Manganese Complexes as Drying Catalysts for Alkyd Paints

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Alkyd paint and paint driers.†

1.1 Introduction

1.1.1 A brief history of paints and coatings[1-4]

Paints and coatings occupy a prominent place in the cultural history of mankind. People have always been fascinated with colors and used paints to decorate and beautify themselves and their environment. Archaeologists found pigments and paint grinding equipment in Zambia (Southern Africa), thought to be between 350,000 and 400,000 years old. The oldest testimony of artistic activity was found in the south of France where some 30,000 years ago our prehistoric ancestors decorated the walls of their cave dwellings with stunning animal drawings. The ancient paints consisted of animal fat and colored earth or natural pigments such as ochre. Hence, they were based on the same principle as the paints that are used today - a binder and a coloring agent. Around 3000 BC, Egyptians began using varnishes and enamels made of beeswax, gelatin and clay – and later protective coatings of pitch and balsam to waterproof their wooden boats. About 1000 BC, the Egyptians created varnishes from Arabic gum. Independently, the ancient Asian cultures developed lacquers and varnishes and by the 2nd century BC, these were being used as coverings on a variety of buildings, artwork and furnishings in China, Japan and Korea. The ancient Chinese knew how to make black lacquer (the true predecessor of modern coatings) from the sap of the lacquer tree *Rhus Vernicifera*. In India, the secrete of the lac insect *Coccus lacca* was used to produce a clear coat to beautify and protect wooden surfaces and objects. The early Greeks and Romans also relied on paints and varnishes, adding colors to these coatings and applying them on homes, ships, and artwork. It was not until the industrial revolution and ensuing mass production of linseed oil, however, that the production of modern house-paints began.

Over the decades, formulations of paints and coatings have become more and more sophisticated. Today, coatings not only protect and beautify the substrate. They also have functional properties: they are used as anti-skid surfaces, they can insulate or act as an electrical conductor, they can reflect or absorb light, etc. Paints and coatings play an indispensable role in our modern world and cover virtually everything we use from household appliances, buildings, cars, ships, airplanes to computers, microchips or printed circuit boards.

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† This chapter is based on: R. van Gorkum and E. Bouwman, *Coord. Chem. Rev.* **2005**, in press

1.1.2 Alkyd paint

A modern paint is a complex mixture of components (Table 1.1).[5] 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 Fig 1.1. Paints based on alkyd resin binders are usually solvent-borne paints, common solvents being white spirit (a mixture of saturated aliphatic and alicyclic C_7-C_{12} hydrocarbons with a content of 15-20% (by weight) of aromatic C_7-C_{12} hydrocarbons), or xylene. Although European legislation drives paint development towards water-borne systems, in order to reduce the amount of VOC's (volatile organic compounds) in the atmosphere, solvent-borne paints often show a number of advantages over water-borne paints. Examples are: 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. As a result solvent-borne coatings will not be totally replaced by water-borne coatings in the foreseeable future, according to the paint industry.[1] Further important components of alkyd paint are pigments and extenders. The pigment is the substance that gives the paint color. Pigments 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 let down colored pigments of great tinting strength.[6] The last important category of components of alkyd paint comprises 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

Table 1.1:
Typical paint composition

Component	Weight-%
binder	30
organic solvent	27
water	10
pigments	19
extenders	12
additives	2

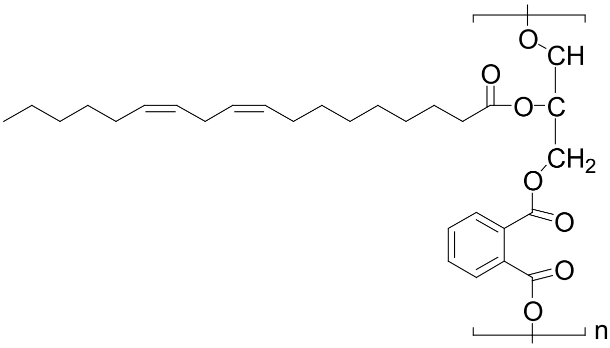


Figure 1.1: Example of an alkyd resin used as a binder compound in alkyd paint. The fatty acid chain shown is linoleic acid.

catalysts, or driers.[5] Driers are metal soaps or coordination compounds which accelerate paint drying, thus shortening the total drying time. Without driers, the drying time of alkyd paint would be over 24 hours, which is clearly undesirable for most applications.

1.1.3 The drying of alkyd paint[5]

During the drying of alkyd paints several 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 forms through coalescence of the binder particles. Then chemical drying (also called oxidative drying) occurs, a lipid autoxidation process, which means that the paint dries by oxidation of the binder compound with molecular oxygen from the air. Autoxidation will be discussed in detail in the next section. During the drying process four overlapping phases can be discriminated:

- Induction period
- Hydroperoxide formation
- Hydroperoxide decomposition into free radicals
- Polymerisation / crosslinking

The induction period is the time between application of the paint to a surface and the start of dioxygen uptake by the paint film. The induction period occurs because the effects of solvent, anti-skinning agent and natural anti-oxidants that may be present in the alkyd resin must be overcome before the drying process can begin. Autoxidation of the unsaturated fatty-acid chains in the alkyd binder then gives rise to hydroperoxides with uptake of atmospheric oxygen. Decomposition of these hydroperoxides results in the formation of peroxide and alkoxide radicals. These radicals initiate the polymerisation of the unsaturated molecules of the binding medium. Polymerisation occurs through radical termination reactions forming cross-links, causing gelling of the film, which is followed by drying and hardening. The number of cross-linked sites that are formed determines the film hardness. Cross-link formation is irreversible; hence when a paint layer has dried it cannot be easily removed.

1.2 Metal-catalysed autoxidation

1.2.1 Autoxidation in general

Autoxidation is the direct reaction of molecular oxygen with organic compounds under relatively mild conditions.[7] More specifically, autoxidation is described as the insertion of a molecule of oxygen into a C-H bond of a hydrocarbon chain to give an alkyl hydroperoxide.[8] Autoxidation and metal-catalysed autoxidation has been extensively studied for numerous substrates under various reaction conditions.[8-15] Generally, an induction time is observed after which the autoxidation reaction abruptly starts and rapidly attains a limiting, maximum oxidation rate.[12, 13, 16, 17] The reaction proceeds by a free-radical chain mechanism and can be described in terms of initiation, propagation and termination. Scheme 1.1 shows the generally accepted reaction steps.

Initiation can occur via several different pathways, either metal mediated or not. Steps **1** and **2** in Scheme 1.1 are often proposed as the initiation steps in non-metal-

Initiation.

$RH + \text{Initiator} \rightarrow R^{\bullet} + \text{Initiator-H}$ **1**

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

$ROOH + M^{n+} \rightarrow RO^{\bullet} + M^{(n+1)+} + {}^{-}OH$ **3**

$ROOH + M^{(n+1)+} \rightarrow ROO^{\bullet} + M^{n+} + H^{+}$ **4**

$M^{n+} + O_2 \leftrightarrow [M^{(n+1)+}(O_2)^{-}]^{n+}$ **5a**

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

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

Propagation

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

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

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

Termination

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

$2\ ROO^{\bullet} \rightarrow R{=}O + ROH + {}^{1}O_2$ **11a**

$2\ ROO^{\bullet} \rightarrow ROOR + O_2$ **11b**

$ROO^{\bullet} + M^{n+} \rightarrow ROO^{-} + M^{(n+1)+}$ **12**

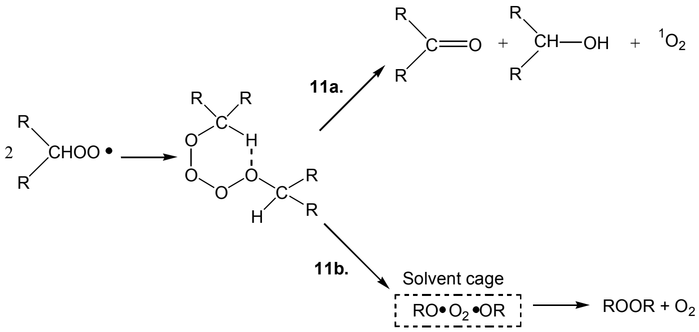
$R^{\bullet} + M^{(n+1)+} \rightarrow [R\text{–}M^{n+}]^{n+}$ **13**

Scheme 1.1: Radical chain reactions as occuring in metal-catalysed autoxidation.

mediated autoxidation.[5, 18] Step **1** is the reaction of some arbitrary initiating species with the substrate, directly forming a carbon-centred radical. Reaction **2** is the thermal homolytic decomposition of a hydroperoxide, which only plays a significant role at elevated temperatures. In metal-mediated initiation, the initiation of radical chains predominantly occurs through steps **3** to **6**. Reactions **3** and **4** are the so-called Haber-Weiss reactions, originally proposed for the decomposition of H_2O_2 by iron in aqueous media.[19] This set of reactions is the generally accepted mechanism by which hydroperoxides are decomposed in polar media by a metal with two stable oxidation states differing one electron. The situation is different in apolar media,[8, 14] however, as will be discussed in the next section. Reaction **4** generally is slower than reaction **3**.[20] Initiation reaction **5a,b** involves the activation of molecular oxygen by the metal in the lower oxidation state, forming a metal-superoxide complex (**5a**). This complex can then abstract a hydrogen atom from the substrate to form a hydroperoxide complex and a carbon radical (**5b**). This initiation pathway operates predominately in apolar media.[21] In the last initiation reaction in scheme 1.1, reaction **6**, a carbon radical is formed by direct reaction of the higher-valent metal ion with the substrate.[8, 15, 22]

The most important propagation reactions are reactions **7** and **8**. Reaction **7** is extremely rapid (diffusion controlled, $k \sim 10^{9}\ \mathrm{l \cdot mol^{-1} \cdot s^{-1}}$) except at very low partial pressures of dioxygen (dissolved-oxygen concentration $<10^{-3}$ M) and therefore in non-metal catalysed reactions only peroxy radicals are of importance in chain propagation.[10, 18, 23] Reaction **8** is relatively slow and thus it is the rate-determining step for the formation of hydroperoxides. Since the peroxy radical in reaction **8** is comparatively unreactive it has a strong preference for the abstraction of the most weakly bound hydrogen atom of the hydrocarbon substrate.[23] One initiation event can set off the cycle between reactions **7** and **8**, which is why these reactions are responsible for a large increase in hydroperoxide concentration during the first stages of autoxidation. Hydroperoxide formation will eventually be balanced by hydroperoxide decomposition, however, resulting in a steady state concentration of hydroperoxides in polar media. This is the main reason for autoxidation to attain a limiting rate.[12-14, 16, 17] Alkoxide radicals can only be formed through metal-catalysed autoxidation, *via* reaction **3**. These alkoxide radicals can also propagate radical chains via reaction **9** or various other reactions, see section 1.3.4 for examples.

Termination reaction **10** is not a dominant reaction. Alkoxide radicals are much too reactive and hence their concentration is rather low. Under most autoxidation conditions, the only significant termination reaction is the reaction of two peroxyl radicals with each other (reactions **11a** and **11b)**.[11] Reaction **11a** proceeds according to the Russell-mechanism,[18, 24] where a tetraoxide intermediate is formed which decomposes to yield non-radical products: an alcohol, ketone and singlet oxygen. The other bimolecular peroxyl radical termination reaction, reaction **11b**, leads to a peroxide cross-link. This reaction is proposed to proceed also via a tetraoxide intermediate,[25] some speculation regarding the validity of that proposal remains, however.[26, 27] In Scheme 1.2 the tetraoxide intermediate and the course of termination reactions **11a** and **11b** is shown.



Scheme 1.2: Bimolecular peroxyl radical termination *via* a tetraoxide intermediate. In reaction **11a** (the Russel mechanism) an alcohol, ketone and singlet oxygen are formed. In reaction **11'**, the tetraoxide intermediate decomposes to yield two alkoxyl radicals, which recombine in the solvent cage to form a peroxide cross-link.

The role of the metal ion in a metal-catalysed autoxidation is to create new radical chains, as can be readily seen in Scheme 1.1. Due to the abundance of hydroperoxides formed trough the cycle of reactions **7** and **8**, this will be mainly by hydroperoxide decomposition, reactions **3** and **4**. Common transition metals capable of hydroperoxide decomposition are Fe, Cu, Co, Mn, Ti, V and Ce.[8, 15] The reactivity of these metal ions towards hydroperoxides depends mostly on the redox potential of the $M^{n+}/M^{(n+1)+}$ pair and thus on the polarity of the solvent and the coordination environment of the metal ion. A metal compound has to be able to perform both reaction **3** and **4**, or **3** and **6** so that each change of its oxidation state starts a new radical chain.[8]

Metal ions can also act as potent *inhibitors* of autoxidation,[14, 28-30] by means of reactions **12** and **13** in Scheme 1.1. Reaction **12** commonly occurs for Mn^{2+} and Co^{2+} metal salts and this reaction can completely suppress autoxidation when the concentration of metal ions is higher than the hydroperoxide concentration.[14, 15] Particularly for manganese(II) complexes, reaction **12** is one of the causes for the induction time that is often observed for metal-catalysed autoxidation reactions. To eliminate this induction time, the $[Mn^{2+}]/[ROOH]_0$ ratio has to be less than one.[31] Higher valent metals might be able to inhibit autoxidation (at low oxygen concentration) by scavenging carbon radicals, reaction **13** in scheme 1.1. Cu^{2+} and Fe^{3+} ions have been shown to readily reduce certain carbon radicals.[32, 33]

An extensive treatment of the general kinetics of metal-catalysed autoxidation will not be given here, but the interested reader is referred to an excellent review by Reich and Stivala.[34]

1.2.2 The autoxidation of alkyd paint

1.2.2.1 General considerations

Several aspects of alkyd paint autoxidation are typical for the alkyd system:

- Autoxidation occurs in an apolar environment
- Oxidations take place at the fatty acid tail of the alkyd resin
- Oxidation leads to cross-link formation.

These different aspects are highlighted in the following sections.

1.2.2.2 Autoxidation in apolar media: metal-hydroperoxide complex formation

Autoxidation drying starts when all solvent is evaporated. Consequently, autoxidation takes place in a mixture of pure alkyd resin and pigments, which is very likely a significantly apolar environment. This has some consequences for the autoxidation reactions, *i.e.* ionization processes will be suppressed and metal salts will not dissociate into ions.[9] The most notable consequence for autoxidation of the alkyd system is that the Haber-Weiss reactions **3** and **4** do not occur in apolar media. Hydroperoxides are decomposed following metal-hydroperoxide complex formation, as shown in scheme 1.3.[9, 10, 14, 35, 36] This has some far-reaching implications for metal catalysis, since reaction **4b** in scheme 1.3 has been reported to be very slow for simple metal salts.[10]

$$ROOH + M^{n+} \rightleftharpoons [(ROOH)M]^{n+} \qquad \mathbf{3a}$$

$$[(ROOH)M]^{n+} \rightarrow RO^{\bullet} + [(M^{(n+1)+}(OH^{-})]^{n+} \qquad \mathbf{3b}$$

$$ROOH + M^{(n+1)+} \rightleftharpoons [(ROOH)M]^{(n+1)+} \qquad \mathbf{4a}$$

$$[(ROOH)M]^{(n+1)+} \rightarrow ROO^{\bullet} + M^{n+} + H^{+} \qquad \mathbf{4b}$$

Scheme 1.3: Metal–hydroperoxide complex formation in media of low polarity

Thus, reduction of the higher valence state metal is proposed not to be accomplished by hydroperoxides, but rather by easily oxidizable autoxidation products such as aldehydes and alcohols or directly by the substrate (reaction **6** in scheme 1.1).[10, 22] Metal-hydroperoxide complex formation is also thought to account for the very sudden conversion of catalyst into inhibitor upon steadily increasing the metal concentration.[14] In apolar media, metal salts will form a complex with a hydroperoxide as long as the hydroperoxide is available. Metal ions that are not coordinated can participate in the inhibiting reaction **12** in scheme 1.1, and thus sudden inhibition of autoxidation occurs if the metal concentration becomes higher than the hydroperoxide concentration.[14, 30, 31]

1.2.2.3 Fatty acid autoxidation

The fatty acid tail of the alkyd resin (Fig 1.1) is where autoxidation takes place. 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.[7, 27]

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,[37] 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 of non-conjugated polyunsaturated fatty acids (or lipids) for autoxidation comes from the presence of *bis*-allylic hydrogen atoms, which have a relatively low bond dissociation energy of 75 kcal/mol (see Fig 1.2)

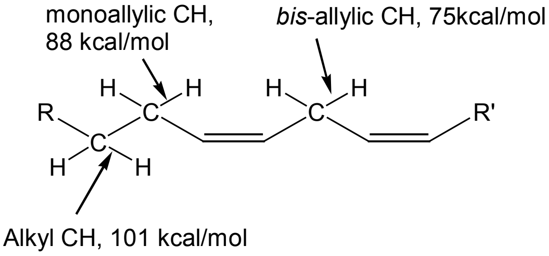
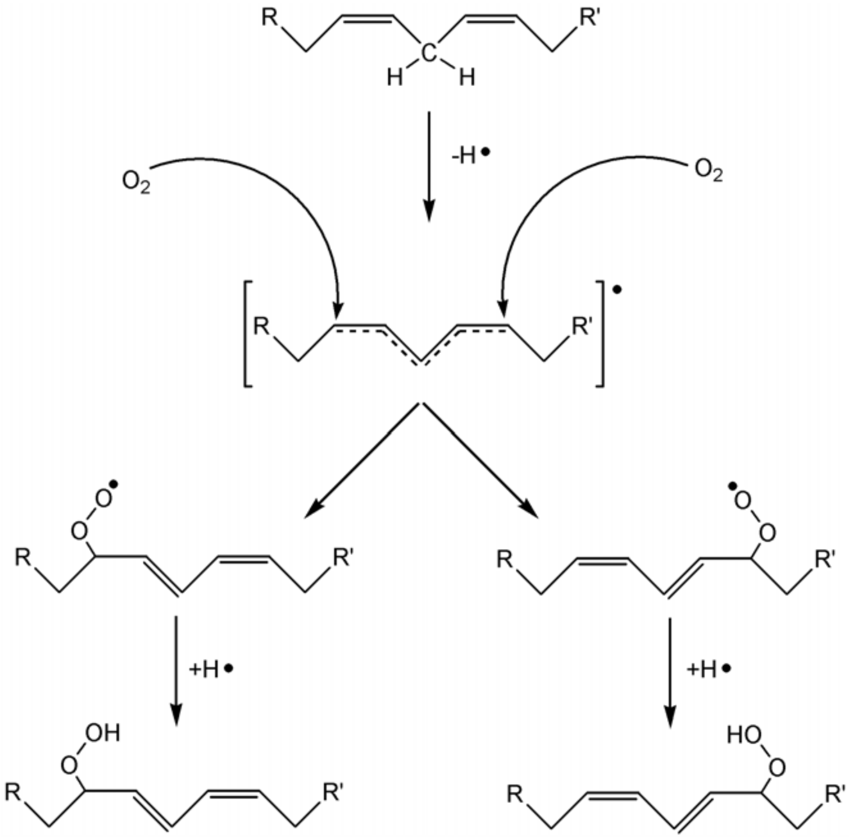


Figure 1.2: Bond dissociation energies of the different CH bonds in fatty acids

and can therefore be easily abstracted, resulting in radical chain initiation and thus autoxidation.[27, 38, 39] Abstraction of one of the *bis*-allylic hydrogen atoms results in the formation of a radical species. This radical species is stabilised by delocalisation due to the local pentanediene structure. Molecular oxygen reacts extremely rapid with this pentanedienyl radical species to form a peroxy radical which has the double bonds dominantly conjugated, since this is the most stable structure.[7] The peroxyl radical can then participate in a host of reactions, as was outlined in section 1.2.1 and scheme 1.1, but in the early stages of autoxidation the dominant reaction will be to abstract a hydrogen atom from another lipid molecule to form a hydroperoxide and propagate the radical chain (reaction **8** in scheme 1.1). Scheme 1.4 shows the initial autoxidation reactions for a fatty acid pentanediene substructure, forming a hydroperoxide. Figure 1.3 shows the total time course of fatty acid 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.



Scheme 1.4: Initial hydroperoxide formation in the autoxidation of the fatty acid chain of an alkyd resin binder unit.

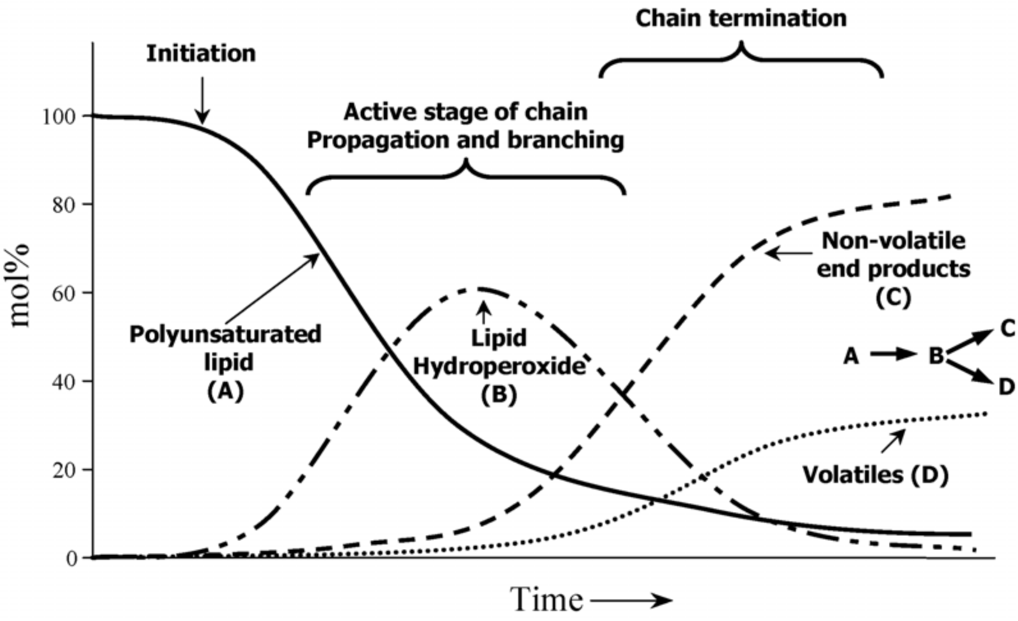


Figure 1.3: time course of fatty acid (lipid) autoxidation,redrawn after Gardner.[41]

1.3 Studies into the drying and cross-linking mechanisms of alkyd paint

1.3.1 General

Since the mechanisms of lipid autoxidation are fairly well understood,[7, 34] in the last decade the most significant advancements in the understanding of 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.

A general review of earlier work regarding all aspects of the polymerisation of drying oils was given by Wexler,[40] and several recent reviews are available covering fatty acid autoxidation.[7, 41] The Paint Research Association has published a report regarding the drying of linoleic-based coatings,[42] and also a recent review is available about the *yellowing* (discoloration over time) of dried oil films, studied with the model compound methyl linolenate.[43] Yellowing is caused by over-oxidation of the coating and is a general problem for alkyd coatings. The yellowing process will not be discussed.

1.3.2 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. In most of the studies discussed in this section, no drying catalysts are used. Autoxidation of the oils is then accomplished thermally or *via* photo-oxidation.

The structure of a dried film of soya oil has been studied by Falla with GLC (gas liquid chromatography) and infrared spectroscopy (IR).[42] Soya oil was dried as a thin film on glass using cobalt and lead driers (see section 1.4 for more information concerning 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 hr 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.[44] 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. 1.4).[42]

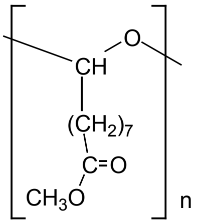


Figure 1.4: A postulated structure for the dried film polymer of soya oil. Terminal groups could include OH, COOH and CHO.[42]

Lazzari *et al.* studied the drying and oxidative degradation of linseed oil by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC) and size exclusion chromatography (SEC).[45] 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-oxidised at 80 °C, or irradiated with wavelengths > 295 nm. Analysing the film dried at 80 °C after 6 hours with FTIR, the same observations were made as reported by van de Voort *et al.* in a study concerning the oxidation of edible oils.[46] After an induction time of 4 hours, the peak due to hydroxyl groups rapidly increased and reached a constant value after 8 hours, while isolated double bonds disappeared.[45] An insoluble polymer was formed after extended oxidation times at 80 °C (up to 150 hours). 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 shows 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.[45]

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.[45]

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.[47-49] 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.[47] Samples were spread out as a thin film on a either a KBr or a glass window, after which they were oxidised in a ventilated oven at 60 °C in the dark. After oxidation for 30 hours a very weak peak at 885 cm^{-1} evidenced the formation of *trans* epoxides.[47] Oxidised samples were treated with NO after increasing reaction times to differentiate between alcohol and hydroperoxide formation. NO reacts with alcohols to form a nitrite ester (R-O-N=O), which has a specific band at 779 cm^{-1}.[47] 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. 1.5.

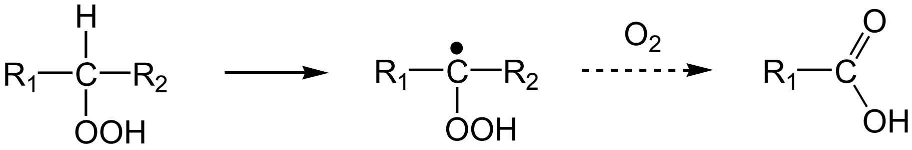


Figure 1.5: Carboxylic acid formation *via* hydrogen atom abstraction and subsequent β-elimination reactions and oxidation.

Raman spectroscopy of a linseed oil film heated at 60 °C up to 50 hours shows a broad band appearing around 850 cm^{-1}.[47] 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.[47]

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.[48] 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.[48] 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.[49] In comparison, the thermo-oxidation of a dried linseed oil film at 100 °C for up to 1000 hours 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.[49]

1.3.3 Studies with fatty acid esters

1.3.3.1 General observations in ethyl linoleate drying

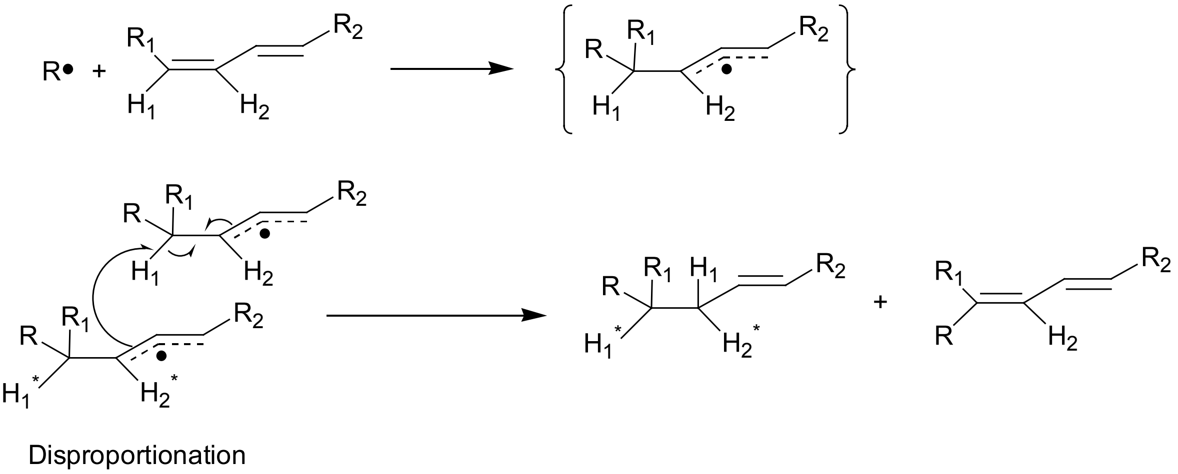
In the last decade, Muizebelt and colleagues made important advancements concerning knowledge of the oxidative crosslinking of alkyd resins.[50-52] Fatty acids or fatty acid esters were used as model compounds to study the cross-linking reactions that occur under the reaction conditions of a drying alkyd paint, *i.e.* a thin film air-dried by a Co/Ca/Zr combination drier (see section 1.4.2) at room temperature. Ethyl linoleate autoxidation was monitored over an extended period of time (up to 1 year) using several analytical techniques.[50] In the oxidation of technical grade EL (composition about 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 even after 110 days there is still some unreacted ethyl oleate left. The relative reactivity of ethyl oleate vs 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.[53] 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 assigned 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.[50]

1.3.3.2 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 spectroscopy, quantitative ^{13}C NMR spectroscopy and ^{13}C NMR spectroscopy with the so-called POMMIE technique.[50, 52] The POMMIE ^{13}C-NMR technique yields sub-spectra 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 yield 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 two 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 an overall formation of ether links from double bonds occurs.[50] The amount of dimeric C-C cross-linked material formed in the autoxidation of EL was determined to be about 5%.[50]

1.3.3.3 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).[51] With SIMS, oligomeric species up to pentamers could be detected after one day of drying.[51] 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 above 300 amu (EL = 308 amu).[51] 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 $[(\mathrm{EL}\text{-}\mathrm{H})_2 + n\mathrm{O}, n = 0\text{-}5]$ and trimers which followed the general formula $[3\mathrm{EL}\text{-}x\mathrm{H} + n\mathrm{O}, x = 2 \text{ or } 4]$. 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 (2EL + *n*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 at the double bonds of dimers, related to the occurrence of peaks with masses of either (3EL-4H), or (3EL-2H), respectively.[51] 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.[54] 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 isomer of linoleic acid (9,11-octadecadienoic acid, methyl ester).[51] The mass spectra of dried reaction mixtures of MR showed all peaks doubled with a mass difference of 2 amu as compared with 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 1.5. 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 in the presence of a cobalt catalyst resulted in the formation of a cross-linked co-polymer.[51]



Scheme 1.5: Radical addition to a conjugated double bond and subsequent disproportionation, yielding species of two mass units apart.

Modern “high-solid” alkyd paints contain so-called “reactive diluents”.[55] 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.[55] 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 found to be 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.

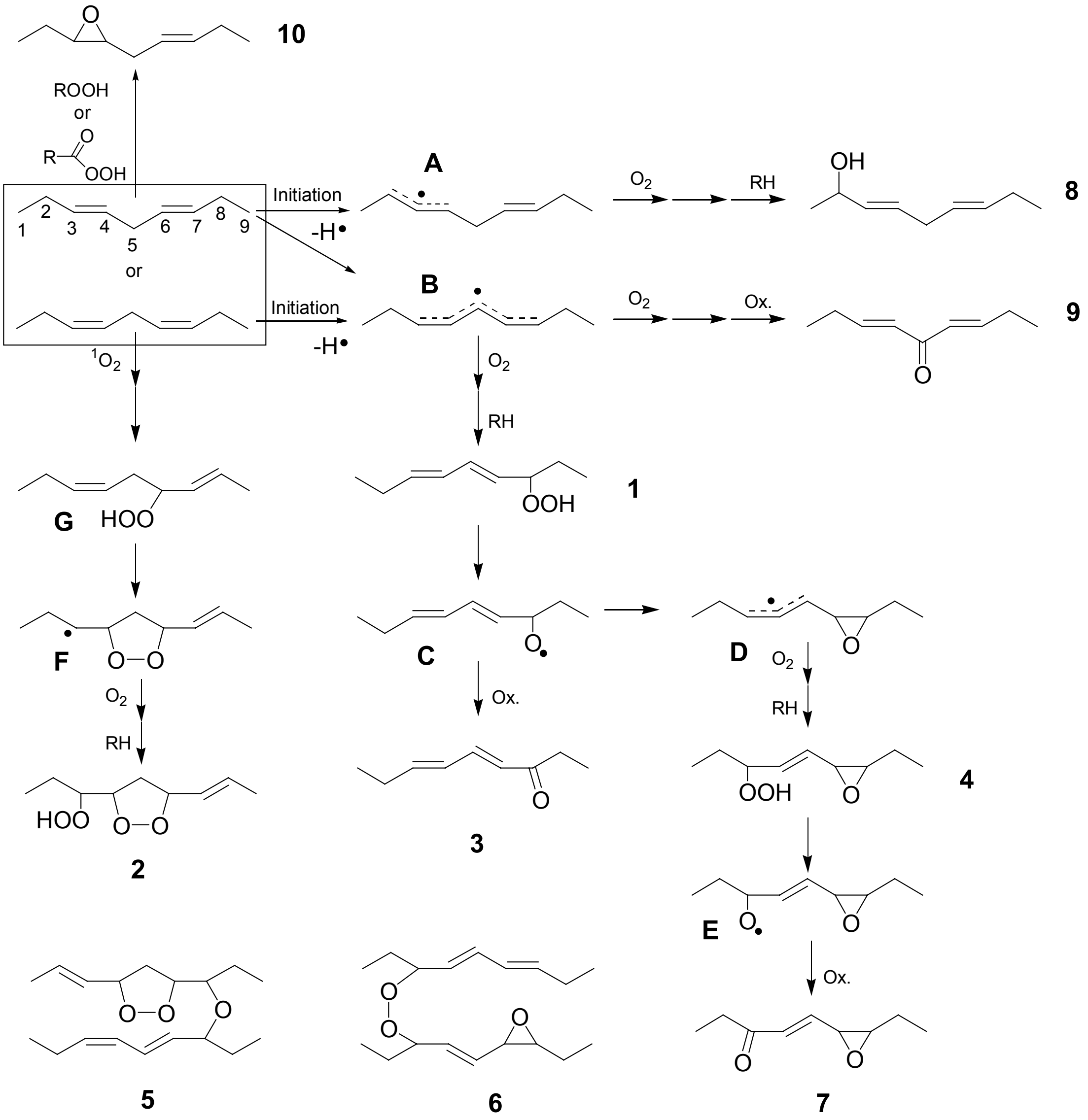
In a recent study, Oyman et al. studied the drying of several fatty acid esters (EL, methyl linoleate (ML), and methyl linolenate (MLn)) emulsified in water, to mimic water-borne alkyd paints.[56] The autoxidation was catalysed by a water-emulsifiable cobalt drier and the reaction was monitored by FTIR and Raman spectroscopy on emulsion films. The main conclusions from that study were that fatty acid ester oxidation does not take place during water evaporation from the emulsion film, and that the oxidation reactions proceed in exactly the same way as for non-aqueous systems once all water has evaporated.[56]

1.3.4 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.[57] 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.[58-60]

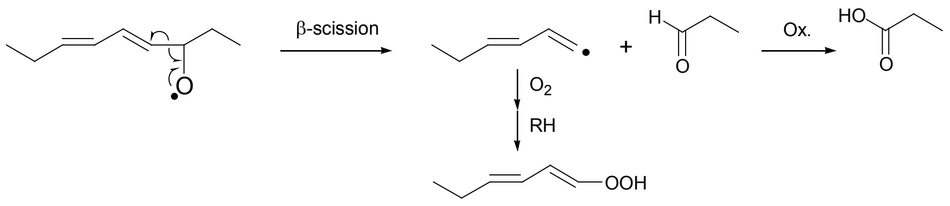
The nonadiene isomers were allowed to react with dioxygen in the presence of a cobalt catalyst for a period of 65 hours up to 1 week. Since the nonadiene isomers are rather volatile, the reaction was performed in a closed vessel with a sufficient amount of air present. The reaction products were separated by preparative HPLC and SEC and analyzed 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 1.6. 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.[57]

Products **1** through **10** shown in Scheme 1.6 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).[57] Aldehydes and carboxylic acids can be formed through β-scisson reactions of alkoxy radicals; see Scheme 1.7 for an example.



Scheme 1.6: 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.[57]

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 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.[61] Peracids can be formed by oxidation of aldehydes. A singlet-oxygen pathway was also found to exist, since the



Scheme 1.7: Example of a β-scission reaction leading to chain breaking and formation of aldehydes and carboxylic acids.[57]

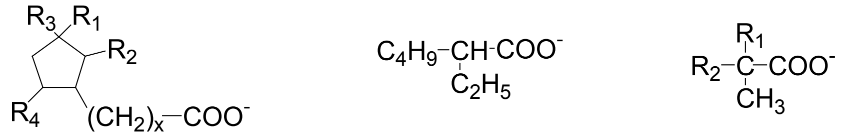
endoperoxide compound **2** was isolated. This compound must be formed from species **G**, which in turn can only be formed by the direct addition of singlet oxygen to a double bond in 3,6-nonadiene. In principle, compound **1** can also be formed by the addition of singlet oxygen. In a separate study, Hubert *et al.* showed that generation of singlet oxygen by photosensitizers added to ethyl linoleate or alkyd mixtures enhances the drying rate.[62] 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, photo-sensitised oxidation (reaction with $^1O_2$) and epoxidation. Normal radical autoxidation was concluded to be the most important mechanism.[57]

1.4 Metal complex driers for alkyd paints

1.4.1 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 1920's with the preparation of metal naphthenates.[63] The driers that are used today are based upon synthetic acids, like 2-ethyl hexanoic acid and versatic acid, shown in Fig. 1.6. 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.



I **II** **III**

Figure 1.6: 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 ten.

The metals that have been used in drier compounds can be 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 1.2.[64, 65]

Table 1.2:
The 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	

Primary driers are autoxidation catalysts, and as such function predominantly as surface driers, where the dioxygen concentration is highest. 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. It is most uncommon to use a primary drier in a coating formulation without an additional secondary or auxiliary drier.

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.[63] 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,[10, 66] and Lombard *et al.* proposed a dinuclear cobalt(III) species to take part in the catalysed autoxidation of α-pinene (Fig. 1.7).[67] Also, the formation of peroxide and hydroperoxide complexes has been proposed, especially in media of low polarity (see Section 1.2.2.2).[34] The formation of insoluble cobalt(III) hydroxides was proposed as the reason for catalyst deactivation in the autoxidation of tetralin.[12]

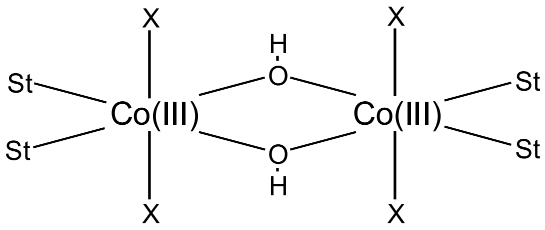


Figure 1.7: Dimeric cobalt complex proposed to be formed in the cobalt stearate catalysed autoxidation of α-pinene. St = stearate anion, X = water or alcohol.

Manganese soaps are also used as primary driers, although they are almost always used in combination with cobalt soaps.[63] The autoxidation activity of manganese soaps can be greatly enhanced by the addition of amine ligands, a topic which will be discussed in Section 1.5.1. 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.[15] Consequently, iron soaps are not used in air-drying alkyd paints, except 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.[63]

Secondary driers are active in the cross-linking steps of drying, they are responsible for an overall drying throughout the entire paint layer.[64] 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.[63, 64]

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.[68, 69] In an account by Ali *et al.* a study is described where organobismuth compounds were evaluated as primary driers.[70]

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.[71] 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. 1.8.[72] The use of aluminium compounds as additional cross-linkers in high-solids alkyd paints has also been studied.[73] 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.[73]

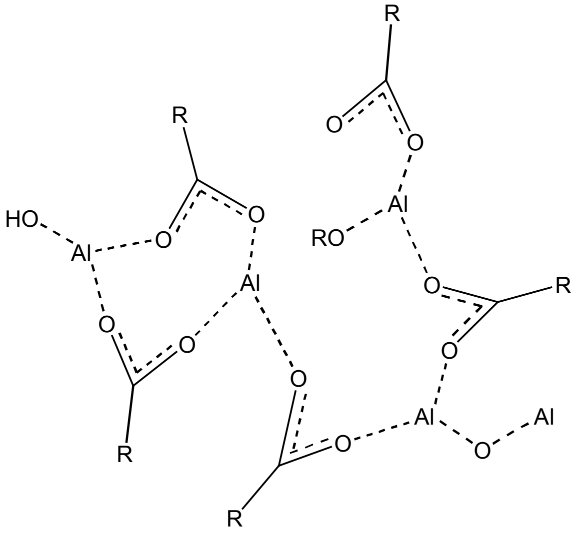


Figure 1.8: Schematic representation of possible alumina cross-links in an oxidised alkyd network.

Auxiliary driers are added to enhance or alter the activity of the primary drier, and thereby improve the appearance and quality of the total paint film. The action of these driers at the molecular level is not known. 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.[64] Potassium driers combined with cobalt driers were found to be very effective in the through-drying of especially water-borne alkyd systems.[69, 74, 75] 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.[63]

1.4.2 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 alkyd paints.[52, 65, 69, 71, 76-81] 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.[65] 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 vs time, the increase of the 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 catalyze oxidation-reduction.[65]

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.[80, 81] 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.[80] 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 for Co *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.*[65] 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.[80] 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 hours, 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.[80]

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.[81] 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.[81] The MR profiling studies have shown that the initial cross-linking rate for *all* different drier combinations, (Co alone, Co/Ca, Co/Zr or Co/Zr/Ca) is spatially *uniform* throughout the paint film. Only after two to three hours, the cross-linking near the surface of the film becomes 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 becomes non-uniform after three hours, only the degree of non-uniformity differs for each drier combination.[81] 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.[81] Conventional drying-time measurements using a drying recorder showed that the Co/Ca system indeed had the shortest through-drying time.[81] 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.[82] The fact that drying was found to be uniform throughout the paint film for the first three hours, 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.

1.5 Enhancing drier activity and the development of new drier systems

1.5.1 The effect of added ligands

In the earliest reports on paint drying, nitrogen-containing ligands were added to paint mixtures containing cobalt-drier soaps to prevent so-called *loss-of-dry*.[83, 84] 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,[85, 86] formation of insoluble drier complexes in the paint mixture and drier hydrolysis (common in waterborne paints).[63] 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-phenantroline show no loss-of-dry upon ageing, in contrast to paint mixtures with the simple metal oleates.[83] Nicholson had already shown in a conductometric study of the adsorption of cobalt acetate and [tris(1,10-phenantroline)cobalt(II)]di(acetate) on titanium dioxide in acetic acid, that the phenantroline complex is apparently adsorbed to a lesser extent on the TiO_2 surface than cobalt acetate.[85]

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.[87] 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-phenantroline, 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*-phenantroline, 2,2'-bipyridine or other aromatic nitrogen containing ligands are added to the paint mixture (Fig. 1.11).[88-90] Canty *et al.*, after studying the drying time of paint mixtures vs the molar ratio of added 1,10-phenantroline for different metal concentrations, proposed that a bis(phenantroline)cobalt complex is formed at the phenantroline concentration which produces most rapid drying. For manganese soaps the presence of a mixture of mono(phenantroline)manganese and bis(phenantroline)manganese complexes was proposed.[91]

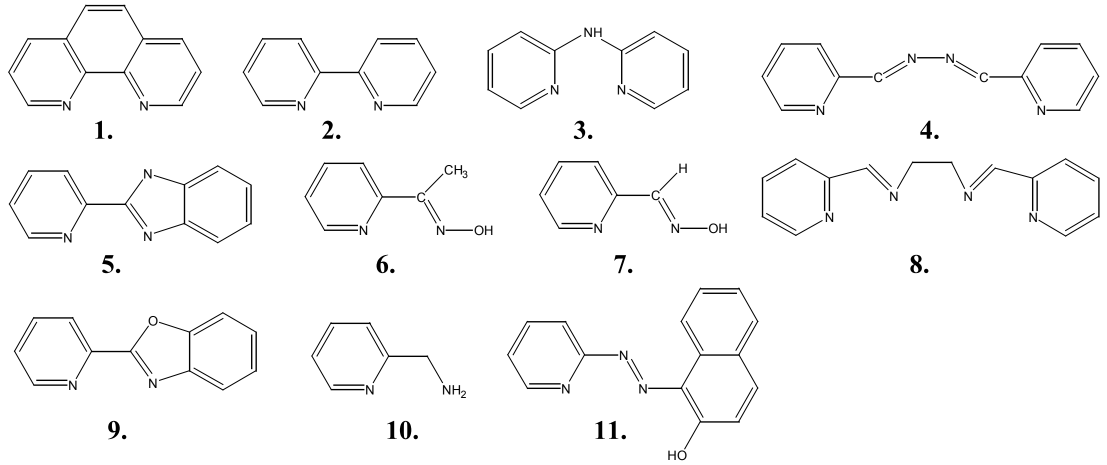


Figure 1.9: Ligands that accelerate paint drying when using manganese (with **1-11**) or cobalt (with **1,2**) carboxylates as driers.[90]

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.[84, 92] 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-phenantroline *in-situ* to a cobalt containing varnish *retarded* the drying time. This contrasting result was attributed to the type of varnish used.[84]

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.[92] 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 unpigmented systems.[92]

Table 1.3 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 sulfur-bearing 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

Table 1.3: Nitrogen ligands added to manganese, iron and lead naphthenate driers to enhance drier activity in the drying of linseed oil, taken from ref [92].

Additive[a]	Activity[b]. 0.03% Co = 1.0			% Improvement[c] more improvement = higher %		
	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-Phenantroline	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-phenantroline			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 = ($Dtime_{Co}/Dtime_{m+l}$) where $Dtime_{Co}$ = the drying time of a sample containing 0.03 weight%-on-oil of cobalt naphthenate as drier and $Dtime_{m+l}$ the drying time of a sample containing another drier with added ligands. [c] $((Dtime_{old} - Dtime_{m+l})/Dtime_{m+l}) \times 100\%$, where $Dtime_{old}$ = the drying time for that metal naphthenate without any ligands added and $Dtime_{m+l}$ = the drying time with ligands added.[92]

speculated in several reports on the catalytic mechanism of manganese complexes with *o*-phenantroline.[91, 93, 94] They supposed that manganese phenantroline 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.[20, 34]

The ligand 2,2'-bipyridine (bpy) is often added to cobalt and manganese driers in water-borne alkyd coatings. Alternatively, the driers are added as the complex $[M(bpy)_3]^{n+}(anion)_n$.[95, 96] In the coordinated 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.

Recently, Warzeska *et al*. studied the influence of bpy on the autoxidation of ethyl linoleate with manganese 2-ethylhexanoate.[97] The autoxidation of EL catalysed by cobalt and manganese 2-ethylhexanoate and manganese 2-ethylhexanoate with bpy was followed by FTIR (see chapter 2 for more information on the exact methods that were used). 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 equivalents 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 *et al*.[92] 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.[97] The complex $[Mn^{II}_2Mn^{III}_2O_2(2\text{-ethylhexanoate})_6(bpy)_2]$ was isolated from a commercial drier solution containing manganese 2-ethylhexanoate and bpy, the molecular structure of which is shown in Fig. 1.10. 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 isolated cluster compound shows a comparable autoxidation activity as for an *in-situ* mixture of manganese and bpy, it was concluded that these kind of cluster

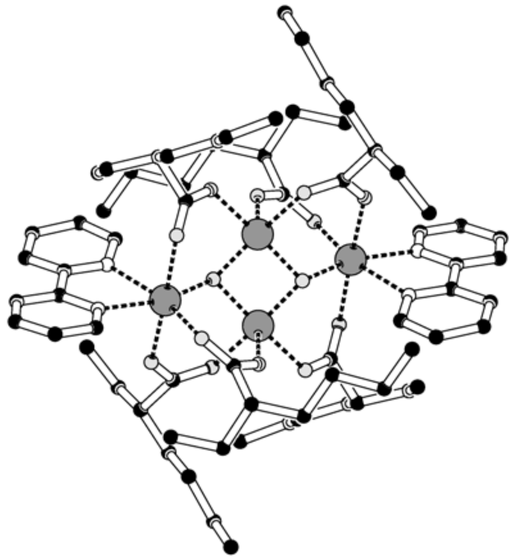


figure 1.10: molecular structure of $[Mn^{II}_2Mn^{III}_2O_2(2\text{-ethylhexanoate})_6(bpy)_2]$, determined by single crystal X-ray crystallography. Due to disorder in the alkyl chains and disordered solvent molecules in the crystal, the structure could not be fully refined (final R_1 value was 30%) The Mn_4O_2 cluster core can be considered as quite proper, however.

compounds might well be present as catalytically active species in the autoxidation reaction.[97]

Wu *et al*. used time-resolved FTIR and Size Exclusion Chromatography (SEC) (see also chapter 2) to study the influence of the ligands 2-aminomethylpyridine (amp, a ligand already proposed by Wheeler, see Fig. 1.9, **10**) and 2-hydroxymethylpyridine (hmp), as compared to bpy, on the autoxidation and crosslink formation rates of ethyl linoleate catalysed by manganese 2-ethylhexanoate.[98] The ligands were also tested in a real alkyd system.[98] 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 crosslink formation. Here, formation of dimers was observed after 4 hours for the system containing hmp, after 6 hours for amp and 8 hours for the bpy system. In a real alkyd paint system, however, manganese + bpy showed the shortest drying time (7.5 h) followed by manganese + amp (9 h) and hmp (13 h).[98] Hence, for these particular ligands, the trends observed with the model compound EL were not reflected in the used real alkyd system.

1.5.2 Driers not based on metal carboxylates

Few reports are available 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.[84] The complex showed rapid drying of drying oils and the 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.[84]

Metal acetylacetonates are simple, readily available metal complexes. Although they have received much attention as catalysts in the fields of autoxidation,[99-101] polymerisation [102-106] and hydroperoxide decomposition,[100, 101, 106-108] 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^{+}.[109-111] 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 autoxidised linseed oil samples were 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. In chapter 3 the activity of manganese acetylacetonate in the autoxidation of EL is evaluated.

1.5.3 New drier systems

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.[98] 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 in the region of interest. After 60 min, all water was evaporated and the decrease of the 3010 cm^{-1} peak could be monitored (see Chapter 2 for more information). The complex [Mn(hfac)$_2$] by itself was found not to be active in the autoxidation, when either one of the ligands hmp or amp (see section 1.5.1) were added, however, induction times (after water evaporation) dropped below 100 min and the autoxidation proceeded at a quite acceptable rate. The results were compared with those obtained for a commercial water-emulsifiable manganese drier (Nuodex WEB Mn9), and the results are summarised in Table 1.4. 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.

Table 1.4: The EL autoxidation activity of [Mn(hfac)$_2$] compared to Mn WEB, with and without added ligands. Taken from ref [98].

Catalyst	Ligands 3 equiv.	20% EL emulsion Induction time (min)	Rate[a] ($\times 10^{-4}$min^{-1})	Real alkyd paint[b] Drying time (h)
Mn WEB	-	220	24.1	15
	amp	70	37.5	7
	hmp	150	54.2	7 ½
Mn(hfac)$_2$	-	>500	-	n.d.
	amp	80	17.5	5 ½
	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[70] at 23 °C and 50% relative humidity.

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.[112] Typical ligands consist of the condensation product of 1,2-diaminocyclohexane and two equivalents of a 2-hydroxy-benzaldehyde with alkyl substituents, to promote solubility in apolar paint mixtures. In Fig. 1.11 two examples of the used ligands are shown.

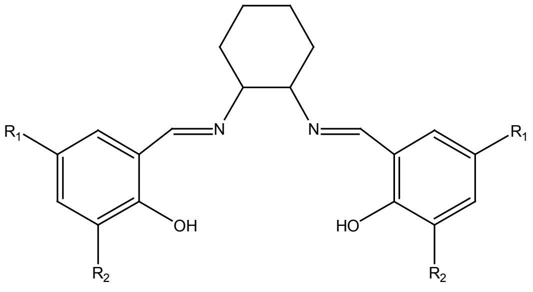


Figure 1.11: Examples of salen type ligands used with manganese as alkyd paint driers. Substituents are R_1=R_2= *tert*-butyl, or R_1 = a dodecyl chain, R_2 = H.

In a patent by Micciché *et al.* a drying system based on an iron carboxylate and a reducing agent is described.[113] As mentioned in Section 1.4.1, iron compounds are not 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 drying results comparable to cobalt driers.[113]

Oyman *et al.* have used SEC, FTIR and Raman spectroscopy as well as oxygen uptake experiments to evaluate the manganese complex $[(Mn^{IV})_2(Me_3tacn)_2(\mu\text{-}O)_3](PF_6)_2$ (see Fig. 1.12) as an oxidation catalyst for EL and a possible drier for alkyd emulsion coatings.[114] 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 the complex 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.[114] With hmteta added to the Me_3tacn complex, the EL oxidation rate was found to be comparable with the rate found for the cobalt drier.[114]

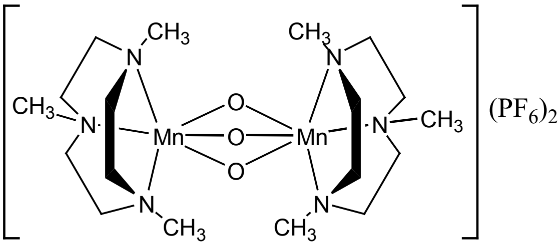


Figure 1.12: $[(Mn^{IV})_2(Me_3tacn)_2(\mu\text{-}O)_3](PF_6)_2$, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane.

1.6 The lipoxygenase enzyme, a biological paint drier?

1.6.1 Structure and function of lipoxygenase

Lipoxygenases are non-heme, nonsulfur iron (or manganese) dioxygenases that act on lipid substrates containing one or more (*Z*,*Z*)-1,4-pentadiene moieties.[115] Common polyunsaturated fatty acids, such as linoleic, linolenic and arachidonic acids are the natural substrates for these enzymes, which are widely distributed among plants and animals. The primary reaction products are hydroperoxides of conjugated (E,Z)-dienes, which is why the activity of this enzyme may be considered when the drying of alkyd paint is discussed.

The active site of most lipoxygenases contains iron, which is bound to three histidine residues, a C-terminal isoleucine, water and a variable sixth ligand.[115, 116] In plants, this sixth ligand is an aspargine residue while in mammals it may be either histidine, aspargine or serine. In Fig. 1.13 a picture of the active site of *soybean* lipoxygenase is shown, which is the most studied lipoxygenase. In the enzyme's resting state iron is present as high-spin iron(II) with a distorted octahedral coordination geometry. When the enzyme is in its catalytically active form iron is present as high-spin iron(III) in an octahedral environment. The reduction potential of the active site Fe(III) ion is known to be high (close to 0.6 V vs NHE), making lipoxygenase a significantly stronger oxidising agent than other non-heme iron-containing enzymes. There are two channels from the enzyme surface to the active site. It is postulated that the existence of the two cavities allows separate access of dioxygen and substrate to the active site iron.[117] There is, however, no consensus on how the substrate gains access to the metal centre or any definite information on substrate binding.[115]

The lipoxygenase enzyme from the fungus *Gäumannomyces graminis* contains manganese instead of iron.[118, 119] EPR studies on the enzyme indicate that manganese is present as octahedral manganese(II).[120] Incubation of the enzyme with linoleate led to a decrease of the Mn(II) signals, supposedly because of oxidation to the EPR silent manganese(III) state. An alignment of the primary structure of soybean lipoxygenase with manganese lipoxygenase over the part that contains the three proximal Fe-ligands, His499, 504 and 690, and the presumed distal ligand Asn694, showed that these ligands are preserved in the structure of manganese lipoxygenase. This finding, coupled with recent EPR results, is an indication that the coordination environments for iron and manganese lipoxygenase are largely the same.[120]

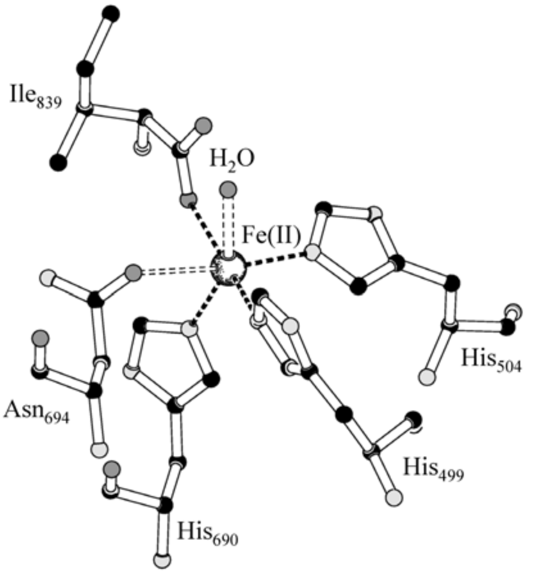
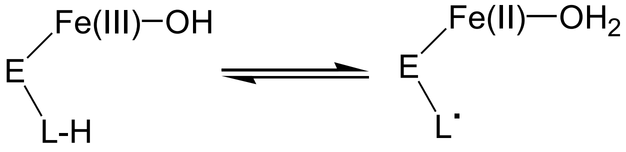


Figure 1.13: Soybean Lipoxygenase L-1 active site iron coordination geometry, taken from a crystal structure determination at 1.4 Å resolution.[116] The enzyme is in the resting state. The aspargine residue probably forms only a weak bond with iron. The Fe-O_{Asn} distance is around 3 Å.

Substrates for manganese lipoxygenase are linoleic and linolenic acid. The main products are 13*R*-hydroperoxy-(9*Z*,11*E*)-octadecadienoic and 13*R*-hydroperoxy-(9*Z*,11*E*,15*Z*)-octadecatrienoic acids. However, the formation of 11*S*-hydroperoxy-(9*Z*,12*Z*)-octadecadienoic acid from linoleic acid was also observed.[120] The formation of such a bis-allylic hydroperoxide from a polyunsaturated fatty acid has not yet been observed with iron lipoxygenases.[120]

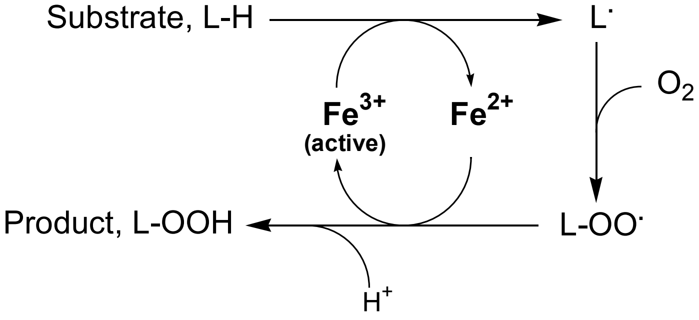
1.6.2 Mechanism for catalytic activity

A proposed mechanism for the activity of the enzyme is unique in that catalysis is achieved via substrate activation instead of by the more familiar dioxygen activation. Schemes 1.8 and 1.9 show a representation of the enzyme's proposed catalytic mechanism. Molecular oxygen has been proposed to neither bind, nor react with the lipoxygenase iron ion, but rather to trap the activated enzyme-substrate complex.[115, 117, 121] Linoleic acid is activated by breaking the C-H bond at carbon-11. The hydrogen atom is supposedly transferred to an enzymatic group, possibly a hydroxide ion coordinated to iron (see Scheme 1.8). The linoleyl radical that is formed reacts rapidly with O_2 to form a



Scheme 1.8: Proposed substrate activation by lipoxygenase·. E = enzyme and LH = substrate

peroxyl radical (see Scheme 1.9) The peroxyl radical is reduced to peroxide anion and protonated to yield bound linoleate hydroperoxide. Release of the product to the solvent completes the catalytic cycle. The enzyme is stereo- and regiospecific. For example, soybean lipoxygenase converts linoleic acid strictly to 13S-hydroperoxy-(9*Z*,11*E*)-octadecadienoic acid.



Scheme 1.9: Representation of the catalytic cycle of the lipoxygenase enzyme

1.6.3 Lipoxygenase as a paint drier.

The enzyme itself will probably not be a good paint drier. Despite the fact that most enzymes operate only under very specific temperature and pH conditions, the function of the lipoxygenase enzyme is to create hydroperoxides, whereas the main function for a paint drier is to decompose hydroperoxides. Still, the enzyme functions via activation of the substrate by hydrogen atom abstraction, which would also be beneficial for paint driers. Consequently, coordination compounds that model the active site of the enzyme could also show the ability to abstract a hydrogen atom from a substrate, for example an alkyd resin molecule, thereby initiating autoxidation. Model complexes for the lipoxygenase active site could thus very well be good paint driers, especially if they are also able to catalytically decompose hydroperoxides.

1.7 Aim and outline of this thesis

The aim of the research described in this thesis was to find new, metal-complex-based driers for alkyd paints, which do not contain cobalt. The use of cobalt compounds in paints is a topic of debate, due to the toxicity and suspected carcinogenity of cobalt.[122-125] The chosen approach has been to synthesise and screen different, and sometimes new, manganese and iron complexes for their activity in paint drying. It was soon found that manganese complexes gave better results than iron complexes. Consequently, synthetic efforts were mainly focused on the development of new manganese driers.

In this chapter an overview has been given of the chemistry that plays a role in the drying of alkyd paint and the metal driers that are used. It also covers the latest studies done to unravel the mechanisms of alkyd paint drying and metal drier action. Chapter 2 is an account of the analytical methods that have been used to study the activity of potential new paint driers, using ethyl linoleate (EL) as a model for real alkyd paint. In Chapter 3, the activity of the simple manganese compound manganese *tris*(acetylacetonate) in the autoxidation and oligomerisation of EL and the drying of real alkyd paint is reported. The oxidation mechanism of EL by commercial cobalt and manganese catalysts, [Mn(acac)$_3$] and [Mn(acac)$_3$] with bipyridine added is discussed. The synthesis and characterisation of new manganese and iron complexes containing tripodal, tetradentate ligands is described in Chapter 4 and the activities of these new complexes in EL autoxidation are compared and discussed in Chapter 5. Chapter 6 is a break-away from paint chemistry, since it is an account of the coordination chemistry of [Mn(acac)$_2$(bpy)]. This complex was found to have the relatively rare trigonal prismatic coordination geometry in the solid state. DFT calculations have been used to answer the question of why the complex adopts the trigonal prismatic geometry. Finally, Chapter 7 contains the general conclusions and outlook.

Parts of this thesis have been published[97, 126, 127] or have been submitted for publication[128, 129] and several other manuscripts are in preparation.

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