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Coordination Chemistry Reviews 249 (2005) 1709–1728

COORDINATION CHEMISTRY REVIEWS

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Review

The oxidative drying of alkyd paint catalysed by metal complexes

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Received 27 September 2004; accepted 1 February 2005

Contents

Abstract

The focus of this review paper is the transition metal chemistry involved in alkyd (paint) drying. A general introduction is given on the composition of a common alkyd paint and the latest insights in the structure of the dried alkyd film are discussed. The drying of an alkyd paint is an autoxidation process catalysed by transition metal salts. Thorough investigations have shed light on the role of the transition metals as catalysts in the drying process and a wealth of spectroscopic techniques have been used to monitor the autoxidation process and to analyse the autoxidation products. More recently, these techniques have been used to develop a test reaction for the rapid screening of new manganese and iron based drier catalysts. Promising new driers based on simple manganese complexes have been proposed as replacements for the environmentally unfriendly cobalt driers that are presently used in alkyd paints.

Keywords: Oxidation; Drying; Alkyd paint; Driers; Cobalt; Manganese

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doi:10.1016/j.ccr.2005.02.002

1. General introduction and scope

A common household paint consists of a complex mixture of chemicals, a rough estimate of the basic ingredients is listed in Table 1 [1]. Oil paint, the oldest form of modern paint, uses a binder that is derived from a vegetable oil, such as obtained from linseed or soya bean. In alkyd paint, the binder is a synthetic resin, which is called an alkyd resin. The term *alkyd* was coined in the early days and originates from the *AL* in polyhydric *ALcohols* and the *CID* (modified to *KYD*) in polybasic *aCIDs*. Hence, in a chemical sense the terms alkyd and polyester are synonymous. Commonly, the term "Alkyd" is limited to polyesters modified with oils or fatty acids. A typical alkyd resin is prepared by heating for example linseed oil, phthalic acid anhydride and glycerol to obtain a fatty-acid containing polyester, as schematically shown in Fig. 1.

Further important components of alkyd paint are pigments and extenders. Pigments produce the paint color and are derived from natural or synthetic materials that have been ground into fine powders. Extenders are inert pigments used to extend or increase the bulk of a paint. Extenders are also used to adjust the consistency of a paint and to reduce the color of pigments with great tinting strength [2].

Finally, the last important category of components of alkyd paint constitutes the additives. A large variety of coating additives is known, which have widely differing functions in a coating formulation. One of the most important groups of additives is that of the catalytically active additives, which includes the paint-drying catalysts, or driers. Driers are metal soaps or coordination compounds which accelerate paint drying by enhancing the rate of cross-link formation between the binder molecules, thus shortening the total drying time [1,3]. Without the addition of driers, the drying time of an alkyd paint would be over 24 h, which is clearly undesirable.

Table 1
Example of a typical composition of an alkyd paint mixture

Component	Weight %
Binder	30
Organic solvent	27
Water	10
Pigments	19
Extenders	12
Additives	2

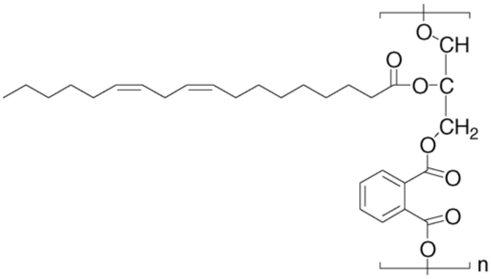


Fig. 1. Schematic impression of an alkyd resin used as a binder compound in alkyd paint. The fatty acid chain shown is linoleic acid.

In the last decade or so, environmental legislation has sparked the research effort concerning the drying chemistry of alkyds. Emission of VOCs (volatile organic compounds) from paints has become a major concern. An important way to achieve reduction of VOC emissions is to switch from solvent-borne paints to water-borne paints. In a water-borne alkyd paint the alkyd resin is *emulsified* in water, whereas in a solvent-borne alkyd paint the resin is *dissolved* in an organic solvent. Although already 70% of all decorative coatings in the EU are water-borne, solvent-borne paints still show a number of advantages over water-borne paints. These advantages are, for example: easier application properties, wider application and drying tolerance under adverse conditions (low temperature, high humidity) and a higher level of performance on difficult substrates, such as heavily stained or powdery substrates. Water-borne emulsion paints also contain significant amounts of surfactants, which can have a negative influence on the activity of the paint drier and the dried film surface [4,5]. As a result, solvent-borne coatings are unlikely to be totally replaced by water-borne coatings in the foreseeable future [6]. An additional way to reduce VOC emissions is the use of solvent-borne products with a lower solvent content, the so-called "high-solids" paints [6].

Another topic of concern is the use of cobalt compounds as driers in alkyd paint. Cobalt compounds generally are the most widely used drying catalysts for the oxidative drying of alkyd paints. Several accounts have recently appeared, however, detailing the toxicity and bioaccessibility of cobalt salts and cobalt driers [7–9]. In order to arrive at new catalysts an improved understanding of the complex chemistry taking place during the drying of alkyd paint is necessary.

In this paper an overview is given of the research into the mechanisms of paint drying, which is closely related to lipid oxidation. The general chemistry and latest trends and developments pertaining to metal paint driers is also reviewed. These two approaches are meant to be illustrative of the chemistry involved and the latest developments in metal catalysed alkyd paint drying. The focus is predominantly on the work done in the last decade.

2. The drying of alkyd paint

2.1. Introduction: autoxidation of the binder

During the drying of alkyd paints two different stages can be identified. The first process is the physical drying of the paint. In this process the solvent evaporates and a closed film is formed. The second process is chemical drying (also called oxidative drying), which is a lipid autoxidation process. The reaction proceeds by a free-radical chain mechanism and can be described in terms of initiation, propagation and termination, as summarised in Scheme 1. Initiation can occur

Initiation

$\mathrm{RH + Initiator \rightarrow R^{\bullet} + Initiator{-}H}$ Eq. **1.**

$\mathrm{ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH}$ Eq. **2.**

$\mathrm{ROOH + M^{n+} \rightleftharpoons [(ROOH)M]^{n+}}$ Eq. **3a.**

$\mathrm{[(ROOH)M]^{n+} \rightarrow RO^{\bullet} + [(M^{(n+1)+}(OH^{-})]^{n+}}$ Eq. **3b.**

$\mathrm{ROOH + M^{(n+1)+} \rightleftharpoons [(ROOH)M]^{(n+1)+}}$ Eq. **4a.**

$\mathrm{[(ROOH)M]^{(n+1)+} \rightarrow ROO^{\bullet} + M^{n+} + H^{+}}$ Eq. **4b.**

$\mathrm{M^{n+} + O_2 \rightleftharpoons [M^{(n+1)+}(O_2)^{\bullet -}]^{n+}}$ Eq. **5a.**

$\mathrm{[M^{(n+1)+}(O_2)^{\bullet -}]^{n+} + RH \rightarrow [M^{(n+1)}(OOH^{-})]^{n+} + R^{\bullet}}$ Eq. **5b.**

$\mathrm{M^{(n+1)+} + RH \rightarrow R^{\bullet} + H^{+} + M^{n+}}$ Eq. **6.**

Propagation

$\mathrm{R^{\bullet} + O_2 \rightarrow ROO^{\bullet}}$ Eq. **7.**

$\mathrm{ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}}$ Eq. **8.**

$\mathrm{RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}}$ Eq. **9.**

Termination

$\mathrm{2\ RO^{\bullet} \rightarrow ROOR}$ Eq. **10.**

$\mathrm{2\ ROO^{\bullet} \rightarrow ROOR + O_2}$ Eq. **11.**

$\mathrm{2\ R^{\bullet} \rightarrow R\text{-}R}$ Eq. **12.**

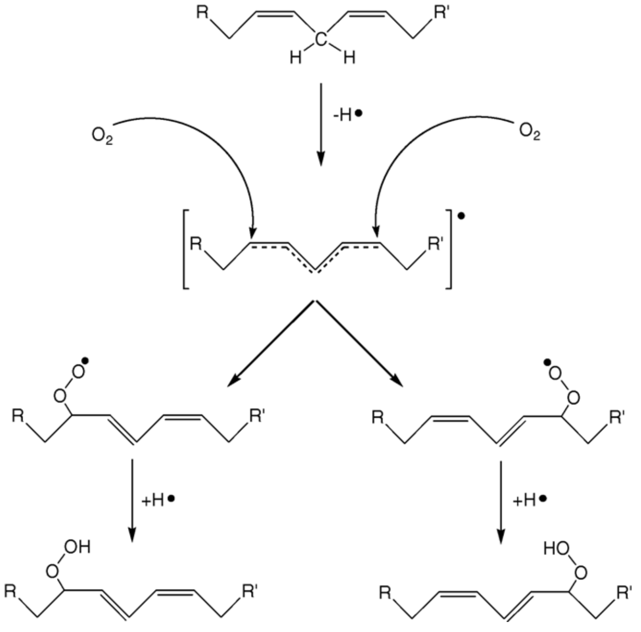
$\mathrm{RO^{\bullet} + R^{\bullet} \rightarrow ROR}$ Eq. **13.**

Scheme 1. Radical reactions taking place in the metal-catalysed autoxidation of an alkyd resin binder [22,23].

through the action of some unidentified initiating species (Eq. (1)) on the substrate, by thermal hydroperoxide decomposition (Eq. (2)) or by action of the metal drier. Initiation via the drier catalyst proceeds through metal hydroperoxide decomposition (Eqs. (3a), (3b), (4a) and (4b) [10,11], metal-dioxygen activation (Eq. (5a) and (5b)) [12], or by direct reaction of the metal complex with the resin (Eq. (6)) [11,13,14]. Propagation reactions involve mainly hydroperoxide formation through Eqs. (7) and (8). The reaction according to Eq. (7) is extremely rapid (diffusion controlled, $k \sim 10^9\ \mathrm{l\,mol^{-1}\,s^{-1}}$), except at very low partial pressures of dioxygen (dissolved-oxygen concentration $<10^{-3}$ M). The reaction described by Eq. (8) is relatively slow and thus it is the rate-determining step for the formation of hydroperoxides [15–17]. Termination occurs via radical recombination to yield peroxy, ether and carbon–carbon cross-links (Eqs. (10)–(13)) [18–20].

The autoxidation takes place at the fatty acid group of the alkyd resin (Fig. 1). Fatty acids are important biomolecules, and are present in lipids as their triester with glycerol. Consequently, a considerable amount of research has been performed on elucidation of their autoxidation mechanism, since lipid autoxidation is known to be the cause of vital issues, such as food spoilage, tissue injuries and degenerative diseases [21,22]. An extensive coverage of the kinetics of fatty acid autoxidation will not be given here, excellent reviews of the early work are readily available in the literature [10,23].

The fatty acids in an alkyd resin are polyunsaturated fatty acids, commonly linolenic acid, (α-linolenic acid = 9*Z*,12*Z*,15*Z*-octadecatrienoic acid and γ-linolenic acid = 6*Z*,9*Z*,12*Z*-octadecatrienoic acid) which is a major constituent of linseed oil [24], or linoleic acid (9*Z*,12*Z*-octadecadienoic acid) which is a major constituent of, for example, sunflower oil and soya oil. The high susceptibility



Scheme 2. Initial hydroperoxide formation in the autoxidation of the fatty acid chain of an alkyd resin binder unit.

of non-conjugated polyunsaturated fatty acids for autoxidation arises from the presence of *bis*-allylic hydrogen atoms, which have a relatively low C–H bond dissociation energy of 75 kcal/mol and can therefore be easily abstracted, resulting in radical chain initiation and thus autoxidation [21,25]. In Scheme 2 the initial autoxidation reactions for a fatty acid pentadiene substructure, forming a hydroperoxide, are summarised. Abstraction of one of the *bis*-allylic hydrogen atoms results in the formation of a radical species, which is stabilised by delocalisation due to the local pentadienyl structure. Molecular oxygen reacts extremely rapid with this pentadienyl radical species to form a peroxy radical which has the double bonds dominantly conjugated, since this is the most stable structure [22]. The peroxyl radical can then participate in a number of reactions, but in the early stages of autoxidation the dominant reaction will be to abstract a hydrogen atom from another resin molecule to form a hydroperoxide and propagate the radical chain (Eq. (8) in Scheme 1). Fig. 2 shows the total time course of lipid autoxidation: the fatty acid concentration will rapidly decrease as hydroperoxides are formed. The hydroperoxide concentration will go through a maximum when hydroperoxide formation is surpassed by hydroperoxide decomposition. Hydroperoxide decomposition leads to further product-formation, forming cross-linked (non-volatile) species and numerous other oxygen containing products such as alcohols, ketones, aldehydes and carboxylic acids. Since the mechanisms of lipid autoxidation are fairly well understood, in the last decade the most significant advancements in alkyd paint drying come from studies concerning the dry film structure of dried oils and fatty acids and the mechanisms of the cross-link formation.

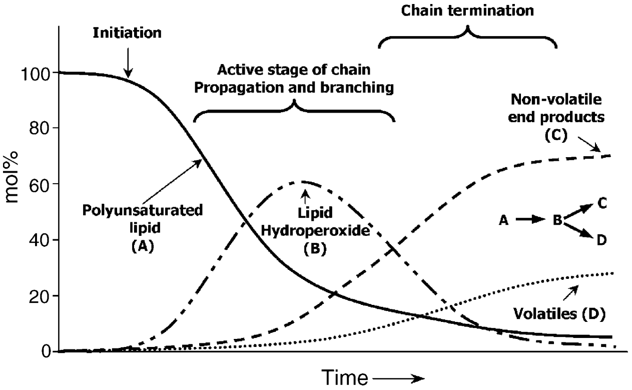


Fig. 2. Schematic impression of the time course of fatty acid (lipid) autoxidation, redrawn after Gardner [27].

A general review of earlier work regarding all aspects of the polymerisation of drying oils was given by Wexler [26], and several recent reviews are available covering fatty acid autoxidation [22,27]. The Paint Research Association has published a report regarding the drying of linoleic-based coatings [28], and also a recent review is available about the *yellowing* (discoloration over time) of dried oil films, studied with the model compound methyl linolenate [29]. Yellowing is caused by over-oxidation of the coating and is a general problem for alkyd coatings. The yellowing process will not be discussed in this review.

2.2. Studies with drying oils

The fatty acids in natural oils are present predominantly as lipids. A natural oil with a high content of polyunsaturated fatty acids, such as linoleic or linolenic acid, can be categorised as a drying oil. Drying oils are prone to autoxidation and, as a precursor to an actual alkyd resin, are often used as a model compound to study paint drying.

The structure of a dried film of soya oil has been studied by Falla with GLC (gas liquid chromatography) and infrared spectroscopy (IR) [28]. Soya oil was dried as a thin film on glass using cobalt and lead driers at 25 °C and 65% relative humidity. The oil was converted to methyl esters prior to analysis with GLC. Two fractions could be obtained from the methyl esters of 16 h dried soya oil, one soluble in heptane and one insoluble. The soluble part yielded peaks corresponding to oleate, stearate and palmitate. The insoluble part was analysed by infrared spectroscopy to yield a spectrum similar to that obtained in studies concerning the drying of linseed oil [30]. The IR spectrum lacked bands characteristic of unsaturation and showed additional bands typical of OH, COOH and other, non-ester, carbonyl containing species. Elemental analysis data of the insoluble material could be fitted to the molecular formula $C_{10}H_{18}O_3$, and on the basis of this result a possible structure for the dried film polymer was formulated (Fig. 3) [28].

Lazzari et al. studied the drying and oxidative degradation of linseed oil by Fourier transform-infrared spectroscopy

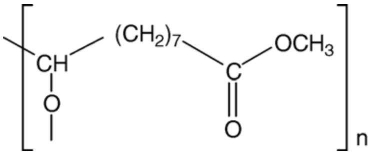


Fig. 3. A postulated structure for the dried film polymer of soya oil. Terminal groups could include OH, COOH and CHO [26].

(FTIR), thermogravimetry (TG), differential scanning calorimetery (DSC) and size exclusion chromatography (SEC) [31]. Linseed oil was spread on selected supports, obtaining a film thickness of 80 μm, and was then exposed to different conditions. Different films were naturally aged, thermo-oxidized at 80 °C, or irradiated with wavelengths >295 nm. Analysing the film dried at 80 °C after 6 h with FTIR, the same observations were made as reported by Vandevoort et al. [32]. After an induction time of 4 h, the peak due to hydroxyl groups rapidly increased and reached a constant value after 8 h, while isolated double bonds disappeared [31]. An insoluble polymer was formed after extended oxidation times at 80 °C (up to 150 h). The soluble part of this polymer was extracted and analysed by SEC and IR. The SEC chromatogram of the soluble part of the aged sample shows a peak due to the original component, as well as a peak assigned to dimers and a continuous distribution of higher molecular weight fractions. The IR spectrum of the soluble (extracted) sample was compared with the IR spectrum of the sample before extraction. The spectrum of the soluble sample showed signals of lower intensity for the ester groups relative to the methylene signals in the sample, which would suggest that a process of fragmentation takes place in which aliphatic chains are preferentially released from the insoluble network [31].

Analysis of a sample film kept at room temperature exposed to the atmosphere (natural aging/drying) by FTIR yields exactly the same spectral changes as seen for samples treated at 80 °C, albeit over a much longer time period. It was thus supposed that treatment of linseed oil at moderately higher temperatures only accelerated the natural drying and degradation processes, not altering the type and extension of the reactions [31].

Mallégol et al. sought to gain insight into the long-term behaviour of oil-based paints by studying the thermo- and photo-oxidation of several different drying oils [33–35]. FTIR was again used as the preferred analytical method, as well as Fourier transform Raman spectroscopy, to study the structure of linseed oil and poppyseed oil films oxidised at 60 °C [33]. Samples were spread out as a thin film on either a KBr or a glass window after which they were oxidized in a ventilated oven at 60 °C in the dark. After oxidation for 30 h a very weak peak at 885 cm^{-1} evidenced the formation of *trans* epoxides [33]. Oxidised samples were treated with NO after increasing reaction times to differentiate between alcohol and hydroperoxide formation. NO reacts with alcohols to form an R–O–N=O nitrite, which has a specific band at 779 cm^{-1} [33]. Studying the time course of hydroperoxide formation and alcohol formation, it was concluded that alcohols are secondary products formed only after hydroperoxides are created. To assess the amount of carboxylic acid present in the oxidised oils, samples were treated with SF_4 to form the acid fluorides. Two new peaks were observed after treatment, i.e. at 1843 cm^{-1}, attributed to non-conjugated acid fluorides, and at 1810 cm^{-1} attributed to conjugated acid fluorides. The formation of carboxylic acids in the curing step evidences chain scission reactions that can weaken the dried film. Carboxylic acid formation was proposed to occur by oxidation of aldehydes or via hydrogen abstraction from the tertiary carbon with a hydroperoxide function and subsequent β-scission after hydroperoxide decomposition, as shown in Fig. 4.

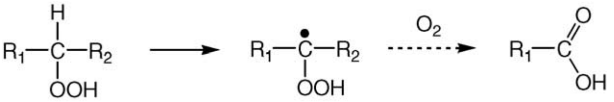


Fig. 4. Carboxylic acid formation via hydrogen atom abstraction and subsequent β-elimination reactions and oxidation.

Raman spectroscopy of a linseed oil film heated at 60 °C up to 50 h showed a broad band appearing around 850 cm^{-1} [33]. This band was attributed to the formation of hydroperoxides and also peroxide cross-links, since the band remained present even after extended drying times (over 100 h), during which period the hydroperoxide concentration decreased notably. From their FTIR and Raman studies Mallégol et al. concluded that the oxidation of the fatty acids in linseed and poppyseed oil at 60 °C proceeds according to the following general sequence:methylene-interrupted *cis* → *trans*-conjugated → *trans*-non-conjugated → saturated. Hydroperoxides are decomposed by homolytic cleavage of their peroxy bond, leading to a mixture of ketones, aldehydes, alcohols and acids by subsequent reactions. The decrease in unsaturation was explained by epoxide formation through addition of peroxyl radicals on conjugated double bonds [33].

The fate of hydroperoxides formed in the oxidation of linseed and poppyseed oil at different temperatures (25, 40, 60, 80, 100 and 120 °C) has been studied in further detail [34]. The hydroperoxide concentration as a function of oxidation time was determined by iodometric titration. The peroxide values (PV) rapidly reached a maximum before decaying slowly. For oxidation reactions carried out at higher temperature, PVs were found to be lower. Under the conditions used by Mallégol et al. it was found that the peroxide value determined by iodometric titration was the sum of the ROOH and ROOR concentrations. By reacting oxidised oil samples with SF_4 prior to PV determination, the contribution of only the dialkylperoxide cross-links to the PV could be determined, as SF_4 reacts with the hydroperoxides. The ROOR concentration for linseed oil dried at 60 °C is lower than the ROOH concentration and follows the same trend when monitored over time: going through a maximum and then decaying. This means that peroxide cross-links are destroyed after prolonged reaction times at this temperature [34]. The photo-oxidation of a dried linseed oil film leads to severe degradation of the dried film network, as was concluded from the observed major changes in the FTIR spectrum, i.e. a rapid decrease of peaks due to double bonds, ester bonds and even alkyl groups [35]. In comparison, the thermo-oxidation of a dried linseed oil film at 100 °C for up to 1000 h did not yield such major changes in the FTIR spectrum. Thus although the cross-linked network is quite photo-labile, the thermostability is relatively high [35].

2.3. Studies with fatty acid esters

2.3.1. General observations in ethyl linoleate (EL) drying

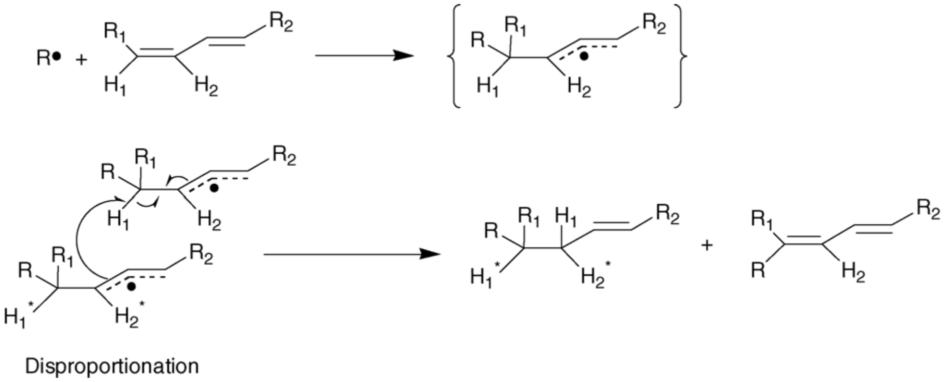
In the past decade, Muizebelt and colleagues made important advancements concerning knowledge of the oxidative cross-linking of alkyd resins [18–20]. Fatty acids or fatty acid esters were used as model compounds to study the cross-linking reactions that occur under the reaction conditions of a drying alkyd paint, i.e. a thin film air-dried by a Co/Ca/Zr combination drier (see Section 3.2) at room temperature. Ethyl linoleate autoxidation was monitored over an extended period of time (up to 1 year) using several analytical techniques [18]. In the oxidation of technical grade EL (70% EL, 30% ethyl oleate, traces of palmitate and stearate) followed by GC–MS it was observed that all ethyl linoleate had been oxidised in three days, while after 110 days there is still some unreacted ethyl oleate left. The relative reactivity of ethyl oleate versus ethyl linoleate was determined using the saturated esters as internal standards. Both compounds decreased according to pseudo first-order kinetics and a reactivity ratio of linoleate to oleate of 17 was found, which has been reported earlier [36]. Size exclusion chromatography (SEC) showed relatively fast oligomer formation and the distribution of oligomers reached after one day did not change substantially upon further reaction. The peak due to hydroperoxides slowly decreased over time (up to 400 days), however. Discrete oligomers slowly disappeared, as was evidenced by a smoothing of the SEC curve after long reaction times. The formation of low-molecular weight material became more apparent over time. From these results it was concluded that cross-linking continues over prolonged reaction times with concurrent degradation [18].

2.3.2. Time evolution of drying and cross-link formation

The cross-linking in the autoxidation of EL (99% purity) was studied in more detail using ^{1}H NMR, quantitative ^{13}C NMR and ^{13}C NMR with the POMMIE technique [18,20]. The POMMIE ^{13}C-NMR technique yields subspectra for methine, methylene and methyl carbons, and the methine carbon spectra yield information regarding cross-linked sites. Spectra were recorded at increasing reaction times and integrated to give the time dependence of the relative amounts of double bonds, ether and peroxy cross-links, as well as carboxylic acids, aldehydes and epoxides. After one week of drying, all non-conjugated double bonds had disappeared. The formed conjugated double bonds decreased to low levels after two months. In the initial stages of the reaction considerable epoxide formation was observed. The epoxide concentration also decreased to zero within 2 months, however. The increasing carbonyl peak at 178 ppm was attributed to carboxylic acid formation from aldehydes, where aldehyde formation was ascribed to β-scission reactions. Ether and peroxy cross-links were formed in roughly equal amounts in a period of 133 days. It was concluded that linoleic acid undergoes cross-linking and β-scission in approximately equal proportions. Over prolonged reaction times (1 year) the POMMIE ^{13}C NMR results showed that the total double bond concentration continues to decrease for the entire duration of the experiment, the peroxy signal remains more or less constant and the ether signal increases. Thus it was concluded that a net formation of ether links from double bonds occurs [18]. The amount of dimeric C–C cross-linked material formed in the autoxidation of EL was determined to be about 5% [18].

2.3.3. Oligomerisation in detail

Oligomerisation products of EL dried by cobalt in air were analysed further with Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS), direct chemical ionisation-mass spectroscopy (DCI-MS) and fast-atom-bombardment mass spectroscopy (FAB-MS) [19]. With SIMS, oligomeric species up to pentamers could be detected after one day of drying. After 60 days of drying peaks are smaller and only dimers remain, with the formation of new compounds with molecular weights between that of specific oligomers. After 240 days of reaction, no features could be detected beyond 300 amu (EL = 308 amu) [19]. These observations again indicated the ease of degradation of the formed oligomers. By FAB-MS and DCI-MS dimers were detected which could be assigned the general formula $[(\mathrm{EL\text{-}H})_2 + n\mathrm{O}, n = 0–5]$ and trimers which followed the general formula $[3\mathrm{EL}\text{-}x\mathrm{H} + n\mathrm{O}$, $x = 2$ or $4]$. Some important mechanistic conclusions were drawn from the mass spectra. Dimerisation was proposed to occur exclusively trough radical termination reactions, since masses related to the general formula $(2\mathrm{EL} + n\mathrm{O})$ would be expected if addition to double bonds had occurred followed by disproportionation. Formation of trimers was attributed to either combination reactions of (dimeric) radicals, or to radical addition to the double bonds of dimers, related to the occurrence of peaks with masses of either (3EL-4H), or (3EL-2H), respectively. The finding that radical addition to double bonds is apparently limited to the formation of trimers (and higher oligomers) was rationalised by the presence of conjugated double bonds in dimerised EL, which are more susceptible to addition reactions [37]. The observation that chains with conjugated bonds cross-link according to a different mechanism than chains with non-conjugated bonds was confirmed by drying studies with methyl ricinoate (MR), which is the methyl ester of a conjugated linoleic acid isomer (9,11-octadecadienoic acid, methyl ester) [19]. The mass spectra of dried reaction mixtures of MR showed all peaks doubled with a mass difference of 2 amu as compared with



Scheme 3. Radical addition to a conjugated double bond and subsequent disproportionation, yielding species of two mass units apart.

spectra for EL. This observation was explained by a cross-link mechanism of radical addition to a double bond and subsequent disproportionation, which leads to masses of 2M-2 and 2M, as shown in Scheme 3. Radical addition to a conjugated double bond generates an allyl radical, which is stabilized by delocalisation and the reason why conjugated double bonds are more reactive in a radical addition than non-conjugated double bonds. Drying a mixture of EL and MR for 2 days in air with cobalt resulted in the formation of a cross-linked co-polymer [19].

Modern “high-solids” alkyd paints contain so-called “reactive diluents” [38]. In these paints the solvent has been replaced by a compound which acts as a solvent but which also forms cross-links with the alkyd resin during drying, thereby becoming part of the network. Muizebelt et al. studied the drying of EL in the presence of reactive diluents (for example butenediol derivatives) by NMR and mass spectroscopy [38]. It was shown by mass spectroscopy that the reactive diluents do form cross-links with EL. The proposed reaction mechanism for cross-link formation of the reactive diluents was the same as shown earlier for EL and MR: compounds with allylic methylene groups cross-link via radical recombination whereas compounds with conjugated double bonds cross-link via addition to the double bond.

In a recent study, Oyman et al. studied the drying of several fatty acid esters (EL, methyl linoleate (ML), and methyl linolenate (MLn)) emulsified in water, to mimic water-borne alkyd paints [39]. The autoxidation was catalysed by a water-emulsifiable cobalt drier and the reaction was monitored by FTIR and Raman spectroscopy on emulsion films. The main conclusions from that study were that no fatty acid ester oxidation takes place during water evaporation from the emulsion film, and that the oxidation reactions proceeds in exactly the same way as for non-aqueous systems once all water has evaporated [39].

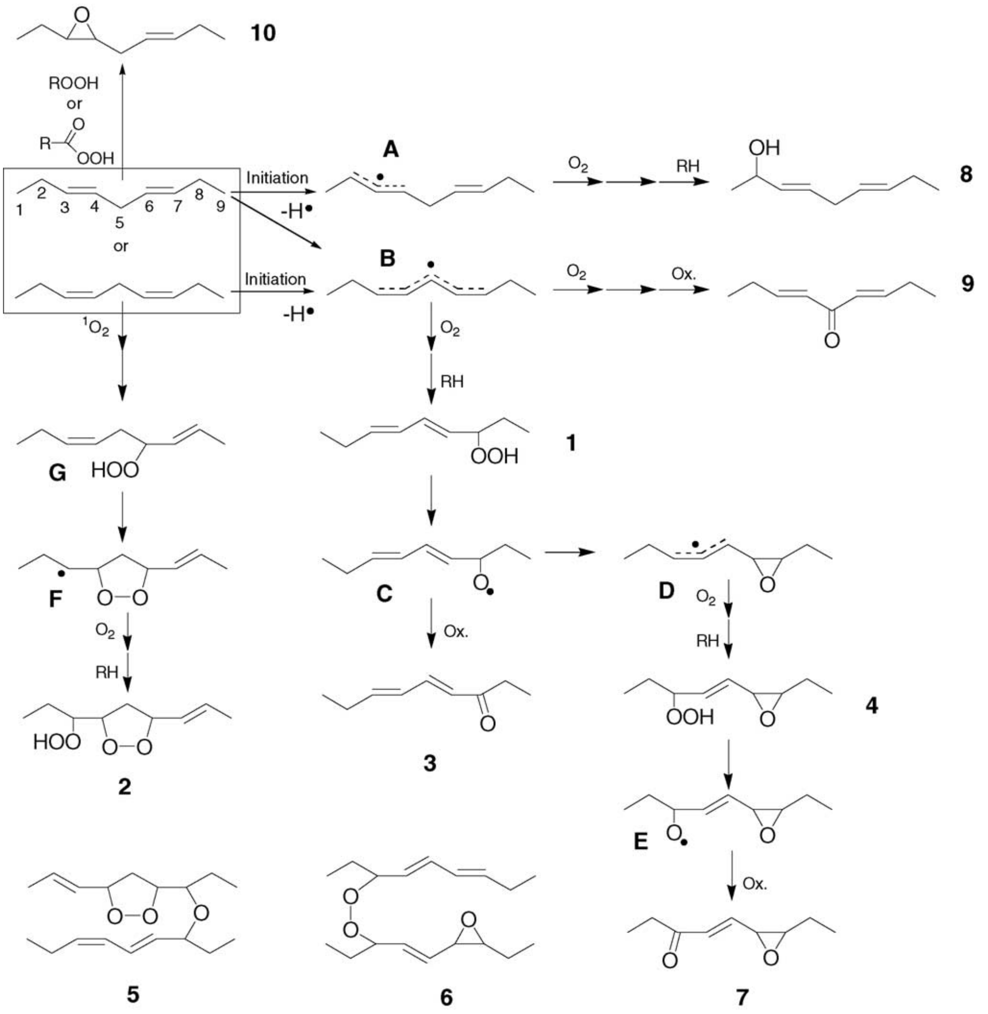
2.4. Studies with the model compounds (*Z*,*Z*)- and (*E*,*E*)-3,6-nonadiene

The symmetrical model compounds (*Z*,*Z*)- and (*E*,*E*)-3,6-nonadiene have been used to get further insight in the cross-link reactions that occur during the drying of alkyd resins [40]. Focus of the study was the product isolation and characterisation of the compounds formed in the cobalt-catalysed autoxidation. Similar studies have been carried out with (*Z*,*Z*)-2,5-heptadiene and (*Z*,*Z*)-4,7-undecadiene [41–43].

The nonadiene isomers were allowed to react with dioxygen in the presence of a cobalt catalyst for a period of 65 h up to 1 week. Since the nonadiene isomers are rather volatile, the reaction was performed in a closed vessel with a sufficient amount of air present. The reaction products were separated by preparative HPLC and SEC and analysed by ^{1}H and ^{13}C NMR. The products that were isolated and characterised and the proposed reaction paths leading to those products are depicted in Scheme 4. Both isomers were observed to react equally fast and the same products were found when starting from either the *E*,*E* or the *Z*,*Z* isomer, due to extensive (*Z*) → (*E*) isomerisation. Only the ratio of the product *E* and *Z* isomers was found to be dependent on the starting material [40].

Products **1** through **10** shown in Scheme 4 were isolated, while compounds **A** through **F** represent proposed intermediates. Only very small amounts of compounds **8** and **9** were observed, as was expected. Compound **8** results from the abstraction of hydrogen from the C-2 position, while hydrogen abstraction of the doubly activated C-5 position would be more favourable. Compound **9** is the evidence that some of the oxygen reacts with C-5, while the C-3 positions are known to be far more reactive. Most compounds are probably formed through reactions of **1**, which itself is formed by hydrogen abstraction at C-5 followed by addition of dioxygen. The hydroperoxide that is formed is decomposed, forming alkoxy radical species **C**. This species is the proposed intermediate in the formation of many different products, not only for compounds **3**, **4** and **7**, but also for many of the aldehyde and carboxylic acid derivatives that were detected and characterized (not shown here) [40]. Aldehydes and carboxylic acids can be formed through β-scisson reactions of alkoxy radicals; see Scheme 5 for an example.

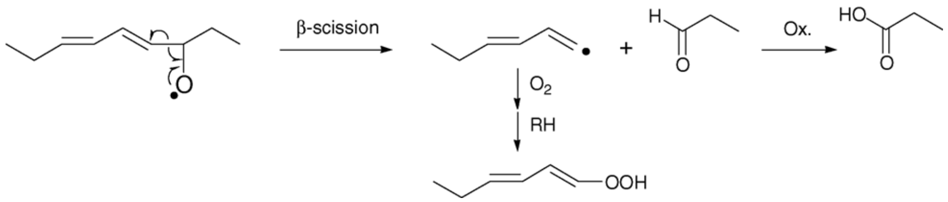
Ketones **3**, **7**, and **9** can be formed by oxidation of alkoxy radicals and epoxide **4** via an intramolecular addition reaction of the alkoxy radical to an adjacent double bond. The



Scheme 4. Products of the cobalt-catalysed autoxidation of (*E*,*E*) or (*Z*,*Z*)-3,6-nonadiene. Products 1–10 were isolated and characterised with ^{1}H and ^{13}C NMR. Species A–F are proposed reaction intermediates. The monomeric products found with the (*Z*,*Z*)-isomer were also isolated starting from (*E*,*E*)-3,6-nonadiene [38].

isolation of small amounts of compound **10** was evidence that direct epoxidation of isolated double bonds also occurs. The most probable routes for direct epoxidation were proposed to be via peracids and via hydroperoxides [44]. Peracids can be formed by oxidation of aldehydes. A singlet-oxygen pathway was also found to exist, since the endoperoxide compound **2** was isolated. This compound must be formed from species **G**, which in turn can only be formed by the direct addition of singlet oxygen to a double bond in 3,6-nonadiene. In principle, compound **1** can also be formed by the addition of singlet oxygen. In a separate study, Hubert et al. showed that generation of singlet oxygen by photosensitizers added to ethyl linoleate or alkyd mixtures enhances the drying rate [45]. Two “dimeric” species, **5** and **6** were isolated. The formation of the dimers is thought to proceed via radical recombination, for instance **5** could be formed by combination of species **C** and **F**.

An important conclusion from the autoxidation experiments with 3,6-nonadiene is that oxidation proceeds via three different mechanisms: normal radical autoxidation,



Scheme 5. Example of a β-scission reaction leading to chain breaking and formation of aldehydes and carboxylic acids [38].

photosensitised oxidation (reaction with $^1O_2$) and epoxidation. Normal radical autoxidation was concluded to be the most important mechanism [40].

3. Metal complex driers for alkyd paints

3.1. Introduction: classification and function of driers

Driers catalyse the uptake of dioxygen and decomposition of hydroperoxides to free radicals, resulting in hardened cross-linked polymer networks that bind the pigment to the painted surface of the treated object. Common driers are metal soaps of carboxylic acids. The first modern driers were developed in the early 1920s with the preparation of metal naphthenates [46]. The driers that are used today are based upon synthetic acids, like 2-ethyl hexanoic acid and versatic acid, shown in Fig. 5. Versatic acids have a tertiary carbon atom adjacent to the carboxylic acid group resulting in a highly branched structure. The reason for using branched carboxylic acids is to achieve a high solubility in the apolar environment that is the oil-paint binder system and to prevent precipitation of the complex. The introduction of water-borne and high-solids alkyd paints has led to the development of new drier systems, however.

The metals that are used in drier compounds are historically grouped in three categories: primary driers (also called active or oxidation driers), secondary driers (also called through-driers) and auxiliary driers. The metals used for the driers in each category are listed in Table 2 [47,48].

Primary driers are autoxidation catalysts. The most important function for autoxidation catalysts is hydroperoxide decomposition and consequently all primary drier metals have two accessible valence states that differ by one electron, which allows for catalytic hydroperoxide decomposition (see Eqs. (3a), (3b), (4a) and (4b) in Scheme 1). It is most uncommon to use a primary drier in a coating formulation without either a secondary or an auxiliary drier added.

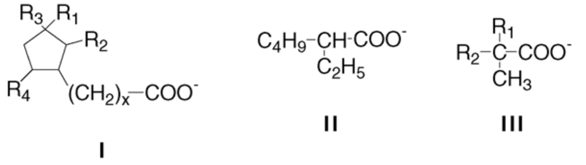


Fig. 5. Carboxylates used in traditional drier metal soaps. **I**: Naphthenoate derivative, R_1, R_2, R_3 and R_4 are short alkyl chains or hydrogens. **II**: 2-ethylhexanoate, often referred to as “octoate”. **III**: Versetate, typically neodecanoate: R_1 and R_2 are alkyl groups and the total number of carbon atoms is 10.

Table 2
Metals that are used in alkyd paint formulations, in each drier category

Primary driers	Secondary driers	Auxiliary driers
Cobalt	Lead	Calcium
Manganese	Zirconium	Zinc
Iron	Bismuth	Lithium
Cerium	Barium	Potassium
Vanadium	Aluminium	
	Strontium	

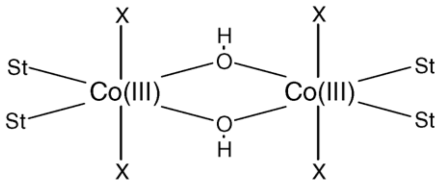


Fig. 6. Dimeric cobalt complex proposed to be formed in the cobalt stearate catalysed autoxidation of α-pinene. St = stearate anion, X = water or alcohol.

The most widely used metal in primary driers is cobalt. As a simple metal soap it shows unequalled effectiveness at room temperature, and it can be used in a broad range of coatings and varnishes [3]. The exact structures of the cobalt species present during alkyd paint drying are not precisely known. Based on general autoxidation literature, some structures can be proposed, however. Cobalt(III) with carboxylate ligands tends to form polynuclear complexes [15,49], and Lombard et al. proposed a dinuclear cobalt(III) species to take part in the catalysed autoxidation of α-pinene (Fig. 6) [50]. Also, the formation of peroxide and hydroperoxide complexes has been proposed, especially in media of low polarity (see Section 2.1) [23]. The formation of insoluble cobalt(III) hydroxides was proposed as the reason for catalyst deactivation in the autoxidation of tetralin [51].

Manganese soaps are also used as primary driers, although they are almost always used in combination with cobalt soaps [46]. The autoxidation activity of manganese soaps can be greatly enhanced by the addition of amine ligands, which will be discussed in Section 3.3.2. A disadvantage of the use of manganese is the brown color of its compounds in the trivalent state, and manganese driers are thus not preferred to be used in high concentration in light colored or white paints.

Iron metal soaps are not very good drying catalysts at room temperature. Although iron complexes are very potent redox catalysts in aqueous solutions, in apolar solvents the Fe(III) ion in metal soaps is not easily reduced, which prevents the redox cycle necessary for catalytic hydroperoxide decomposition [14]. Consequently, iron soaps are not used in air-drying alkyd paints, only sometimes in baking enamels. Iron complexes are also very strongly colored, which prevents their use for the same reasons as for manganese complexes. Cerium and vanadium are only used as primary drier metals in specialty coatings [46].

Secondary driers are active in the cross-linking steps of drying, they are responsible for an overall drying throughout the entire paint layer [48]. Auxiliary driers are said to enhance or alter the activity of the primary drier, and thereby improve the appearance and quality of the total paint film. However, it is not understood what auxiliary driers do on the molecular level. Some metals, which have been termed as “auxiliary” driers, actually function as secondary driers. For example potassium driers combined with cobalt driers were found to be very effective in the through-drying of especially water-borne alkyd systems [52–54]. The classification "auxiliary driers" is thus not really defining a unique group, and use of the term may therefore be discontinued. All driers that are not primary driers are thus better categorised as secondary driers.

Lead has been widely used as a secondary drier metal, but now the use of lead in paints is banned in most western countries, due to its toxicity. Zirconium, bismuth, barium and strontium have all been labelled "lead-replacements", but zirconium is the most widely accepted replacement for lead [46,48].

Bismuth soaps combined with cobalt driers were found to improve the drying times of alkyd paints especially under adverse conditions of low temperature and high humidity [53,55]. In an account by Ali et al. a study is described where organobismuth compounds were evaluated as primary driers [56].

Aluminium compounds greatly enhance cross-linking. It has been reported that alkyd paint formulations containing cobalt drier and an aluminium drier have a significantly increased hardness [57]. Turner et al. have proposed that the increased polymerisation drying for aluminium is accomplished by the formation of extra cross-links formed with alumina and polar groups in the oxidised alkyd network, as schematically shown in Fig. 7 [58]. The use of aluminium compounds as additional cross-linkers in high-solids alkyd paints has also been studied [59]. It was concluded that in the case of high-solids paints, special tailor-made alkyd systems need to be used together with aluminium to avoid severe embrittlement of the dried paint layer [59].

Zinc, lithium and potassium driers are added to paints with a cobalt drier to inhibit wrinkling of the paint film, which is caused by differential hardening of the surface relative to the remainder of the film. Zinc prevents wrinkling by retarding the cobalt drier [48].

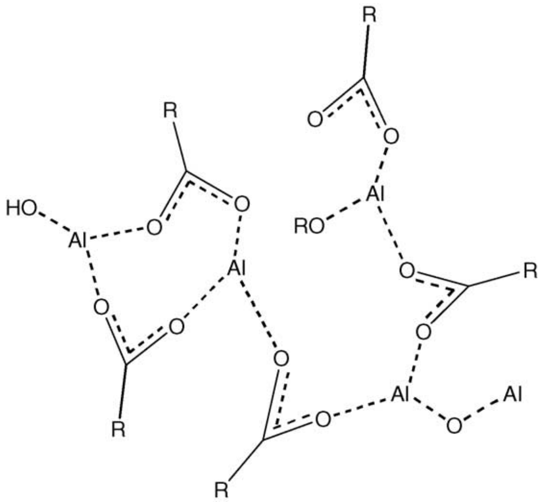


Fig. 7. Schematic representation of possible alumina cross-links in an oxidised alkyd network.

Calcium driers help improve a multitude of different characteristics, such as hardness and gloss as well as drying under adverse weather conditions. Judged by volume, calcium is one of the most used driers [46].

3.2. The efficiency of different drier combinations

Quite a number of studies have been reported comparing the efficiency of different combinations of driers in both water-borne and solvent-borne alkyds [47,53,57,59–65]. Frequently used drier combinations are, for example Co/Zr/Ca, Co/Pb/Ca or Mn/Zr/Ca. In a recent publication, Meneghetti et al. have compared the use of cobalt plus zirconium octoate with cobalt plus lead octoate in the autoxidation of linseed oil at 60 °C [47]. The increase of the linseed oil viscosity was monitored over time for different concentrations of Co, Co/Pb and Co/Zr catalysts. Two rate constants could be obtained from logarithmic plots of viscosity versus time, the increase of ln(viscosity) in a first time domain (0–12 h) was attributed to oxidation and in a second time domain (14–23 h) to polymerisation. The use of Co/Zr catalyst mixtures in a molar ratio of 1:3 showed a significant increase in the overall rate of viscosity change, more so than when the same ratio of Co/Pb catalyst mixtures was used. The observation that a Zr catalyst alone (no cobalt) did not show any activity and the observation that for Co/Zr combinations the increase in the rate of viscosity change was predominantly in the time domain attributed to polymerization, led to the conclusion that Zr did not catalyse oxidation-reduction reactions [47].

Mallégol et al. reported two detailed studies examining the effects of combinations of Co, Zr and Ca on the autoxidation reactions taking place during linseed oil or alkyd resin drying [64,65]. The peroxide value (PV) of linseed oil drying at 25 °C was monitored over time with Co drier alone or combinations of Co/Zr or Co/Zr/Ca [64]. The PV maxima for the different drier systems occurred all after the same drying time and the PVs followed the order: Co alone > Co/Zr > Co/Zr/Ca. The lower PVs in the case of Co/Zr and Co/Zr/Ca were attributed to an increased activity in hydroperoxide decomposition in the presence of Zr and Zr/Ca. Peroxide values for linseed oil dried by Ca/Zr and Zr alone resembled the PV time curve observed for linseed oil dried without any driers added; Zr and Ca/Zr thus did not catalyse peroxide decomposition, as was also found by Meneghetti et al. [47]. Consequently it was concluded that Zr and more so Ca/Zr function by allowing the cobalt drier to conserve its efficiency for long oxidation times [64]. This conclusion was further supported by the fact that peroxide decomposition kept slowly continuing for the drier systems Co/Zr and Co/Zr/Ca even after 3000 h, where the linseed oil PV for the mixture with cobalt alone levelled off. It was hypothesised that Zr and Ca/Zr driers function by coordinating to fatty acid carboxylates formed in the various oxidation reactions, thereby preventing these carboxylates to coordinate to the cobalt drier and decrease its mobility [64].

The autoxidative cross-linking in an alkyd film, cast from a water-borne alkyd emulsion and dried by different drier combinations was studied by magnetic resonance (MR) profiling [65]. With this technique, the cross-link density could be qualitatively determined at different film depths. Alkyd mobility in the film is related to the spin-spin relaxation time, T_2: solids have a low molecular mobility and a short T_2 time, whereas viscous liquids (such as an oil) have a greater mobility and a longer T_2 time [65]. The MR profiling studies showed that the initial cross-linking rate for *all* different drier combinations, (Co alone, Co/Ca, Co/Zr or Co/Zr/Ca) was spatially *uniform* throughout the paint film. Only after 2–3 h, the cross-linking near the surface of the film became faster than near the substrate, (in this case, "the substrate" means "the surface where the film is applied upon") and drying became non-uniform. For all drier combinations, drying became non-uniform after 3 h, only the degree of non-uniformity differed for each drier combination [65]. The difference between T_2 values near the surface and the substrate was observed to follow the order Co > Co/Zr > Co/Zr/Ca > Co/Ca. Hence, for the alkyd system used, the combination Co/Ca was found to be the most uniform through-drying system [65]. Conventional drying-time measurements using a drying recorder (see Section 3.3.1) showed that the Co/Ca system indeed had the shortest through-drying time [65]. The occurrence of non-uniform drying was attributed to the development of a gradient in the concentration of molecular oxygen in the depth of the film, due to diffusion limitations, which is an established concept in alkyd drying [66]. The fact that drying was found to be uniform throughout the paint film for the first 3 h, led to the conclusion that the improvements in cross-link formation by the addition of secondary driers should be accomplished by their action *in the initial* drying stages and not, as one might assume, during later stages of drying.

3.3. Enhancing drier activity and the development of new drier systems

3.3.1. Techniques to evaluate drier activity

In order to improve drier activity it is required to have access to an accurate way of measuring and comparing the activity of different driers. Conventional methods for determining the drying time of an oil or paint film often involved a *drying time recorder*. The basic principle behind such a recorder is that a needle is dragged over a wet film at a constant speed. The kind of trace the needle makes in the film determines in which stage of drying the film is. For a Braive drying recorder these stages are defined as (1) stage a: the paint is wet and flows together, the end of this stage is called the "open time", (2) stage b: a scratchy line is visible, the paint begins to polymerise, the end of this stage is the "dust-free time" and (3) stage c: the needle traces a straight line in the film, the end of this phase is the "surface dry time" [56,67]. Other methods for determining the activity of driers included, for example, the measurement of viscosity change and sample weight increase over time [68,69]. In the previous sections more modern techniques such as ^{13}C NMR [18,20,40,42], GC [18], HPLC [40,42,43], FTIR [18,28,30,33], SEC [18,20], MS [19], SIMS [19] and MR profiling [65] have been used to study the effects of the drier on the paint film. In most of these studies the focus was on elucidating the structure of the dried paint film and not on the specific activity of the drier, or the mechanism of action.

It was recently reported by Warzeska et al. that the oxidation reaction of ethyl linoleate as monitored with time-resolved FTIR spectroscopy and size exclusion chromatography is very suitable as a high-throughput screening model reaction for evaluating different drying catalysts for alkyd paint [70]. The kinetics of EL oxidation can be studied efficiently by time-resolved FTIR spectroscopy [32]. The *cis* **H**–**C**=CH stretching vibration at 3010 cm^{-1} is especially suitable to follow the disappearance of EL in time. In the first step of the reaction a hydrogen atom is abstracted from the reactive methylene group of the *cis*, *cis*-1,4-diene moiety. After rearrangement of the resulting pentadienyl radical and reaction with dioxygen (see also Scheme 2), a hydroperoxide is formed and one of the *cis* **H**–**C**=CH hydrogens has now become a hydrogen on a secondary carbon atom. The decrease of the infrared vibration due to the disappearance of this cis **H**–**C**=CH hydrogen can thus be associated directly to the first step of the autoxidation reaction. To follow the autoxidation of EL in time, an FTIR spectrum is recorded (automatically) every 5 min. Fig. 8 shows (part of) several example spectra of an oxidation experiment. For each spectrum, integration is carried out for the area between 2992 and 3025 cm^{-1}. As a result a table is obtained with the integral of the 3010 cm^{-1} peak at different times. The logarithmic plot of these data gives a straight line and thus, in first approximation, the oxidation of EL follows pseudo first-order kinetics. From the slope of this graph the pseudo first-order reaction rate of H$^{\bullet}$ radical abstraction can be estimated [70].

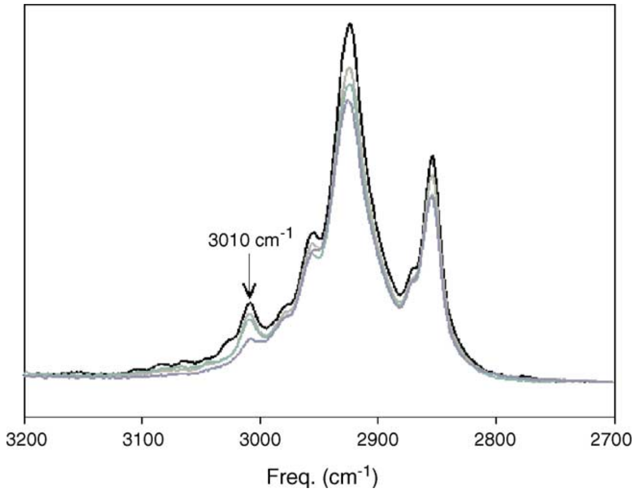


Fig. 8. 2700–3200 cm^{-1} region of the FTIR spectra of EL at increasing reaction times during an autoxidation reaction. The peak at 3010 cm^{-1} decreases as the autoxidation reaction proceeds.

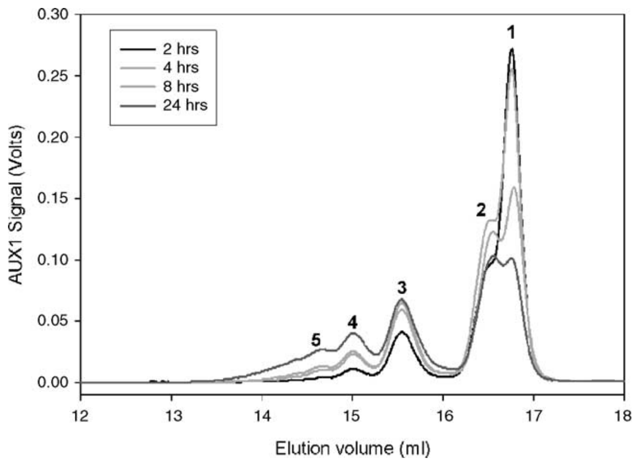


Fig. 9. Several size exclusion diagrams; samples taken after 2, 4, 8 and 24 h reaction time of an autoxidation reaction mixture of EL with a metal complex drying catalyst. Peak assignments: (1) EL; (2) EL-hydroperoxide; (3) dimmers; (4) trimers; (5) oligomers.

To measure the *extent* of the cross-linking, size exclusion chromatography (SEC) was used. Fig. 9 shows several chromatograms taken at different times during an autoxidation reaction. The EL peak decreases in time as EL-hydroperoxides are formed. The hydroperoxide peak will first increase and then decrease, as hydroperoxides are decomposed to form cross-linked species. The intensity of the peaks due to these cross-linked species increase over time: first dimers are visible, then trimers and given sufficient reaction time, higher oligomers are subsequently detected.

3.3.2. The effect of added ligands

In the earliest accounts, nitrogen-containing ligands were added to paint mixtures containing cobalt-drier soaps to prevent *loss-of-dry* [71,72]. Pigment-containing paints often experience loss of drying upon aging, which means that their drying times are longer after a certain storage time. Loss-of-dry can be attributed to failing of the paint drier, which may have several reasons, such as: adsorption of the drier on the pigment surface [73,74], formation of insoluble drier complexes in the paint mixture and drier hydrolysis (common in waterborne paints) [4,5,46]. In one of the first reports concerning nitrogen ligands and paint driers, Nicholson observed that pigmented paint mixtures with manganese and cobalt complexes containing the ligand 1,10-phenanthroline showed no loss-of-dry upon ageing, in contrast to paint mixtures with the simple metal oleates [71]. Nicholson had already shown in a conductometric study of the adsorption of cobalt acetate and cobalt(II) tris(1,10-phenanthroline)diacetate on titanium dioxide in acetic acid, that the phenanthroline complex is apparently adsorbed to a lesser extent on the TiO_2 surface than cobalt acetate [73].

Inspired by Nicholsons work, Wheeler studied the influence of several hundreds of nitrogen-containing ligands on the drying rate of a paint dried by cobalt oleate and lead naphthenate [75]. No differences were found in adding the ligands in situ to the paint, or by using pre-formed complexes. Only the aromatic heterocyclic didentate ligands 2,2′-bipyridine and 1,10-phenanthroline, and to a lesser extent, the monodentate ligand pyridine were found to shorten the drying time, both initially and upon ageing.

In general, aromatic or heterocyclic nitrogen-containing ligands (except pyridine) or aromatic and aliphatic primary and secondary (di)amines were found to prolong the drying time to a considerable extent. Tertiary amines were found to have little or no effect on the drying rate. Wheeler also claimed in several US patents that manganese carboxylates (naphthenates, oleates, octoates) show a remarkably enhanced drying activity (produce shorter drying times) when *o*-phenanthroline, 2,2′-bipyridine or other aromatic nitrogen containing ligands are added to the paint mixture (Fig. 10) [76–78]. Canty et al., after studying the drying time of paint mixtures versus the molar ratio of added 1,10-phenanthroline for different metal concentrations, proposed that a bis(phenanthroline)cobalt complex is formed at the phenanthroline concentration which produces most rapid drying. For manganese soaps the presence of a mixture of

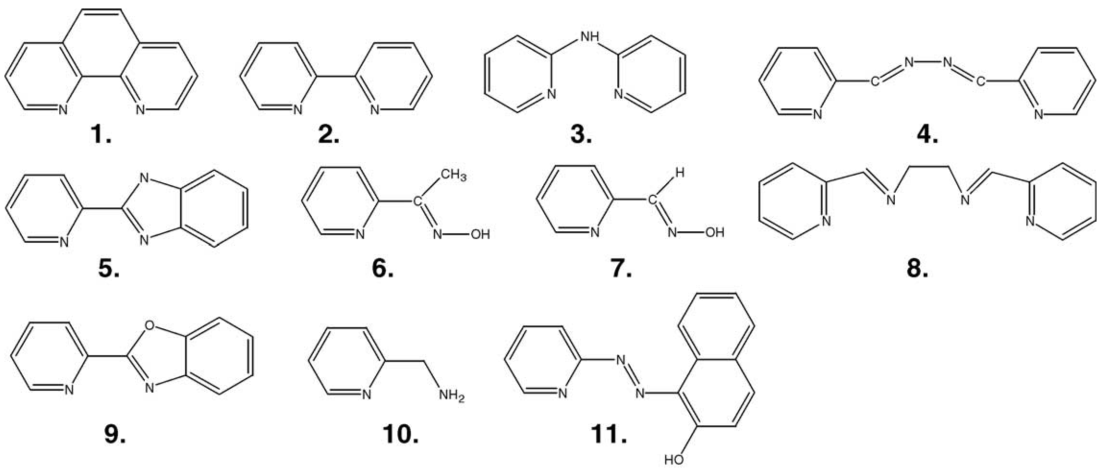


Fig. 10. Ligands that accelerate paint drying when using manganese (with 1–11) or cobalt (with 1,2) carboxylates as driers [76].

Table 3
Nitrogen ligands added to manganese, iron and lead naphthenate driers to enhance drier activity in the drying of linseed oil

Additive[a]	Activity (0.03% Co = 1.0)[b]			Improvement on self (%)[c]		
	Mn	Fe	Pb	Mn	Fe	Pb
N,*N*′-bis(salicylaldehyde)ethylenediamine	1.4	0.46		180	210	
N,*N*′-bis(salicylaldehyde)-1,2-phenylenediamine	1.35		0.70	170		50
1,10-Phenanthroline	1.35	0.60		170	300	
Dicyclohexylamine	1.10			120		
Hexamethylenetetramine	1.00			100		
Cyclohexylamine	1.00			100		
N,*N*′-bis(benzaldehyde)ethylenediamine	1.00			100		
Pyridine-2-carboxylic acid	0.95			90		
2,6-(*N*,*N*′-dimethylaminomethyl)-4-octylphenol	0.95			90		
2,6-(*N*,*N*′-dimethylaminomethyl)-4-butylphenol	0.95	0.35		90	130	
Dicyandiamide	0.90			80		
2-Naphtylamine	0.90			80		
Methyldiethanolamine	0.90			80		
2-Methyl-6-aminopyridine	0.80			60		
Lauryl pyridinium chloride	0.80			60		
2-(2-Dimethylaminoethylamino)pyridine	0.75			50		
Tris(hydroxymethyl)aminoethane	0.75			50		
N-Dicyanoethylbenzenesulfonamide	0.70			40		
Quinaldine	0.70	0.35		40	130	
2-Vinylpyridine	0.70			40		
2-Aminopyrimidine	0.70			40		
Triphenylguanidine	0.70	0.40		40	170	
Acetoacetanilide	0.70			40		
DL-alanine	0.70			40		
Pyridine		0.35			130	
Allylamine		0.35			130	
1,2-Phenylenediamine		0.35			130	
4-Bromoacetanilide		0.35	0.50		130	10
Tribenzylamine		0.35			130	
2,2’-Bipyridine			0.65			40
2-Aminoethyl hydrogen sulfate			0.60			30
sym-Diphenylcarbazide			0.55			20
Nitro-1,10-phenanthroline			0.55			20
Salicylaldoxime			0.55			20
Urea			0.50			10
DL-Leucine			0.50			10
Methylacetylurea			0.50			10

[a] A molar ratio of 2:1 of ligand-to-metal was used.

[b] Activity = $(\mathrm{Dtime}_{\mathrm{Co}}/\mathrm{Dtime}_{\mathrm{m+l}})$ where $\mathrm{Dtime}_{\mathrm{Co}}$ = the drying time of a sample containing 0.03 wt.% on-oil of cobalt naphthenate as drier and $\mathrm{Dtime}_{\mathrm{m+l}}$ the drying time of a sample containing another drier with added ligands.

[c] $((\mathrm{Dtime}_{\mathrm{old}} - \mathrm{Dtime}_{\mathrm{m+l}})/\mathrm{Dtime}_{\mathrm{m+l}}) \times 100\%$, where $\mathrm{Dtime}_{\mathrm{old}}$ = the drying time for that metal naphthenate without any ligands added and $\mathrm{Dtime}_{\mathrm{m+l}}$ = the drying time with ligands added [78].

mono(phenanthroline)manganese and bis(phenanthroline)-manganese complexes was proposed [79].

Zettlemoyer et al. studied the use of different nitrogen ligands as loss-of-dry agents with cobalt, manganese, iron, lead, chromium and zinc carboxylate driers [72,80]. Only manganese and cobalt were found to be positively influenced by the addition of nitrogen-donor ligands. In contrast to the findings of Nicholson, Zettlemoyer found that adding 1,10-phenanthroline in situ to a cobalt containing varnish *retarded* the drying time. This contrasting result was attributed to the type of varnish used [72].

Zettlemoyer et al. also conducted a large, systematic study comparing the drying activities of cobalt, manganese, iron and lead naphthenates with 160 different nitrogen ligands added in the drying of linseed oil [80]. The ligands were added in situ in a 2:1 molar ratio of ligand-to-metal. For the cobalt drier, it was found that the activity was hardly improved by any ligand. From this and earlier findings it was concluded that although aromatic heterocyclic didentate nitrogen ligands accelerate cobalt driers in pigmented systems, this is apparently not the case in un-pigmented systems [80].

Table 3 shows the results of the manganese, iron and lead driers with the ligands that produced the highest activities for each drier. Activities are relative to the activity of the normal cobalt naphthenate drier without any amine added. The manganese drier was accelerated mainly by bifunctional heterocyclic nitrogen ligands or Schiff-base compounds and retarded by strongly basic diamines, substituted phenylenediamines, diphenylamine, diethylenetriamine, L-cysteine, tetrabutylethylenediaminetetraacetate and sulfurbearing amines. The iron drier could be accelerated up to 300%, but the resulting activity was found to be still less than that of the cobalt drier.

Myers, Wheeler and Canty speculated in several reports on the catalytic mechanism of manganese complexes with *o*-phenanthroline [79,81,82]. They supposed that manganese phenanthroline complexes perform better in the coordination and activation of molecular oxygen, and that oxygen activation followed by addition of the dioxygen molecule to the paint resin is the primary mode of action of the complex. Although oxygen activation might play a role for some complexes, it will not be the primary role for manganese complexes once hydroperoxides are formed, since that will then be hydroperoxide decomposition [23,83].

The ligand 2,2′-bipyridine (bpy) is often added to cobalt and manganese driers in water-borne alkyd coatings, or the driers are added as the complex $[M(bpy)_3]^{n+}(anion)_n$ [4,5,84,85]. In the complexed case, the counterions usually are carboxylates, phosphonates, sulfonates or sulfates. As in the case for solvent-borne paints, the purpose of the ligand is to accelerate the drier and shorten the drying time, but more so to protect the drier metal from adverse effects such as hydrolysis, chemisorption on the pigment or other reactions which lead to loss-of-dry [4,5]. In two recent papers, Weissenborn et al. reported that the loss-of-dry upon aging of water-borne alkyd emulsions containing pigments was reduced when a cobalt drier complexed with 2,2-bipyridine was used, as compared to cobalt driers without any ligands added [4,5].

Recently, Warzeska et al. studied the influence of bpy on the autoxidation of ethyl linoleate with manganese 2-ethylhexanoate [70]. The autoxidation of EL catalysed by cobalt and manganese 2-ethylhexanoate and manganese 2-ethylhexanoate with bpy was followed by FTIR. The rates for the autoxidation of EL with either manganese or cobalt 2-ethylhexanoate were found to be similar, only the manganese compound showed a prolonged induction period whereas the cobalt compound did not. Addition of 0.25 equiv. of bpy to the manganese catalyst already drastically shortened the induction time. Adding more than 0.5 equiv. did not change the rate or the induction time any further. The addition of bpy to cobalt 2-ethylhexanoate resulted in a *decrease* of the reaction rate, but did not give rise to an induction time. This result is in agreement with the earlier observations by Zettlemoyer and Myers [80]. Warzeska et al. proposed that coordination of bpy to the cobalt drier results in a lowering of the concentration of the catalytically active species, and consequently, in a decrease in reaction rate [70]. The complex $[Mn_2^{II}Mn_2^{III}O_2$(2-ethylhexanoate)$_6$(bpy)$_2]$ was isolated from a commercial drier solution containing manganese 2-ethylhexanoate and bpy, the molecular structure is shown in Fig. 11. The fact that after addition of 0.5 equiv. of bpy the autoxidation rate and induction time of the manganese catalysed reaction did not change any further is well in agreement with the formation of the obtained tetranuclear cluster compound. Since the cluster compound showed a comparable autoxidation activity as for an in situ mixture of manganese and bpy, it was concluded that this type of cluster compounds might well be a catalytically active species in the autoxidation reaction [70].

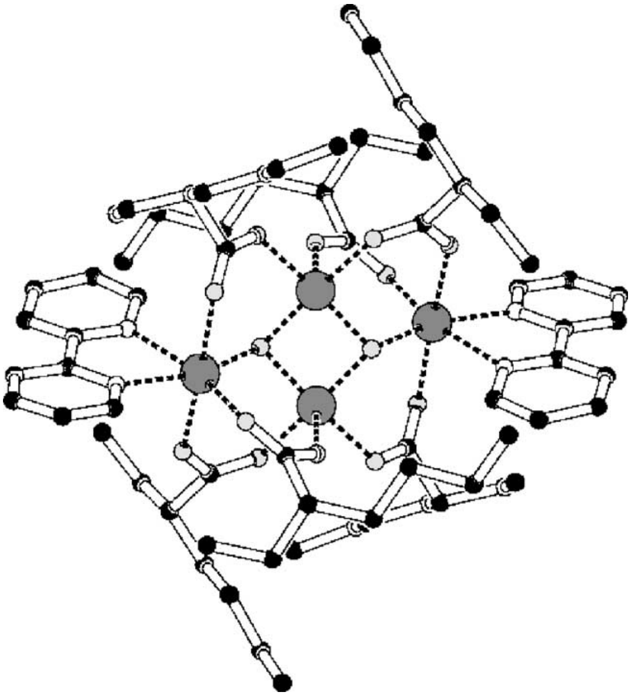


Fig. 11. Molecular structure of $[Mn_2^{II}Mn_2^{III}O_2$(2-ethylhexanoate)$_6$(bpy)$_2]$, determined by single crystal X-ray crystallography. Due to disorder in the alkyl chains and disordered solvent molecules in the crystal, the structure could not be fully refined (final R_1 value was 30%) The Mn_4O_2 cluster core can be considered as quite proper, however.

Wu et al. used time-resolved FTIR and size exclusion chromatography (SEC) to study the influence of the ligands 2-aminomethylpyridine (amp) (a ligand already proposed by Wheeler, see Fig. 10, **10**) and 2-hydroxymethylpyridine (hmp), as compared to bpy, on the autoxidation and cross-link formation rates of ethyl linoleate catalysed by manganese 2-ethylhexanoate [86]. The ligands were also tested in a real alkyd system [86]. The ligand amp was reported to show a comparable effect on the rate and induction time as for bpy, while hmp shows a slightly shorter induction time and a larger rate. SEC was used to obtain insight in the rate of cross-link formation. Here, formation of dimers was observed after 4 h for the system containing hmp, after 6 h for amp and 8 h for the bpy system. In a real alkyd system, however, manganese + bpy showed the shortest drying time (7.5 h) followed by manganese + amp (9 h) and hmp (13 h). Hence, for these particular ligands, the trends observed with the model compound EL were not reflected in the used real alkyd system.

3.3.3. Driers not based on metal carboxylates

There are not many accounts of driers for alkyd paints not based on metal carboxylates. Zettlemoyer et al. did some drying experiments with modified hemin, the iron(III)–porphyrin complex isolated from hemoglobin [72]. The complex showed rapid drying of drying oils and the

Table 4
EL autoxidation activity of [Mn(hfac)$_2$] compared to Mn WEB, with and without added ligands

Catalyst	Ligands 3 equiv.	20% EL emulsion		Real alkyd paint drying time (h)[b]
		Induction time (min)	Rate ($\times 10^{-4}$ min^{-1})[a]	
Mn WEB	–	220	24.1	15
	amp	70	37.5	7
	hmp	150	54.2	71/2
Mn(hfac)$_2$	–	>500	–	n.d.
	amp	80	17.5	51/2
	hmp	50	18.5	8

[a] Relative rate calculated from: $-\ln([EL]_t/[EL]_{60} \times 100)$, a plot of the natural logarithm of the integral of the 3010 cm^{-1} peak in the FTIR spectrum, vs. time.

[b] White, water-borne paint based on a medium-oil alkyd emulsion siccativated with 0.06% Mn on solid binder. Drying time measured with a Braive drying recorder at 23 °C and 50% relative humidity.

prevention of loss-of-dry in pigmented systems (printing inks). The properties of dried ink films were not satisfactory, however, and this combined with the high cost of hemin made the complex unattractive as a commercial drier [72].

Metal acetylacetonates are simple, readily available metal complexes. Although they have received much attention as catalysts in the fields of autoxidation [87–89], polymerisation [90–94] and hydroperoxide decomposition [88,89,94–96], few studies have been performed on the use of metal acetylacetonates as possible paint driers. Indictor et al. and Bear et al. studied the autoxidation of linseed oil with acetylacetonates of the metals Co^{2+}/Co^{3+}, Cr^{3+}, TiO^{2+}, Cu^{2+}, Fe^{2+}/Fe^{3+}, Zn^{2+}, Mn^{2+}/Mn^{3+}, Al^{3+}, V^{3+}, VO^{2+}, Zr^{4+}, Pb^{2+}, K^{+} [68,69,97]. For each metal acetylacetonate, the viscosity change over time in the absence and presence of *tert*-butyl hydroperoxide, the dioxygen uptake of the sample, the weight change of the sample at different temperatures by thermogravimetry and the infrared spectra of autoxidized linseed oil samples was studied. The viscosity experiments showed the largest increase in viscosity (over a period of 13 days, at room temperature) for the acetylacetonates of Mn^{2+}, Mn^{3+}, Co^{2+}, V^{3+} and VO^{2+}. The thermogravimetric experiments at 60, 80 and 100 °C showed the highest rates of weight increase for the acetylacetonates of Co^{2+}/Co^{3+}, Mn^{2+}/Mn^{3+} and Fe^{2+}. Thus, not surprisingly, the acetylacetonate complexes that are active in the autoxidation of linseed oil are those containing the same metal ions as used for the metal carboxylates as primary driers in alkyd paint.

3.3.4. *New drier systems*

Recently, van Gorkum et al. and Wu et al. published reports concerning the possible use of manganese acetylacetonates as driers in alkyd paint [86,98]. To study the drier activity, FTIR and SEC were used to monitor the oxidation of EL, as described in Section 3.3.1.

Wu et al. tested bis(1,1,1,5,5,5-hexafluoroacetylacetonate)manganese(II) as a catalyst in the autoxidation of EL emulsified in water [86]. The reason for using [Mn(hfac)$_2$] was that the complex has a good solubility in both water and the alkyd phase.

The first 60 min of autoxidation could not be followed by FTIR due to the large absorption of water. After 60 min, all water was evaporated and the decrease of the 3010 cm^{-1} peak could be monitored. [Mn(hfac)$_2$] by itself was found not to be active in the autoxidation, when either one of the ligands hmp or amp were added however, induction times (after water evaporation) dropped below 100 min and the autoxidation proceeded at quite an acceptable rate. The results were compared to those obtained for a commercial water-emulsifiable manganese drier (Nuodex WEB Mn9), and the results are summarised in Table 4. The Mn WEB drier and [Mn(hfac)$_2$] were also tested in a real water-borne alkyd system, with and without additional ligands. Upon addition of the ligands amp or hmp, a lower activity than the Mn WEB drier was found for [Mn(hfac)$_2$] in the model system, in real paint however, the hexafluoroacetylacetonate complex showed comparable or better drying times than the commercial drier.

Van Gorkum et al. studied the use of [Mn(acac)$_3$] in the autoxidation of EL, and the effect of bipyridine on the autoxidation catalysed by [Mn(acac)$_3$] [98]. The results were compared to the activities of two commercial paint driers, Co 2-ethylhexanoate and Mn 2-ethylhexanoate, the FTIR results are shown in Fig. 12. It was found that [Mn(acac)$_3$] had a higher autoxidation activity than Mn 2-ethylhexanoate. When [Mn(acac)$_3$] was used together with 1 equiv. of bipyridine, the autoxidation rate surpassed even that of Co 2-ethylhexanoate. Since all reactions were done using purified

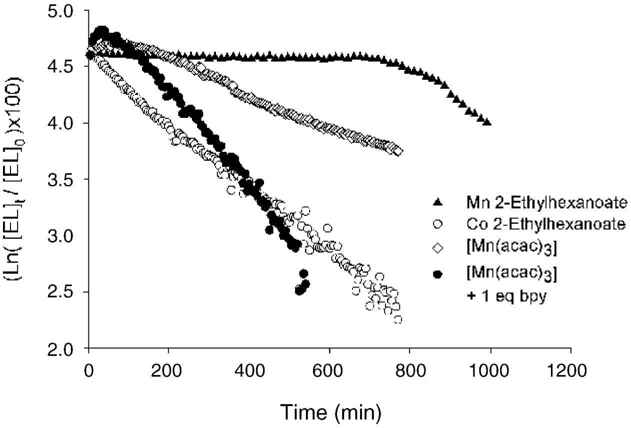
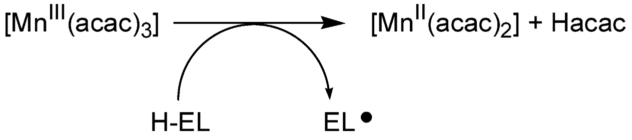


Fig. 12. Time-dependent integral plots of the 3010 cm^{-1} IR peak of purified EL, reaction with different autoxidation catalysts.



Scheme 6. Radical initiation by [Mn(acac)$_3$] trough hydrogen atom abstraction of the activated methylene group in ethyl linoleate.

EL (hydroperoxides had been removed), the induction times are a measure of the ability of the metal complexes to initiate the autoxidation reaction. [Mn(acac)$_3$], with and without bipyridine showed a short induction time, especially compared to Mn 2-ethylhexanoate. It was therefore, proposed that [Mn(acac)$_3$] is able to initiate the radical autoxidation *via* direct reaction with the substrate, as is depicted in Scheme 6.

The addition of bipyridine to [Mn(acac)$_3$] was found to drastically increase the autoxidation rate. To study the exact influence of bpy, the complex [Mn^{II}(acac)$_2$(bpy)] was prepared and studied with cyclic voltammetry. The voltammograms showed that for the complex [Mn^{II}(acac)$_2$(bpy)], the Mn(II)/Mn(III) oxidation and reduction peaks shift to a more positive potential compared to the Mn(II)/Mn(III) peaks for [Mn^{III}(acac)$_3$], as shown in Fig. 13. From these data it was concluded that [Mn^{III}(acac)$_3$] is more easily reduced in the presence of bpy, since it can form the stable complex [Mn^{II}(acac)$_2$(bpy)]. It was further proposed that both initiation and hydroperoxide decomposition are enhanced by the facilitated reduction of Mn(III) to Mn(II). In catalytic hydroperoxide decomposition according to the Haber-Weiss reactions (Section 2.1), the reduction of Mn(III) is always the slowest step. Addition of bpy clearly accelerates this step and thus removes the bottleneck for the autoxidation.

[Mn(acac)$_3$] was also tested in real alkyd systems, and the drying times obtained were compared to the results obtained with conventional drier systems [67]. An example of the results is presented in Table 5. As can be concluded from these results, [Mn(acac)$_3$] performs even better than the commercial manganese and cobalt driers. The enhancing effect of bipyridine is not apparent in real paint, however.

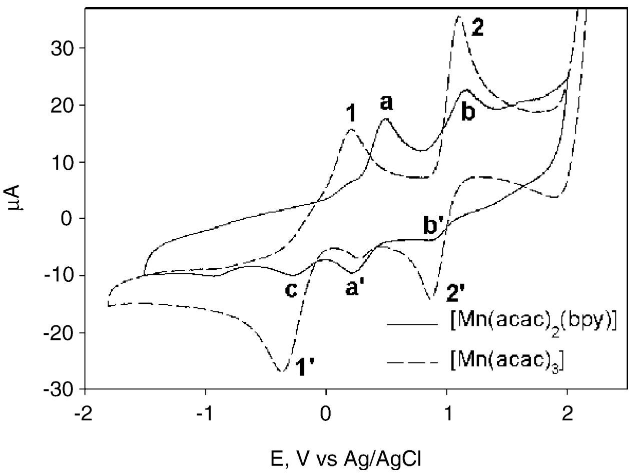


Fig. 13. Cyclic voltammograms of [Mn(acac)$_3$] and [Mn(acac)$_2$(bpy)] in CH$_3$CN, [nBu$_4$N](PF$_6$) as electrolyte, scan rate 200 mV/s. Selected potentials: 1/1′ 0.222/−0.373 V; a/a′ 0.50/0.203 V; 2/2′ 1.111/0.862 V; b/b′ 1.165/0.891 V; c −0.28 V.

Table 5
Drying times in real alkyd paint[a]

Drier	Drying time in hours (Braive recorder), 76 µm at 23 °C and 50% relative humidity		
	Stage a	Stage b	Stage c
Co–Ca–Sr[b]	1.15	2.15	6.45
Mn–Ca–Zr[c]	1.30	12.30	16.00
Mn-bpy[d]	1.30	6.30	10.00
[Mn(acac)$_3$]	1.15	2.15	4.00
[Mn(acac)$_3$] + bpy	1.15	3.00	5.00

[a] The drying time was measured in a clear varnish based on Uralac AD 152 WS-40 from DSM Resins (a medium oil alkyd resin based on soy-bean oil, 47% oil).

[b] Commercial cobalt combination drier.

[c] Commercial manganese combination drier.

[d] Commercial manganese drier based on manganese 2-ethylhexanoate and bipyridine.

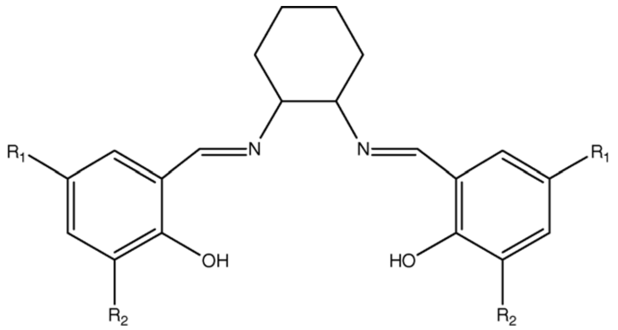


Fig. 14. Examples of salen type ligands used with manganese as alkyd paint driers. Substituents are $R_1 = R_2 =$ *tert*-butyl, or $R_1 =$ a dodecyl chain, $R_2 =$ H.

In a recent patent by Boomgaard et al., new manganese driers for alkyd paints are described based on manganese complexes with substituted *salen*-type ligands [99]. Typical ligands consist of the condensation product of 1,2-diaminocyclohexane and two equivalents of a 2-hydroxybenzaldehyde with alkyl substituents, to promote solubility in apolar paint mixtures. In Fig. 14 two examples of the used ligands are shown.

In a patent by Micciché et al. a drying system based on an iron carboxylate and a reducing agent is described [100]. As was mentioned in Section 3.1, iron compounds are not

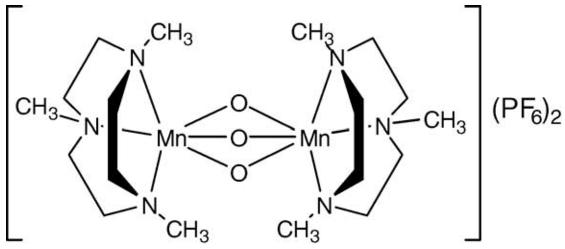
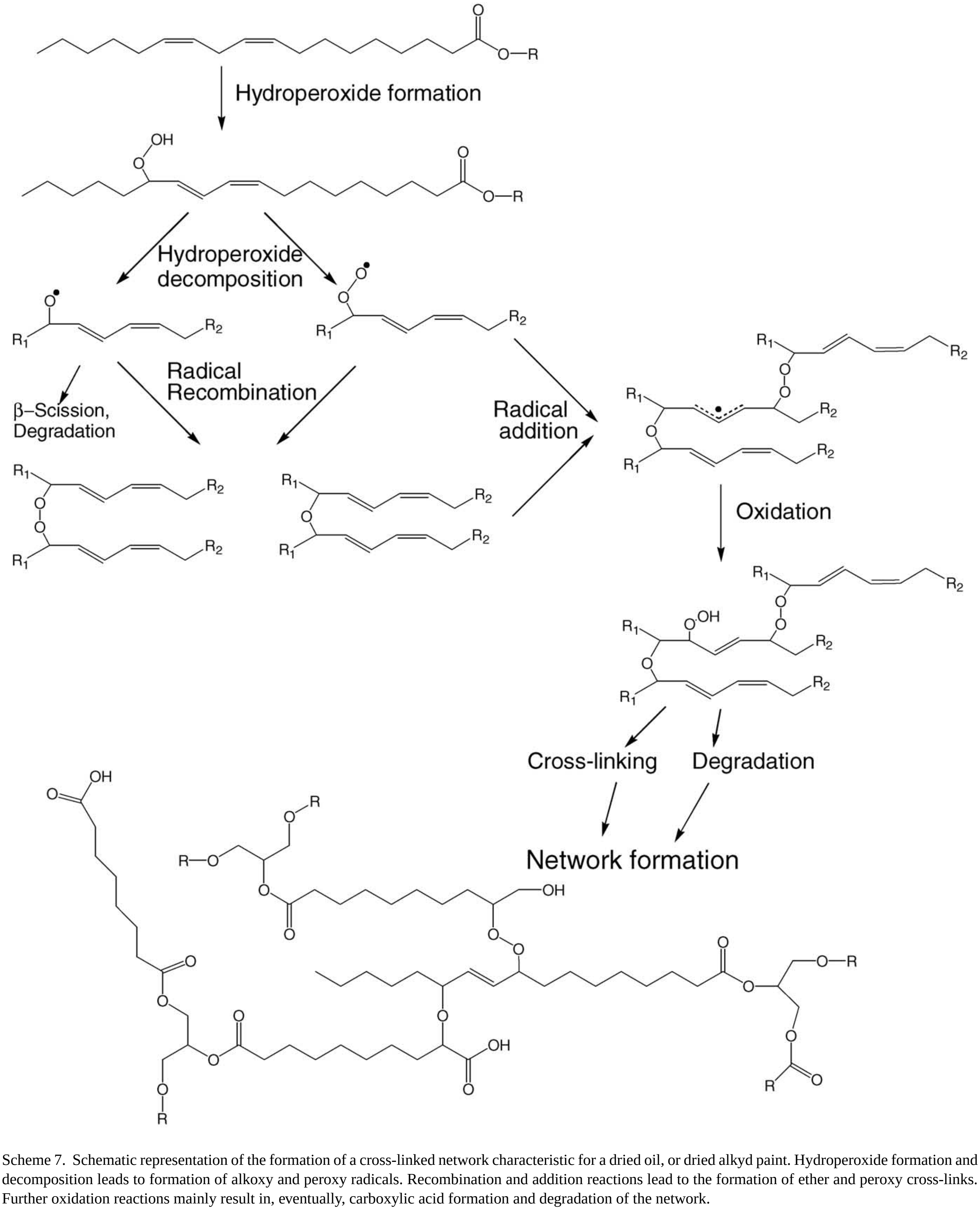


Fig. 15. [Mn(IV)$_2$(Metacn)$_2$(µ-O)$_3$](PF$_6$)$_2$, Metacn = 1,4,7-trimethyl-1,4,7-triazacyclononane.



Scheme 7. Schematic representation of the formation of a cross-linked network characteristic for a dried oil, or dried alkyd paint. Hydroperoxide formation and decomposition leads to formation of alkoxy and peroxy radicals. Recombination and addition reactions lead to the formation of ether and peroxy cross-links. Further oxidation reactions mainly result in, eventually, carboxylic acid formation and degradation of the network.

effective driers at room temperature, since the reduction of iron(III) to iron(II) by hydroperoxides proceeds slow in apolar media. By adding a reducing agent such as ascorbic acid or derivatives thereof, a drying system was obtained which showed comparable drying results as were obtained with cobalt driers [100].

Oyman et al. have used SEC, FTIR and Raman spectroscopy as well as oxygen uptake experiments to evaluate the manganese complex $[Mn(IV)_2(Metacn)_2(\mu\text{-}O)_3](PF_6)_2$ (MnMetacn, see also Fig. 15) as an oxidation catalyst for EL and a possible drier for alkyd emulsion coatings [101]. The complex was found to have a slightly higher EL oxidation activity than the commercially available manganese catalyst Nuodex-Web-Mn but a much lower activity compared to a cobalt drier (Nuodex-Web-Co). Adding 1 or 3 equivalents of the compound 1,1,4,7,10,10-hexamethyl triethylenetetraamine (hmteta) to MnMetacn resulted in higher oxidation rates and lower maximum peroxide values in the oxidation of EL. These observations together with SEC results, which showed that adding more than 3 equiv. of hmteta resulted in a *decrease* in oligomer formation, led to the conclusion that hmteta probably only increases the hydroperoxide decomposition rate, not the rate of oligomerisation [101]. With hmteta added to MnMetacn, the EL oxidation rate was found to be comparable with the rate found for the cobalt drier [101].

4. Concluding remarks

4.1. A summary of alkyd paint drying

The work described in Section 2 draws a clear picture of the reactions involved in the drying of a fatty acid ester, drying oil or alkyd paint binder resin. Based on these data, a scheme can be drawn (Scheme 7) that summarises the different steps of the formation of a dried paint network. In all cases the first step is hydroperoxide formation, with concomitant formation of conjugated double bonds in the case of fatty acids that contain the pentadienyl moiety. The drier catalyses hydroperoxide decomposition, which results in the formation of peroxy and alkoxy radicals. Through recombination of these radicals, ether and peroxide cross-linked dimers are formed. The species with conjugated double bonds are prone to radical addition reactions, and thus in the later stages of drying this is the most important route to cross-link formation. Alkoxy radicals give rise to β-scission reactions which leads to degradation of the network, and results in the formation of numerous oxidation products such as epoxides, aldehydes and ketones, most of which will be oxidised further to alcohols and carboxylic acids. Over time, all unsaturation disappears, as do the peroxide cross-links. What most likely remains is a network of predominantly carboxylic acid C_9 chains, linked via ester bonds and ether cross-links.

4.2. The need for improved knowledge of paint drier chemistry

Early research into paint drier chemistry has mostly been on a trial-and-error basis, seemingly with the motive that if a drier dries paint, no further attention is needed. Only a few publications go into detail on the mechanisms of drier action [64,65,70,98]. The increase in environmental regulations make knowledge of drier chemistry of the utmost importance, however. Many water-borne coatings require new and improved drier systems, as do high-solids paints. Replacement of the toxic cobalt salts as driers in alkyd paint still poses a challenge. The replacement of other toxic compounds in alkyd paint, such as the anti-skinning agent methylethylketoxime (MEKO), also requires knowledge of how this compound interacts with the drier [102,103]. It is opportune that coordination chemists take a more detailed look at the chemistry involved in paint drying.

Acknowledgements

Financial support from the Dutch Ministry of Economic Affairs, as part of the SENTER/Innovation Oriented Research Program on Heavy Metals (IOP) No. IZW99241c, is thankfully acknowledged. Support by the Netherlands Research Council for Chemical Sciences (CW) with financial aid from the Netherlands Technology Foundation (STW) in the Priority Program Materials and by the Netherlands Ministry of Economic Affairs (BTS 98141) is also kindly acknowledged. Professor Dr. Jan Reedijk and Dr. Sabine Warzeska are acknowledged for most helpful discussions.

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