A VERY EFFECTIVE STABILIZER FOR PERFLUOROPOLYETHERTR LUBRICANTS

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ABSTRACT

A new stabilizer for fluorinated lubricants, either oils or greases, was developed stemming from the chemistry of perfluoropolyethers. The additive shows good efficiency in improving the stability of perfluoropolyether oils at very high temperatures in presence of metals and under oxidative environments, extending thus the life of the formulated lubricants. Some specific tests were carried out in order to assess performances in applications.

Furthermore, as a first approach, grazing infrared reflection-absorption spectroscopy was used as a probe for studying structural and topological issues relative to additive-surface interactions.

1. INTRODUCTION

It is well-known that perfluoropolyether oils suffer from thermo-oxidative environments in combination with metals [1]. Many mechanisms were suggested to explain this behavior [2-4] and the common opinion is that –O-CF₂-O- sequences, acetal units, are reasonably weak points of the chain. In oxidative environment at high temperatures and in presence of metals, a two-stage reaction is observed [5]. In the first stage the metal oxide is converted into metal fluoride and, in the second one, a fast decomposition of the fluid occurs catalyzed by the new surface so formed. Thus, a wide variety of additives were synthesized to stabilize these fluids [6-10] in order to improve their endurance in high-temperature applications.

Recently, a new additive without phosphorous atoms was proposed. Preliminary results [11] have shown a good activity as thermo-oxidative stabilizer for perfluoropolyether lubricants. The present work reports experimental results obtained from specific tests, in order to clarify the real efficiency of the new structure in improving perfluoropolyether performances in high- temperature applications.

2. MATERIALS AND METHODS

Experiments were carried out with a base oil having the following structure:

\[
\text{CF}_3\cdot[\text{(O-CF}_2\text{CF}_2)_m\cdot\text{(O-CF}_2\text{CF}_2)_n]\cdot\text{O-CF}_3.
\]

This lubricant has an average molecular weight of about 10000 and a kinematic viscosity at 20°C around 270 cSt; the m/n ratio is about 1.

The additive (DA410) used in this work has the following chemical structure:

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{OCH}_2\text{CF}_2\text{R}^f\cdot\text{O} \quad \text{CF}_2\text{CH}_3\text{O} \\
\end{align*}
\]

where R\(^f\)=\[[\text{O-CF}_2\text{CF}_2]_m\cdot\text{(O-CF}_2\text{CF}_2)_n]\cdot\text{O-CF}_3 and the average molecular weight was about 2500.

Two grease samples were prepared by thickening the oil with 30% by weight of PTFE’s powder; one sample was stabilized with 2% by weight of DA410. After refining a cone penetration of about 280 mm/10’ was measured for both.

Stability tests for oils.

The micro-oxidation corrosion test was carried out on oils according to a previously described method [11]. Isotherms were imposed from 250°C up to 300°C in presence of a 1 l/h air flow rate, and of stainless steel and Ti-Al-V alloy metal specimens.

Another series of tests was carried out by using a metal specimen made of 100Cr6, whose surface was previously activated with fluorine. The COF₂ production rate due to degradation reactions at 260°C was detected as function of the DA410 concentration in the oil formulation.

Stability tests for greases.

Glass cups, filled with 45 g of grease samples and 10% of iron powder, were placed in a ventilated oven at 250°C for 100 h. Weight loss was checked during the time.

Functional life of greased ball bearings was determined according to the ASTM D1741 method, without the grease reservoir.

Moreover, in order to verify some effects anti-wear under severe conditions, extreme pressure (E.P.) four-ball wear tests were carried out according to the IP239 method.

3. RESULTS AND DISCUSSION

In micro-oxidation tests, after a slow induction time corresponded on a weight loss up to 2% (step I), a very fast degradation occurred (step II). The addition of DA410 at 1% by weight in oil formulations gave a 40 times improvement in terms of the first step duration. In fact, the formulation with DA410 lasted at 250°C for 800 hours versus only 20 hours without additive. During these reactions a surface modification was clearly observed. SEM (Scanning Electron Microscopy) analyses of metal specimens (100Cr6) were performed during
step I and II. In Fig. 1 is shown the surface appearances. In the step I (Fig.1-B) the formation of metal fluoride generated catalytic sites active on the degradation reaction of the step II (Fig.1-C). In order to verify the DA410 activity under very harsh conditions, oil formulations were tested in presence of a surface ad hoc activated with F₂. These tests were carried out by immersing the metal specimen in oil formulations having different DA410 concentrations, from 0.003% up to 3% by weight. We found that DA410 works already at 0.03%; actually, at lower concentrations the gas evolution rate, due to degradation reactions monitored over 2 days, began to substantially increase (Fig.2). These results suggest that DA410 is able to increase the energetic barrier of the reaction catalyzed by metal surface and also to protect the oil even when metal fluorides are already formed.

![Figure 1](image)

**Figure 1** – Steps of surface modification during thermal oxidation test: A) not exposed; B) step I; C) step II

The good stability imparted from DA410 to oil formulations was reflected on grease performance improvement. The stability test carried out in glass cup with iron powder showed at 250°C after 100 h a weight loss of the formulated grease of about 4% with respect to the blank test where the grease lost about 50% after 24 h. The failure time registered at 150°C, with functional life of greased ball bearings test, was around 3000 h against 800 h for the bearing filled with grease without additive. Moreover, no weld point was observed for the formulated grease under E.P. 4-ball wear test in the whole range of applied loads in comparison with the blank test that showed a weld point at 501 kg.

![Figure 2](image)

**Figure 2** – Gas evolution rate vs. DA410 concentration at 260°C on activated metal surface

The good performances of DA410 as stabilizer for PFPE oils in presence of metals suggest specific activity on metal surface. Thus, a first approach to investigate the additive-surface interaction was attempted by using Grazing Angle InfraRed Reflection Absorption Spectroscopy (GA-IRRAS). The comparison with the GA-IRRAS spectrum of a very thin layer of DA410 on a 100Cr6 surface and an usual transmission IR spectrum clearly revealed differences in terms of the relative intensity among normal modes of vibration of substituted aromatic moiety (NO₂ stretching, C=C stretching and in plane ring deformation) and of the perfluoropolyether chain (cooperative motions involving C-C, C-O-C and CF stretching). This phenomenon could be attributed to specific topology of the metal-additive interface, through a physicochemical interaction causing, *inter alia*, PFPE chain conformational changes.

### 4. CONCLUSION

We demonstrated that DA410 additive improved PFPE performances, either for oil or grease formulations, on high temperature applications, under oxidative environment and in presence of metals. A first attempt to explain this behavior in terms of additive-surface interaction was made by infrared reflection-absorption spectroscopy.


