Controlled Oxidative Curing of Tung Oil

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Antiskinning agents are used to control the oxidative curing of tung oil catalyzed using a cobalt drier. Additives agents that are too volatile result in the premature formation of a cured oil (e.g., skin), whereas antiskinning agents that are slow to release from the fatty oil may delay drying altogether. Methyl ethyl ketoxime is currently the most popular antiskinning agent; but due to its relatively high volatility coupled with associated health hazards, new antiskinning agents are being sought for aqueous and solvent-based alkyds. In this article, new formulations containing an antiskin agent and a co-promoter to activate the metallic drier, providing excellent antiskinning performance while providing improvement in dry-through performance, are presented.

INTRODUCTION

Alkyd resins are combinations of polyesters with oils that cure oxidatively involving fatty acids within the oils. The rate of alkyd drying is governed to a large measure by the composition of the fatty oils as curing involves the reaction of singlet oxygen at the unsaturation sites in the acid.[1-3] Common oils in alkyds include linseed, oleic, tung, and safflower—and the rate of drying of the alkyds is dependent upon the composition of the fatty oils and their concentrations. Alkyds that contain high levels of unsaturation sites in the fatty acids usually dry faster as intermediate oxy-compounds such as hydroperoxides[4-6] and cyclic peroxides[7,8] are produced at these sites via oxidative attack. Free radical formation assisted by a cobalt catalyst[9,10] aids in chain propagation reactions forming the fully cured resin.

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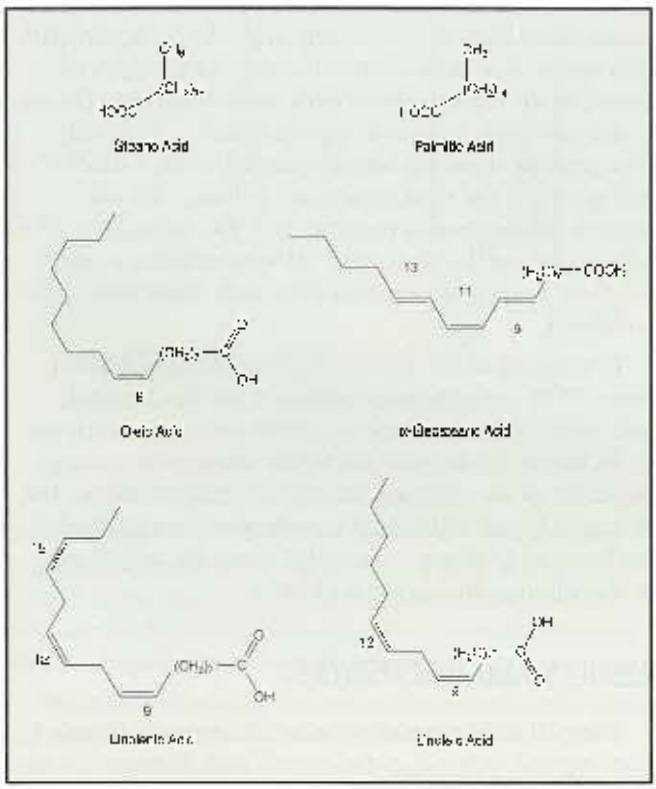
Figure 1—Common fatty acids found in tung oil.



Tung oil is common in many fast-drying alkyd formulations and is composed of several fatty acids as shown in *Figure* 1. It contains small amounts (~5%) of saturated fatty acids such as stearic and palmitic acids along with 8% oleic acid. It also contains small fractions of linoleic (4%) and linolenic (3%) acids. The major fatty acid in tung oil is α-eleostearic acid (about 80%). *Figure* 1 shows that α-eleostearic contains three double bonds—9-trans, 11-cis, and 13-trans—which causes alkyds formulated with tung oil to quickly dry and, in some cases, to skin prematurely.

Alkyd resins formulated with tung oil typically contain an antiskinning agent to control the premature drying of the resin in the storage can. Methyl ethyl ketoxime (MEKO) is today's most popular antiskinning agent but it has several drawbacks including high volatility; it is listed as a category 3 carcinogen in Europe causing liver tumors in mice and rats. It may also cause blood effects (methemaglobinemia) following repeated oral and dermal exposure and it has been shown to be a skin sensitizer in animal studies as well as irritating to skin and eyes.

Therefore, a new antiskinning agent is warranted that not only overcomes many of the health and exposure issues associated with MEKO, but also one that allows the user to *control* the rate of desired dry-through of the resin and at the same time minimize the onset of premature skin formation at the alkyd-air interface. A new antiskinning additive, Prevaskin™,[1] combines an antiskinning agent and a cobalt co-promoter. The combination allows for rapid dry-through in solvent and aqueous-based alkyds while minimizing the formation of the skin commonly encountered with fast-drying alkyd systems. This study shows the controlled skinning of tung oil using the new additives compared to MEKO. Air-drying and infrared studies show the benefits of the two-additive system, the antiskinning agent in its ability to control skin formation and the cobalt co-promoter in providing rapid dry-through of the resin.

EXPERIMENTAL

Samples for air-oxidation studies were prepared using tung oil (purchased from Aldrich) and cobalt 12 (obtained from OMG America, Inc.), and in all cases 0.1% Co was added to the tung oil based on weight. A total of seven samples were prepared in glass bottles: tung oil alone (no Co catalyst), tung oil with Co only (no antiskinning agent), and tung oil with cobalt containing the various antiskinning agents. MEKO (25% active in mineral spirits) was added at 0.1%. Prevaskin additives were prepared in mineral spirits (14% active) and also added at 0.1% based on resin solids. This material contains an antiskin agent along with an organic co-promoter to activate the metal drier. Four additive formulations that varied in the ratio of the antiskin agent to the co-promoter were tested: 410 (four parts antiskin

Figure 2a—Formation of 1:6 cyclic peroxide in tung oil.

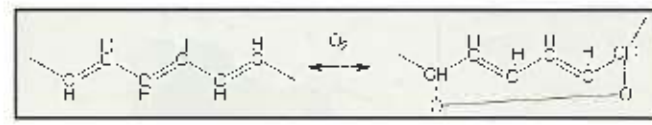


Figure 2b—Oxidation of unsaturated fatty oil to a 2:4 cyclic peroxide.

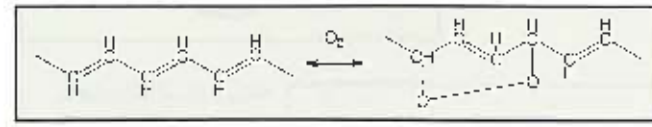


Figure 2c—Formation of the 1:2 cyclic peroxide.

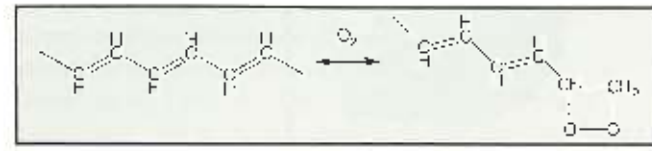


Figure 3—Onset of skinning in tung oil formulations.

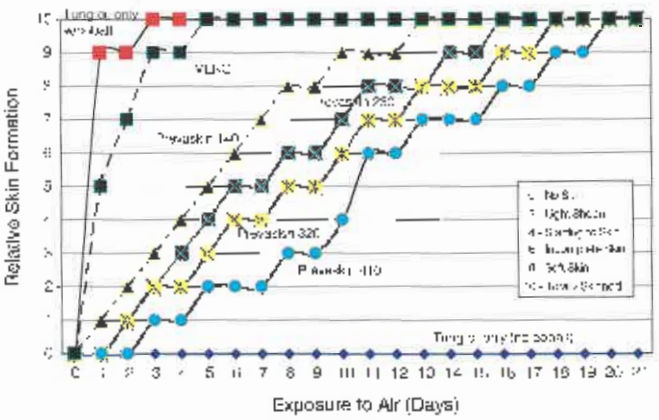


Figure 4—Tung oil only (no cobalt; left image) and skin formation in tung oil using MEKO after four days (right).

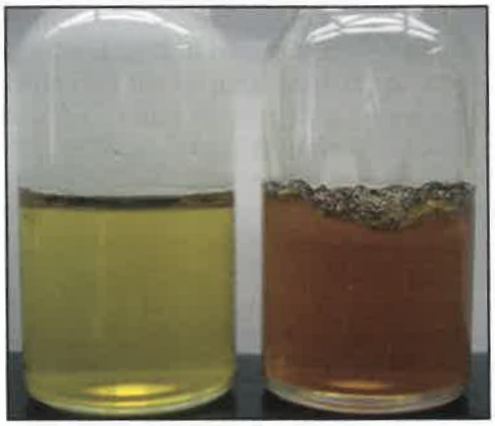
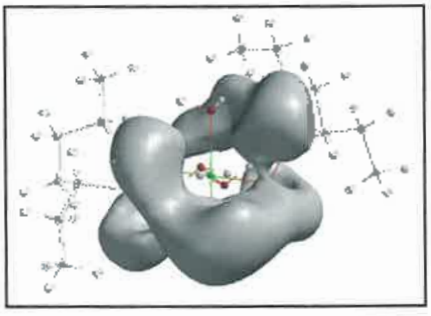


Figure 5a—Electrostatic potential isosurface of Co(II) octoate.



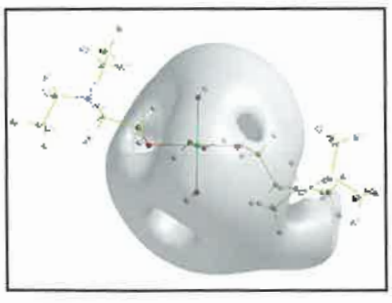


Figure 5b—Electrostatic potential isosurface of Co(II) with a co-promoter.

agent; one part co-promoter), 320 (three parts antiskin agent; two parts co-promoter), 230 (two parts antiskin agent; three parts co-promoter) and 140 (one part antiskin agent; four parts co-promoter). The samples were placed in an exhaust hood with air flowing over the top of the unsealed bottles at approximately 100 ft/min. The onset of skinning was monitored using a load of 200 g/cm^2. If the load penetrated through the oil quickly, it was given a ranking of 0. The formation of a light sheen on the top of the oil was ranked a 2 until the load no longer penetrated the skin (see *Figure* 2 for rankings).

The drying of the seven samples was also studied using FTIR. Samples were prepared on NaCl crystals and infrared spectra were recorded every two hours up to 24 hours. To account for subtle changes in coating thickness of the coatings during the curing process, the IR bands for an individual sample were normalized to the band at 1700 cm^{-1} since this band did not change in absorbance during the 24 hours.

RESULTS AND DISCUSSIONS

Tung oil is composed of several fatty acids (*Figure* 1). The largest fraction is α-eleostearic acid (9-trans, 11-cis, 13-trans) with minor amounts of oleic, linoleic, linolenic and saturated fatty acids. The mixture of conjugated (α-eleostearic) and nonconjugated (linoleic, linolenic) acids results in a complicated drying process. For example, Faulkner[12] showed methyl eleostearate forms 1:2, 1:4, and 1:6 endo-peroxide intermediates such as those in *Figure* 2. However, as discussed by Wexler,[13] oxidation of conjugated triene fatty oils such as eleostearic acid also forms hydroperoxides (O–O–H), commonly found in many fatty acids.[14,15]

Skinning studies shown in *Figure* 3 clearly show the beneficial effects of an antiskinning agent in slowing the onset of skinning on the surface of tung oil. The oil itself without any cobalt catalyst never cures (data along the x-axis). Tung oil with only cobalt and no antiskinning agent cures very quickly as a heavy skin formed after only one day of drying. An impenetrable skin formed on the surface of the oil after three days.

The sample containing MEKO skins at a slightly slower rate than the sample containing no antiskinning agent but a noticeable skin was observed after one day. The skin thickened after two days and the oil was completely skinned after four days, as seen in *Figures* 3 and 4. MEKO is currently the most common antiskinning agent in today's alkyd formulations. It is commercially available as a 25% active solution and is typically used at about 0.1% in the final alkyd. Because of its relatively high volatility, MEKO quickly escapes from the tung oil during use and as such produces the skin seen in *Figure* 4. With MEKO being a *single-component* anti-

Figure 6a—IR spectra of tung oil with MEKO showing curing.

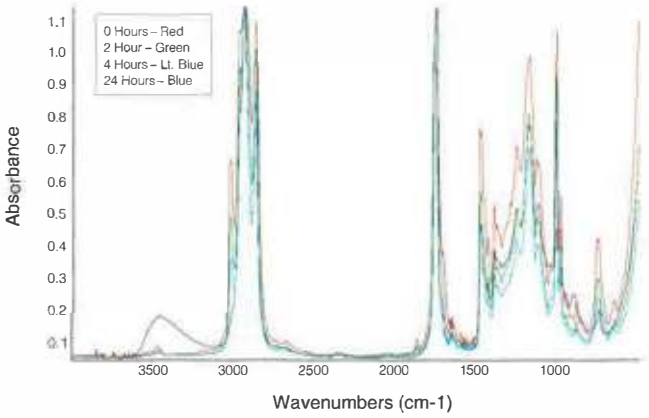
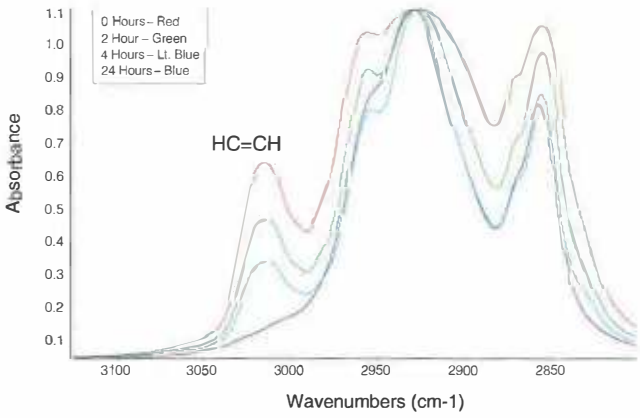


Figure 6b—Loss of unsaturation in tung oil after five hours.



skinning agent, it is difficult to properly balance the skinning requirements (necessitating high levels of MEKO in the alkyd due to its high volatility) and dry-through performance (requiring low concentrations of MEKO to ensure rapid dry-through).

Samples containing Prevaskin skin more slowly than the sample containing MEKO. Unlike MEKO, *Figure* 3 shows it is possible to control the skinning rate by controlling the ratio of the antiskin agent to co-promoter. Changing the concentration of the antiskinning agent in the samples to meet the skinning requirements of a given alkyd formulation is offset by changing the activity of the cobalt drier. The activity of the drier is controlled by the addition of a co-promoter to the antiskinning formulation. For example, *Figure* 5 shows two electrostatic potential maps[16] of a cobalt drier, one without and one with a cobalt co-promoter. It is clearly seen that the co-promoter alters the activity of the cobalt drier. Therefore, if a high level of antiskinning is required, the concentration and composition of the co-promoter is concomitantly adjusted to ensure a high level of cobalt activity—thus ensuring rapid dry-through of the tung oil in the alkyd. The use of a high concentration of MEKO would address the antiskinning problem but its high concentration would undoubtedly cause serious delays in the dry-through of the alkyd.

The correct ratio of the antiskinning agent to the cobalt co-promoter permits one to control the rate of skinning of tung oil (and therefore alkyds formulated using tung oil). At a ratio of 1:4 (Prevaskin 140), skinning is slowed compared to MEKO, whereas alkyds using high concentrations of tung oil in an alkyd formulation may require a higher ratio of antiskinning agent to co-promoter (Prevaskin 320 or 410). In fact, at the highest level of antiskinning agent (Prevaskin 410) complete skinning was delayed until about 20 days.

The drying of tung oil monitored using infrared spectroscopy is seen in *Figures* 6a–6d. The spectrum in

Figure 6c—Disappearance of *cis*-unsaturation in tung oil during drying.

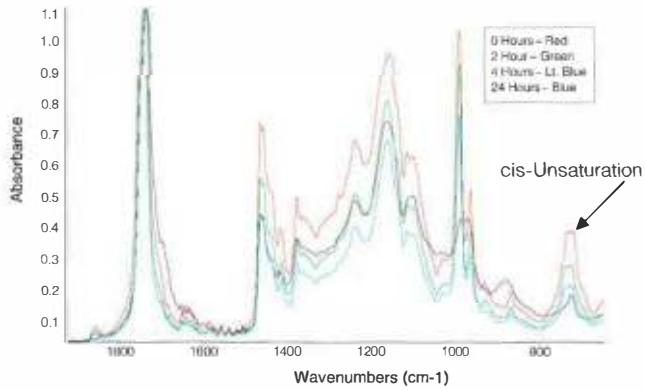


Figure 6d—Typical changes in IR band intensities during drying of tung oil.

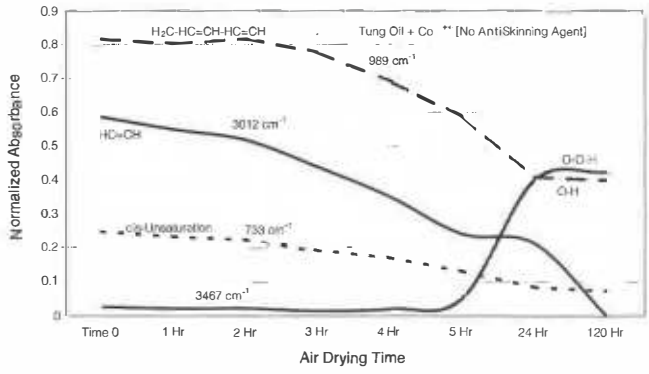


Figure 6a for the drying of tung oil with MEKO is representative of all the IR spectra recorded for tung oil with the various antiskinning agents. The spectra typically show the HC=CH bands at 3015 cm^{-1}; the C–C stretches at about 2950 cm^{-1} and 2850 cm^{-1}; the carbonyl band, C=O, at 1740 cm^{-1}; the C–C bands at 1456 cm^{-1}; the C–O–R bands at about 1100 cm^{-1}; and

Figure 7a—Formation of the hydroperoxide from 1,2 endo-peroxide intermediate.

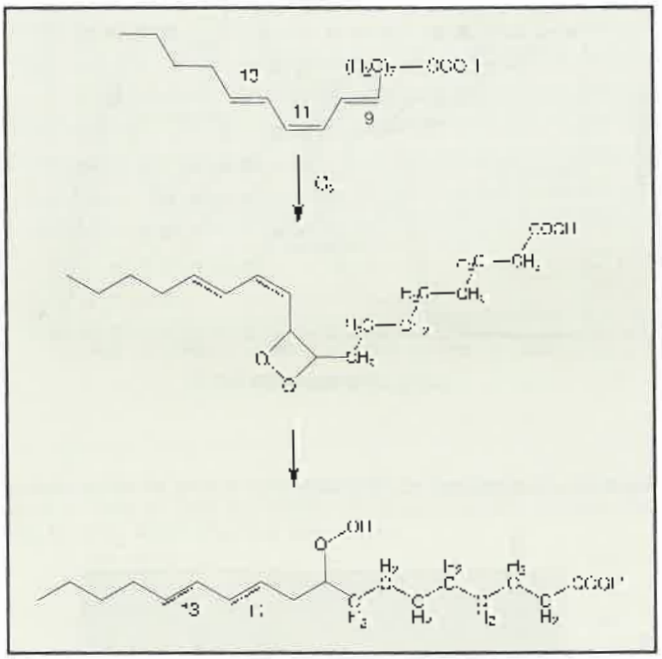


Figure 7b—Loss of *cis*-unsaturation and migration of double bonds formed from the 1,4 endo-peroxide.

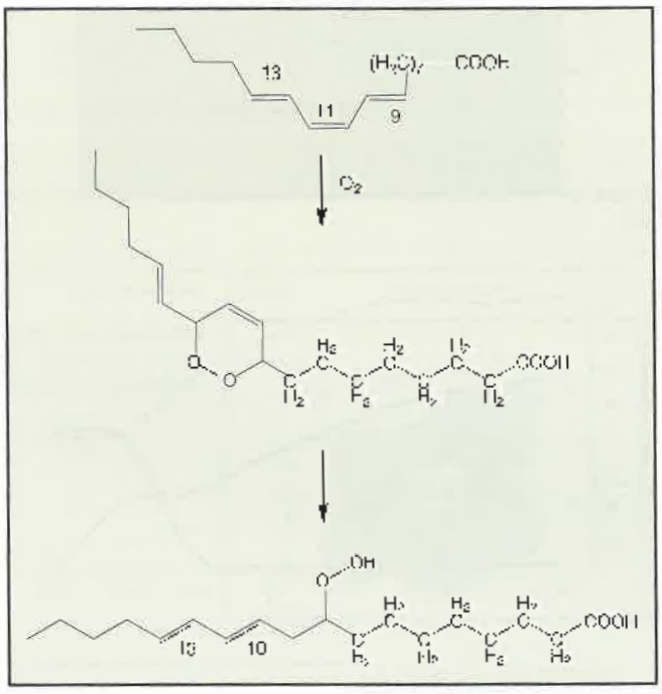
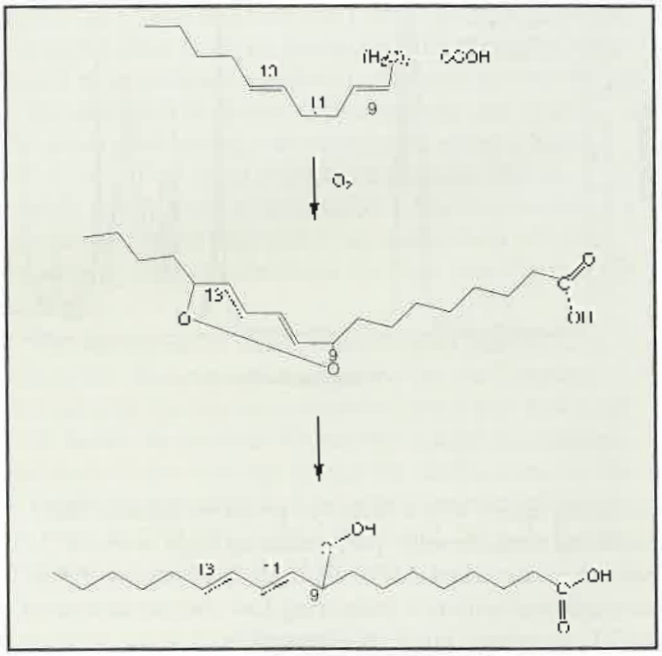


Figure 7c—Loss of *cis*-unsaturation during the formation of the 1,6 endo-peroxide.



the H_2C–CH=CH-CH_2 bands at about 990 cm^{-1}. The bands seen at about 720 cm^{-1} are associated with those at 3015 cm^{-1} and are due to *cis*-unsaturation.[4] Drying of tung oil produces changes in the structure of the oil easily followed with IR. The most noticeable changes are seen in *Figure* 6d: loss of intensity of the bands at 3015 cm^{-1} and 720 cm^{-1}; the decrease in intensity of the bands at 1456 cm^{-1}; and the increase in intensity of the band at about 3400 cm^{-1}.

The loss in intensity at 3015 cm^{-1} and 720 cm^{-1} is indicative of a loss in *cis*-unsaturation within α-eleostearic acid and at 3400 cm^{-1}, the hydroperoxide entity forms during curing.[5] There are several routes to the formation of this hydroperoxide seen in *Figures* 6a and 6d and all involve intermediate endo-peroxides of the types seen in *Figures* 7a–7c, which eventually transform into the stable O–O–11 structures. In each case, the loss of *cis*-unsaturation occurs and in *Figures* 7a–7c it is also seen that the *trans*-unconjugation may change positions, similar to that seen during the drying of methyl oleate.[17–19] The isomerization from *cis* to *trans* isomers can be envisioned similar to the free-radical mechanism as proposed by Knight and co-workers.[20]

The effects of the new additives on the controlled curing in tung oil monitored using IR are seen in *Figures* 8a and 8b. Slowing the loss in *cis*-unsaturation is indicative of slowing the drying rates. Tung oil containing MEKO shows a rapid loss in unsaturation during the first four hours of air exposure whereas tung oil containing high ratios of co promoter (Prevaskin 140 or 320) exhibits a slower loss in unsaturation. If a particular alkyd is formulated using various concentrations of tung oil, it is possible to adjust the formulation by

Figure 8a—Slowed loss of *cis*-unsaturation (delayed curing) in tung oil by additives combining antiskinning agent and co-promoter (Prevaskin 140 and 320).

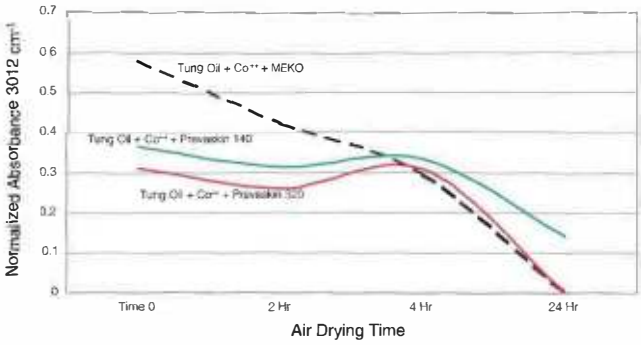
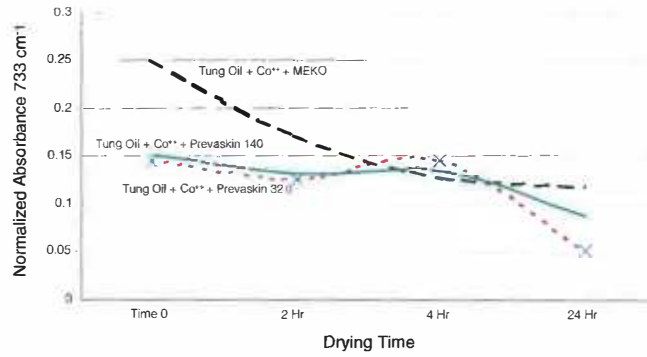


Figure 8b—Slowed loss of *cis*-unsaturation (delayed curing) in tung oil by additives combining antiskinning agent and co-promoter (Prevaskin 140 and 320).



monitoring the rate at which *cis*-unsaturation disappears and then balancing the ratio of the antiskinning agent to the co-promoter.

CONCLUSIONS

A new type of additive designed to prevent premature drying of tung oil shows promise in selectively controlling the drying profile of the oil. Combining an antiskinning agent with a cobalt co-promoter allows one to tailor the drying characteristics of tung oil. Structural changes during drying are easily followed using infrared spectrometry.

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