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Improvement of oxidative stability of trimethylolpropane trioleate lubricant

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ABSTRACT

The aim of this study was to determine the optimum formulation for vegetable oils-based synthetic ester lubricant (trimethylolpropane trioleate, TMPTO) by searching for suitable antioxidants to extend its service life. The oxidative stability was evaluated by rotary bomb oxidation test (RBOT), pressurized differential scanning calorimetry (PDSC) and oven oxidation stability test (OOST). The results indicated that *N*-phenyl-alpha-naphthylamine (Am2) exhibited superior antioxidant activity compared to other selected antioxidants and thus could be used as the optimal primary antioxidant for TMPTO. Synergistic antioxidant effect between Am2 and a sulfur-containing auxiliary antioxidant (DLTDP) was also carefully investigated. The results suggested that the combination of Am2 and DLTDP revealed a good antioxidant synergism and could effectively improve the anti-oxidation ability of TMPTO. The best anti-oxidation result was achieved by the combination of 0.9 wt.%/0.1 wt.% Am2/DLTDP. Good antioxidant synergism between Am2 and DLTDP could be attributed to their complementary anti-oxidation mechanisms (Am2: radical scavenger and DLTDP: peroxide decomposer).

1. Introduction

In recent years, increasing environmental awareness and more restrictive regulations have accelerated the development of biodegradable lubricants all over the world [1–3] The lubricants of the future have to be more environmentally friendly and to have a higher level of performance and lower total life-cycle costs (LCC) than commonly used lubricants today [2,4]. Synthetic esters lubricants derived from renewable resources have been developed for applications in environmentally sensitive areas such as forests and agriculture areas due to their high biodegradability, low toxicity, and environmentally benign nature [2,3]. Moreover, such lubricants exhibit better lubricity, excellent viscosity index, and lower volatility than petroleum-based lubricants [3,5,6]. Most of synthetic esters are the branched polyol esters derived from neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE). The alcohol moiety of this type of synthetic esters is usually petrochemical origin, whereas the fatty acids are almost exclusively based on renewable resources, namely vegetable oils [2,3,7]. Trimethylolpropane trioleate (TMPTO) prepared by the esterification of trimethylopropane and oleic acid has been utilized as high performance base fluids for industrial applications such as hydraulic fluids, two-stroke engine oils, and metal working oils, etc. [2,6,8].

Though TMPTO exhibits superior properties compared to mineral oils, it has been slow in gaining wide acceptance as lubricant base fluid. The main drawback to restrict its wide application is its poor oxidative stability due to the presence of abundant unsaturated bonds ($C{=}C$) in the fatty acids moiety of TMPTO molecule, which are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxygen-containing compounds [2,6,9]. This phenomenon results in insoluble deposits and increases the oil acidity and viscosity, which eventually strongly affects the lubricating process during their industrial in-life service [10]. In order to avoid or temporally delay these problems, lubricants need to possess superior oxidation stability. Therefore, antioxidants are the key additive which can delay or prevent the oxidation process by protecting the lubricant from oxidative degradation, allowing the oil to meet the demanding requirements for use in industrial applications [10,11]. Antioxidants interrupt the auto-oxidation process in different ways, according to their different structure and antioxidant mechanism. Oxidation inhibitors are classified into two groups: hydroperoxide decomposers and free radical scavengers, depending upon the mode of their controlling action. Hindered phenols and arylamine antioxidants as radical scavengers function by donating hydrogen atoms to terminate alkoxy and alkyl peroxy radicals, thus interrupting the radical chain mechanism of the auto-oxidation process.

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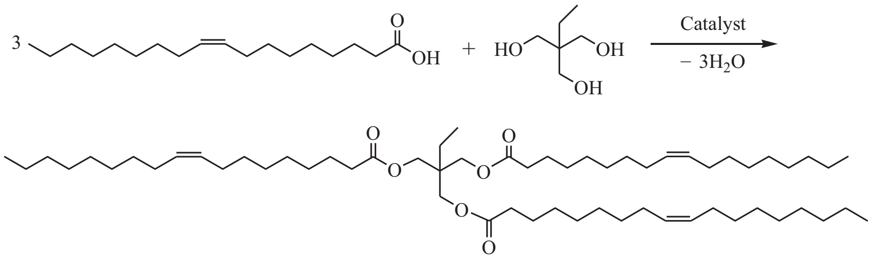

Fig. 1. Outline of synthesis of trimethylolpropane trioleate (TMPTO).

Organosulfur compounds as hydroperoxide decomposers function through the formation of oxidation and decomposition products. The antioxidant action starts with the reduction of an alkyl hydroperoxides to a less reactive alcohol, with the sulfide being oxidized to a sulfoxide intermediate [12]. Several types of antioxidants are widely used to increase oxidative stability of lubricants [13–17]. Becker and Knorr [18] reported that hindered bisphenols, polyhydroxybenzenes, zinc and bismuth dithiocarbamates performed better in vegetable oils than monophenol/aromatic amine based commercial formulations. Duncan et al. [19] evaluated oxidative stability of ashless additives for the biodegradable polyol ester base oils. Previous studies [11,20–23] have shown that combinations of different antioxidants can exhibit better oxidation inhibition than any individual antioxidant, revealing a good synergistic effect on oxidation stability.

A variety of methods have been reported to evaluate the thermal oxidative stability of lubricating oils and the oxidation inhibition capacity of antioxidants, including rotary bomb oxidation test (RBOT), thin film micro-oxidation test (TFMO), turbine oil stability test (TOST), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and pressurized differential scanning calorimetry (PDSC). RBOT is a rapid method and has been used to study the oxidation stability of lubricating oils by many workers [9–11,24–26]. Recent studies have shown that PDSC is an effective way to evaluate the antioxidant efficiency and oxidation stability of base oils, which is rapid, requires very little sample and provides good precision for measurement of oxidative degradation [9,25,27–30].

The purpose of this study was to improve oxidation stability of TMPTO to extend its applicability by searching for suitable antioxidants. The oxidative stability of antioxidants in TMPTO was evaluated by RBOT, PDSC and oven oxidation stability test (OOST). Additionally, the synergistic effect of antioxidants on the oxidative stability of TMPTO was carefully investigated.

2. Experimental

2.1. The base stock and additives

The base oil used in this work was trimethylolpropane trioleate (TMPTO). Trimethylolpropane (TMP), oleic acid (C18&Below < 10 wt.%; C18:1, 75–80 wt.%; C18:2 < 14 wt.%; others <1.5 wt.%) and solid acid catalyst (SO_4^{2-}/M_xO_y, M = Zr, Ti, Sn) were commercially obtained from domestic market (China) and were used to synthesize TMPTO without further purification. The esterification process was monitored by produced water and acid value. When the reaction was completed, the catalyst was removed from the product by filtration and excess oleic acid was removed by distillation under reduced pressure. After further refining process of the crude product, a clear, pale yellow liquid was obtained. The synthetic process and IR spectra of TMPTO were shown in Figs. 1 and 2, respectively. It was seen from IR figure, the peak of the hydroxy group (—OH) at 3468 cm^{-1} was very small and even could be neglected, indicating that the esterification reaction was considerably close to completion. At the same time, esterification rate calculated by acid values of the system before and after the reaction reached above 98 wt.%. The typical properties of TMPTO were listed in Table 1. In order to keep TMPTO from oxidation, it was stored sealed in dry and airy place to protect from high temperature and fire. The acid value of TMPTO was often tested and changed little. Therefore, TMPTO may not be subjected by oxidation within a short time at room temperature and normal atmospheric pressure.

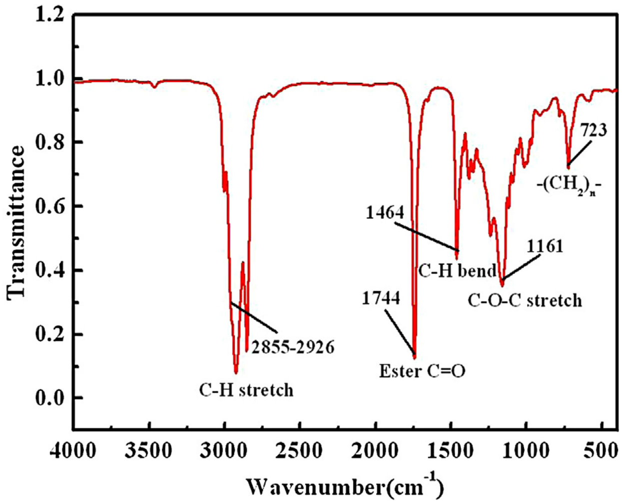

Fig. 2. Infrared (IR) spectra of the trimethylolpropane trioleate (TMPTO).

The antioxidant additives used were commercial available products, which were Irganox L115 (Ph-S) and Irganox L57 (Am1) purchased from the Ciba Company, T531 (Am2), SONOX 1010 (Ph) and SONOX DLTDP obtained from domestic market (China). These additives were selected based on their excellent performance at high temperatures. The chemical structures of five antioxidants were displayed in Fig. 3. All the additive concentrations were expressed in weight percentage.

Table 1
Typical properties of TMPTO.

Properties	TMPTO	Test method
Total acid number (mg KOH/g)	0.41	ASTM[a] D 974-97
Kinematic viscosity at 40 °C ($mm^2\,s^{-1}$)	51.36	ASTM D 445-86
Kinematic viscosity at 100 °C ($mm^2\,s^{-1}$)	10.11	ASTM D 445-86
Viscosity index	189	ASTM D 2270-98
Pour point (°C)	−41	ASTM D 97-96a
Flash point (°C)	309	ASTM D 92-05a
Copper strip corrosion (100 °C, 3 h)	1b	ASTM D 130-83

[a] American Society for Testing and Materials (ASTM).