



# Catalytic activity of primary and secondary driers towards the oxidation and hydroperoxide decomposition steps for the chemical drying of alkyd resin

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## ABSTRACT

The autoxidation of fatty acid methyl esters (FAMES) derived from colza, sunflower, linseed and tung oils and the oxidation of sunflower FAMES in the presence of several commercial driers based on Co(II), Mn(II), Fe(II), V(IV), Sr(II), Zr(IV), Ca(II), Zn(II) have been investigated. The oxidation step was studied through oxygen uptake measurements with an automatic O<sub>2</sub> pressure recorder (RapidOxy<sup>®</sup>) and by ATR-FTIR spectroscopy. Pure methyl linoleate hydroperoxides (ROOH) were prepared by photooxidation to follow their decomposition by HPLC in the presence of the driers. Only Co(II), Mn(II) and Fe(II) as primary driers have catalytic effects both on the oxidation and on the ROOH decomposition steps. However, the Co-based drier shows the higher oxidation rate while the Fe-based drier has the greater ROOH decomposition rate. On the other hand, oxidation runs faster by increasing the amount of driers from 2.5 to 25–50 mM but an antioxidant behavior is observed at higher levels. Secondary driers show poor or no catalytic activities both on the oxidation and the ROOH decomposition steps with a conversion ranging from 5 to 9% over 24 h. Combinations of driers were finally investigated to highlight possible synergistic or antagonist effects during the oxidation and hydroperoxides decomposition steps. Synergistic effects were found only on the oxidation stage with Co(II)-Zn(II), Mn(II)-Zn(II) and Fe(II)-Ca(II), while these latter do not have influence on the decomposition step.

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## 1. Introduction

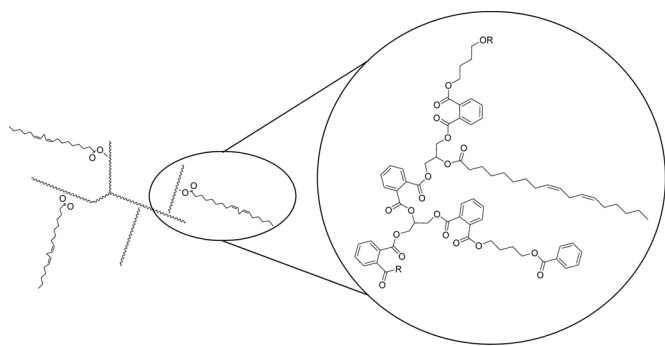
Autoxidation is the spontaneous reaction between molecular oxygen <sup>3</sup>O<sub>2</sub> and organic molecules leading to the formation of hydroperoxides and peroxides as primary oxidation products. It involves a radical chain mechanism which has been studied since the mid-twentieth century [1–3]. Since several years, researches on the oxidation of lipids in chemical, biochemical, food and medical fields have multiplied. Indeed, such uncontrolled chain reactions can be problematic as they can induce undesired oxidative degradation. Products that contain fats and oils turn rancid when exposed to air generating unpleasant flavors and odors. In the human body, the lipid oxidation would be involved in several diseases (e.g. diabetes, cancers, neurological illnesses, etc.) [4–7]. In the field of

fragrances, this degradation can cause an olfactory loss, unpleasant smells, change of colors and the formation of allergenic compounds [8]. In all these cases, autoxidation must be avoided and the use of antioxidants is necessary.

On the contrary, autoxidation can be advantageous in other fields. This is the case in paints and coatings where the film formation results from an oxidative chemical drying of alkyd resins. Indeed, the radical chain reactions involved in the autoxidation of unsaturated fatty acids present in alkyd resins and the decomposition of the resulting hydroperoxides are responsible for the crosslinking of the binder, implying the formation and the hardening of the film [9]. Alkyd coatings are emulsion systems composed of alkyd resin, pigments, fillers and additives. Alkyd resins are complex viscous three-dimensional polyesters grafted with fatty acids obtained by polycondensation of linoleic acid, glycerol, 2,4-butanediol, phthalic anhydride and benzoic acid for example (Scheme 1).

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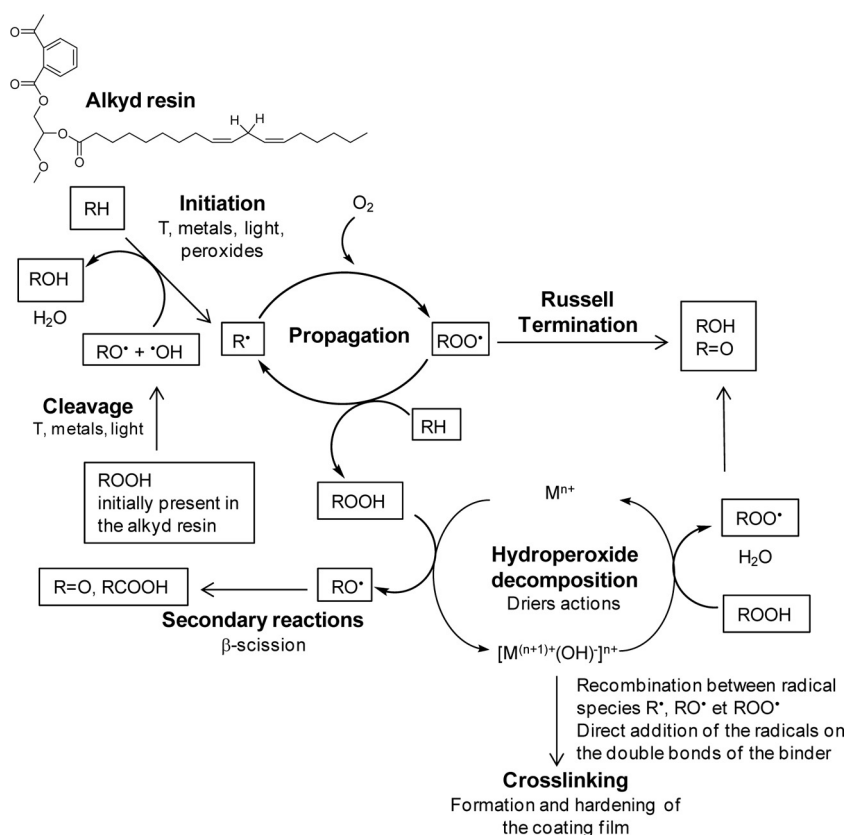


**Scheme 1.** Example of a 3-dimensional alkyd resin structure obtained by polycondensation from phthalic anhydride, glycerol, 1,4-butanediol, linoleic acid and benzoic acid.

The study of the autoxidation of such complex formulations, especially from a mechanistic viewpoint, is not straightforward but can be simplified by using model compounds such as fatty acids or fatty acid methyl esters which constitute the part of the alkyd binder that undergoes the oxidative process [10]. The autoxidation of fatty acid and esters is largely documented [3,11–15]. The radical chain process starts with the initiation step which generates alkyl radicals  $R^\bullet$  by abstraction of a hydrogen atom with an initiator. Then, peroxy radicals  $ROO^\bullet$  are rapidly formed by addition of oxygen, which abstract a hydrogen atom from another molecule of fatty acid/ester, leading to the formation of the primary oxidation compounds, *i.e.* the hydroperoxides abbreviated as  $ROOH$ . This is the kinetically more important step and is also the rate limiting step in the autoxidation process. It is noteworthy that hydroperoxides can also be formed through a singlet oxygen ( $^1O_2$ ) pathway. In vegetable oils, for example, the presence of natural photosensi-

tizers can lead to the generation of this excited species resulting in the formation of  $ROOH$  [16]. Additionally, secondary oxidation products like conjugated ketones, resulting from the  $ROOH$  decomposition, can also contribute to photosensitized  $^1O_2$  generation as reported by Muizebelt et al. [17,18]. Indeed, hydroperoxides  $ROOH$  are relatively unstable and readily decompose through the action of UV light, temperature and metals providing secondary more stable oxidation products along with other radical species such as  $RO^\bullet$  and  $ROO^\bullet$ . Also, the radicals  $ROO^\bullet$ , in the presence of oxygen, can undergo a reversible reaction as suggested by Porter et al. to form the corresponding  $R^\bullet$  radicals [11]. Finally, radical species recombine thus ensuring the crosslinking of the resin and creating a complex network, which at a macroscopic scale, corresponds to the film formation [19]. Scheme 2 illustrates the radical reaction involved in the crosslinking process of an alkyd resin.

Autoxidation is however a relatively slow process. To accelerate the chemical drying of alkyd resins, catalysts, the so-called driers, are used as additives. These latter are typically metal salts of fatty acids (*e.g.* 2-ethylhexanoate, neodecanoate), which are divided into two categories. Cobalt-, iron-, manganese-, vanadium-, and cerium-based catalysts are classified as primary driers which play a catalytic role in the chemical drying. They catalyze the formation of alkyl radicals ( $R^\bullet$ ) through hydrogen abstraction which is followed by the formation of peroxy radicals ( $ROO^\bullet$ ) through oxygen absorption. Such radicals give then hydroperoxides which can decompose into active radical species like  $RO^\bullet$  and  $ROO^\bullet$  via the Haber-Weiss cycle process, resulting *in fine* in the crosslinking of the resin and the film formation [22]. The driers thus shorten the induction period of the autoxidation process which can be sometimes longer due to natural antioxidants present in raw seed oil mixtures. On the other hand, secondary driers, including *e.g.* zirconium, zinc, calcium, aluminum, are claimed to improve the stability and the solubility of the primary driers in the paint formulations,



**Scheme 2.** Radical reactions involved during the autoxidation and chemical drying of alkyd resins [19–21].

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