New insights on the anti-skinning effect of methyl ethyl ketoxime in alkyd paints

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In order to shed light on the role of oxime additives as blocking agents of the cobalt-catalyzed autoxidative drying in alkyd paints, various techniques have been applied. Spectroscopic studies (Vis-NIR, ^{1}H NMR) of different model solutions show, together with investigations on the coordination chemistry of cobalt salts with oximes, that only weak interactions between cobalt and oximes can be evidenced; in several cases the residual water that is present is a stronger ligand than oximes for the cobalt ion. From $CoCl_2$ and methyl ethyl ketoxime (meko) the highly unstable complex $[Co(meko)Cl_2]_n$ has been isolated. The polymerization inhibition properties of different oximes were studied by TR-FTIR and SEC techniques. From EPR and GC-MS model experiments, it has been established that the free radicals formed in the coating compositon may readily add to the C=N double bond of the oxime, producing stable radical addition products that could inhibit further free radical chain reactions.

Among the environmental challenges arising in the last decade, the one concerning the substitution of suspected toxic components in common organic coating materials is of great importance. The search for acceptable alternatives for toxic chemical additives in alkyd paints, especially the anti-skinning agents and the cobalt drier catalysts, recently became a subject of intense industrial and academic interest.[1–3] Alkyd paints are based on alkyd resins; this general term describes polyesters that incorporate a fatty-acid chain like, for instance, oleic, linoleic, linolenic, palmitic, stearic or ricineic acid (Fig. 1). These resins are used as binders and form the hard paint film as a result of an autoxidation process that occurs by a free radical mechanism catalyzed by transition metal driers in the presence of atmospheric oxygen.[4] Thus, the metal driers, and among them the most used cobalt-based driers, are essential additives to alkyd paints.

Formation of a film in air due to the autoxidation is an inherent property of paints. Unfortunately, this feature of air-drying coatings causes a storage problem, resulting in early film formation on the surface of the liquid coating material in the can. The prevention of skin formation is the role of the additives called anti-skinning agents. These additives are included in the formulation of the paint and are added to the coating material to prevent skinning during production or storage of the coating material. The different types of anti-skinning agents described in the literature are based on hydroquinones, phenols or amines.[4,5] Since the early 1980s the class of oximes (Fig. 2) has been the most widely applied group of anti-skinning agents. However, several recent reports suggest the toxicity of these oximes,[6] and particularly their likely hepatocarcinogenicity.[1,7] Consequently, there is an urgent need to propose substitutes for this class of compounds. For this purpose a detailed knowledge of the exact mechanism occurring during alkyd paint storage and drying is required.

The mechanism associated with the anti-skinning performance of oximes in general, and of methyl ethyl ketoxime (meko) in particular, still remains unclear. One of the current hypotheses concerns the coordination of meko to the cobalt octoate during storage, thus inhibiting the activity of the catalyst.[3,4,5] The possibly formed complexes would be unstable and upon application of the paints in air the oxime would evaporate,[8] releasing the metal in the active form for the oligomerization drying process. Another possible hypothesis involves the reaction of meko with peroxide radicals formed in the presence of oxygen,[5] thus inhibiting the association of radical

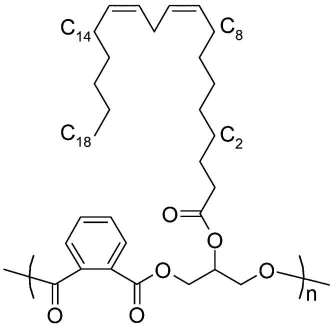
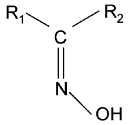


Fig. 1 Idealized structure of an alkyd made from 1 mol phthalic anhydride, 1 mol glycerol, and 1 mol of linoleic acid.



R_1 = H, R_2 = Me, acetaldoxime (aax)
R_1 = H, R_2 = Et propanaldoxime (pax)
R_1 = H, R_2 = Pr butyraldoxime (bax)
R_1 = Me, R_2 = Me, acetonoxime (mmko)
R_1 = Me, R_2 = Et, methylethyl ketoxime (meko)

Fig. 2 General formula of oximes. R_2 = alkyl, R_1 = alkyl (ketoxime) or H (aldoxime).

monomers that ultimately leads to the hard paint coating. Clearly, the lack of experimental data and results supporting these hypotheses forbids a complete understanding of the anti-skinning phenomenon associated with oximes.

Alternative products for oximes as anti-skinning agent displaying similar properties, but more environmentally friendly, could be proposed from the basis of a general understanding of the mechanism of action of oximes in paints. We now report new results from an attempt to clarify the role of meko as a blocking agent for the autoxidation process in paints.

Experimental

Materials

The additives used for these studies are commercial components of industrial paints. They were chosen with the view to keep the model studies as close as possible to the actual alkyd paint formulations. Commercially available cobalt octoate drier (10 wt·%) in C_{10}–C_{12} paraffin or naphthenic solvents (Nuodex Co 10) and anti-skinning oxime additives were provided by Sasol Servo (Delden, The Netherlands). Technical ethyl linoleate (EL, 65–70%, remainder ethyl palmitate and ethyl stearate) was obtained from Fluka. Test experiments have shown that the results with technical EL (70%) are comparable to those obtained with pure EL (99%). The palmitate and stearate are not reactive in the autoxidation reaction. Commercial *tert*-butyl hydroperoxide, ^{t}BuOOH (5.0–6.0 M solution in decane), from Aldrich was used.

Analytical techniques

Vis-NIR spectra were obtained on a Perkin–Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique with the pure solvent used as a reference. A solution of cobalt octoate (1.75×10^{-3} mol·l^{-1} of Co) and a solution of meko (3.76×10^{-1} mol·l^{-1}), both in toluene, were prepared.

^{1}H-NMR measurements were performed at 200 MHz on an upgraded Jeol FX-200 spectrometer driven by a Techmag computer system using benzene-d$_6$ as deuterated solvent. In a typical experiment 10.67 mg of cobalt octoate (10 wt ·%) was added to 1 ml of C_6D_6 to give a 1.8×10^{-2} M solution in cobalt. Meko (4.50 mg, 5.165×10^{-5} mol) in 0.5 ml of C_6D_6 was added to 0.1 ml of the previous solution to give a solution having a 1:30 molar ratio of cobalt to meko. ^{1}H NMR (200 MHz, benzene-*d*$_6$) of meko shows *Z* (60%) and *E* (40%) isomers: δ 0.9 (CH_3CH_2, t, $Z+E$), 1.65 (CH_3C, s, *E*), 1.70 (CH_3C, s, *Z*), 2.02 (CH_2, q, *Z*), 2.25 (CH_2, q, *E*). ^{1}H NMR (200 MHz, benzene-*d*$_6$) of the solution having a 1:30 molar ratio cobalt to meko shows broad signals for which no accurate integrals can be given: δ 10.0 (v br), 1.9 (br), 1.5 (br), 1.0 (br), 0.8 (br).

Time-resolved FTIR spectra (TR-FTIR) were obtained on a Bio-RAD FTS-60A spectrometer equipped with a Specac ATR device (ZnSe crystal, angle of incidence 45°), using the reflectance technique (4000–400 cm^{-1}, res. 2 cm^{-1}). Every 5 min an absorption spectrum was automatically recorded. After measurement in the range of interest a baseline correction was performed and the peak at 3010 cm^{-1} was integrated. As output of this processing a file containing the integral of this peak at different times was obtained. Two procedures were employed. (i) In a typical experiment for oxidative oligomerization of ethyl linoleate, 500 μl of EL were mixed with 14.5 μl of a Co octoate solution in toluene (Nuodex 10 in toluene, 0.169 M), the molar ratio being EL:Co = 400:1. Two hundred microliters of the mixture was spread in a thin layer on a sample holder to undergo time-resolved infrared measurements. (ii) In a typical experiment done with the objective to test the inhibiting properties of oximes on the EL oligomerization test reaction, to the same mixture of EL–Co was added, for example, 2.5 μl of a meko solution in toluene (0.983 M); thus, the molar ratio was EL:Co:meko = 400:1:6. Then, 200 μl of the mixture was spread in a thin layer to undergo time-resolved infrared measurements.

X-Band solution EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Samples for measurements were prepared by mixing of components in the presence of oxygen. Concentrated ^{t}BuOOH was quickly added to 0.2 ml of a 0.169 M solution of Co octoate in toluene. The mixture was stirred at ambient temperature for 2 s. Immediately after mixing, the cell was inserted in a resonance cavity through which a stream of nitrogen was passing. The products of the oxidation of meko by ^{t}BuOOH were generated using the same procedure by adding 6 equiv. of meko to a mixture of Co octoate–^{t}BuOOH.

Size exclusion chromatography (SEC) measurements were performed in chloroform on two PL-gel Mixed-E columns (300 × 7.5 mm i.d., Polymer Laboratories) and an interferometric refractive index detector (Optilab DSP, Wyatt Technology) as concentration detector. The flow rate was 1 ml·min^{-1} and the sample load was 100 μl of a solution of 2.5 mg·ml^{-1} in chloroform.

Synthesis

Synthesis of [Co(meko)Cl$_2$]$_n$. $CoCl_2 \cdot 6H_2O$ (1.3 g, 5.4 mmol) in an Erlenmeyer flask were covered by 1.5 ml of trimethyl orthoformate and then dissolved in 5 ml of methanol. In another flask a solution of 1.8 g (21.6 mmol) of methyl ethyl ketoxime in 5 ml of methanol was prepared. The two solutions were warmed (to 50 °C) and mixed; the resulting mixture was boiled for 1–2 min. The resulting blue-purple solution was left to stand under normal atmosphere for 8 h to give a deep blue solution, which was evaporated to dryness. The resulting oil was extracted with 30 ml of THF and the solution was filtered using filter paper. The clear solution obtained was concentrated to approximately 5 ml by rotary evaporation. The addition of 25 ml of diethyl ether to the concentrated solution resulted in the immediate precipitation of a light blue powder. The product was filtered and washed with 5 ml of diethyl ether, yielding 0.75 g of the powder (65% based on Co). This hygroscopic product was stored under an argon atmosphere. Anal. (%): calcd for $C_4H_9Cl_2CoNO$: Co, 27.2; C, 22.2; H, 4.0; N, 6.5; Cl, 32.7; found: Co, 27.4; C, 22.4; H, 4.2; N, 6.4; Cl, 30.5. Selected IR (cm^{-1}): 807 m, 1059 s and 1134 vs (CC stretch); 1370 m and 1458 s (CH bend); 1620 s (C=N stretch); 2978 w (CH stretch); 3094 m br and 3187 w (OH stretch). Vis-NIR (solid state, cm^{-1}): v = 7400, 14 800, 16 835, and 40 400.

Drying time determinations

The drying time was determined with a Beck Koller (B.K.) drying recorder (wet film thickness: 76 μm; ASTM D5895-96) and a Braive recorder (wet film thickness: 76 μm; ASTM D5895-96). After application of the film on a glass strip (B.K. recorder: 69 × 2.5 cm; Braive recorder: 30.5 × 2.5 cm) a vertical blunt needle is positioned into the freshly applied film by a 5 g load and then dragged through the drying paint in a direction parallel to the length of the coating. The three stages in the Braive recorder experiment are described as: *stage a*, the paint flows together (leveling), meaning that the paint is wet; *stage b*, a line is visible, the paint begins to polymerize, this is the basis trace; *stage c*, this is the so-called "surface dry time". This condition is reached when the drying reactions have proceeded sufficiently. At this condition the film is no longer displaced. The drying was further established by hand according to ASTM D1640 (wet film thickness: 60 μm). The performance of the various anti-skinning agents has been evaluated in a white air-drying paint of following composition:

53.4 wt·% SETAL 16 LV WS-70 (long-oil linseed alkyd resin, AKZO Nobel Resins B.V.); 28.5 wt·% Kronos 2190 (titanium dioxide, Kronos GmbH); 0.3 wt·% SER-AD FA601 (anionic pigment dispersant, Sasol Servo B.V.); 3.75 wt·% Nuodex COMBI APB (cobalt-containing combination drier, Sasol Servo B.V.); $14.05 - a$ wt·% Shellsol D60 (mineral solvent, Shell), and a wt·% anti-skinning agent. A test on skin of 100 g of paint in a closed glass bottle of 300 ml during storage has been done.

Results and discussion

Interaction between the cobalt octoate drier and meko in the absence of hydroperoxides

The first step towards a better understanding of the mechanism of action of meko in paints could be to confirm or to refute the hypotheses proposed until now. For this reason spectroscopic studies (Vis-NIR, ^{1}H-NMR) of different model solutions have been conducted to highlight the possible interactions between cobalt octoate and methyl ethyl ketoxime. The most widely accepted hypothesis concerns the formation of inactive cobalt complexes upon addition of meko to the cobalt-containing solution, as in eqn. 1. The second part of this hypothesis suggests that the weak complexes formed lose their oxime ligands under atmospheric conditions. The oxime would evaporate, thus releasing active drying cobalt species.

$$\mathrm{Co(RCOO)}_x + n\cdot\mathrm{meko} \rightarrow [\mathrm{Co(meko)}_n]^{x+} + x\cdot\mathrm{RCOO}^- \quad (1)$$

Vis-NIR experiments have been carried out to try to get some insights into these species. In commercial alkyd paints the optimum anti-skinning effect is obtained for a cobalt:meko molar ratio around 1:6. Nevertheless, the ligand field spectra obtained in any case do not correspond to the general pattern expected for an octahedrally surrounded cobalt cation, since the maxima are at too low energy for homoleptic CoL_6 species.[9] Fig. 3 shows the spectrum obtained for the deep blue starting solution of original Co octoate in toluene, with a maximum at 590 nm and a shoulder at 550 nm. These characteristics suggest the presence of high-spin Co(II) in a tetrahedral environment of oxygen atoms.[10] By adding six molar equivalents of meko, a color change from deep blue to pink is observed and a new absorption band around 440 nm appears, indicating the formation of a new cobalt species. While the peak observed in this region has been assigned to different environments of the Co(II) center, no firm conclusions can be drawn on the basis of UV-VIS spectroscopy.[11–13] Only minor changes are observed by successive additions of meko to Co octoate in solution, from a 1:1 to 1:25 Co octoate:meko ratio.

The species formed in solution are unstable: after several hours the pink color of the resulting solution turns yellow-green. Most of the original bands remain in the 580 nm range, but a new absorbing band at 500–540 nm appears. Experiments in the presence of various quantities of air have been conducted. The final steady state for the Co octoate–meko solutions is reached after 24 h under atmospheric conditions, after 33 h when the sample is closed to air, and after 64 h when the solution is kept under argon.

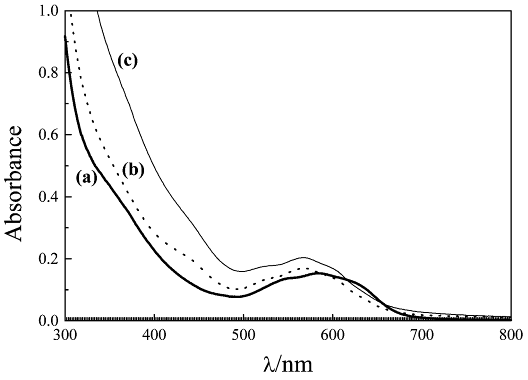


Fig. 3 Vis-NIR spectra of (a) cobalt octoate solution in toluene (1.75 mM), (b) Co octoate:meko (1:6 molar to Co), and (c) Co octoate–meko after 4 days.

The changes observed in the ligand field spectroscopy strongly suggest that the hypothesis of meko evaporation cannot be the only one. As shown in Fig. 3, after 4 days the expected return to the original pattern of Co octoate in toluene, due to the supposed meko evaporation, is not observed. The observed color changes might be attributed to partial oxidation of the metal ion to Co^{3+}.

Instead of evaporation, another hypothesis may be that meko is hydrolyzed to give the ketone (mek) and hydroxylamine *via* a process assisted by cobalt. In order to check this hypothesis NMR spectroscopy has been carried out on the above-described model solutions. The ^{1}H-NMR spectrum in benzene-d$_6$ of Co octoate–meko mixtures with ratios varying from 1:6 until 1:30 shows the predominance of paramagnetic species inducing patterns with broad peaks, which are shifted from the values for pure meko in C_6D_6. This observation suggests that meko is in the close vicinity of the paramagnetic cobalt centers, probably forming species in which cobalt is associated with several meko molecules. The possibility of meko hydrolysis catalyzed by Co octoate, in the presence of air, is not supported by the NMR measurements, since the formation of the non-coordinating methyl ethyl ketone has not been detected, even after several weeks. The persisting paramagnetic perturbations during NMR measurements demonstrate that the oxidation of Co^{2+} to diamagnetic Co^{3+} does not occur, or at least not to completion.

Coordination studies

The information given by Vis-NIR spectroscopy and ^{1}H NMR on the model solutions suggests the possibility of species associating cobalt and meko. For this reason, it was decided to attempt to synthesize and structurally characterize coordination compounds of cobalt with oximes, with the possibility to study the reactivity of these compounds as models under atmospheric conditions.

The first attempts to yield cobalt meko species have been performed using cobalt octoate, cobalt versatate and cobalt acetate as starting salts, but were unsuccessful. The use of cobalt precursors with weakly coordinating anions, such as BF_4^-, ClO_4^-, and NO_3^-, also did not result in the isolation of meko complexes. In general, either sticky oils were obtained, or the starting cobalt salt was obtained after evaporation of solvent. Nevertheless, the infrared spectra of typical solutions in some cases suggested the coordination of meko to cobalt (shift of the characteristic C=N stretching band from 1664 cm^{-1} to 1620 cm^{-1}), the problem being the isolation of the species likely in equilibrium in solution. Finally, a reaction of cobalt chloride and meko in the presence of trimethyl orthoformate as a dehydrating agent gave, after treatment with THF, a compound with formula $[\mathrm{Co(meko)}]\mathrm{Cl}_2]_n$ as indicated by elemental analysis and infrared spectroscopy. FTIR measurements on the meko complex in air show that it reacts readily with water from the atmosphere. The changes with time indicate that water molecules progressively replace the oxime ligand, leading to cobalt chloride hydrate. Recrystallization attempts resulted in interesting new cobalt compound with an unusual linear chain of alternating octahedral and tetrahedral cobalt sites, which no longer contains meko as a ligand.[14] It is worth mentioning that two other oximes have been used in coordination studies: acetaldoxime and butyraldoxime. From these compounds, several complexes of the general formula $[\mathrm{M^{(II)}X_2(L)_4}]$ (M = Co or Mn; X = Cl or Br; L is one of the

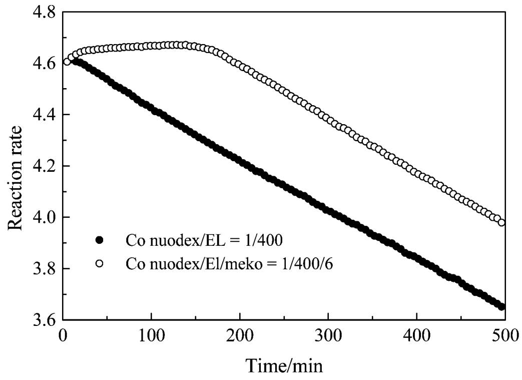


Fig. 4 Autoxidation of a mixture of Co Nuodex and EL in the presence and absence of meko. FTIR graphs represent the pseudo-first-order rates $-\ln(100 \times [\mathrm{EL}]_t/[\mathrm{EL}]_0)$ *versus* time.

aldoximes), stabilized by strong hydrogen bonding, have been isolated and characterized by single crystal X-ray diffraction studies.[15] The structural details and the reactivity of these coordination compounds show that the oxime ligands are in fact weakly bonded to the metal; indeed, for most of these species water appears also to be a stronger ligand.

The effect of meko on the radical-mediated autoxidation of EL

Based on the observations described above it may be concluded that the interaction between meko and the cobalt drier in alkyd paints is at best only very weak. At this point it was decided to investigate the influence of meko on the cobalt-catalyzed autoxidation of ethyl linoleate. TR-FTIR spectroscopy is a useful tool to follow the reaction of linoleate with O_2.[3,16] The rates of disappearance of EL in the reaction with dioxygen as catalyzed by the commercial cobalt and manganese driers correlate reasonably well with the actual drying times as found in the real alkyd paints.[3]

The method seems to be quite sensitive to changes in the catalyst's structure,[16] and it has been used to check the real inhibition properties of meko and the difference between various oximes as potential antioxidants, on cobalt octoate drier activity. The first step of ethyl linoleate autoxidation is the formation of the first radical species by the breaking of the C–H bond of the activated methylene group at C_{11} (Fig. 1). Thus, the kinetics of this reaction can be followed by measuring the decrease of intensity of the characteristic[16] infrared stretching C–H band at 3010 cm^{-1}.

In Fig. 4 plots of EL C_{11}–H radical abstraction rate *versus* time for the commercial drier Co Nuodex, in the presence or absence of methyl ethyl ketoxime, are depicted. For the sample containing Co Nuodex only, the consumption of EL starts immediately and the decrease of the EL concentration is linear in time; the curve can be treated with a pseudo-first-order fit. From the slope of this graph the pseudo-first-order rate of $H^{\bullet}$ radical abstraction can be determined (Table 1). The TR-FTIR studies show that the radical initiation in the autoxidation of a mixture of Co octoate with EL is blocked for about 3 h when 6 equiv. of meko to cobalt are added at the beginning of the process (Fig. 4).

The same experiments conducted with addition of 2 to 15 equiv. of meko to cobalt have shown that the induction times vary between 90 min (2 equiv.) and 240 min for 10 equiv., after which a constant value is obtained. The results are similar when the classical radical-trap compounds nitrosobenzene, C_6H_5NO, or nitrosotoluene, $CH_3C_6H_4NO$, are used instead of meko under the same conditions. The autoxidation process of EL is inhibited for 70 min when 6 equiv. of nitrosobenzene to Co octoate are added and for 40 min if 6 equiv. of nitrosotoluene are added. A noticeable difference between the nitroso compounds and meko in general is that after inhibition or after the induction period, meko does not slow the rate of conversion of the ethyl linoleate. This observation is in agreement with one of the specific properties of meko in actual alkyd paints, which is that no retarding effect on the drying time of the coated paint is observed (Table 1).[4]

The effect of meko in the TR-FTIR experiments can be interpreted as either resulting from the formation of unstable (towards atmospheric conditions) Co meko species or from a radical trap action of the oxime. However, the fact that an inhibition of the autoxidation of EL also occurs when meko is added in the course of the experiment, and that the resulting inhibition time depends on the amount of meko (1:18 Co:meko for 40 min, < 15 min for 1:6) unambiguously demonstrates the dominance and the importance of the radical trap activity of meko in this case. The observation of similar results for well-known spin trap radicals,[17–19] like nitrosotoluene and nitrosobenzene, establishes also the radical trap properties of meko. The polymerization process of EL catalyzed by Co Nuodex has been followed using size exclusion chromatography (SEC). The results for a mixture of EL and cobalt octoate in the presence of meko show that after 4 h only a very small amount of dimer is formed, as compared to the reaction in the absence of meko (Fig. 5).

These results confirm the inhibiting action of the oxime. To clarify the possible role of meko acting as a radical trap and to investigate the influence of the hydroperoxides that are present in alkyd paints, EPR studies on the decomposition of hydroperoxides by Co Nuodex in the presence of meko have been performed.

Table 1 The effect of different oximes on the catalytic activity of Co Nuodex in the EL model system and in an alkyd paint[a]

	EL FTIR		Paint[c]			
				Drying time/h		
Anti-skinning agent[b]	Induct. time/min	Reaction rate[d]/10^{-3} min^{-1}	Skin formation/days	Stage a	Stage b	Stage c
None	0	4.2	< 1 day	0.30	1.15	2.00
Aax	140	3.8	14	0.45	3.15	5.45
Pax	126	3.1	8	0.30	3.30	4.00
Bax	219	1.2	15	0.45	3.00	5.00
Mmko	80	4.0	9	0.30	1.15	2.00
Meko	160	4.3	11	0.30	1.15	2.00

[a] The induction times (min) and reaction rates ($\times 10^{-3}$ min^{-1}) are average values from several measurements; a deviation of ±10% has been found between different measurements, due to the radical nature of the autoxidation reactions. [b] For abbreviations see Fig. 2. Six equivalents of the agent was used. [c] White oil alkyd paint based on long-oil alkyd resin, siccatived with 0.08% cobalt drier on solid binder. Drying time, 76 μm with a Braive drying recorder at 23 °C and 50% relative humidity, see Experimental for explanation of stages. [d] Relative rate calculated from the graph $-\ln(100 \times [\mathrm{EL}]_t/[\mathrm{EL}]_0)$ *versus* time, linear fit of the data after the induction period.

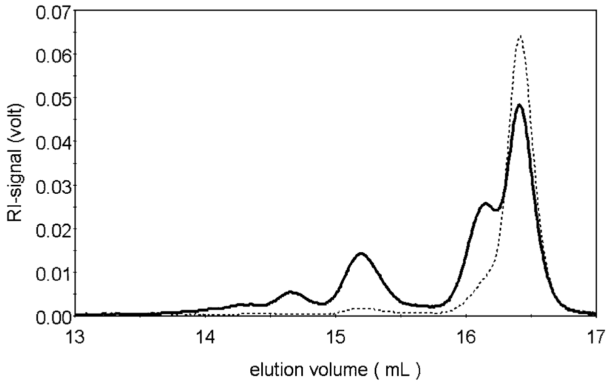


Fig. 5 SEC traces of polymers obtained from polymerization of EL catalyzed by Co Nuodex with meko (---) and without meko (—) after 4 h reaction time.

The behavior of meko in the presence of hydroperoxides

The effect of peroxides has been studied with EPR, using ^{t}BuOOH as the hydroperoxide source. Immediately after addition of ^{t}BuOOH to a Co octoate solution in toluene, a symmetrical singlet ($g = 2.016$) is observed (Fig. 6, trace a). The deep blue color of the Co octoate solution turns green within a few seconds, suggesting the formation of Co(III), which is also indicated by the ligand field spectrum.[20] The intensity of the EPR signal changes upon changing both the molar ratio of the components and their absolute concentrations. These results suggest the presence of a long-lived radical coordinated to the cobalt ion in the toluene solution. The observed g value is typical for a coordinated ^{t}BuOO$^•$ radical.[21] Several groups have reported the g values for oxygen-containing radicals: the g values observed between 2.014–2.015 were attributed to $RO_2^•$ radicals,[22] whereas g values ranging from 2.004 to 2.009 have been assigned to RO$^•$ radicals.[23] Brandon and Eliot[24] reported the formation of long-lived radicals produced by the reaction of ^{t}BuOOH with cobalt acetylacetonates and Symons[25] has shown that RO$^•$ cannot be easily detected in the liquid phase by EPR, because of its very short relaxation time. Eqns. (2)–(4) could describe the mechanism involved to form the observed peroxide radical. Moreover, the formation of ^{t}BuOH has been confirmed using GC analysis and comparison with an authentic sample. The kinetics and a similar mechanism of cobalt octoate catalyzed decomposition of hydroperoxides has been reported.[13]

$$Co^{2+} + {}^tBuOOH \rightarrow Co^{3+} + {}^tBuO^• + OH^- \quad (2)$$

$$^tBuO^• + {}^tBuOOH \rightarrow {}^tBuOO^• + {}^tBuOH \quad (3)$$

$$Co^{3+} + {}^tBuOO^• \rightarrow {}^tBu\text{–}O\text{–}O^•\text{–}Co^{3+} \quad (4)$$

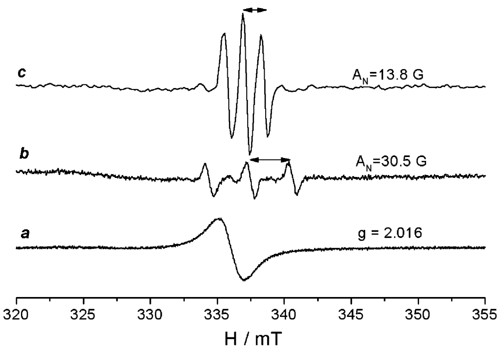


Fig. 6 EPR spectra in toluene solution at room temperature of (a) Co Nuodex–^{t}BuOOH; (b) Co Nuodex–^{t}BuOOH–meko just after mixing; (c) Co Nuodex–^{t}BuOOH–meko after 2 min.

By adding 6 equiv. of meko to the Co octoate–^{t}BuOOH mixture the EPR spectrum shows a new signal (Fig. 6, trace b), which is ascribed to the iminoxy radical derived from meko [eqn. (5)]. Here the ^{t}BuO$^•$ radicals formed during the initial homolysis of the O–O bond of the [LCo^{III}–OO^{t}Bu] complexes abstract H atoms from methyl ethyl ketoxime.[11] The iminoxy radical shows hyperfine splitting into three lines because of the nearby nitrogen atom, but meaningful examination for further hyperfine splittings was not possible because of the low concentration of the radical. The nitrogen splitting ($A_N = 30.5$ G) is in good agreement with similar reported data.[26,27] The iminoxy radical has a very short lifetime and within a few minutes the formation of a new radical with $A_N = 13.8$ G is observed (Fig. 6, trace c), which is stable in air and at room temperature for approximately 4 h.

$$^tBuO^• + (CH_3)(C_2H_5)C{=}N\text{–}OH \rightarrow {}^tBuOH + (CH_3)(C_2H_5)C{=}N\text{–}O^• \quad (5)$$

The nitrogen hyperfine splitting of this radical suggests that it is the signal of a nitroxide radical, which could be formed by the addition of a *tert*-butoxy radical to meko followed by a prototropic shift [eqn. (6)].[27] This nitroxide radical appears to be extremely stable and can still be detected after one day by keeping the mixture under a closed atmosphere. The addition of a ^{t}BuO$^•$ radical to the C=N bond of a meko radical is strongly supported by the identification of a nitroso compound [eqn. (7)] which has been isolated and characterized by GC-MS.

$$^tBuO^• + (CH_3)(C_2H_5)C{=}N\text{–}OH \rightarrow ({}^tBuO)(CH_3)(C_2H_5)C\text{–}NH\text{–}O^• \quad (6)$$

$$^tBuO^• + (CH_3)(C_2H_5)C{=}N\text{–}O^• \rightarrow ({}^tBuO)(CH_3)(C_2H_5)C\text{–}N{=}O \quad (7)$$

Other radicals[28] are known to add to oximes in a similar manner, including HO$^•$, $H_2N^•$, and $HOH_2C^•$.

Since Ingold[26b] and co-workers have reported that the majority of iminoxy radicals give self-reactions, it was decided to carry out further experiments to identify secondary products. However, in our experiments only one additional compound, which is formed *via* reaction (8), could be identified by GC-MS.

$$(CH_3)(C_2H_5)C{=}N\text{–}O^• + (CH_3)(C_2H_5)C{=}N\text{–}O^• \rightarrow (CH_3)(C_2H_5)C{=}N\text{–}O\text{–}(CH_3)(C_2H_5)C\text{–}N = O \quad (8)$$

The concentration of secondary products, relative to the concentration of the iminoxy radicals, is highly dependent on the oxime structure. In general, the secondary products described by eqns. (6) and (8) are more pronounced for unhindered dialkyl oximes.[27] The same EPR experiments have been performed using acetaldoxime and acetonoxime. The nitroxide type radicals formed during the reaction are stable for 3–4 h, but after one day the reaction mixture does not show any EPR signal. In this case the formation of a stable nitroso compound described by eqn. (7) is not supported by GC-MS experiments.

Implications for the anti-skinning effect in alkyd paints

While the most accepted theory of autoxidation is that it is a chain reaction, which proceeds by a free radical mechanism, it is to be expected that the presence of hydroperoxides in low concentrations in the alkyd paint composition is quite important. Right after the production of the alkyd paint, and during the storage of the paint, the decomposition of the peroxides will be initiated by the added drier, leading to RO$^•$ and ROO$^•$ radicals (according to equations analogous to eqns. (2) and (3)) followed by the formation of R$^•$ as described by eqn. (9).[4] In the radical chain propagation reactions [eqns. (9) and (10)] a larger amount of hydroperoxides is formed and the cobalt catalyst generates more radicals [eqn. (2)].

$$\mathrm{ROO}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\bullet} \qquad (9)$$

$$\mathrm{R}^{\bullet} + \mathrm{O}_2 \rightarrow \mathrm{ROO}^{\bullet} \qquad (10)$$

Finally, in the termination reactions [*e.g.* eqns. (11) and (12)] the radicals are recombined, thus forming the cross-links.[4,29]

$$2\mathrm{R}^{\bullet} \rightarrow \mathrm{RR}\ (\text{C–C-linked dimer}) \qquad (11)$$

$$\mathrm{R}^{\bullet} + \mathrm{ROO}^{\bullet} \rightarrow \mathrm{ROOR}\ (\text{peroxy-linked}) \qquad (12)$$

To prevent the latter skin-forming reactions, meko is included in the paint formulation. The radicals that are formed in eqns. (2) and (3) may react with meko by addition to the C=N bond, producing the stable radical addition products described by eqn. (6), which due to their high stability inhibit further free radical chain reactions. This hypothesis is confirmed by GC-MS measurements on a Co Nuodex–EL–meko mixture in toluene and comparison with an authentic sample of individual components, showing the formation of a new compound. The molecular mass of this compound corresponds to the $[(\mathrm{EL}-\mathrm{H})+\mathrm{meko}]^+$ fragment.

Finally, by exposure of the paint to air the stable radical addition products are destroyed by reaction with dioxygen. The remaining radical addition products may even enhance the drying process, because of the rapid formation of new radicals by reaction with dioxygen. After evaporation of possible unreacted meko the radical chain reaction can thus proceed to form the solid coating.[29]

Regarding the data presented in Table 1, a variation of the induction time and the first skin formation can be observed for the class of oximes (acetaldoximes or ketoximes). For acetaldoxime, propanaldoxime and acetonoxime short induction times and early film formation have been observed. This feature can be ascribed to the formation of a relatively unstable radical addition product, as has been observed for the unhindered oximes.[27] In this case, the reactions described by eqns. (5) and (8) are probably more pronounced than reaction (6).

Comparing with other oximes, meko has the best performance in paints because there is little or no loss of drying properties. The hindered oximes (*e.g.* butyraldoxime) retard the drying too much to be suitable for use in oxidative drying paints and coatings. This behavior can be due to the higher stability of the radical addition products, which cannot be easily destroyed, even by reaction with dioxygen. Another possible explanation could be the low volatility of hindered oximes. By exposure of the paint to air, these oximes still remain in the paint composition and scavenge the radicals formed by eqns. (9) and (10), thereby retarding the drying.

Conclusions

Vis-NIR and ^{1}H NMR spectroscopic studies have shown, together with coordination chemistry of cobalt salts with oximes, that at the best only weak interactions between cobalt and oximes are present. The presence of water seriously reduces the stability of the coordination compounds in the solid state. These data do not support the hypothesis concerning the coordination of meko to cobalt octoate during storage, which would thus inhibit the activity of the cobalt catalyst.

On the basis of experimental observations it has been established that the free radicals formed in the coating composition may readily add to the C=N double bond of the oxime, producing stable radical addition products that could inhibit further free radical chain reactions. Looking at the anti-skinning effect of different oximes, a good correlation between the oxime's general formula and the stability of the radical addition products was found. This is in excellent agreement with the performance of the different oximes in alkyd paints.

In subsequent studies the presented knowledge will be applied to find potential antioxidants as anti-skinning agents for alkyd paints. Due to the continuing shift from cobalt-based driers to manganese and iron driers, attention will also be directed to the decomposition of hydroperoxides by manganese and iron complexes.

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