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Influence of Drier Combination on Through-Drying in Waterborne Alkyd Emulsion Coatings Observed with Magnetic Resonance Profiling

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Achieving fast and uniform crosslinking in alkyd coatings poses a challenge to formulators that demands a fundamental understanding of drier efficiency. In recognition of this, we have examined the physical changes that accompany autooxidative crosslinking in alkyd films (cast from waterborne emulsions) in the presence of various combinations of metal carboxylate driers. A newly developed type of magnetic resonance (MR) profiling was used in conjunction with conventional techniques: Beck-Koller drying tests, pendulum hardness, and mass uptake. MR profiling noninvasively probes the molecular mobility of the alkyd as a function of depth (with a pixel resolution of about 9 μm), over drying times ranging from minutes to weeks. It thereby indicates drier efficiency via its sensitivity to viscosity build-up during drying and to subsequent film hardening. We show unequivocally that more uniform crosslinking is achieved using a combination of a primary (Co) and a secondary (Ca) drier, in support of conventional belief. Furthermore, these results yield new insight into the chemical mechanisms induced by the driers and are thus of clear benefit to coatings researchers and formulators. Notably, the secondary driers improve the efficiency of the hydroperoxide decomposition reactions, but they are only active during an initial period, after which crosslinking nonuniformity develops.

INTRODUCTION

Ever since modern paints were developed, alkyds have been used as binders. Increasingly tighter environmental regulations[1,2] restricting the emission of volatile organic compounds are driving the development of waterborne alkyds (either as emulsions[3] or water-soluble alkyds) to replace conventional solvent-based systems. However, paints cast from waterborne alkyds typically suffer from longer drying times[3-5] compared to their solvent-based analogues, and they require two to three times more drier for satisfactory drying.[6] They are likewise prone to adhesive failure. Additional problems with cohesive film failure and wrinkling have long been attributed to nonuniform crosslinking density with depth into the film.[7] This crosslinking profile is the main focus of this paper.

Autooxidative polymerization mechanisms of drying oils and alkyd resins used in coatings have been studied for decades.[8-11] It has been established[12] that alkyd resin curing is a complex process consisting of (a) an induction period, (b) oxygen uptake, (c) hydroperoxide formation, (d) hydroperoxide decomposition leading to oxidation products, and (e) crosslinking. But only in recent years has significant progress been made in elucidating the oxidation mechanisms leading to the polymerization and the hardening of oils and alkyd films in air.[12-16]

In 1954, Fitzgerald proposed a few principles that are very relevant here.[7] He suggested that the chemistry of crosslinking reactions in alkyds is influenced by *physical* processes, especially oxygen diffusion. Fitzgerald attributed the growth of a so-called "skin layer" in alkyds to faster peroxide formation and decomposition near the surface in comparison to near the substrate. He proposed that the origin of the gradient in crosslinking density is a gradient in oxygen content resulting from diffusion from the surface. These basic concepts have persisted over the last five decades and are now commonly held beliefs.

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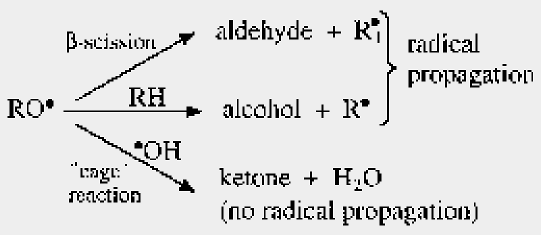


Scheme 1—Reactions of the alkoxyl radicals to produce aldehydes or alcohols (and propagate radicals) and to produce ketones (without propagating radicals).

Here we consider both the chemical and the physical aspects of film formation from alkyd emulsions, and we test Fitzgerald's concept of a gradient in crosslinking density resulting from an oxygen diffusion-limited reaction. Using a newly developed magnetic resonance profiling methodology,[17] we determine why and when the alkyd skin layer forms and explore the influence of the drier chemistry.

In comparison to the numerous studies of the oxidation and crosslinking reactions, very little effort has focused on the catalytic effects of metal salts (commonly referred to as driers), which are added to accelerate drying in alkyds. This topic did, in fact, attract a lot of attention prior to the mid-1960s, however explanations for the effects of driers did not reach much beyond the speculative stage.[18-20] Primary driers (also known as surface driers), such as cobalt carboxylates, were found to speed up all five of the basic reactions (a to e, mentioned earlier). This effect has recently been explained by an increase in the rate of the overall oxidative polymerization mechanism, which relies primarily on the radical concentration.[21]

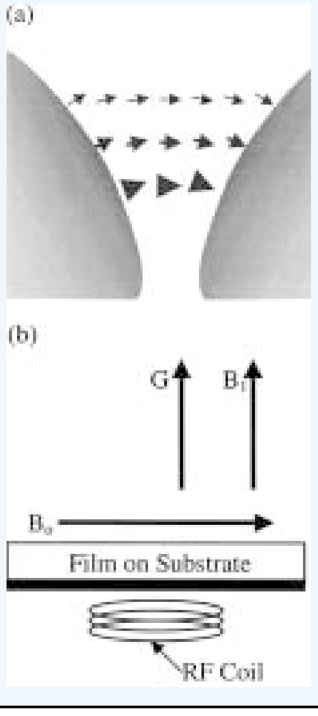


Figure 1—(a) Cross-section of the pole-pieces on the GARField magnet. The arrows show the direction of the magnetic field. The size of the arrows indicates the relative strength of the magnetic field at the various heights. (b) Configuration of magnetic fields in the GARField magnet. The film rests horizontally above a planar-spiral surface RF coil. A static magnetic field, B_o, is oriented parallel to the sample plane. A gradient in the magnetic field, G, is permanently in the vertical direction (i.e., at a right angles to the main field). The magnetic field of the RF coil, B_1, is likewise in the vertical direction.

When used alone, primary driers, such as cobalt, often result in surface wrinkling that is attributed to nonuniform crosslinking.[7] Secondary driers are therefore added in combination with at least one primary drier, to "fine tune" the drying process.[22] Their exact roles in autooxidation are not always chemically defined, but their effects on drying times and film properties have been determined in comparative studies.[23-28] Secondary driers are sub-classified as polymerizing-through driers (e.g., Zr) and as auxiliary driers (e.g., Ca).

The classification of driers is based on tests that measure drying times by drawing either a needle (i.e., the Beck-Koller method) or a ball through a film. Cotton wool, sand, or finger touching are also commonly employed to measure surface drying times. Most drying tests do not offer any explanations for the effects of the different driers and hence selection is made on an empirical basis, usually involving as much art as science. Newer methods to measure the degree of cure in alkyd coatings have been developed.[29-31] These techniques do not, however, offer resolution in the vertical direction to determine any spatial variation in the degree of crosslinking. The use of chemical profiling by confocal Raman microscopy[32] and by infrared microscopy[33] has been envisaged, but it has been shown that they are only sensitive to the chemical evolution of the alkyd film leading to oxidation products. They are not sensitive to the important crosslinking reactions and do not determine crosslinking density. Hence, it is true to say that all existing drying tests—both conventional and new—do not determine crosslinking depth profiles. Progress in understanding drier mechanisms has been impeded by the lack of adequate analytical techniques.

We have exploited the enormous potential of magnetic resonance (MR) profiling to follow the crosslinking of alkyd resins from their moment of casting through 64 days of drying. A novel permanent magnet,[17] which was specifically designed to probe planar films and coatings, is employed. We have previously shown that MR profiling is a highly effective probe of crosslinking density with depth in films of a photo-initiated latex formulation.[34] The technique is sensitive to hydrogen (^1H) nuclei mobility with a spatial resolution of about 9 µm. In alkyds, ^1H mobility is related to the viscosity build-up of the film and to the progression of crosslinking during drying. Variations in the degree of crosslinking through the film depth reveal the effects of metal carboxylates on the nonuniform curing of alkyd resins. The analysis thereby facilitates the selection and optimization of driers for alkyd resins.

Importantly, MR profiling is used for the first time in conjunction with two conventional methods: pendulum

Table 1—Comparison of Drying Times for Different Drier Combinations

Drying Combination and Concentration (wt% on the Alkyd)	Surface/Touch -Dry Time (hr)	Through-Dry Time (hr)
No drier	>24	>24
0.05% Co	7	12
0.10% Co	6.5	11
0.10% Co + 0.15% Zr	6.25	19
0.10% Co + 0.25% Ca	5	10.5

hardness tests and Beck-Koller (BK) drying tests. The MR parameters are thereby compared with other physical parameters and are found to be generally consistent with them. However, MR profiling is a much more sensitive and reliable technique. Notably, it can be applied to viscous liquids, and so it enables the evaluation of drier efficiency in freshly cast alkyd films. MR data on alkyd mobility are obtained noninvasively, when other techniques would be insensitive or would damage the specimen. Moreover, when coupled with oxygen uptake measurements, MR profiling yields new insight into the mechanisms of driers.

Mechanisms of Alkyd Drying

A review of the chemistry of alkyd drying[12] is useful for subsequent data interpretation. When considering the drying of an alkyd resin, it is more important to focus on the evolution of radicals, because they are the key species in both the oxidation and the crosslinking reactions. Initially, radical concentration is very low. It is dependent on the level of radical impurities ($X^\bullet$) able to initiate hydrogen abstraction on a fatty acid chain, R, via the reaction:

$$X^\bullet + RH \rightarrow R^\bullet + XH \tag{1}$$

Once created, radicals propagate via reactions in which hydroperoxides are formed but in which the overall radical concentration remains constant:

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{2}$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \tag{3}$$

If the only means of chain radical evolution was by propagation, then oxidation—which relies on the presence of radicals—would continue at a constant and very low rate. Fortunately, for the useful applications of drying oils, hydroperoxides formed via reaction 3 are not very stable. They thermally decompose in monomolecular or bimolecular reactions to produce new radicals:

$$ROOH \xrightarrow{\Delta} RO^\bullet + {}^\bullet OH \tag{4}$$

$$2\,ROOH \rightarrow RO^\bullet + ROO^\bullet + H_2O \tag{5}$$

Through these two reactions, the concentration of radicals is increased. However, at room temperature their rates of reaction, especially 4, are relatively slow. Another mechanism of hydroperoxide decomposition, recently proposed by Mallégol et al.,[16] is likely to be dominant at room temperature:

$$\underset{\displaystyle OOH}{\sim CH \sim} \xrightarrow{X^\bullet, O_2} \underset{\displaystyle OOH}{\sim \overset{\bullet}{C} \sim} \tag{6}$$

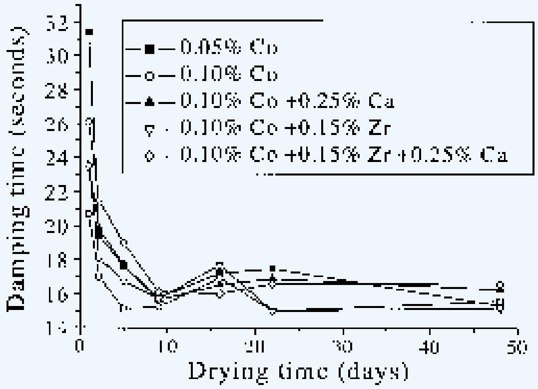


Figure 2—Development of pendulum hardness (expressed as damping time) over one to 48 days for different drier combinations and concentrations, as indicated in the legend. The data for the pure alkyd are not shown here because they would be off of this scale; after 48 days its damping time is still very high (31.8 sec).

This reaction requires the presence of oxygen. The production of new radicals, created in reactions 4 through 6, results in a faster oxidation rate. Furthermore, alkoxyl radicals ($RO^\bullet$), formed in reactions 4 and 5, can go on to propagate radicals, as in *Scheme* 1, while also producing ketones, alcohols, and aldehydes.

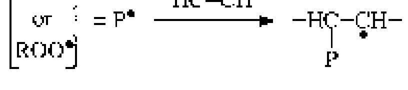
When the radical concentration increases, there is likewise an increase in the probability of radical recombination through one of three reactions:

$$R^\bullet + R^\bullet \rightarrow R-R \tag{7}$$

$$RO^\bullet + R^\bullet \rightarrow ROR \tag{8}$$

$$ROO^\bullet + R^\bullet \rightarrow ROOR \tag{9}$$

These reactions are at the heart of alkyd technology, as they create crosslinks. Alkyl (C–C), ether (C–O–C) or peroxy (C–O–O–C) "bridges" are formed to join two alkyd chains in reactions 7, 8 and 9, respectively. In each of the reactions, radicals are not propagated but are destroyed. Crosslinking can also occur with radical propagation through an addition reaction on double bonds[14] (mainly conjugated):



$$\begin{bmatrix} R^\bullet \\ \text{or} \\ ROO^\bullet \end{bmatrix} = P^\bullet \xrightarrow{-HC=CH-} -\underset{\displaystyle P}{HC}-\overset{}{\underset{\bullet}{C}H}- \tag{10}$$

It is obvious that without an efficient decomposition of hydroperoxides (reactions 4 and 5), the oxidation rate will remain very low. Because of the need for fast drying in industrial and commercial alkyd paints, driers are inevitably incorporated. A transition metal (M) with two valence states (n and n+1) participates in a reaction to break down a hydroperoxide via the Haber-Weiss mechanism:

$$M^{n+} + ROOH \rightarrow M^{(n+1)+} + RO^\bullet + OH^- \tag{11}$$

$$M^{(n+1)+} + ROOH \rightarrow M^{n+} + ROO^\bullet + H^+ \tag{12}$$

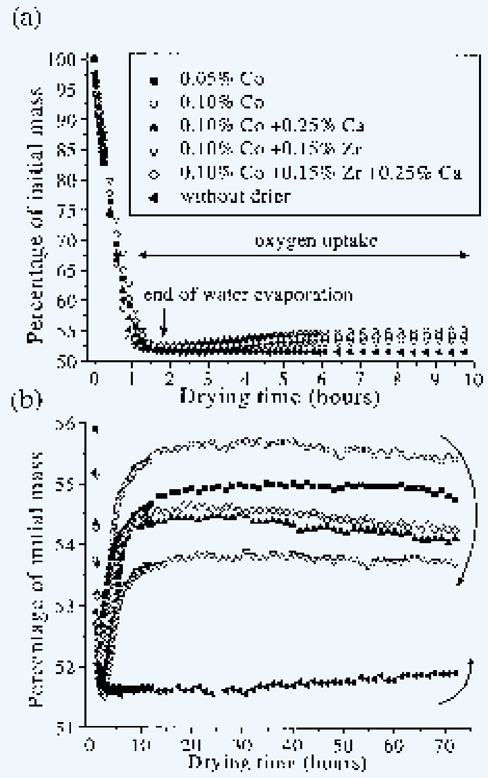


Figure 3—Mass changes for the different alkyd systems dried in air. (a) Evidence for water evaporation over the first couple of hours and (b) evidence for oxygen uptake and slow mass loss over 70 hr. The symbols used are identical to those in Figure 2, for ease of comparison.

The radicals created by these reactions go on to promote the oxidation of fatty acid chains. The net effect of reactions 11 and 12 is equivalent to that of equation (5), but in the presence of metal catalyst, the activation energy drops from 90-170 kJ/mol to 40-50 kJ/mol,[35] and the reaction rate is therefore faster.

MATERIALS AND EXPERIMENTAL METHODS

Materials

An alkyd resin (Jotun A/S, Norway), based on tall oil fatty acids, isophthalic acid, and pentaerythritol was used. Its oil length (i.e., fatty acid content) was 83%, and its acid value was between 6 and 9 mg KOH/g alkyd. Atsurf 3969 (Uniqema, Belgium), which consists of a blend of a high molecular weight ethylene oxide/propylene oxide (EO/PO) copolymer and oleyl ethoxylate (with 20 EO), was used in the emulsification.

Three commercial driers (metal carboxylates) for alkyd resins were employed: cobalt 5 hydro-cure II E, zirconium 12 hydro-cem E, and calcium 5 hydro-cem E (provided by OMG Europe GmbH, Germany). The numbers in the trade names refer to the metal content. These driers are self-emulsifiable in water and consist of the metal carboxylate and proprietary surfactants in a mineral spirits carrier. The cobalt drier also contains 2,2′-bipyridyl, which functions as a drying accelerator and minimizes loss of dry upon storage.[36]

Emulsification

Atsurf 3969 was dissolved in double-distilled water to make a 5 wt% solution. The alkyd resin was then added to yield a 1:1 weight ratio. The mixture was stirred with a motor-driven propeller for five minutes at 45°C. The pH was adjusted to approximately 7 by addition of a 50 wt% solution of KOH. The coarse emulsion was introduced into a high pressure homogenizer (Microfluidizer TM-120, Microfluidics, Newton, U.S.) equilibrated at 50°C. Emulsification was carried out at 600 kPa for 15 min. The final droplet diameters were <0.9 µm, as measured by laser light scattering (Malvern Mastersizer MS20, Malvern, UK). Driers were added to the alkyd emulsion and agitated vigorously in a shaker for two minutes. The pH was readjusted if necessary. The emulsion was left for at least one day and shaken for two minutes prior to casting.

Drying Time Measurement

Beck-Koller drying tests were carried out using a standard BK drying recorder (Mickle Laboratory Engineering Co., UK) in a room controlled at 23 ±1°C and at 50% RH. Films (wet thickness of 80 µm) were cast on clean glass plates using an automated six-holed film applicator that moved at a constant, controlled speed. (Thicker films were prone to de-wetting.) Rounded steel needles (shaft diameter of 1.0 mm) were drawn through the films. Surface-dry time was recorded as the point when the needle started to lift out of the bulk film and to skim along the surface, leaving a jagged furrow in the surface. At the onset of this point, the surface was also finger-touch dry. The through-dry time was taken to be the point when no observable furrow or indentation was seen in the film. In some cases, it was difficult to distinguish the exact surface or through-dry times, hence times should be taken as approximations to within ± 0.5 hours, at best. All samples were measured in duplicate and the results averaged. To improve precision, all measurements were carried out by the same operator.

Hardness Measurement

Film hardness was measured on drying alkyd films (80 µm wet thickness) using a pendulum hardness

Table 2—Mass Loss for Alkyd Emulsions Containing Various Driers

Drying Combination and Concentration (wt% on the Alkyd)	% of Initial Mass at Minimum (m_{min})	% of Initial Mass at Plateau (m_p)	m_p–m_{min} (%)
0.05% Co	51.80 (2.42)[a]	55.00	3.20
0.10% Co	52.19 (2.08)	55.70	3.51
0.10% Co + 0.15% Zr	51.51 (2.58)	53.88	2.37
0.10% Co + 0.25% Ca	52.60 (1.98)	54.46	1.86
0.10% Co + 0.15% Zr + 0.25% Ca	52.24 (2.42)	54.62	2.38

(a) Values in parentheses are the time in hours necessary to reach the minimum value. The maximum values were reached after around 20 hr for the five compositions and are not indicated in the table.

tester (Erichsen model 299) according to the König method. This method continues to follow the through drying (or hardness development) at later times when the BK methods has no sensitivity. Results are expressed as the time taken for the pendulum to reduce in amplitude from 6° to 3°. Measurements were made at selected drying times (nominally 1, 2, 4, 8, 16, 32, and 64 days) at five different positions across the film and averaged.

Mass Changes

Mass loss/gain measurements were carried out on an analytical balance interfaced to a computer. Films of the alkyd emulsion were cast on glass plates (total film area 60-70 cm^2) using a 120 µm applicator (6 cm wide). The mass of the film (initially about 0.6 g) was recorded to the nearest 0.1 mg with a sampling frequency that was varied to suit the different rates of mass change. The films were protected from fluctuating air currents in environmental conditions identical to those in the BK tests.

Magnetic Resonance Profiling (GARField)

A small purpose-built permanent magnet, called Gradient-At-Right-angles to the Field (GARField) and described elsewhere,[17] was used to obtain MR profiles from alkyd films. The magnet is designed to give a horizontal magnetic field of constant magnitude in a horizontal plane around a central region of 20 mm width. Tapered pole pieces (shown in *Figure* 1a) give rise to a large magnetic field gradient, which is oriented in the vertical direction, perpendicular to both the constant magnetic field and to the plane of the sample (*Figure* 1b). The presence of the field gradient causes nuclei to resonate at different frequencies depending on their vertical position in the sample. In the experiments performed here, samples were located in the magnet at a position corresponding to a magnetic field strength of 0.7 T and a field gradient strength of 17.5 T m^{-1}. A surface coil (with a diameter of 3 mm) was tuned to a resonant frequency of 30 MHz and placed beneath the sample, where it was used to examine the area of the film directly above it. The coil transmits a radiofrequency excitation signal to the sample and then acts as a receiver for the nuclear magnetic resonance (NMR) signal emitted by the sample.

Shaken alkyd emulsions were cast onto clean microscope coverslips (2 cm × 2 cm) using a 120 µm applicator. Immediately after casting, the film was placed in the magnet and the MR profiling was commenced in the open atmosphere at 21°C. Profiles were obtained using a spin-echo excitation pulse sequence[37]: $90_x - \tau - (90_y - \tau - \text{echo} - \tau)_n$ for n = 32 echoes and a pulse gap of τ = 95.0 µs. Usually, 1024 averages were obtained in a total acquisition time of five minutes. To obtain a profile, the echoes were Fourier transformed, thus giving the NMR signal intensity profile as a function of depth with a pixel resolution of 8.75 µm.

The spin-spin relaxation time (T_2) was then determined at each vertical position by fitting the profile decays to a single exponential function, $M_o\exp(-nT_E/T_2)$, where $T_E = 2\tau$ is the echo time. The T_2 values correspond to a local average for the alkyd, which is likely to have a distribution of relaxation times. Typically, solids, such as fully dried alkyd resins, have a low molecular mobility and a short T_2 time, whereas viscous liquids, such as an oil, have a greater molecular mobility and a longer T_2. The level of alkyd mobility can thus be gauged by T_2 values. We show herein that T_2 is sensitive to changes during the drying stage (up to the through-dry time) and during the later hardening stage.

Profiles were recorded after drying times of 1, 2, 4, 16, 32, and 64 days to coincide with the times used for hardness measurements. After drying times ≥ 4 days, the NMR signal intensity from the hardened alkyd decayed rapidly. To measure the very short T_2 values, a "shifted k-space" technique was used with echo times as short as 50 µs.[37] It was necessary to increase the number of averages to 6000 to improve the signal-to-noise ratio. Data acquisition then took 30 min (rather than the usual five) with a reduced pixel resolution of 17.5 µm.

RESULTS AND DISCUSSION

Drying Times and Hardness Development

Results from conventional tests will first be reported, and then MR profiling data will be considered in this light. For a waterborne alkyd film without any drier, *Table* 1 shows that after 24 hr, surface- (i.e., touch) and through-dry points have not yet been achieved. In contrast, an alkyd film containing 0.10% Co plus 0.25% Ca driers (wt% on the alkyd) has the shortest surface-dry time of five hours and the shortest through-dry time of 10.5 hr. When the Co drier is used alone at low concentrations (0.05 %), surface drying is slower than in any other drier system. The Co through-dry time of 12 hr, however, is faster than that achieved with a mixture of 0.10% Co and 0.15% Zr driers (19 hr), consistent with previous findings.[28] Drying tests enable a comparison of the efficiency of the various drier

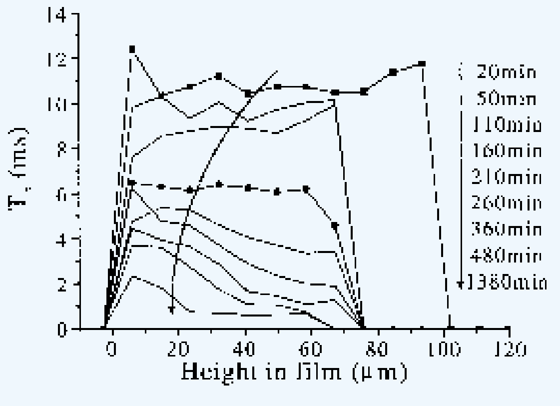


Figure 4—T_2 profiles obtained with the GARField magnet from an alkyd emulsion film containing 0.05% Co drier. The final film thickness is seen to be about 75 µm. Profiles are presented for drying times of 20, 50, 110, 160, 210, 260, 360, 480, and 1380 min. The direction of the arrow shows the progression of time. Individual pixels are shown by the symbols for the profiles at 20 and 160 min.

combinations, but they yield no information on the chemical mechanisms nor do they provide information on the spatial dependence of crosslinking. Presumably, however, surface-dry times are more sensitive to crosslinking near the surface in comparison to through-drying times.

Hardness measurements were only possible after through-drying was achieved. *Figure* 2 shows the hardness development between drying times of one and 48 days. Normally, the König damping time is short when the coating is not dried and then the damping time increases as the coating becomes harder. In our experiments, the damping time was initially high, and it decreased over a narrow range of time before approaching an apparent plateau value. These results suggest that at the early stages of drying, when the films were liquidlike, the hard glass substrate influenced the hard measurement, because the film was too thin. At later times, when the film was harder, a more reliable measurement of the film hardness was obtained without an artefact from the substrate.

Of course a reliable comparison of driers systems cannot be made in these conditions. One can only observe the obvious increase in the drying rate brought on by the driers. An alkyd resin without added driers, as a control sample, still has a damping time of 32 sec after 48 days, which is comparable to the value for the alkyd with 0.05% Co drier after one day. After drying times of about nine days, it is found that there is no more influence of the glass plate. All films reach similar final damping times of about 16 sec, regardless of the driers used. After longer times, there are some variations in hardness, but these are attributed to experimental uncertainties. In any case, the measurements are not a direct probe of crosslinking depth profiles.

Mass Changes upon Drying

Mass measurements for six different alkyd systems are plotted in *Figure* 3a. For all compositions, the mass initially decreases linearly with time as water evaporates at a constant rate. The minimum in the mass, m_{min}, is considered here to represent the end of the water evaporation stage. *Table* 2 shows that m_{min} lies in the range between 51.51 and 52.60% of the initial mass for all compositions, which is consistent with the composition of the emulsions (47.5 wt% water).

Upon completion of water evaporation, the observed increase in mass is attributed to the uptake of oxygen. Without the addition of a drier, the mass uptake rate is very slow. In alkyds containing driers, mass uptake occurs primarily between times of two and 10 hours. The mass uptake then reaches a maximum plateau value (m_p) before decreasing again slightly (*Figure* 3b). The mass loss after m_p is most likely due to the progressive loss of volatile oxidation products that are formed from the breakdown of fatty acid chains. These products are typically aldehydes (as in *Scheme* 1) and carboxylic acids.[33] The pure alkyd does not exhibit a mass loss over this time scale because the oxidation reactions without driers are extremely slow under ambient conditions, as already discussed.

We propose that the differences between m_p and m_{min}, listed in *Table* 2, can be used as a measure of the relative activity of the driers. Values of ($m_p - m_{min}$) are found to vary with the driers used. The alkyd films containing Co driers alone have the largest ($m_p - m_{min}$) values (3.20 and 3.51%). These two systems also had the longest surface dry times (*Table* 1). The smallest ($m_p - m_{min}$), and hence the lowest amount of oxygen uptake, is achieved with a combination of 0.10% Co and 0.25% Ca driers. A low oxygen uptake indicates that fewer radicals are available to participate in the oxidation reactions. We suggest that fewer radicals remain available because they have recombined to create crosslinks. The Co/Ca system is therefore the most efficient. In support of this interpretation, this system likewise exhibits the fastest through-dry times (*Table* 1). The harder surface in the alkyd with Co only is achieved with poorer overall drying efficiency. (Incidentally, the rate of oxygen uptake indicates the *oxidation* rate but does not provide information about *crosslinking* rates.)

T_2 Depth Profiles

MR profiles indicate molecular mobility as a function of depth.[17,34] When most of the water has evaporated from an emulsion (after about 30 min), the NMR signal is mainly due to ^1H in the alkyd resin. As the resin undergoes crosslinking, the ^1H mobility decreases, and T_2 falls.

Figure 4 shows a series of T_2 depth profiles obtained from an alkyd film containing 0.05% Co drier. The first profile, obtained after 20 min of drying, shows that at this point in time the film is about 110 µm thick. The film still contains water, and thus the T_2 value is a weighted average for the alkyd and the water. T_2 is uniform with depth. After 50 min, most of the water has evaporated, and from this time forward, T_2 indicates the mobility of the alkyd only. The film thickness decreases to about 80 µm, where it stabilizes. Over the next 100 min, T_2 decreases with time, suggesting that crosslinking is underway in the alkyd. (Recall that the surface dry time for this film was found to be 420 min.) T_2 remains uniform with depth. After 210 min of drying, however, T_2 near the air surface has fallen to less than 4 ms, indicative of some solidification. Near the substrate, in contrast, T_2 is nearly 6 ms and has not decreased much during the previous hour. A spatial gradient in T_2, and presumably crosslinking, has developed.

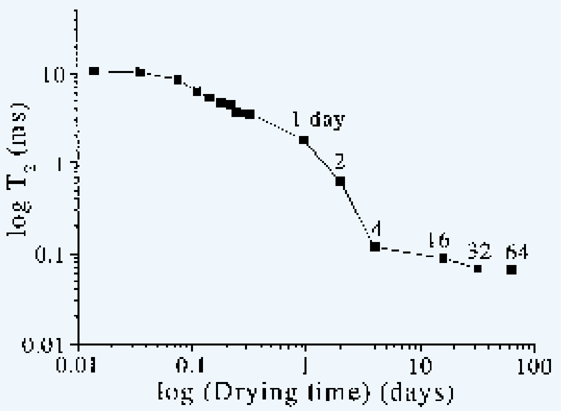


Figure 5—T_2 as a function of drying time (up to 64 days) (on a log-log scale) for an alkyd containing 0.05% Co. (Full depth profiles from this same film at the earlier times are shown in Figure 4.) The T_2 values were obtained at a position 10 µm above the substrate.

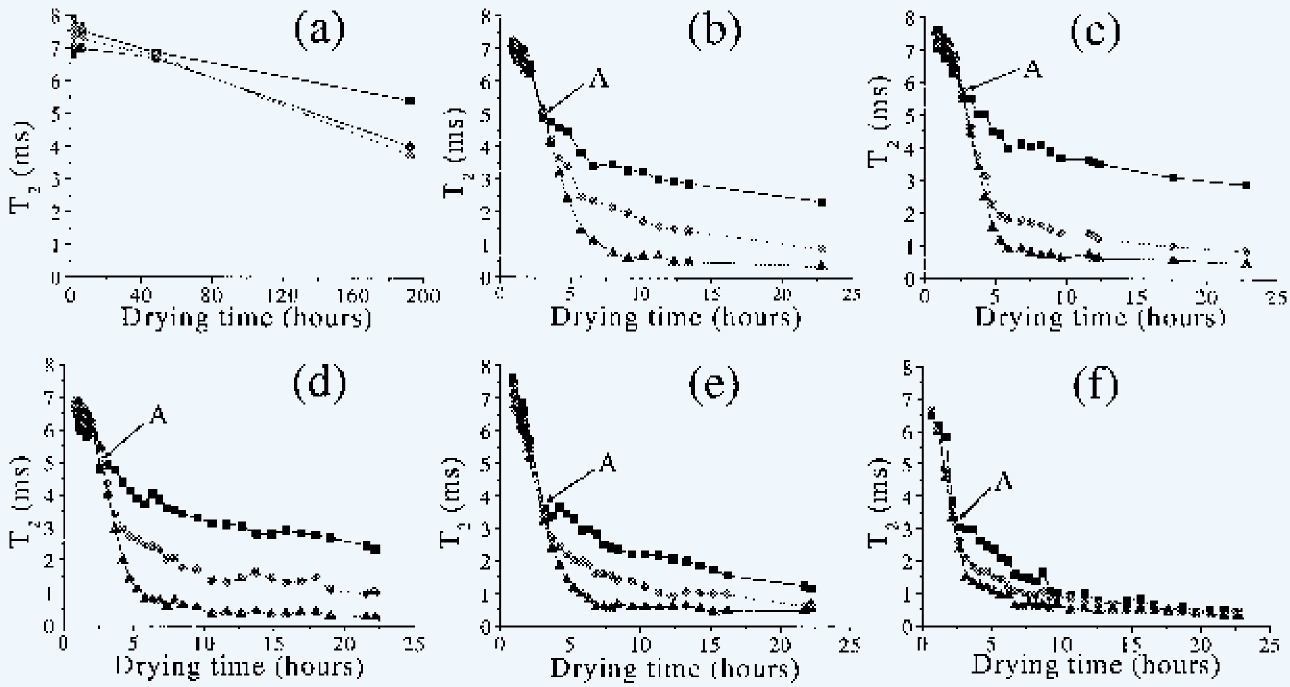


Figure 6—T_2 as a function of time at three different depths from the surface (typically 10 (▲); 35 (●); and 70 (■) µm) of alkyd films containing various drier concentrations and combinations: (a) neat alkyd, (b) 0.05% Co, (c) 0.10% Co, (d) 0.10% Co and 0.15% Zr, (e) 0.10% Co, 0.15% Zr, and 0.25% Ca, and (f) 0.10% Co and 0.25% Ca. Point A indicates the time at which inhomogeneity develops, and T_2 begins to be lower near the surface than near the substrate.

This gradient, which persists in the profile for drying times up to two days, has been proposed previously in the literature[7] on the basis of simple observations, but—until now—its existence has never been directly proven.

T_2 in this same alkyd film with 0.05% Co was monitored during 64 days of drying. *Figure* 5 illustrates how it evolves. There is not a straightforward mathematical relationship between T_2 and any other physical property (such as viscosity or crosslink density), although correlation between T_2 and thermomechanical properties has been demonstrated experimentally. Comparison of T_2 evolution to the development of the pendulum hardness, shown in *Figure* 2, is worthwhile (taking into account the differences in wet film thickness (80 versus 120 µm) and the artefacts before the films have hardened). The T_2 decrease is very strong during the first four days. Similarly, over five days of drying, the pendulum damping time of the alkyd with 0.05% Co decreases sharply to ca. 18 sec., where it remains (within the uncertainty of the measurement). After four days of drying, the rate of decrease in T_2 for the same system (*Figure* 5) strongly slows down. Between four and 64 days, the T_2 falls from about 0.12 ms to about 0.06 ms, whereas it falls from 10 ms to 1 ms during the first two days. T_2 measurements indicate hardening for up to 64 days but at a much slower rate, as likewise found recently from peroxide value measurements,[16] whereas there is no evidence in the pendulum hardness tests for any subsequent crosslinking (although sensitivity in the hardness measurements might have been improved if it had been possible to use thicker films.)

To confirm further that the decrease in T_2 observed in *Figures* 4 and 5 is indeed the result of crosslinking, a comparison can be made to an alkyd film without any drier. *Figure* 6a reveals a very gradual decrease in T_2 over time. As one would expect, crosslinking takes place in the absence of a drier but at a very slow rate. After 200 hr, the T_2 near the air surface is 4 ms, and it is about 5.5 ms near the substrate. A gradient has developed in the T_2 depth profile. This profile is roughly the same as that found after 210 min in the alkyd containing 0.05% Co drier. We note from comparison with *Figure* 4 that the presence of Co has no appreciable effect on the T_2 of the initial alkyd. There is no evidence that Co, at the concentrations used, influences relaxation times.

T_2 depth profiles obtained at various times of drying contain a wealth of information, so much, in fact, that it becomes difficult to compare different series of profiles. To aid in comparing the influence of various drier concentrations and combinations, *Figures* 6b-f show T_2 evolution during the first day of drying (starting from the time when the water has evaporated) at three positions in each alkyd film. The positions were chosen to correspond to points near the surface, substrate, and middle of the film. Co, a primary drier, is examined on its own at two concentrations (*Figures* 6b and 6c) and in combination with secondary driers.

Regardless of the drier concentrations and combination, a similar pattern is observed, illustrated schematically in *Figure* 7. (The meanings of Stages I, II, and III in *Figure* 7 will be given in the next section.) Over the first two

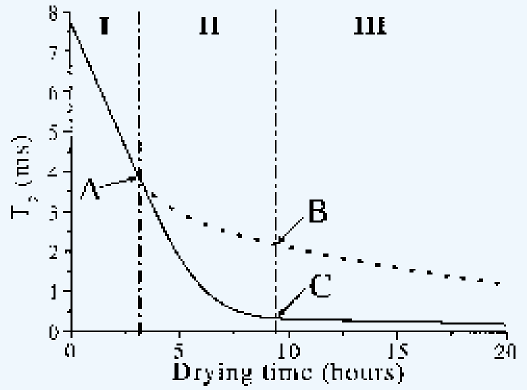


Figure 7—Schematic illustration of T_2 as a function of time near the surface of an alkyd film (—) and near the substrate (- - -). Three stages (I, II and III, as explained in the text) are illustrated. Point A indicates the point where the crosslinking rate near the surface is faster than near the substrate interface. At point C, the crosslinking rate near the surface slows down.

or three hours of drying, T_2 decreases at a roughly constant rate, and this rate is identical at all depths from the surface. Initially, T_2, and hence crosslinking, is spatially uniform.

At the point marked "A" in *Figures* 6 and 7, a change in the drying pattern develops. Near the surface, the T_2 continues to fall approximately at the same rate. Near the substrate, in contrast, the rate of decrease in T_2 is markedly slower. A spatial gradient in T_2 emerges. None of the drying combinations result in uniform crosslinking. Over time, the T_2 near the air surface approaches a limiting value corresponding to the crosslinked alkyd, and its rate of decrease slows. At drying times greater than about five hours, the rate of decrease in T_2 is approximately uniform with depth, but the spatial gradient in T_2 persists.

Despite the broad similarities in behaviors observed in *Figures* 6b through f, clear differences are also apparent. In particular, the T_2 value at point A varies between 3.0 ms (for the alkyd with 0.1% Co and 0.25% Ca driers) to 5.5 ms (for 0.10% Co). The rate of decrease in T_2 up to point A is greater in alkyds containing Co/Ca and Co/Ca/Zr driers. It is slower in alkyds containing only Co or Co/Zr driers. The difference between T_2 values at points B and C in *Figure* 7 gives an indication of the extent of the nonuniformity in crosslinking. The difference in T_2 between the vicinities of the surface and the substrate, listed in *Table* 3, is greatest for an alkyd with Co drier alone compared to alkyds with other driers. Interestingly, Ca is highly effective at promoting crosslinking uniformity when used in combination with Co. Zr, on the other hand, although classified as a through-drier,[28] has a negative impact on the drying uniformity when used in combination with Co and Ca. Elsewhere it has been pointed out that the effectiveness of Zr driers is very dependent on the nature of the alkyd.[27]

In a film formed with a primary drier alone (Co), the conventional belief is that the surface is dried while the interior of the film is still a viscous liquid. The T_2 profiles presented here support this idea. On the other hand, mixtures of cobalt with metals like calcium (an auxiliary drier) and zirconium (a through-drier) are thought to lead to more homogeneous drying in the film depth. This idea is supported for the case of Co with Ca (*Figure* 6f). The faster decrease in T_2 found in this system is consistent with its relatively short surface dry time (five hours) and lower mass uptake, both of which suggest a faster crosslinking rate.

In an attempt to relate the T_2 relaxation times to a physical property of the alkyd, it is sensible to review the BK drying measurements in the light of the current results. *Figure* 8 shows the correlation between the touch-dry and through-dry times and T_2 values (measured at depths of 10 and 35 μm from the surface, respectively) for all alkyd systems. The depth of 10 μm corresponds to the "near surface," whereas the depth of 35 μm is equivalent to the region near the substrate in the 40 μm thick films used in the BK measurements.

All of the T_2 values at the touch-dry times lie between 0.8 and 1 ms, regardless of the drier concentration or combination. This touch-dry T_2 value should be seen in comparison to the initial value of the alkyd, which is typically about 7 to 8 ms. The correlation between the through-dry point and T_2 is not as strong. There is some scatter in the data, but nevertheless T_2 lies in the range between 0.9 and 1.5 ms, which comprises the range obtained at the touch-dry point. Conventional wisdom says that the touch-dry time corresponds to the point when the surface has crosslinked enough to create a "skin" layer. The through-dry time corresponds to the point when there is crosslinking "through" the depth of the film. Our results support this concept. We suggest that a T_2 relaxation time in an alkyd film on the order of 1 ms corresponds to a network that is sufficiently crosslinked to have some mechanical integrity. Hence the needle used in the BK test skims along the alkyd surface when T_2 has fallen to about 1 ms near the surface. When the film has this same level of mechanical integrity throughout its depth, T_2 is 1 ms near the substrate, and the film is "through-dry" according to the BK test.

NEW INSIGHTS INTO ALKYD DRIER MECHANISMS

As already discussed, three mechanisms of hydroperoxide decomposition can generate radicals that induce crosslinking. At room temperature, thermal decomposition (reactions 4 and 5) is very slow. Consequently, the "oxygen-induced" mechanism (reaction 6) and the Haber-Weiss drier mechanisms (reactions 11 and 12) are the dominant means of decomposition. We propose that the "oxygen-induced" mechanism for hydroperoxide decomposition holds the key to understanding drier effects.

To simplify the discussion of drier mechanisms, we will only consider three drier compositions: Co alone, Co/Zr, and Co/Ca/Zr. This choice will allow a qualitative comparison with the results obtained previously by Mallégol et al.[21] with the same driers in linseed oil films. Alkyd drying has been shown to be very similar to linseed

Table 3—Differences between T_2 Relaxation Times Near the Substrate (Point B) and Near The Surface (Point C) at the Start of Stage III

Drying Combination and Concentration (wt% on the Alkyd)	T_2 near the Substrate at Point B (ms)	T_2 near the Surface at Point C (ms)	Difference between Points B and C (ms)
0.05% Co	0.6	3.1	2.5
0.10% Co	0.7	3.7	3.0
0.10% Co + 0.15% Zr	0.5	3.3	2.8
0.10% Co + 0.25% Ca	0.6	1.7	1.1
0.10% Co + 0.15% Zr + 0.25% Ca	0.6	2.7	2.1

oil drying in the presence of cobalt driers,[29] so the comparison is justifiable. Previous measurements of the hydroperoxide concentration over time[21] are shown schematically in *Figure* 9. In comparison, *Figure* 10 summarizes how T_2 evolves over time for the same three drier combinations (Co, Co/Zr, and Co/Ca/Zr) near the air surface and near the substrate interface. *Figure* 7 was divided into Stages I, II and III, and the first two of these stages are likewise identified in *Figures* 9 and 10. Each stage will now be discussed in turn.

Stage I: Peroxide Build-Up

During Stage I, *Figure* 9 shows there is a build-up of the peroxide concentration. The cobalt drier is active as soon as the oil is spread out as a film. Oxygen is assumed to be dissolved in the alkyd, and initially the oxidation reactions are not limited by the diffusion of oxygen into film. Presumably in the alkyd, many radicals are produced and crosslinking reactions occur alongside oxidation reactions, leading to the viscosity increase as indicated by the decrease in T_2 during Stage I (*Figure* 10). During the first hour, peroxide values increase at the same rate for the three drier combinations, because the cobalt activity is sufficient to yield a radical concentration allowing the maximum propagation rate.

Figure 7 illustrates the significant MR result that crosslinking is essentially uniform with depth in the alkyd film during Stage I. Whereas Fitzgerald suggested that gradients in crosslinking density resulted from faster peroxide decomposition near the air surface,[7] we find that initially crosslinking (and presumably peroxide decomposition) is uniform throughout the film. It is sometimes assumed in the field of alkyds that drying uniformity is influenced by the drier combination during the initial stages, but we observe in Stage I uniform drying for Co alone as well as with secondary driers.

The maximum oxidation rate depends on the particular composition of the alkyd or oil. Indeed, radical propagation is limited by the reactivity of polyunsaturated fatty acid chain to hydrogen abstraction or addition to double bonds. The oxidation rate (of intact fatty acid chains), therefore, cannot be significantly accelerated by a higher concentration of primary drier.[38] Comparison of *Figures* 6b and c, and examination of *Table* 1, shows that increasing the concentration of the Co drier from 0.05 to 0.10 wt% has a negligible effect on the rate and the spatial variation of crosslinking. Competitive reactions between metallic species and alkylperoxy radicals, which are very strong oxidants, have been suggested to explain this result.[39] High concentrations of a primary drier can therefore be poisonous to the catalytic reaction. Of course, the addition of Zr or Ca/Zr cannot increase the oxidation rate either.

The rate of crosslinking, on the other hand, is indeed affected by the presence of secondary driers. *Figure* 10 shows how T_2 decreases faster when a Zr drier is used along with the Co drier, and the fastest decrease in T_2 (associated with faster crosslinking) is found with the combination of all three driers. *Figure* 9 shows that the maximum of the peroxide concentration is reached at the same drying time for Co, Co/Zr, and Co/Ca/Zr driers. However, after one hour, a separation of the curves is observed and the maximum peroxide value (PV) is lower in mixtures containing secondary driers. The lower maximum in PV suggests that the driers have encouraged the peroxide decomposition reactions. It is likely that cobalt is quickly deactivated by the increasing concentration of oxidation products in the alkyd. Co either reacts with aldehydes (produced via *Scheme* 1) or, more likely, it forms a complex with carboxylic acids on fatty acid chains, losing its mobility in the crosslinked alkyd film. When a second metal (e.g., Ca or Zr) is present in the alkyd, it can instead form a complex with carboxylic acids, thereby keeping the Co free. Cobalt thus remains active for a longer time and continues its role in causing peroxide decomposition. The resultant increased concentration of free radicals leads to faster crosslinking, because the radical propa-

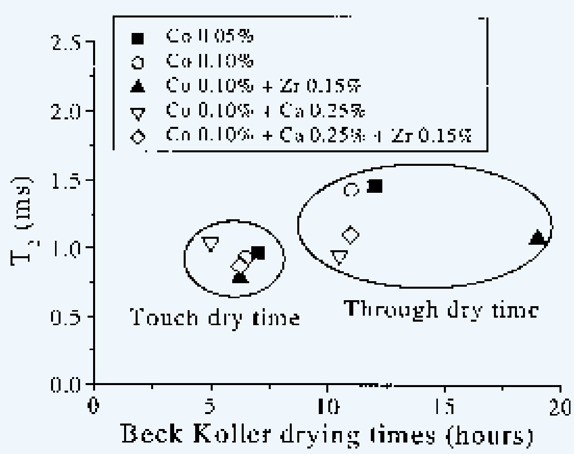


Figure 8—Correlation between T_2 relaxation times for alkyd films containing various drier combinations and the BK drying times. T_2 was determined at depths of 10 and 35 μm from the surface at the touch and through-dry times, respectively. The symbols are the same as used previously in Figures 2 and 3.

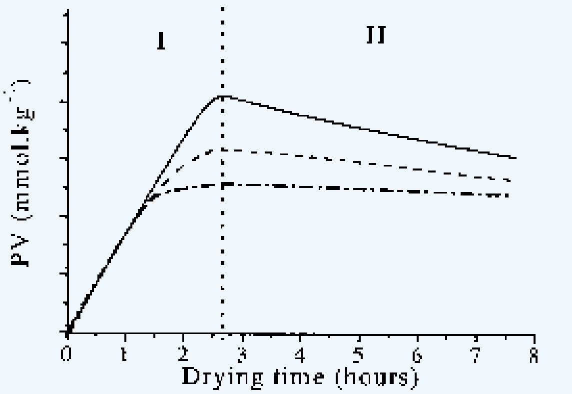


Figure 9—Peroxide value (PV) in linseed oil as a function of time for three different drier combinations: Co only (—), Co and Zr (- - -), and Co, Zr, and Ca (- · · -). Stages I and II are illustrated. The drying time at which the maximum is achieved is indicated by the vertical dashed line. Three drier combinations are considered. Data after Mallégol et al.[21]

gation rate is at its maximum. Whereas one might assume that secondary driers are active during later stages of drying, our data show that the improvement made by the addition of Ca or Ca/Zr to the alkyd/Co mixture is due to differences in the level of their "initial" activity during the first three or four hours of drying.

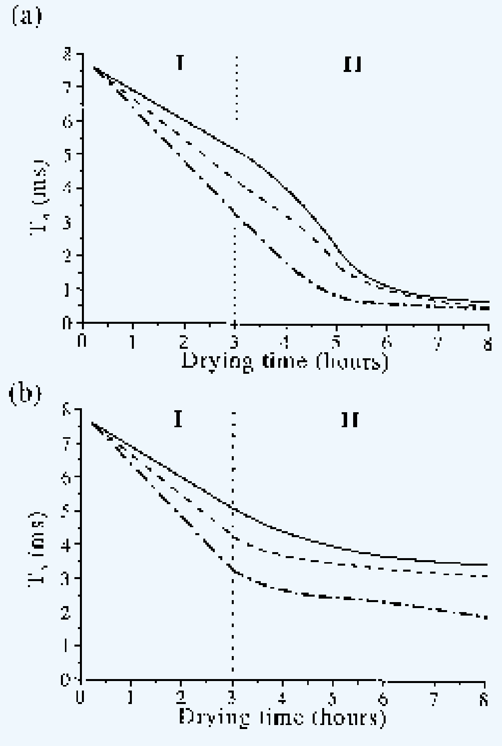


Figure 10—A schematic illustration of the experimental differences in the evolution of T_2 relaxation times with drying time (a) near the surface and (b) near the substrate. Three drier combinations are considered: Co only (—), Co and Zr (- - -), and Co, Zr, and Ca (- · · -). Stages I and II are illustrated.

Stage II: Oxygen-Induced Decomposition of Peroxides

At the end of Stage I, we suggest that the peroxide value is still very high but the cobalt has very low activity, if any, because of its reaction with aldehydes and/or its complexation. Thereafter, peroxide decomposition via reactions 11 and 12 becomes very slow. It is at this point that a difference between the rates of the surface-drying and the through-drying develops. This slowing down of the crosslinking rate near the substrate, seen in *Figures* 7 and 10b, is the bane of application scientists requiring uniform through-drying. An explanation of its origin, as proposed here, is vital to technological improvements.

When reactions 11 and 12 are blocked, we propose that the oxygen-induced mechanism (reaction 6) becomes the dominant means of hydroperoxide decomposition in alkyds at room temperature. We support Fitzgerald's concept that skin formation results from a vertical concentration gradient of oxygen.[7] The diffusion of oxygen through the alkyd is presumably inhibited by the partially crosslinked network that has developed by the start of Stage II. An oxygen concentration profile then develops as a result of diffusion into the alkyd film from the atmosphere. The concentration of oxygen is higher near the air surface, and so more hydroperoxides are decomposed there via reaction 6, and hence more crosslinking takes place in comparison to deeper in the film. Our data do not support the idea that the Haber-Weiss mechanism for peroxide decomposition[12,20] is dominant throughout the entire drying process.

The onset of an oxygen diffusion-limited reaction explains why the alkyd mobility near the surface and the mobility near the substrate diverge at the start of Stage II (*Figure* 7). Furthermore, we observe that the crosslinking rates near the substrate are nearly the same for all three drier combinations during Stage II, as in *Figure* 10b, because the driers have lost most of their efficiency in hydroperoxide decomposition. Thermal decomposition of peroxides (reactions 4 and 5) is the dominant mechanism, and so it makes no difference if there is only a primary drier or a combination of driers.

In support of this interpretation, observe that oxygen uptake (*Figure* 3) is significant for the first 10 hours of drying, which corresponds to both Stages I and II. This high oxygen uptake after reaching the maximum peroxide value is a new result that cannot be inferred from PV measurements alone. We propose that the mass uptake is mainly the result of reaction 6 followed by further oxidation. Although the precise oxidation reactions that occur following reaction 6 are not known, a likely result is the formation of new hydroperoxides in adjacent chains. The net peroxide value has therefore been found elsewhere to decrease very slowly.[21,29]

Stage III: Further Crosslinking and Film Hardening

The starting point of Stage III in *Figure* 7 at about nine hours is defined by the time when T_2 near the air surface approaches a constant value on the time scale of the measurements (shown as point C). Beyond point C, the T_2 near the surface decreases only slightly, suggesting that the film has "dried" there. Around the start of Stage III, wrinkling of the alkyd film's surface can be observed, especially in thick films containing only a Co drier. The cause of this wrinkling is undoubtedly related to the nonuniformity in crosslinking observed experimentally here. Note that even though the wrinkling problems attributed to the heterogeneity of drying appear during Stage III, the improvement in the uniformity of drying offered by secondary driers occurs during Stage I. The differences between the surface and bulk of the films, present at the end of Stage I, are still observed after one day (*Figure* 6) and persist over a very long time.

SUMMARY AND CONCLUDING REMARKS

The use of a new technique of MR profiling, along with the complementary techniques of the BK drying test, pendulum hardness measurement, and mass uptake analysis, has made a significant contribution to the understanding of the role of driers (singly or in combination) in determining crosslinking uniformity in films cast from alkyd emulsions. The spin-spin relaxation time, T_2, being sensitive to ^1H mobility, has been used to indicate the extent of crosslinking as a function of depth, with a pixel resolution as good as 9 µm. In contrast, the data from conventional tests are influenced by all depths.

We find that the influence of drier combination on the rate of crosslinking develops at very early stages, even before the film is touch-dry. A combination of primary (Co) and secondary driers (Ca and Zr) leads to faster crosslinking in comparison to the primary drier on its own or combined with Zr. The probable explanation is that the efficiency of the primary Co drier is decreased by complexation with carboxylic acids. Importantly, and contrary to popular assumptions, crosslinking during the first two hours after casting (Stage I) is uniform with depth.

At later times, but before through-dry has been achieved, the crosslinking rate near the substrate becomes lower than near the surface. This result is attributed to a concentration gradient in molecular oxygen in the depth of the film. Near the surface, where the oxygen concentration is higher, hydroperoxides are decomposed via an oxygen-assisted reaction and thereby generate radicals that lead to crosslinking. Deeper in the film, there is less oxygen and crosslinking is inhibited. The extent of the crosslinking nonuniformity is dependent on the drier combination. A Co/Ca mixture leads to the most uniform crosslinking, whereas when Co is used alone, the crosslinking profile is strongly nonuniform.

MR profiling shows excellent sensitivity to the influence of driers prior to the touch-dry time point (before conventional techniques can be used) as well as when the film hardens over several days. Drying rates can be quantitatively measured and compared with MR profiling. This capability is particularly relevant to the current development of waterborne alkyds for paints, because it can potentially aid in the search for alternative driers. The more uniform drying achieved with certain drier combinations is expected to minimize the occurrence of wrinkling, cohesive film failure, poor gloss, pigment flotation, and water sensitivity.

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