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Roles of peroxides and unsaturation in spontaneous heating of linseed oil

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ABSTRACT

This contribution aims to elucidate the chemical aspects of the autoxidation of linseed oil that may lead to self-heating and fires, especially for linseed oil doped with salts of transition metals, in the presence of an additional fuel, such as cotton. We examine the formation of peroxides, which function as important intermediates in the autoxidation reaction. In particular, we describe the relationship between the formation of peroxides and changes in the degree of unsaturation, together with other structural and compositional modifications occurring in the molecules of unsaturated fatty acid esters. Transition metal salt catalysts were found to decompose peroxides which had built up during the autoxidation reaction of linseed oil, thereby increasing the number of reactive radicals and resulting in higher product yields. Higher temperatures increased the rate of peroxide decomposition. The overall activation energy for peroxide formation corresponds to $71 \pm 1 \text{ kJ mol}^{-1}$. FTIR analysis of oil film demonstrated the progressive decrease in the concentration of *cis* non-conjugated double bonds, formation of *trans* conjugated double bonds, appearance of hydroxyl groups and the broadening of the carbonyl peak. The overall rate of disappearance of double bonds follows first order kinetics with a rate constant of $0.030 \pm 0.007 \text{ h}^{-1}$.

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1. Introduction

Linseed oil finds application in the formulation of alkyd paints and wood treatment agents, and in the production of linoleum. In its processing, raw linseed oil is heated, and then the transition metal salts, especially those of cobalt, are added to act as catalysts to accelerate the oil drying in air, in a process facilitated by the so-called oxypolymerisation reactions [1]. The resulting material named as *boiled* oil, when soaked in rags, will also undergo autoxidation reactions (similar to oxypolymerisation reactions) that induce self-heating which may lead to spontaneous ignition and fires, as frequently reported in news; see References [2–4] for three examples. In spite of the practical importance of fires triggered by low-temperature catalytic oxidation of linseed oil, the chemistry of the oxidation process remains incompletely understood. This contribution aims to gain improved insights and further elucidate the chemical reactions that underpin the autoxidation of linseed oil.

Typical composition of fatty acids, present as glycerides esters, consists of 6–7% of palmitic acid (16:0), 3–6% of stearic acid (18:0), 14–24% of oleic acid (18:1), 14–19% of linoleic acid (18:2) and

48–60% of linolenic acid (18:3) [5], where the first number in each ratio corresponds to the length of the carbon chain and the second to the number of double bonds in the compound. Thus, linseed oil comprises a significant proportion of linolenic acid. The number of bis-allylic methylenes (i.e., $-\text{CH}_2-$ groups inserted between two $-\text{CH}=\text{CH}-$ groups as in $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$) in unsaturated fatty acid affects linearly the oxidisability of the acid [6]. The $-\text{CH}_2-$ groups lie on the same side of the double bond resulting in the distinct *cis-cis* arrangements observed in linoleic and linolenic acids. Each of the two hydrogens of the methylene groups forms part of one or two allylic chains (i.e., $-\text{CH}_2-\text{CH}=\text{CH}-$ or $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$), hence the name of single allylic or double allylic hydrogens used to describe them. These polyunsaturated fatty acids are more susceptible to oxidative damage due to the lowered bond dissociation energy of their allylic hydrogens [7]. The rate of autoxidation reaction depends on the number and position of the double bonds with the relative rates of oxidation for oleates, linoleates and linolenates of 1, 41 and 98, respectively [8].

The oxidation of linseed oil involves reactions between unsaturated fatty acid esters and oxygen, to form organic peroxides. These reactions, also known as lipid peroxidation, proceed by way of a free radical mechanism called autoxidation [9] and involve an initiation step and a propagation sequence which continues until termination takes place [10,11]. The oxidation process usually

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requires a catalyst since the triplet state of oxygen forbids direct reaction of molecular oxygen with closed-shell biomolecules [10]. Transition metals, light, heat and several initiators accelerate the oxidation process [11]. Allylic hydroperoxides, such as $-\text{CH}=\text{CH}-\text{C}(\text{OOH})\text{H}-$, are the primary oxidation products of these reactions in which the number of double bonds remains intact while the positions and/or configurations of these bonds may change from the original structure [11]. The formation of hydroperoxides is a useful indicator of the early stages of lipid oxidation [12]. In the absence of decomposing factors such as redox-active metals, heat, ultraviolet light or antioxidants, lipid hydroperoxides constitute relatively stable intermediates [12]. Alkyl hydroperoxides are readily decomposed in the presence of transition metals [7]. Peroxyl radicals, as in $-\text{CH}=\text{CH}-\text{C}(\text{OO}\bullet)\text{H}-$, are considered as the key intermediates in many oxidative chain processes [13].

Among other metals, cobalt has been recognised as the most effective and widely used additive to promote the oxidative drying of alkyd paints [11,12]. Most transition metal ions could be considered to behave as radical species since many of their biological effects involve the ability to accept or donate a single electron [14]. Transition metals can catalyse undesirable free radical reactions such as autoxidation and formation of hydroxyl radicals [14]. A variety of organic molecules can be oxidised by a combination of hydrogen peroxide and iron(II) salts [14]. New environmentally friendly iron based dryers have been developed for alkyd-based paint systems to replace cobalt based dryers [15]. The mechanism of drying of alkyd paint conveys some similarities with the oxidation of lipid in biological systems [15].

Drying of paint films proceeds in two stage process involving solvent evaporation (physical drying) and oxidation of linseed oil (chemical drying). Metal salts accelerate the chemical drying through the oxidative polymerisation of linseed oil, that involves the formation of peroxide ($-\text{O}-\text{O}-$) links between adjacent fatty acid chains, the so-called oxypolymerisation. Metal catalysts also induce the decomposition of hydroperoxides ($-\text{O}-\text{OH}$) that form during oxidation by initiating the radical chain branching reaction ($-\text{O}-\text{OH} \rightarrow -\text{O}\bullet + \text{OH}$), which increases the overall rate of paint drying [17] but may also lead to ignition. The exact role of the metal ion, in hydrogen abstraction, supporting a radical reaction chain by catalysing the oxidation or reduction of alkyl hydroperoxides, has not been elucidated as yet [6]. It would appear that abstraction of hydrogen from the fatty acyl moieties to give an alkyl radical is the initiating process; once alkyl hydroperoxide is formed, it also becomes a site for initiation of a radical reaction chain [6].

During oxidation reactions of linseed oil, chemical changes take place in the structure of compounds in the oil such as the position and the number of double bonds. The addition of the peroxyl radical to the conjugated double bonds can form epoxides [18]. Carbon-carbon double bonds of unsaturated vegetable oils undergo an epoxidation reaction without a molecular rearrangement [19]. These epoxides are present as intermediates in saturation reactions due to their instability [18]. Fully epoxidised vegetable oils cannot be used as reactive diluents for alkyd resins since they do not have the capacity to dry in air due to the absence of carbon-carbon double bonds [19]. Epoxidisable plant oils have many applications such as plasticisers and stabilisers in PVC, and in the production of linoleum floor coverings [20]. During oxypolymerisation, the double bonds in linseed oil are consumed and peroxides are formed [21]. Iodine value decreases during oxypolymerisation reaction due to the consumption of double bonds [21]. The average amount of unsaturation of fats and oils is calculated as iodine value, normally expressed in terms of grams of iodine added per 100 g of oil [8].

Two pathways operate for the oxidation reactions, a slow pathway that proceeds at a controlled rate and an ignition pathway characterised by high reaction rates [22]. Both chain-branching (i.e., multiplication of the number of radicals involved in the oxidation) and exothermic reactions (which cause rapid increase of temperature in the system) promote the uncontrollable rate of increase of oxidation reactions [22]. Catalysts play an important role in the initiation reactions which are followed by the autocatalytic processes; the oxidation products catalyse the reaction resulting in an exponentially increasing reaction rate as oxidation proceeds [10].

The classical models of self-ignition, such as those of Frank-Kamenetskii, Semenov and Thomas, are based on single-step kinetics and do not account for complex radical reactions that underpin the initiation and propagation of self-heating of materials impregnated with linseed oil [23]. Recently, Worden [24] performed a series of experiments with boiled linseed oil, without being able to identify conditions that do not lead to self-ignition, the so-called subcritical conditions. Worden's findings indicate the limitations of classical models to describe the ignition behaviour governed by radical reactions. Without a detailed understanding of both the initiation and propagation reactions, one cannot formulate models able to predict the ignition of materials that display self-heating behaviour similar to that of lignocellulosics soaked with linseed oil. This contribution studies the propagation reactions that operate during self-heating of materials soaked with linseed oil; i.e., reactions that involve ground state oxygen, and assume prior formation of radical species. Although the reactions of singlet oxygen, that forms from ground state oxygen in the presence of light and organic sensitiser (such as chlorophyll), have been identified to be responsible for the initiation of the self-heating process [23], their role in setting off the self-heating remains to be investigated.

In particular, in the present experiments, we aim to study the chemical changes during oxidation of linseed oil doped with the salts of transition metals, by investigating the formation and disappearance of peroxide species and the evolution of the unsaturation values. This study is important as it gains an understanding of the behaviour of linseed oil during oxidation, explaining the chemistry of the propagation reactions in the self ignition process, and discussing the relationship between temperature and the build-up of peroxide species.

2. Material and methods

2.1. Materials

Nitrates and chlorides of Ce(III), Co(II), Cu(II) and Mn(II) (thereafter denoted as catalysts) were purchased from Sigma Aldrich and Chem Supply. Note that nitrates of transition metals tend to explode on heating, limiting their sample size in the experiments. Sodium thiosulfate 99%, cyclohexane 99%, cobalt(II) 2-ethylhexanoate 65% and potassium iodide 99% were obtained from Sigma Aldrich. We purchased glacial acetic acid from Ajax-Finechem Pty. Ltd. and chloroform from Lab-Scan Analytical Science. Hydrogen peroxide, 30%, was provided by Chem-Supply. Iodine monochloride and 1-hexene were supplied by Merck. Ultra high purity (UHT) oxygen and nitrogen gases were obtained from Air Liquide. We employed commercial raw linseed oil (Sceney's Pty. Ltd., Australia) purchased in a local hardware store.

2.2. Experimental apparatus

We employed two reactor systems, with the evolution of gaseous species studied in a flow-through tubular reactor, and

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