

CHAPTER II

THEORETICAL CONSIDERATIONS

2.1 Oxidation of based lubricants

The based stocks used for lubricants are a mixture of C₂₀- C₄₅ hydrocarbons which can be subdivided into three main groups : paraffins, naphthenes and aromatics. When hydrocarbons are heated in the presence of oxygen, oxidation occurs and hydrocarbons are degraded [1-2].

2.1.1 Auto-oxidation of hydrocarbons.

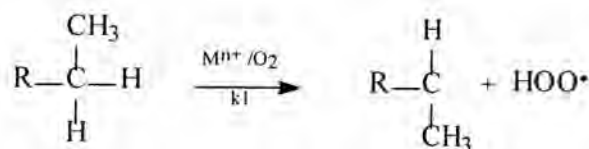
2.1.1.1 Oxidation of hydrocarbons at low temperature (30-120 °C)

The self-accelerating oxidation of hydrocarbons is called auto-oxidation. Its initial stage is characterized by a slow reaction with oxygen followed by a phase of increased conversion. The degradation is driven by an auto-catalytic reaction which can be described by a well-established free radical mechanism. It consists of four distinct stages:

- initiation of the radical chain reaction
- propagation of the radical chain reaction
- chain branching
- the radical chain reaction
- chain termination

Initiation of the radical chain reaction

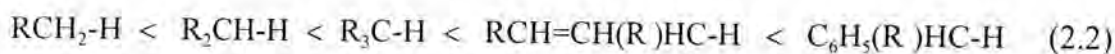
Under normal conditions, i.e. moderate temperature and oxygen partial pressure greater than 50 torr, the first step is a process which is catalyzed by traces of transition metal ions .



(2.1)

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

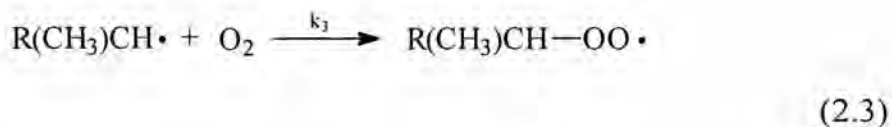
The site of the oxygen attack is determined by the strength of the C-H bond, and the reactivity for hydrogen abstraction increases in the following order:



Hence oxidation of an n-paraffin normally commences by abstraction of a hydrogen at the second carbon atom (alpha-position to the CH_3 group).

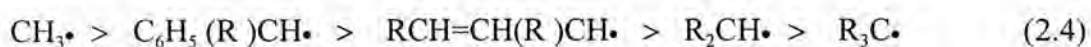
Propagation of the radical chain reaction

Once an alkyl radical has been formed this reacts irreversibly with oxygen to form an alkyl peroxy radical:



Reaction (2.3) is extremely fast ($k_3 = 10^7 - 10^9 \text{ l mol}^{-1}\text{s}^{-1}$) 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:

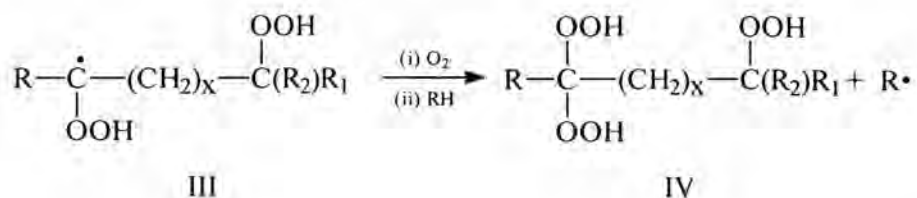


The next step in the chain propagation scheme is the hydrogen abstraction from another hydrocarbon by the peroxy radical:



This leads to a hydroperoxide and an alkyl radical which can again react with oxygen according to reaction (2.3). The rate of reaction of step (2.5) is slow ($k_5 = 10^{-1} - 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ at 30°C , depending on the type of hydrocarbons) when compared with step (2.3) and is therefore the rate determining step for chain propagation. Due to their low reactivity, peroxy radicals are present in a relatively high concentration in the system when compared with other radicals (determined via electron spin resonance)[1].

Since peroxy radicals possess a low energy status, they react selectively and abstract tertiary hydrogen atoms in preference to secondary and primary hydrogen atoms (C-H primary: C-H secondary: C-H tertiary = 1:30:300 as relative rate). Their reactivity is also influenced by steric effects: primary and secondary peroxy radicals show a three to five times higher reactivity than tertiary peroxy radicals.

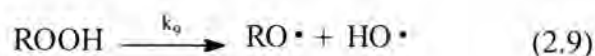


(2.8)

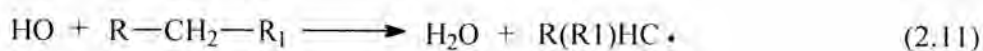
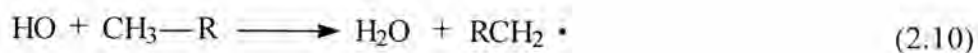
The occurrence of these intramolecular reaction sequences leads to an increased rate of formation of hydroperoxide which results in a reinforced auto-catalytic degradation of the hydrocarbons.

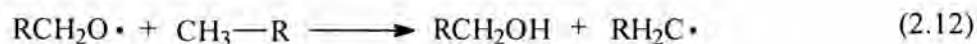
Chain branching

During the early stage of auto-oxidation various types of hydroperoxides are generated. At low concentrations they may be cleaved homolytically to yield an alkoxy radical and a hydroxy radical:

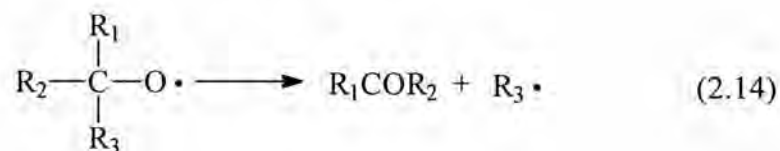


However, this process is thwarted because of a high activation energy, hence reaction (2.9) only plays a significant role at higher temperatures or under catalyzed conditions. Once formed, hydroxy and especially primary alkoxy radicals are so active that they abstract hydrogen atoms in non-selective fashions:

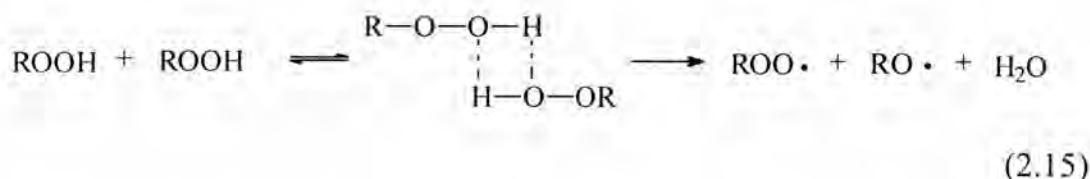




Secondary and tertiary alkoxy radicals prefer undergoing elimination to form aldehydes and ketones:



At high concentrations, i.e. at an advanced state of oxidation, hydroperoxides may react via a bimolecular mechanism:



As a consequence of hydroperoxide accumulation and subsequent cleavage, the concentration of reactive free radicals initiating new chains increases. The time from the beginning of the oxidation to the auto-catalytic phase of the auto-oxidation is called the 'induction period'.

The relation between hydroperoxide accumulation and oxygen uptake of a hydrocarbon is schematically presented in Figure 2.1. As can be seen, during the induction period hydroperoxides are accumulated. After the induction period, the oxidation is auto-catalyzed.

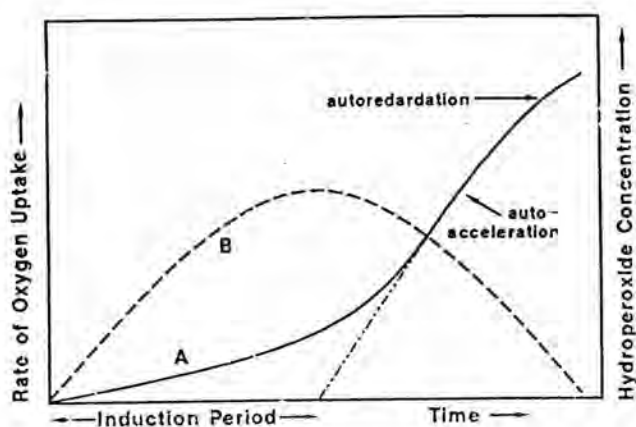
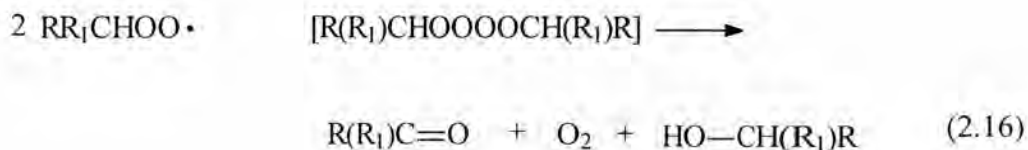


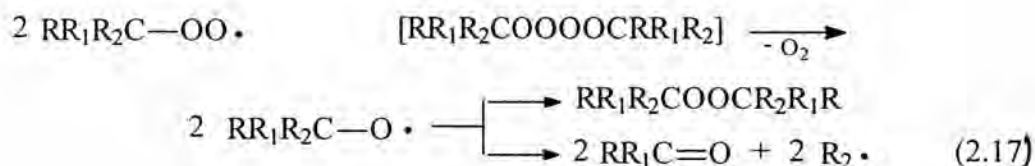
Figure 2.1 Influence of hydroperoxide concentration on the rate of oxygen uptake over time; A = rate of oxygen uptake; B = hydroperoxide concentration (schematic drawing)

Termination of the radical chain reaction

As the reaction proceeds, auto-oxidation is followed by an auto-retardation stage resulting in a standstill before combination of radical species (such as peroxy radicals) to yield unreactive species (such as ketones and alcohols):

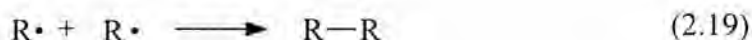


In this example, primary and secondary peroxy radicals form intermediates which disproportionate to non-radical degradation products. In contrast, tertiary peroxy radicals may either combine to give di-tertiary alkyl peroxides or undergo a cleavage reaction leading to ketones and alkyl radicals:



Generally, the rate of termination increases across the series tertiary peroxy < secondary peroxy < primary peroxy.

If the oxygen concentration in the bulk liquid phase is limited (oxygen partial pressure below 50 torr) two additional ways of radical recombination result:



In summary, the uncatalysed oxidation of hydrocarbons at temperatures of up to 120 °C leads to alkylhydroperoxides (ROOH), dialkylperoxides (ROOR), alcohols (ROH), aldehydes (RCHO) and ketones $\text{R}(\text{R}^1)\text{C}=\text{O}$. In addition, cleavage of a dihydroperoxide II of reaction (4.6) leads to diketones ($\text{RCO}(\text{CH}_2)_x\text{COR}^1$), keto-aldehydes ($\text{RCO}(\text{CH}_2)_x\text{CHO}$), hydroxyketones ($\text{RCH}(\text{OH})-(\text{CH}_2)_x\text{COR}^1$) and so forth.

Under metal catalyzed conditions or at higher temperatures, which will be dealt with in sections 2 and 3, degradation leads to a complex mixture of final products.

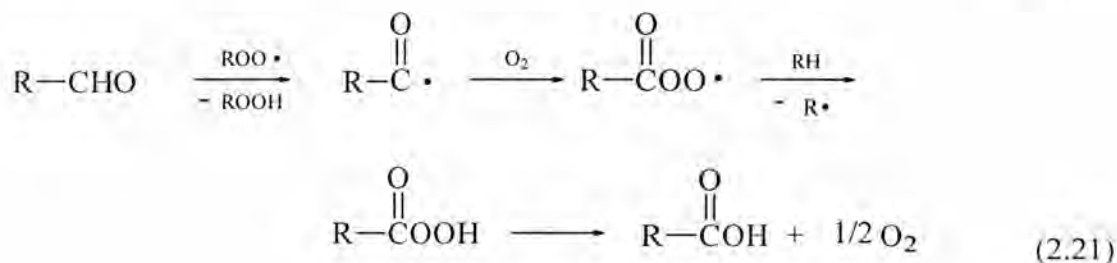
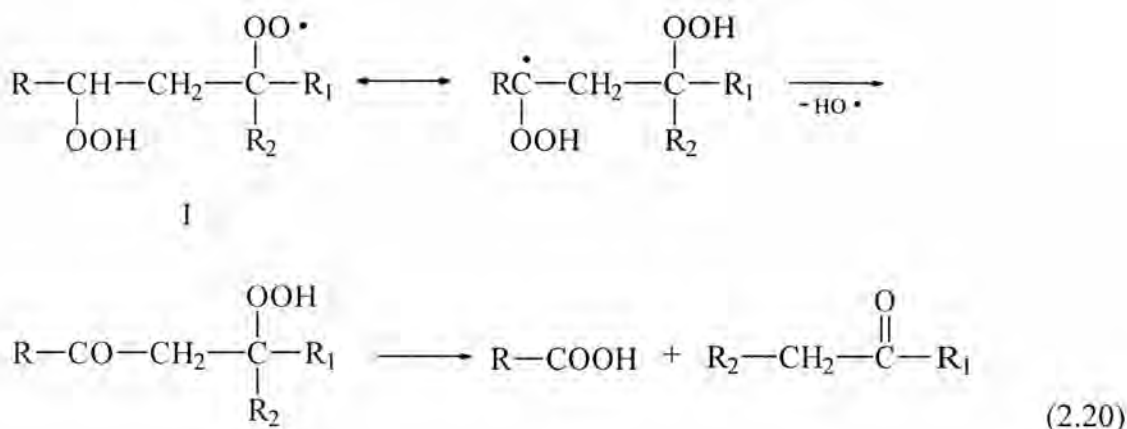
2.1.1.2 Oxidation of hydrocarbons at high temperature ($> 120^{\circ}\text{C}$)

Above 120°C the degradation process can be divided into a primary and a secondary oxidation phase.

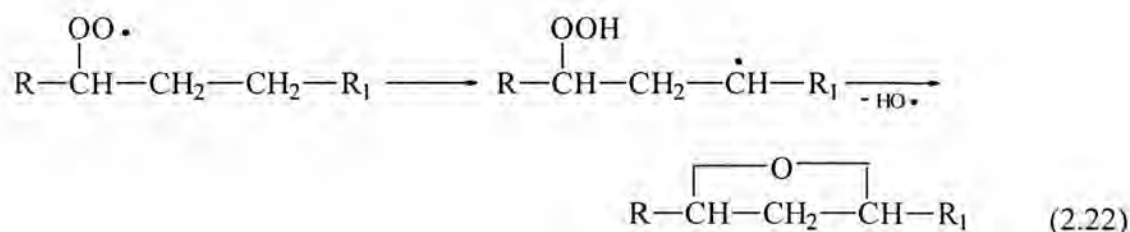
Primary oxidation phase

Initiation and propagation of the radical chain reaction are the same as discussed under low-temperature conditions, but the selectivity is reduced and the reaction rate is increased. At high temperature the cleavage of hydroperoxides plays the most important role.

Reaction (2.9) leads to a proliferation of hydroxy radicals, which non selectively abstract hydrogen atoms (see reaction (2.10) and (2.11)). Acids are formed by the following two reactions, which start from a hydroperoxy peroxy radical (see reaction (2.6)) and an aldehyde :



In addition, when the rate of oxidation becomes limited by diffusion, ethers are formed.



The termination reaction proceeds through primary and secondary peroxy radicals according to reaction (2.16), but at temperatures above 120°C these peroxy radicals also interact in a non-terminating way to give primary and secondary alkoxy radicals:

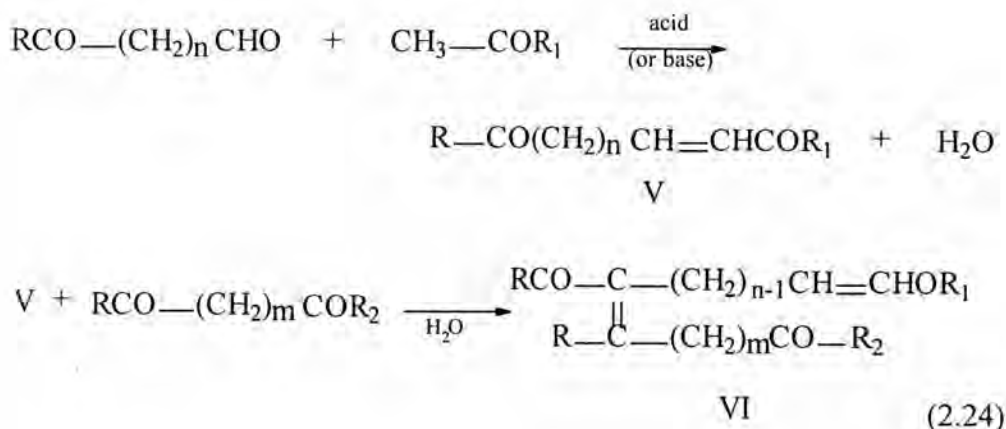


These radicals again contribute to the formation of cleavage products via reactions (2.12) and (2.13).

Secondary oxidation phase

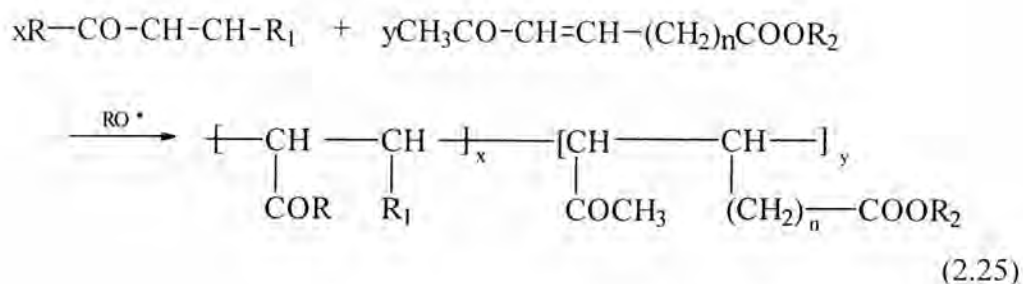
At higher temperatures the viscosity of the bulk medium increases as a result of the polycondensation of the difunctional oxygenated products formed in the primary oxidation phase. Further polycondensation and polymerization reactions of these high molecular weight intermediates result in products which are no longer soluble in the hydrocarbon. The resulting precipitate is called sludge. Under thin-film oxidation conditions, as in the case of a lubricant film on a metal surface, varnish-like deposits are formed. The polycondensation reactions which lead to high molecular weight intermediates (sludge precursors) can be described as follows: In a first step, aldehydes or ketones

formed in the primary oxidation phase combine *via* an acid-or base-catalyzed aldol-condensation to form α , β -unsaturated aldehydes or ketones:



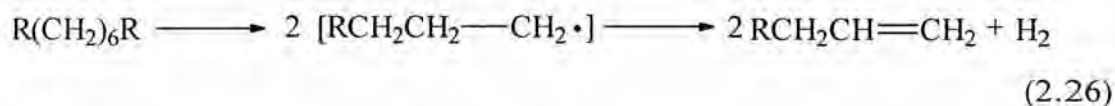
Further aldol-condensations with species VI lead to high molecular weight but still oil-soluble polycondensation products (molecular weight about 2000).

When the reaction becomes diffusion controlled as a result of the increased viscosity of the oil, alkoxy radicals can initiate polymerization of polycondensation products. This leads to sludge and deposit formation as well as to additional oil-soluble high molecular weight products, which contribute to the viscosity increase. This process can be described as copolymerization of two different polycondensation species in which the alkyl groups R, R₁ and R₂ could represent oxo- or hydroxy-functionalised long hydrocarbon chains:



Condensation polymerizations are accelerated in the presence of metals such as iron, but lead suppresses polycondensation.

Under high-temperature conditions there is always the possibility of thermal cleavage of a hydrocarbon chain, especially when the availability of oxygen is limited by diffusion:



Reaction (2.26) leads to unsaturated molecules with lower molecular weight and higher volatility.

The model for high temperature oxidation can be described by Figure 2.2.

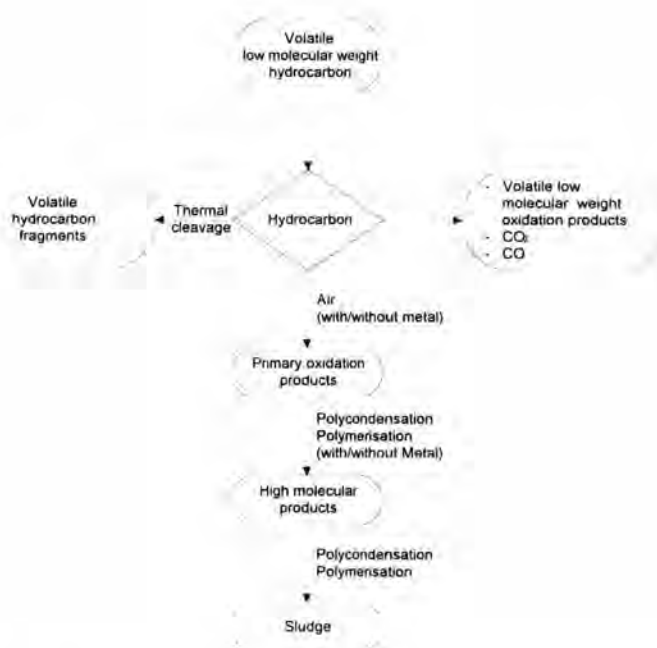
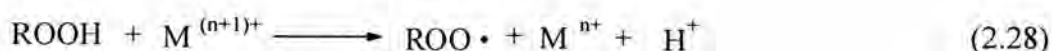
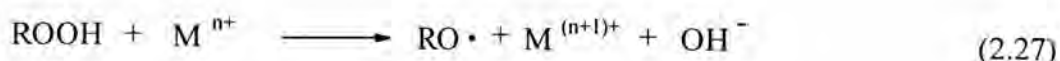


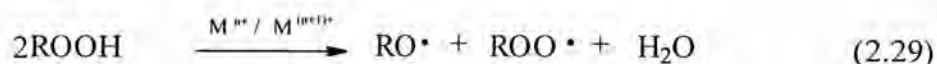
Figure 2.2 Model of lubricant degradation under high temperature conditions.

2.1.1.3 Metal catalyzed auto-oxidation of hydrocarbons

The decomposition of an alkyl hydroperoxide molecule occurs at temperatures of about 150°C. Transition metal ions having two ionic valence states, such as Fe^{2+/3+}, Pb^{2+/4+} and Cu^{1+/2+}, reduce the activation energy of this decomposition process. These ions must be present as metal soaps otherwise they are not catalytically active. Hence the homolytic hydroperoxide decomposition is accelerated at ambient temperature by small concentrations (0.1-50 ppm) of these metals:



Reaction (2.27) and (2.28) can be summarized as (2.29).



Chain branching under the influence of a catalyst at a given temperature proceed faster when compared with the uncatalyzed reaction. The consequence is a high rate of hydroperoxide formation (and hence oxidation) as illustrated in Figure 2.3

The precursor steps of soap formation, shown below with Fe as the metallic surface, arise from the attack of the metal surface by alkylperoxy radicals and alkylhydroperoxide. This process may be called 'corrosive wear'.

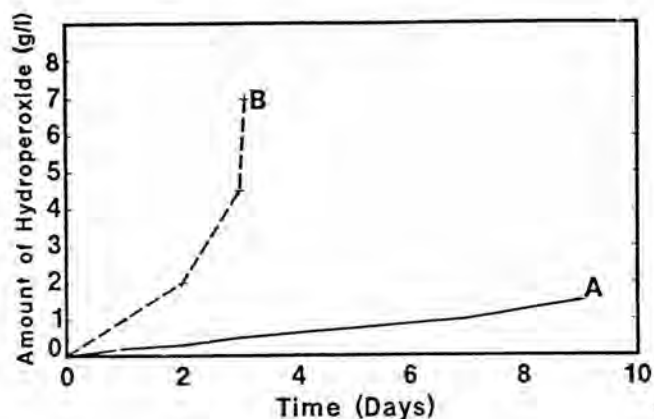
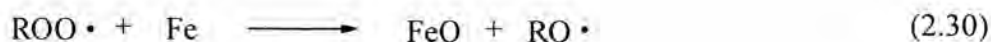
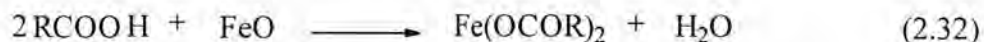


Figure 2.3 Increase of hydroperoxide concentration under the influence of $\text{Fe}(\text{OOCC}_7\text{H}_{15})_3$ catalysis: (A) pure model hydrocarbon; (B) pure model hydrocarbon plus 500 ppm $\text{Fe}(\text{OOCC}_7\text{H}_{15})_3$. Condition 95°C bath temperature; 300ml oil volume; 3 l/hour oxygen flow.

The FeO reacts further with organic acids and forms the iron soaps:



The catalytic activity of copper and iron is summarized as follows[1]:

- In the presence of iron, copper soaps in general retard oxidation and polycondensation/polymerization reactions. On iron ion-free systems organocopper salts behave as pro-oxidants.
- Iron soaps accelerate oxidation and polycondensation/polymerization reactions with increasing concentration.

An example concerning the retardation of oxidation by a copper salt during the oxidation of a model hydrocarbon (tetralin) in the presence of 0.5% iron stearate is given in Figure 2.4

In conclusion, the oxidation of model hydrocarbons proceeds via a radical chain mechanism and is strongly influenced by temperature and by certain transition metal ions. This results in the formation of insoluble sludge with a continuous increase in viscosity.

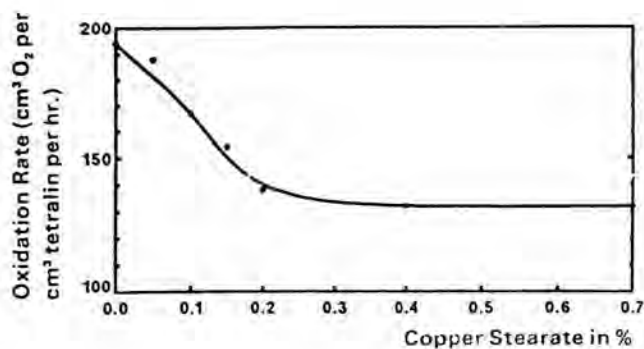


Figure 2.4 Influence of copper stearate on the oxidation rate of the iron stearate (0.5 %) catalyzed oxidation of tetralin.

2.2 Antioxidants in lubricating oil

The use of additives to control lubricant degradation requires a focus on alkyl radicals ($R\cdot$), alkylperoxy radicals ($ROO\cdot$) and hydroperoxides ($ROOH$). Primary alkoxy radicals ($RCH_2O\cdot$) and hydroxy radicals ($HO\cdot$) rapidly abstract hydrogen from the substrate. It is therefore very unlikely that they can be deactivated by natural or synthetic antioxidants, In practice three additive types have proven to be successful in controlling the degradation of lubricating oils:

- radical scavengers
- hydroperoxide decomposers
- synergistic mixtures of these

2.2.1 Radical scavengers

The most widely used types of radical scavengers are phenolic and aminic antioxidants. Recently, organo-copper salts have been introduced to control the oxidative degradation of engine oils[1].

2.2.2 Hydroperoxide decomposers

These compounds convert hydroperoxides into non-radical products thus preventing the chain propagation reaction. Traditionally organosulfur and organophosphorus additives have been used for this purpose. They can be divided according to their structure as follows:

- Organosulfur compounds
- Zinc dialkyl dithiocarbamates
- Organophosphorus compounds

2.2.3 Multifunctional additives

2.2.3.1 Zinc dithiophosphates or metal dithiophosphates

The dominating position of ZnDTPs as additives for lubricating oils is due to their multifunctional performance. Not only do they act as antioxidants, but they also improve the wear inhibition of the lubricant, and protect metals against corrosion. ZnDTPs are mainly used to formulate anti-wear hydraulic fluids and engine oils

2.2.3.2 Organomolybdenum compounds.

These compounds are of general interest in the engine oil area. They are antioxidants and in addition improve the frictional and anti-wear characteristics of the lubricants.

2.2.3.3 Overbased phenates and salicylate

Both phenates and salicylates of magnesium or calcium behave as antioxidants at high temperature.

2.2.3.4 Sulfur/nitrogen and sulfur/phosphorus compounds.

Other multifunctional sulfur/nitrogen, sulfur/phosphorus based additive have antioxidant and anti-wear properties. These additives interact with peroxy radicals and hydroperoxides thus stabilizing industrial lubricants and engine oils.

2.3 Zinc dithiophosphates and metal dithiophosphates

ZDDP and MDDP are antioxidants which have reaction mechanism and are prepared by reaction as follow:

2.3.1 *Reaction mechanism*

The performance of ZnDTPs is strongly influenced by the types of alcohol used for their synthesis. Table 2.1 gives an overview of the variance of performance with type of alcohol[1].

The way ZnDTP performs as an antioxidant is a complex interaction pattern involving hydroperoxides and peroxy radicals. The performance matrix is additionally influenced by other additives which are present in industrial or engine oil formulations.

In a model system comprising cumene hydroperoxide and various ZnDTPs it was demonstrated that the antioxidant mechanism proceeds by an acid catalyzed ionic decomposition of the hydroperoxide. The catalyst species is O,O'-dialkylhydrogendithiophosphate, (RO)₂PSSH, derived from the ZnDTP.

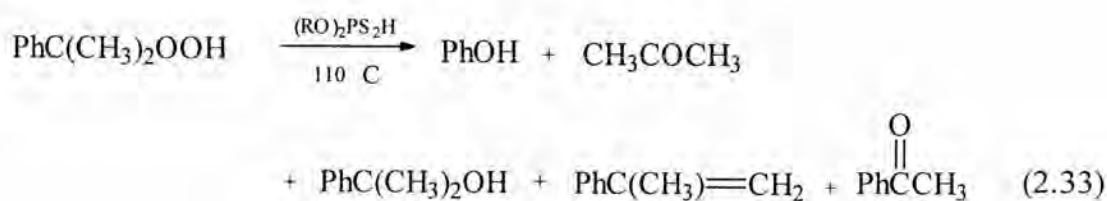
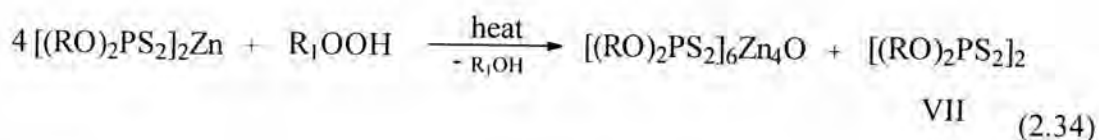


Table 2.1 Structure activity dependency of ZnDTPs

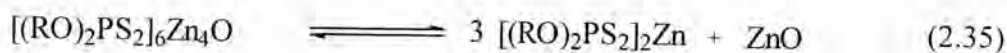
Structure	Function		Property	
	Oxidation inhibition	Wear protection	Thermal stability	Hydrolytic stability
Primary ZnDTP $\text{Zn} \left[\text{S}-\overset{\text{S}}{\parallel}{\text{P}}(\text{OCH}_2\text{R})_2 \right]_2$	satisfactory	satisfactory	good	satisfactory
Secondary ZnDTP $\text{Zn} \left[\text{S}-\overset{\text{S}}{\parallel}{\text{P}}(\text{OCHR}_1\text{R}_2)_2 \right]_2$	good	good	moderate	good
Aryl ZnDTP $\text{Zn} \left[\text{S}-\overset{\text{S}}{\parallel}{\text{P}}(\text{O}-\text{C}_6\text{H}_4-\text{R}_2)_2 \right]_2$	moderate	bad	very good	bad

While the first four products are the result of an acid-catalyzed cationic chain reaction, the acetophenone is formed by a free radical mechanism.

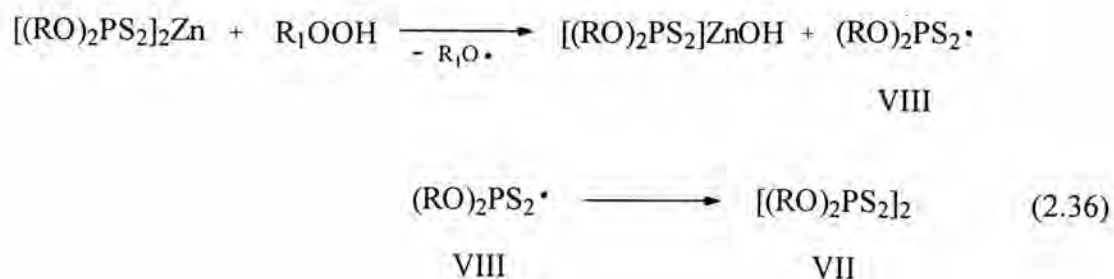
There are two inter-related mechanisms for the formation of the acid catalyst. In the first mechanism, a rapid, initial reaction of ZnDTP and hydroperoxide forms a basic ZnDTP and a disulfide (VII).



An induction period follows where the rate of decomposition of the hydroperoxide is slow. In this reaction phase the basic ZnDTP dissociates to form ZnDTP and ZnO.



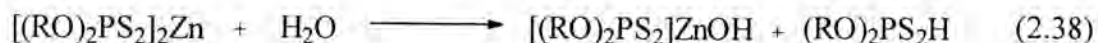
The ZnDTP then reacts with hydroperoxide to form additional disulfide(VII) via the dtp radical (VIII):



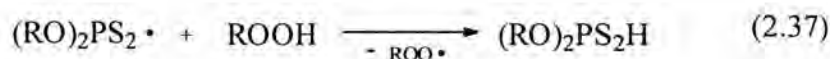
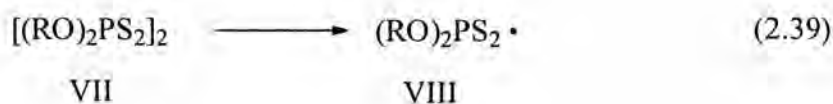
The kinetics of the reaction result in a final rapid decomposition of the hydroperoxide provided the concentration of the basic ZnDTP is low. Under these conditions the sulfur radical is unable to dimerize. Instead it reacts with hydroperoxide leading to the catalytically active acid:



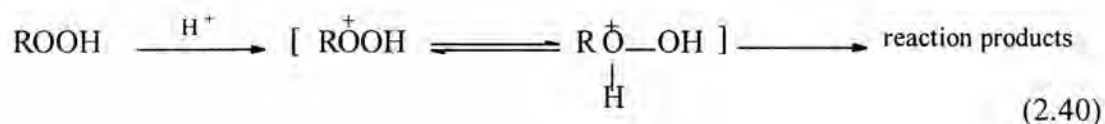
The second source of this acid arises when the ZnDTP concentration falls below a critical level. The traces of water interact with the ZnDTP forming the acid catalyst:



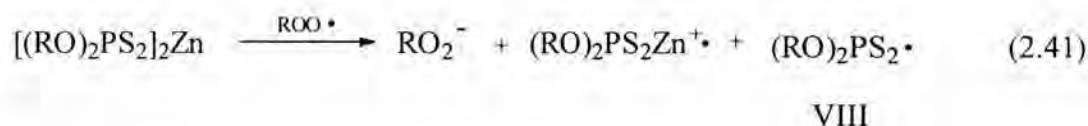
It was demonstrated that at temperatures above 125°C, the disulfide(VII) could be an additional source of the acid catalyst via reaction (2.16) followed by reaction (2.37):



A general scheme for the decomposition of hydroperoxides may be:



ZnDTP may also interact with peroxy radicals according to the following mechanism:



The radical (VIII) may react again with hydroperoxide according to reaction (2.39) thereby regenerating the DPTA, $(\text{RO})_2\text{PSSH}$, which is a better inhibitor than the ZnDTP.

2.3.2 Synthesis

ZDTPs or ZDDPs can be synthesized in two steps, as shown in Figure 2.5. The synthesis of O,O-dialkylphosphorodithioic acids (DTPA or DPDA) followed by their conversion to zinc dialkyl dithiophosphates or metal dialkyl dithiophosphated (ZDDP) [3-6].

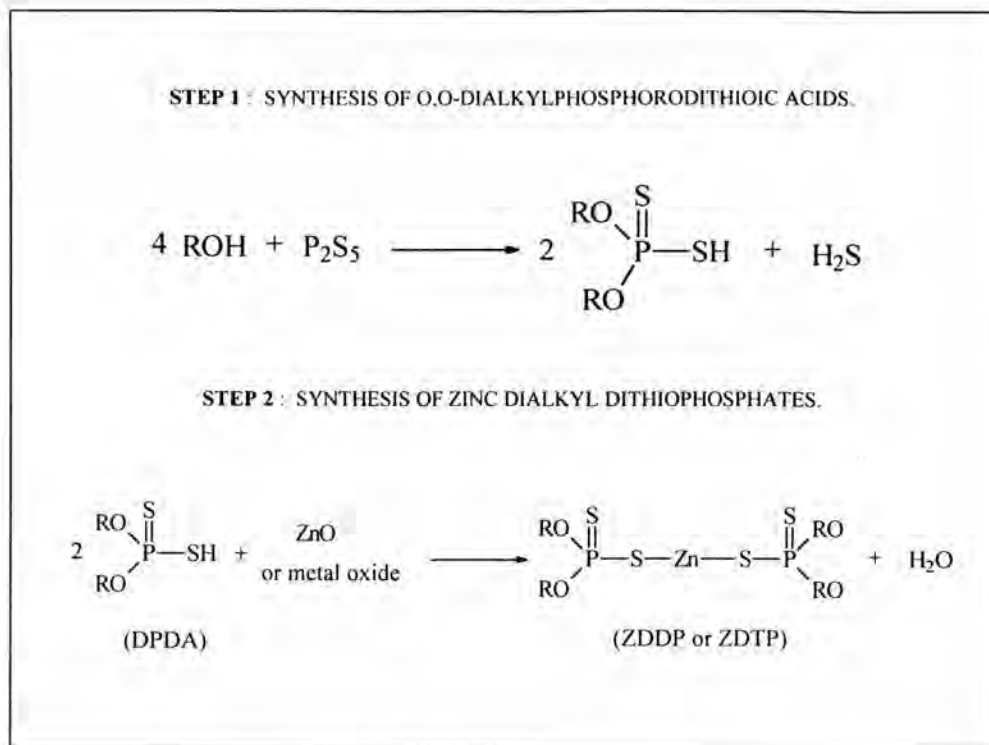


Figure 2.5 Reaction scheme

2.4 Isoamyl alcohol

3-methyl-1-butanol, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$, (isoamyl alcohol, isobutyl methanol or primary isoamyl alcohol) is a water-white, primary alcohol which is chief ingredient of amyl alcohol in fusel oil, that is a by-product of the ethyl alcohol fermentation industry (the fermentation of crude potato starch to ethyl alcohol). Refined amyl alcohol from this source contains about 85% isoamyl alcohol and 15% 2-methyl-1-butanol[7-10].

2.4.1 *Physical properties*

Isoamyl alcohol has melting point at -117.2°C , boiling point at 130.5°C and has density of 0.812 g/cm^3

2.4.2 Chemical properties

The chemical properties of isoamyl alcohol is determined by the hydroxyl group. The most important reactions are dehydration, oxidation and esterification.

2.4.3 Uses

Isoamyl alcohol is used mainly as a solvent and an extracting agent in several practical applications. The important use is in the production of di(isoamyl)ether; which is a component of a catalyst system used for industrial production of polypropylene(PP). It is also used in the production of herbicides and employed for the synthesis of fragrances and flavors.

2.4.4 Storage and Transportation

Isoamyl alcohol can be stored or dispatched in normal or enameled steel containers, provided that ingress of moisture is prevented. Stainless steel containers can also be used. National and international safety regulations relating to air, sea, inland water, rail and road transport and current safety data for isoamyl alcohol must be observed.

Flash point of isoamyl alcohol is 44 °C, It belongs to safety class A II (VbF).

2.5 Previous work

Early studies for preparation and performance evaluation of metal dithiophosphate have been demonstrated in the following patent literatures.

Georges [11] has reported that metallic dithiophosphates could be prepared from metal of groups II B, III B, IV B or VIII of the Periodic System of Elements, preferably zinc. They are obtained by the action of P_2S_5 on a monoester alcohol and then by the reaction of zinc oxide with the dithiophosphoric acid formed.

Roberts [12] has found that molybdenum(IV) compounds of dialkyldithiophosphates could be prepared by reducing Mo(V) or Mo(VI) with H_2S . He used molybdenum(V) dithiophosphates of the type $Mo_2O_3(dtp)_4$ or molybdenum(VI) dithiophosphates of the type $MoO_2(dtp)_2$ as reactants.

Stephen [13] has found that novel oxymolybdenum dialkyldithiophosphate having the general formula $[(RO)_2PS_2]_2Mo_2O_4$, could be prepared by reaction of sodium molybdate with hydrochloric acid, then reacted with dialkylphosphorodithioic acid. The products were tested for wear-performance and oxidation performance.

Gunter [14] has shown that metal dithiophosphates could be prepared by neutralizing dithiophosphoric acid with zinc, cadmium or nickel base in the presence of an acidic promoter. Metal dithiophosphate derived from zinc oxide was preferred.

Maurice [15] has reported compounds of the metal dihydrocarbyl-dithiophosphyl-dithiophosphate type, their preparations and uses. The metals selected were zinc, cadmium, lead and antimony .

Colclough [16] has suggested the preparation of metal dithiophosphates. The preparation was performed by reacting a basic compound, preferably ZnO, with a dithiophosphoric acid and this acid was obtained by reacting P_2S_5 with alcohol and acid catalyst was used. The products were tested in the four ball friction tests (1 rpm, 5 kg, 110 °C) and the results showed that metal dithiophosphates have good friction properties.

Wolfram [17] has demonstrated the preparation of dialkyl-dithiocarbamates of multivalent metal by reacting metal oxides with a secondary amine and carbon disulfide while simultaneously heating to 50-95 °C and removing water of the reaction. Suitable metal oxide was zinc oxide .

Abbas [18,19] has suggested a process for preparing an overbased metal salt of hydrocarbyl dithiophosphoric acid with metal oxide, such as ZnO, an amount sufficient to form overbased metal salt of hydrocarbyl dithiophosphoric acid. The metal oxides had a surface area of not less than about 4 m²/g up to 12 m²/g.

Yoshihiro [20] has reported that lubricating oil compositions containing molybdenum and zinc dialkyldithiophosphates were excellent in prevention of abrasion in internal combustion engines.

Sarin [21] has shown that O,O-dialkylphosphorodithioic disulfides have good anti-wear, extreme pressure and anti-oxidation performances. These additives were studied in a 150 SN mineral base oil for testing anti-wear and extreme-pressure properties by using a four-ball machine and tested anti-oxidation performance by using differential scanning calorimetry. It has concluded that these additives showed good anti-wear, antioxidant and EP properties.