

Experimental Investigation on the Influence of Engine Oil Additives on Silicone Rubber

Shintaro Kusuhara

JXTG Nippon Oil and Energy Corporation

Kenichi Yoshimura, Kenichi Kunieda, and Nozomu Suzuki

NOK Corporation

Shingo Matsuki and Yuji Shitara

JXTG Nippon Oil and Energy Corporation

ABSTRACT

In developing engine oils, it is crucial to consider their compatibility with the rubbers used for seals. Among the different seal rubbers, silicone rubber is particularly susceptible to attack by acids and bases, which means it would be more likely to be affected by certain engine oil additives. In this study, the effects of some major additives, namely detergents, zinc dialkyl-dithiophosphate (ZDDP) and molybdenum dithiocarbamate (MoDTC), on silicone rubber were investigated. Silicone rubber test specimens were immersed in sample oils containing these additives for a prescribed period at 150°C, then the physical properties of the test specimens were measured to compare the effects of the different additives. It was found that ZDDPs dramatically reduce the tensile strength of silicone rubber, with primary ZDDP having a greater effect than secondary ZDDP. Analyses of the test specimens by means of Fourier Transform Infrared Spectroscopy (FT-IR) revealed that the silicone rubbers had degraded, causing changes in the polymer structure. The test specimen immersed in sample oil containing primary ZDDP was degraded to a deeper section than that immersed in secondary-ZDDP-containing oil. This may be because primary ZDDP reduces tensile strength more than secondary ZDDP. In addition, analyses of the sample oils were conducted in order to determine which of the ZDDP-derived species were degrading the silicone rubber. The phosphorus compounds in the sample oils after immersion were identified by means of ^{31}P NMR. When silicone rubber specimens were immersed in sample oils containing these phosphorus compounds, it was found that acidic phosphorus compounds, such as alkyl acid phosphate and phosphorothioate, had major effects. It would appear that these are the compounds which degrade the silicone rubber. Silicone rubber specimens were also immersed in test oils containing a detergent together with ZDDP or an acidic phosphorus compound. In these cases, the drop in tensile strength of the silicone rubber was much smaller. The reason may be that the overbased salt in the detergent neutralizes the acidic phosphorus compound to help prevent degradation of the silicone polymer.

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INTRODUCTION

The performance of engine oils has improved in step with the evolution of engine technologies. Stricter emissions and fuel economy regulations are being imposed on automobiles for environmental reasons. Because some problems cannot be solved with better engine technologies alone, engine oils are being asked to meet a broader range of requirements (1-2). There is particular emphasis on fuel economy improvement, longer drain intervals and compatibility with emission control systems (3, 4, 5). In newer engines, the introduction of new mechanisms and materials aimed at improving fuel economy means there is a need for engine oils which are compatible with these technologies (6-7). As the requirements for engine oils become stricter and more varied, their formulations are being improved, using new types of base oils or additives and experimenting with new combinations of additives (8, 9, 10, 11).

For engine oils, compatibility with engine parts is a critical requirement. Rubber seals are often in contact with engine oils, and so it is especially important to consider the potential for chemical interaction with rubber materials in developing engine oils. The engine oil specifications issued by the International Lubricant Specification Advisory Committee (ILSAC) and Association des Constructeurs Européens d'Automobiles (ACEA), for example, include requirements for compatibility with rubber materials such as fluoro rubber (FKM) and silicone rubber (VMQ), which are used to make crank shaft seals.

Silicone rubber has excellent heat resistance, cold resistance and oil resistance. Silicone rubber's heat resistance comes from its polysiloxane backbone (made up of Si-O-Si units), due to the fact that Si-O bonds have higher bond energy than C-H bonds. However, the polysiloxane backbone is susceptible to attack from acids or bases and

can be degraded even at relatively low temperatures, due to the ionicity of Si-O bonds (12). This can often lead to compatibility problems with engine oils. Silicone rubber was once widely used as an engine seal material, but has been largely replaced by fluoro rubber because of the degradation problem. Yet silicone rubber is still found in engine compartments, due to its performance in low-temperature applications and as a room-temperature-vulcanizing (RTV) rubber.

In developing engine oils, compatibility with silicone rubber is still a key issue. However, there have been few comprehensive, systematic studies on the effects of engine oil additives on silicon rubber (13). In particular, almost nothing has been published on the mechanisms of degradation of silicone rubber by these additives. There are thus many unknowns as to the active species (originating in the additives) involved in the decomposition of silicone rubber and the decomposition mechanism.

In this study, the effects of some commonly used engine oil additives which were thought likely to affect silicone rubber were investigated. Specifically, detergents, ZDDPs and MoDTC were. Detergents are metal salts of organic surfactants (soaps) that help preventing deposits and neutralize acidic products in an engine. In these detergents, the surfactants, typically sulfonates, salicylates and phenates, are bonded to metals such as calcium, magnesium, sodium, potassium, or barium. Calcium-based detergents are most commonly added to lubricants. Further, detergents that contain an overbased salt (e.g. calcium carbonate) are very often used and essential for engine oils which are required to neutralize acidic components. Typically, detergents containing overbased salts are referred to as “overbased”, and those that contain no or very little overbased salts are called “neutral”. ZDDPs have been widely used as engine oil additives due to their excellent anti-wear, anti-oxidation, and extreme-pressure properties. They are generally categorized as primary, secondary or aryl types, depending on the type of their alkyl chains. The primary and secondary types are typically used in engine oils. Meanwhile, MoDTCs are oil soluble organomolybdenum compounds that are used as friction modifiers in modern fuel-efficient engine oils in Japan and elsewhere. Silicone rubber test specimens were immersed in sample oils containing these additives and the changes in the rubber properties were measured. The additives found to have significant effects were investigated further in order to determine the species involved in breaking down the silicone rubber and the mechanisms of decomposition.

EXPERIMENTAL

Sample Oils

Five types of detergents, two types of ZDDPs and one type of MoDTC were evaluated in this study. The detergents were overbased calcium sulfonate (**O-SU**), neutral calcium sulfonate (**N-SU**), overbased calcium salicylate (**O-SA**), neutral calcium salicylate (**N-SA**), and overbased calcium phenate (**O-PH**) (Figure 1 and Table 1). All contain a core of overbased calcium carbonate. The ZDDPs were a primary type having C8 alkyl chains (**P-ZDDP**) and secondary type having C6 alkyl chains (**S-ZDDP**) (Figure 2). The MoDTC is mainly composed of di-sulfide-bis [oxo(dialkyl)dithiocarbamate] molybdenum and has a

mixture of C8 and C13 alkyl chains (Figure 3). To simplify the comparisons, the test oils were all formulated with the same base oil (API Group III) and anti-oxidants (amine type and phenol type).

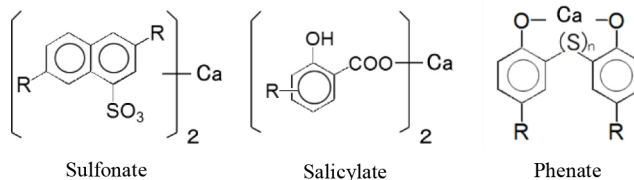


Figure 1. Chemical structures of calcium detergents

Table 1. Characteristics of calcium detergents evaluated in this study

		O-SU	N-SU	O-SA	N-SA	O-PH
Detergent Type		Sulfonate		Salicylate		Phenate
TBN (ASTM D2896)	mgKOH/g	320	20	170	50	250

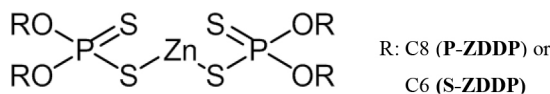


Figure 2. Chemical structure of ZDDP

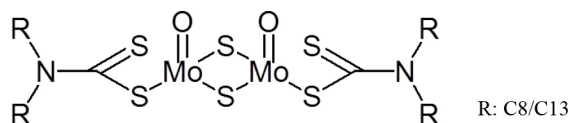


Figure 3. Chemical structure of MoDTC

Silicone Rubber for Test Specimens

The silicone rubber used in this study is a vinyl specific peroxide-cure type compounded with fumed silica and wollastonite as fillers. Rubber sheets of 2 mm thickness were prepared by compression molding at 165°C for 10 minutes and post-curing at 200°C for 4 hours.

Immersion Test

Measurements of initial volume, hardness and tensile properties are made on specimens of specified dimensions cut from sheets of reference VMQ rubbers. The VMQ rubber specimens were immersed in the sample oils and aged at 150°C. The effects of the sample oils on the rubbers were determined by measuring the changes in volume, hardness and tensile properties brought about by the immersion. The test was performed in accordance with JIS (Japanese Industrial Standards) K6258 (14).

Analysis of Silicone Rubber Test Specimens

After immersion, the rubber samples were extracted with hexane for 3 days to remove solubles, then dried in a vacuum oven to remove the solvent. The hexane extracts were condensed with a rotary evaporator. FT-IR measurements of the rubber surfaces were performed on a JASCO FT/IR-6300 FT-IR spectrometer equipped with a Ge single-reflection ATR accessory. ATR FT-IR images of cross sections of the rubber were obtained using a PerkinElmer Spotlight 400 FT-IR imaging system with an ATR imaging accessory. The hexane extracts were analyzed using a JASCO FT/IR-6300 FT-IR spectrometer.

Analysis of Sample Oils

Elemental analysis and quantification of the sulfate or bisulfate ions (SO_4^{2-} , SO_3^-) in the sample oils and precipitates after the immersion tests were conducted by means of ICP (Inductively Coupled Plasma) spectrometry and ion chromatography. Quantification of ZDDP in the sample oils was conducted by means of the HPLC (High Performance Liquid Chromatography) techniques (15). In preparing the test solutions for HPLC analysis, 9-chloromethyl-anthracene was added to the sample oils to react with ZDDP. The test solutions were injected into the silica-based column to detect ZDDP derivatives and determine the quantity of ZDDP in the oils.

^{31}P NMR measurement was carried out to characterize the phosphorus compounds in the sample oils after the immersion tests. The ^{31}P NMR spectra of solutions of the sample oils in CDCl_3 were recorded on a Bruker AVANCE 400NMR spectrometer operating at 162.0 MHz. The chemical shifts of the ^{31}P spectra were calibrated against phosphoric acid.

RESULTS AND DISCUSSION

Immersion Test for Engine Oil Additives

Table 2. Formulations of sample oils for immersion test

Sample Oil	R	A	B	C	D	E	F	G	H
Base Oil	x	x	x	x	x	x	x	x	x
Anti Oxidant	x	x	x	x	x	x	x	x	x
Additive		O-SU	N-SU	O-SA	N-SA	O-PH	P-ZDDP	S-ZDDP	MoDTC

x; contained in sample oil

Table 3. ILSAC elastomer (VMQ) compatibility test results

Test Oil	ILSAC GF-5 limit	a	b
Tensile Strength Changes, %	-50 / 5	-29	-83
Volume Changes, %	-5 / 40	27	30
Hardness Changes, points	-30 / 10	-20	-19

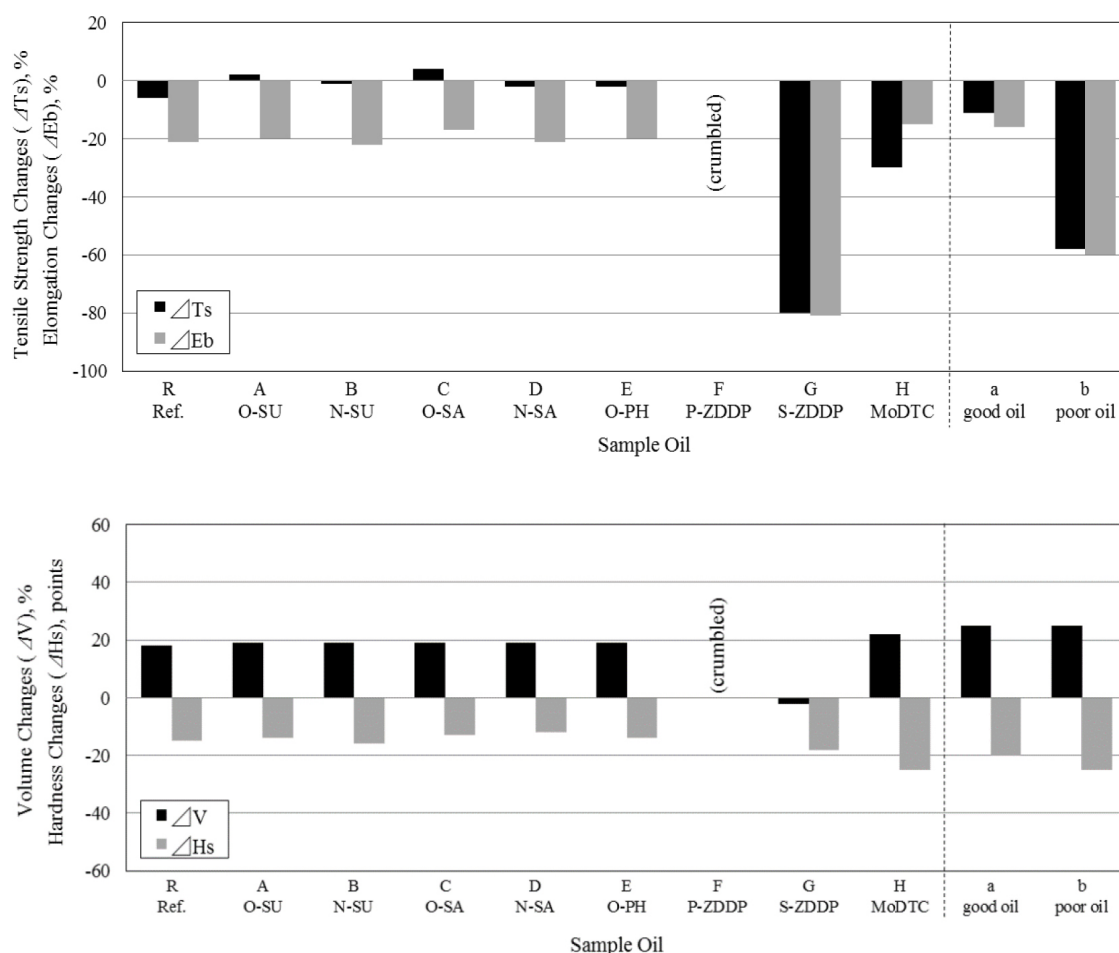


Figure 4. Immersion test results