4 Oxidative degradation and stabilisation of mineral oil based lubricants

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4.1 Introduction

The reactions of oxygen with most organic materials are important from an economical and ecological standpoint. Processes such as the biological O₂/CO₂ cycle, the targeted oxidation of defined organic molecules, or the enzymatic oxidation of waste are all useful reactions. In contrast, the reactions of atmospheric oxygen with hydrocarbon polymers and liquid hydrocarbons (lubricants), as well as with certain biological systems, under varying conditions of temperature and oxygen pressure are undesirable processes. Such reactions lead to a deterioration of these materials. All oxidative processes with oxygen have a common reaction pattern attributable to the biradical status of oxygen.

The aim of this contribution is to present the reaction mechanisms of the degradation processes of lubricants and the factors influencing them. In addition, the mechanisms by which antioxidants inhibit lubricant oxidation with respect to specific industrial and engine oil applications are suggested.

4.2 Autoxidation of hydrocarbons

4.2.1 Oxidation of hydrocarbons at low temperature (30–120°C)

The self-accelerating oxidation of hydrocarbons is called autoxidation. Its initial stage is characterised by a slow reaction with oxygen followed by a phase of increased conversion until the process comes to a standstill. The degradation is driven by an autocatalytic reaction which can be described by the well-established free radical mechanism (Lazar et al., 1989; Denisov and Khudyakov, 1987). It consists of four distinct stages:

- initiation of the radical chain reaction
- propagation of the radical chain reaction
- chain branching
- termination of the radical chain reaction
4.2.1.1 Initiation of the radical chain reaction  Under normal conditions, i.e. moderate temperature and oxygen partial pressure greater than 50 torr, the first step is a process which is catalysed by traces of transition metal ions (Veprek-Siska, 1985):

\[
\begin{align*}
\text{CH}_3 \quad \text{H} \\
\text{R} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{CH}_3
\end{align*}
\]

\[\text{R} \overset{M^{n+}/O_2}{\rightarrow} \underset{k_1}{\text{R} + \text{HOO}^-} \]

(4.1)

R refers to a long chain alkyl substituent and the catalyst \(M^{n+}\) is a transition metal such as Co, Fe, V, Cr, Cu or Mn. The rate of initiation is very slow (\(k_1 = \text{rate constant} = 10^{-9} - 10^{-10} \text{ mol}^{-1} \text{ s}^{-1}\); Emanuel et al., 1967; Sheldon and Kochi, 1973).

The site of the oxygen attack is determined by the strength of the C–H bond, and the reactivity for hydrogen abstraction increases in the following order:

\[\text{RCH}_2\text{H} < \text{R}_2\text{CH} \text{H} < \text{R}_3\text{C} \text{H} < \text{RCH} \equiv \text{CH}(\text{R})\text{HC} \text{H} < \text{C}_6\text{H}_5(\text{R})\text{HC} \text{H} \]

(4.2)

Hence oxidation of an n-paraffin normally commences by abstraction of a hydrogen at the second carbon atom (alpha-position to the CH₃ group).

4.2.1.2 Propagation of the radical chain reaction  Once an alkyl radical has been formed this reacts irreversibly with oxygen to form an alkyl peroxy radical:

\[\text{R(CH}_3\text{)}\text{CH} \cdot + \text{O}_2 \overset{k_3}{\rightarrow} \text{R(CH}_3\text{)}\text{CH} \cdot \text{OO}^- \]

(4.3)

Reaction (4.3) is extremely fast (\(k_3 = 10^7-10^9 \text{ mol}^{-1} \text{ s}^{-1}\)) and has a very low activation energy (\(k_3\) is independent of temperature).

The rate of reaction of carbon centered radicals with oxygen depends on the type of substituents attached to the C-atom and increases in the following order:

\[\text{H}_3\text{C} \cdot < \text{C}_6\text{H}_5(\text{R})\text{CH} \cdot < \text{RCH} \equiv \text{CH}(\text{R})\text{CH} \cdot < \text{R}_2\text{CH} \cdot < \text{R}_3\text{C} \cdot \]

(4.4)

For instance, a tertiary alkyl radical reacts 10 times faster with oxygen than a methyl radical. This difference in reactivity explains why hydrocarbons with tertiary hydrogens (iso-paraffins) are oxidised faster than n-paraffins.

The next step in the chain propagation scheme is the hydrogen abstraction by a peroxy radical from another hydrocarbon:

\[\text{R(CH}_3\text{)}\text{CHOO}^- + \text{RH} \overset{k_5}{\rightarrow} \text{R(CH}_3\text{)}\text{CHOOH} + \text{R} \cdot \]

(4.5)