobalt chloride used at 0.10% w/w Co per alkyd. The cobalt caprioate and neodecanoate was at 0.05% w/w Co per alkyd.*

neodecanoate. The cobalt concentrations used were based on earlier studies on the effect of cobalt concentration for each drier on drying time of pure alkyd emulsions. As shown in the top graph in *Figure* 5, the emulsifiable cobalt drier and cobalt chloride had slightly shorter drying times than cobalt caprioate and neodecanoate. In hindsight, it would have been better to test all driers at the same cobalt concentration to allow a valid comparison between the different types of cobalt. Nevertheless, one way of overcoming loss of dry is to use higher cobalt concentrations such that not all of the cobalt will be deactivated.

### Drying Properties of Emulsions Containing Pigments

The high molecular weight anionic block copolymer was chosen as the dispersant for the pigments because it did not affect drying time or loss of dry. Its concentration was not optimized and kept the same for all pigments. Instead, pigment concentration was kept constant in terms of adsorption surface area allowing direct comparison between the pigments.

The effects of four titanium dioxide pigments and four colored pigments on surface drying time and loss of dry are shown in *Figures* 7 and 8. Pigmented fresh emulsions had slightly longer surface drying times than the non-pigmented emulsions (compare with the top graph in *Figure* 5). For all but one of the pigments, aging of the emulsions caused longer surface drying times, and, for the first time, the anticipated gradual loss of dry was observed. The colored pigments showed slightly more or earlier loss of dry than the $TiO_2$ pigments. Carbon black and red organic had the greatest effect on loss of dry. The suspension pH during aging decreased from

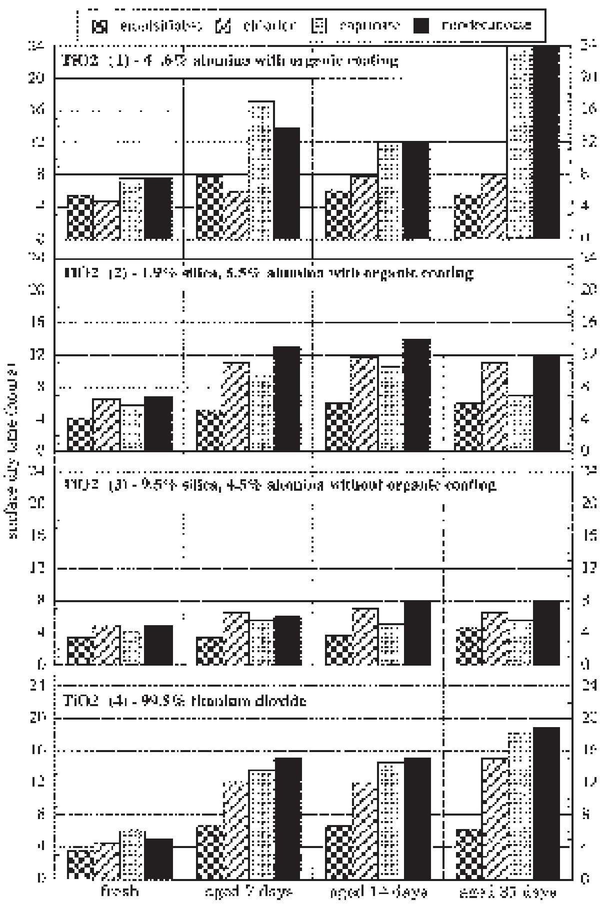

*Figure 7—Effect of titanium dioxide and surface treatment on surface drying time and loss of dry after aging at 50°C of LO83 alkyd emulsions prepared using 5% $C_{12}/C_{14}EO30$ w/w per alkyd. Constant pigment surface area was 180 $m^2$ in sample suspension except $TiO_2$ (4) which had 90 $m^2$. Pigment dispersant was the anionic block copolymer from Figure 5 used at the concentration of 0.5 g per 180 $m^2$ of pigment (1 wt%). The emulsifiable cobalt drier and cobalt chloride was 0.10% w/w Co per alkyd. The cobalt caprioate and neodecanoate was 0.05% w/w Co per alkyd.*

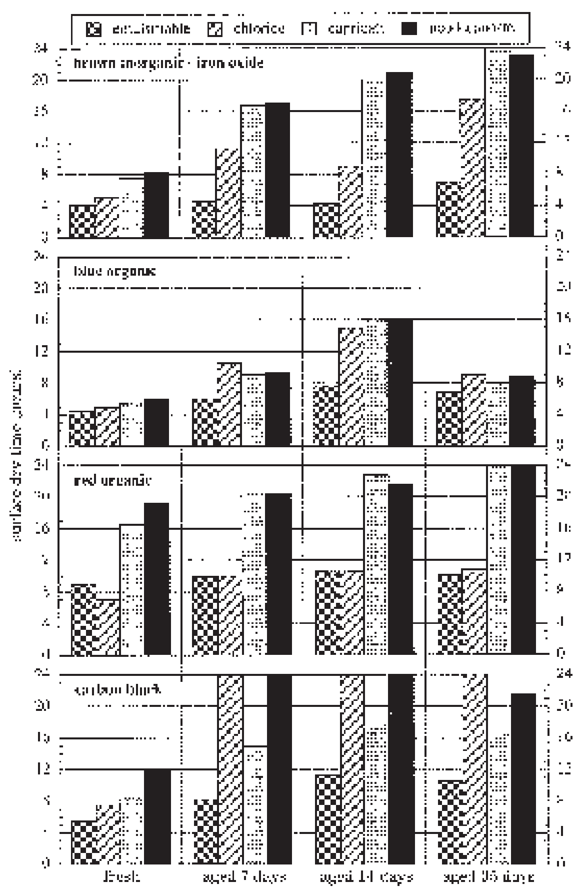

*Figure 8—Effect of colored pigments on surface drying time and loss of dry after aging at 50°C of LO83 alkyd emulsions prepared using 5% $C_{12}/C_{14}EO30$ w/w per alkyd. Constant pigment surface area was 180 $m^2$ in sample suspension. Pigment dispersant was the anionic block copolymer from Figure 5 used at the concentration of 0.5 g per 180 $m^2$ of pigment (1 wt%). The emulsifiable cobalt drier and cobalt chloride was 0.10% w/w Co per alkyd. The cobalt caprioate and neodecanoate was 0.05% w/w Co per alkyd.*

between 7.0-6.5 to between 6.0-5.5, similar to that of the non-pigmented emulsions.

The emulsifiable cobalt drier had the least loss of dry, and after 35 days aging at 50°C still gave reasonable surface drying times. Note, however, that its concentration was double that of the cobalt caprioate and neodecanoate. Comparison between the emulsifiable cobalt drier and cobalt chloride shows that the former suffered from less loss of dry presumably due to presence of the 2,2′ bipyridyl complexing agent.

The results for $TiO_2$ pigments reveal that at an approximately constant level of alumina surface treatment (4.5 to 5.5%), the loss of dry decreases as silica concentration is increased from 0 to 1.9 to 9.5%. This suggests that a silica surface helps minimize loss of dry upon storage. The type of organic treatment could also play an important role, since the treatment is usually based on either polyols, amines, or silicone derivatives which could also interact with the cobalt. Pure titanium dioxide clearly showed that a titanium dioxide surface also causes loss of dry, however, since commercial titanium dioxide pigments have some form of surface treatment, the level of titanium dioxide exposed to aqueous solution would be very small or zero.

The deactivation of cobalt in the presence of pigments is proposed to be due to interaction with the pigment surface and is most probably based on specific adsorption (chemisorption) of cobalt. The exact form of the adsorbed cobalt and adsorption mechanism will be dependent on solution pH, cobalt concentration, and pigment surface. For metal ion adsorption on oxide surfaces in general, the favored model is interfacial precipitation of the metal hydroxide, which due to interfacial effects, can occur at pH values below bulk precipitation in solu-

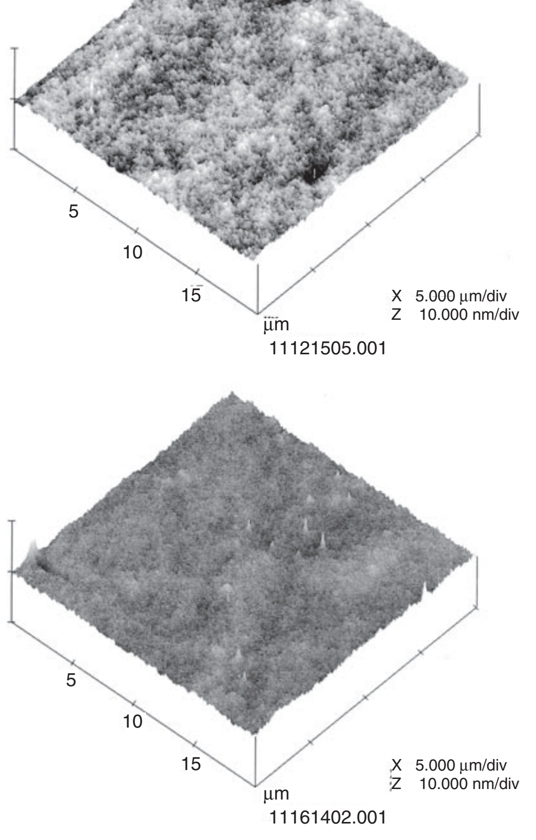

*Figure 9—AFM topographic surface images of dry films formed from the LO70 alkyd resin dissolved in mineral spirits (top) with an average surface roughness ($R_a$) of 0.214 nm and LO70 alkyd resin emulsified with conventional surfactant (bottom) with average surface roughness ($R_a$) of 0.216 nm. $R_a$ values measured on a selected region of the film excluding spikes, peaks and pits (i.e., on defect free). Alkyd concentration of 50 wt% and drier was the emulsifiable cobalt neodecanoate used at 0.10% Co w/w per alkyd. Note exaggerated z-scale.*

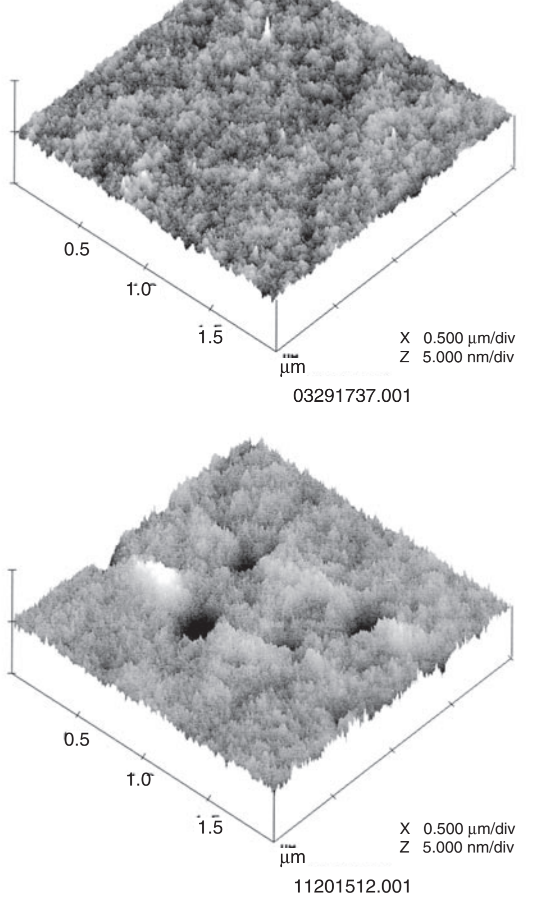

*Figure 10—AFM topograhic surface images of films shown in Figure 9 which have been washed with water, dried, and re-scanned. Top is solventborne alkyd film with average surface roughness ($R_a$) of 0.19 nm. Bottom is alkyd emulsion film showing holes or pits of diameter 0.2 to 0.3 μm and with $R_a$ (excluding the holes/pits) of 0.30 nm.*

tion.[6-9] Cobalt has shown some anomalous behavior for adsorption on MnO$_2$.[9] Our own zeta potential studies on concentrated TiO$_2$ pigment dispersions have shown that cobalt shifts the isoelectric point (iep) of the pigments to higher values, even for the pure TiO$_2$ pigment, which had an iep of 2.2.[10] This suggests specific adsorption of cobalt ions, which at a higher pH (above 5-6) precipitates as the hydroxide. Loganathan et al.[11] have obtained similar results for cobalt adsorption on MnO$_2$.

The time dependence of loss of dry due to cobalt interaction on pigments has not been investigated. The fact that surface drying time gradually decreases over 35 days at 50° suggests a very complex mechanism whereby the cobalt distribution between alkyd, alkyd/water interface, water, and water/pigment interface is continually changing, driven by the adsorption affinity and capacity of the cobalt on the pigment surface. In practice, to maintain drying activity of the cobalt, it is necessary to prevent or slow down precipitation of cobalt hydroxide. This is achieved, in part, by complexing the cobalt with a chelating agent such as 2,2-bipyridyl, present in the emulsifiable cobalt neodecanoate. An excess of 2,2-bipyridyl (in terms of complexing all cobalt and to account for possible interaction with other species or dissolution) should provide adequate protection of the cobalt over the expected storage lifetime of the alkyd emulsion paint.

## Film Formation

The formation of a dry hard film from an emulsion involves evaporation of water, coalescence of emulsion droplets, oxygen uptake, and crosslinking. The crosslinking mechanism of alkyd resins has been thoroughly researched[12,13] compared with the actual process of forming a water free flat alkyd film. Beetsma[2] and Beetsma and Hofland[14] have proposed a general mechanism for film formation of alkyd emulsions based on visual observations. They proposed that the emulsion phase inverts at a critical water concentration to form an alkyd continuous phase and water droplets. The water continues to evaporate and the alkyd resin flows together to give a flat film. The phase inversion point, its occurrence, and flattening depend on droplet viscosity and onset of crosslinking. The effect of various surfactants and additives has not been investigated.

In this study on film formation of alkyd emulsions, films were formed from an alkyd (LO70) emulsion containing a conventional surfactant and from the same alkyd (LO70) dissolved in mineral spirits. Atomic force microscopy images of the dry films are shown in *Figure* 9. Both films appear flat and smooth. The film from the emulsion had some very small but distinct peaks (few nanometers high). The films were washed with water, dried, and re-scanned. *Figure* 10 shows that the solventborne alkyd film was not affected by washing, whereas the alkyd emulsion film had distinct pits or holes in replace of the peaks. It is most likely that the peaks in the unwashed film were surfactant which had migrated to the surface and which was washed away to leave the pits/holes. Similar results have been obtained for latex dispersions.[15] A larger top view of the washed film (*Figure* 11) shows many pits, which are concentrated in a hexagonal pattern grooved about 10 nm below the surface. Such hexagonal patterns have been observed earlier in films cast from solventborne paints and arise due to surface tension and/or temperature gradients generated during solvent evaporation. Formally, they are known as Bénard cells and are considered a film defect which can lower gloss and cause pigment flotation.[16] The size of the hexagonal cells would be expected to be related to film viscosity (drying) and reach their terminal size at a critical alkyd viscosity related to the onset of crosslinking. Further research into this phenomenon is necessary to help understand the mechanism of surfactant migration in alkyd films.

The film formation studies are ongoing and will be complemented with measurements of film properties (e.g., water absorption). Investigation of additive migration and attempts to overcome any detrimental effects will be made in an effort to further improve the performance properties of alkyd emulsion paints.

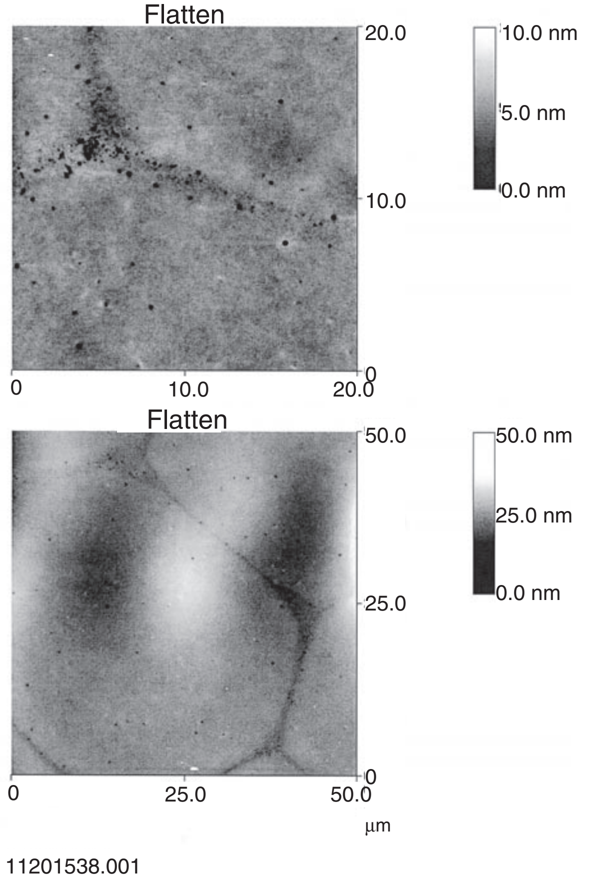

*Figure 11—AFM top-view topographic images of washed alkyd emulsion film from Figure 10 bottom. Top image 20 x 20 µm showing pits or holes in the film (dark circles) concentrated in a Y shaped pattern. Bottom image shows an enlarged view (50 x 50 µm) of a hexagon shaped groove, approximately 10 nm deep, in which surfactant had migrated during film formation and drying.*

## SUMMARY AND CONCLUSIONS

Loss of dry upon storage of long oil alkyd emulsions was due to the presence of pigments. At the pH of normal alkyd emulsion paints (pH 6-8), the cobalt is precipitated as a hydroxide, and its catalytic effect on autooxidation is diminished. Titanium dioxide pigments having silica surface treatment had the least effect on drying time and loss of dry. Emulsions without pigments showed much less loss of dry, however, drying time was increased to > 24 hr by addition of "free" acrylate- and phosphate-based dispersants. This was observed for fresh emulsions and was an instantaneous deactivation of cobalt relative to the gradual increase in drying time observed for pigmented emulsions. Emulsion pH and resin neutralization with ammonium hydroxide also influence drying time and their effects were already apparent in fresh emulsions. These results led to the general conclusion that the effect of additives on drying time of non-pigmented emulsions are observed relatively quickly (24 hr) compared to pigmented emulsions which show a gradual loss of dry upon long-term storage.

Loss of dry is also dependent on the type of drier. Conventional cobalt carboxylate driers used in solventborne alkyd paints performed relatively poorly in alkyd emulsions, in terms of preventing loss of dry. The emulsifiable cobalt neodecanoate drier, which contained 2,2′-bipyridyl as complexing agent, showed the best resistance towards loss of dry. Surprisingly, cobalt chloride also gave good drying times, but was more susceptible to loss of dry. Location of the cobalt (added to alkyd or added to water) does not appear to influence drying time.

The formation of a dry film from a long oil alkyd emulsion made from a conventional surfactant appears to suffer from the migration of the surfactant to the film surface. Washing the dry film leads to holes or pits in the film which are distributed in a hexagonal pattern (Bénard cells). This suggests that water evaporation and surfactants cause sufficient surface tension and/or temperature gradients in the film for the formation of Bénard cells.

## ACKNOWLEDGMENTS

This work has been carried out as part of government and industrially sponsored consortium projects. The Swedish Council for Work Life Research (Rådet för Arbetslivsforskning) is thanked for its financial support of our alkyd emulsion research over the past several years. The following companies are also thanked for their sponsorship and participation in the consortium projects: Alcro-Beckers, Akzo Nobel, DSM Resins, FINA Research (Sigma Coatings), Jotun, OMG Europe, Tikkurila Paints, and Uniqema (ICI Surfactants).

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