

Effect of Viscosity Index Improvers in Ethanol/Gasoline/Water Emulsions Formed with E25 and E85 in Passenger Car Motor Oils

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ABSTRACT

Concern about the consequences of fuel dilution on engine oil properties are intensifying due to the increasing use of E25 and E85 fuel in passenger cars. Notably, such concerns are about the effect of emulsion formation and stability in crankcase oils by E25 or E85 fuel and water dilution on vehicle operation at cold-start conditions. Different types of Viscosity Index Improver (VII) chemistries were evaluated for their effects on emulsion formation and engine oil characteristics. Emulsions were prepared with fresh and used passenger car motor oils using the ASTM D7563 method for emulsion retention. The emulsion properties were evaluated after storage for 24 hours at two different temperatures. Separate oil/gasoline and emulsion (ethanol/water/oil) phases were observed for fresh oil emulsions. None of the emulsions exhibited a separate water phase, regardless of the type of VII in the oil. Analysis of the emulsion composition by Fourier Transform Infrared spectroscopy and Gel Permeation Chromatography confirmed ethanol and water were present in the emulsion phase, while the gasoline and other oil soluble components, including the VII, were present in both phases. When used field test oils were assessed for their emulsion characteristics with E85/water, the used oil emulsions formed a single emulsified phase. This was in contrast to fresh oil behavior. Both fresh and used oil emulsions were tested in a Cold-Cranking Simulator, and Mini-Rotary Viscometer. The results confirmed that the low temperature emulsified oil properties were independent of the type of VII used in the formulation.

INTRODUCTION

The use of bio-fuels such as ethanol for passenger cars is increasing worldwide. Two of the primary motivators for this increased usage are legislative requirements driven by global

warming concerns regarding the use of fossil fuels and the desire to reduce dependence on imported oil. For example, the United States will require refiners to mix 15 billion gallons of ethanol per year into the gasoline supply by the year 2012 and 31 billion gallons by the year 2022 [1]. Gasoline blended with less than 10 vol% ethanol (E5 or E10) is in widespread use in United States and Europe today. To meet future requirements, use of fuels with larger proportions of ethanol (such as E15 or higher) is increasing in the US and other countries. OEMs such as General Motors are reported [2] to be increasing the production of Flex Fuel vehicles capable of running on ethanol blends of gasoline up to 85 vol % ethanol.

The effect of alcohol fuels (such as methanol and ethanol) on engine oils has been studied since the early 1980s [3]. Earlier reports indicated wear, corrosion and rust formation to be the primary concerns with use of the alcohol fuels [4]. Recent studies have found an increase in hydrocarbon emissions from vehicles running on fuels containing high levels of ethanol, such as E25 and E93 [5]. A few studies have demonstrated fewer injector deposits and improved engine performance at full load with fuels containing ethanol [6]. One important concern with the use of ethanol in fuels is emulsion formation by fuel dilution. A recent field test [7] conducted in a cold climate found that E85 fuel usage can lead to significantly higher ethanol and water dilution of the motor oil. This was the case for vehicles operated at low ambient temperature in start/stop driving conditions where the oil temperature was not high enough to evaporate the ethanol and water in the oil. Engine blow-by of fuel and combustion products, such as water, is greater in an engine operating on ethanol-based fuels due to lower engine temperatures and ethanol's relatively high heat of vaporization and boiling point compared to gasoline [8]. Water can condense in the oil pan if the vehicle is idle for a

long time at cold temperatures. Engines operating on ethanol fuel have been reported to have poor cold start-up characteristics attributed to ethanol's high heat of vaporization [9].

There are two consequences related to oil performance from emulsions formed by fuel/water dilution: emulsion instability caused by water/ethanol separation and the effect on the low temperature viscometric properties. Emulsion instability causes water to separate from the oil, potentially resulting in corrosion, rust formation, and oil starvation of engine parts. These concerns were considered during the development of PCMO specifications such as ILSAC GF-4 and GF-5. A bench test (ASTM D6557) was included in ILSAC GF-4 to ensure rust prevention in acidic and low temperature conditions. An emulsion stability bench test, ASTM D7563 (formerly known as ILSAC FF-1), was included in the new ILSAC GF-5 category to ensure that water did not separate from oils emulsified with 10wt% E85 and 10wt% water after 24 hours at 0°C and room temperature. The impacts of emulsion formation on the low temperature properties are less understood. A previous study on methanol/water/oil emulsions found that the absolute viscosity measured at -25°C and 50°C and at shear rates less than 3000 s⁻¹ increased as the proportion of water was increased [10]. There are no current standard industry tests to measure the viscometric properties of emulsions of either fresh or used oils.

Components of fully formulated oils, such as dispersant-inhibitor (DI) packages, can affect emulsions formed in engine oils. It is generally known that the amount and type of dispersants and detergents in the DI package can affect the emulsion formed [11] and its stability, but the effects of the other engine oil components, such as Viscosity Index Improvers (VII), are less known. This paper presents studies on the effect of different types of VII used in PCMO, such as olefin co-polymers (OCP), styrene-isoprene polymers (SI) and poly(alkyl methacrylate) polymers (PMA), on emulsion stability and the low temperature viscometric properties of fresh and used oils.

EXPERIMENTAL DETAILS

FRESH OILS

A baseline of API Group II base oils and an ILSAC GF-4 Dispersant-inhibitor (DI) additive package was first blended and then treated with different VII to make the 5W-30 lubricating oils shown in Table 1. The baseline was also used as control in the study since it did not contain any VII. The 5W-30 oils were blended to an ASTM D445 Kinematic Viscosity at 100°C of 10.4 cSt. Three commercial VIIs available in North America and appropriate for use in passenger car motor oils were selected for study: a 50 SSI high ethylene content OCP, a 55 SSI star SI polymer, and a

45 SSI dispersant PMA polymer. The oils in Table 1 incorporated 0.3 wt% PPD which was suitable for the type of VII. The PPDs were selected based on prior experience with similar GF-4 oils made with these viscosity index improvers.

Table 1. Composition of oils

	Control	Oil 1	Oil 2	Oil 3
Baseline: GF-4 DI and API Group II base oils, wt%	100.0	90.7	92.5	93.9
OCP VII, wt%	--	8.9	--	--
SI VII, wt%	--	--	7.2	--
PMA VII, wt%	--	--	--	5.8
PPD-1, wt%	--	0.3	--	--
PPD-2, wt%	--	--	0.3	--
PPD-3, wt%	--	--	--	0.3
Kinematic viscosity at 100°C, cSt	5.2	10.4	10.4	10.4
CCS (-30°C), cP	4887	5296	5318	6316
MRV (-35°C), cP	n/a	21554	54830	21678

The low temperature SAE J300 viscosities of each 5W-30 oil were measured by Cold Cranking Simulator (CCS) according to ASTM D5293 and Mini-Rotary Viscometer (MRV) according to ASTM D4684.

USED OILS

Used oil samples were collected from field test vehicles run with ILSAC GF-5 quality SAE 5W-20 oils which contained either of two commercial OCP VII with API Group II base oils. The oils contained either the 50 SSI high ethylene content OCP which was used in the 5W-30 fresh oils or a 50 SSI low ethylene content OCP. The compositions and viscometric properties of the fresh 5W-20 oils in the field test are summarized in Table 2. Each oil was blended with an appropriate PPD for the VII used and at an optimized treat rate to provide the lowest fresh oil measured MRV viscosity. Representative samples of used oils were obtained by combining oil from four fleet vehicles run between 4000 and 5000 miles with regular unleaded fuel and operated in city driving conditions. Gas Chromatography (GC) analysis on the field test used oils indicated that the most of the used oil samples had negligible fuel dilution. Used oil from one of the four vehicle of Field Test Oil 1 sample contained 2.9 wt% fuel.

Table 2. Fresh oil compositions of 5W-20 field test oils

	Field Test Oil 1	Field Test Oil 2
GF-5 DI and Group II base oils, wt%	94.1	95.4
High ethylene OCP VII, wt%	5.6	---
Low ethylene OCP VII, wt%	---	4.2
PPD-4, wt%	0.3	---
PPD-5, wt%	---	0.4
Kinematic viscosity (100°C), cSt	8.3	8.6
CCS (-30°C), cP	5106	6371
MRV (-35°C), cP	17500	18100

EMULSION PREPARATION

Emulsions of the oils in [Table 1](#) were prepared according to the ASTM D7563. E25 and E85 fuels were obtained by mixing 25 and 85 volume percent, respectively, of fuel-grade CDA20 denatured ethanol with additive-free regular, unleaded gasoline. The emulsions were prepared at room temperature by adding either E25 or E85 and purified water to the oil in the proportions listed in [Table 3](#), followed by vigorous mixing in a Silverson Model L4RT-W mixer at 4000 rpm for 60 seconds. The amount of fuel in Mixture Ratio I was based on the average fuel dilution observed in the crankcases of vehicles operated for short start/stop driving distances at lower temperatures [7]. Mixture Ratio II represents the fuel/water/oil mixtures prescribed in the emulsion method. The used oils were emulsified following the same procedure, but blended according to Mixture Ratio III. These proportions represent the worst case of fuel/water dilution reported in a published field test run with E85 fuel [7].

Table 3. Types of emulsion prepared in the study

Composition	Mixture Ratio I	Mixture Ratio II	Mixture Ratio III
Fresh oil, wt%	70	80	---
Used oil, wt%	---	---	75
Fuel, wt%	30	10	15
Purified water, wt%	---	10	10

Each of the emulsified blends was poured into two, 1 by 6 inch cylindrical flat bottom glass bottles. Each bottle was filled with about 80 ml of emulsified oil and capped. Following ASTM D7563, one bottle was stored at room temperature, the other was stored in a refrigerator at 0°C for 24 hours.

OIL AND EMULSION TESTS

The low temperature viscosities of the fresh and used oils were measured at SAE J300 5W grade temperatures. The CCS viscosity was measured at -30°C according to ASTM

D5293. Both fresh and used oil MRV viscosities were obtained at -35°C according to ASTM D4684.

The fresh and used oil emulsions were visually inspected for phase separation after 24 hours of storage. The CCS viscosity was measured at -30°C according to ASTM D5293. The initial conditioning step at 80°C in ASTM D4684 was eliminated when measuring the MRV of emulsified phases for safety reasons and to prevent fuel evaporation. Blends of E85, water and oil were further evaluated to determine the composition of the two phases formed. The phases were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to detect the presence of ethanol and water. The FTIR absorbance spectra were obtained from 4000 cm⁻¹ to 600 cm⁻¹ with a Perkin-Elmer FTIR spectrometer. Gel Permeation Chromatography (GPC) analysis was used to detect the presence of VII in the oil-rich phases. The GPC measurements were carried out on an Agilent 1100 Gel Permeation Chromatograph using Mixed D (PLGel) and 50Å (PLGel) columns in series in tetrahydrofuran flowing at 1 ml/min at 25°C with evaporative light scattering detection. The area of the VII elution peak in the GPC data was integrated to give approximate polymer content in the phase. The distribution of VII polymer between the phases was then estimated by mass balance compared to the known amount of VII used in blending the oil.

RESULTS AND DISCUSSION

After 24 hours at 0°C, all blends remained single phase homogeneous mixtures. Phase separation was observed in samples stored for 24 hours at room temperature. The results discussed below therefore relate to the room temperature samples.

EMULSION STABILITY AND CHARACTERISTICS

Fuel/ oil Emulsions

The lubricating oils in [Table 1](#) were first emulsified with only fuel at Mixture Ratio I. As seen in the photographs in [Figure 1a](#), all of the E25/oil blends, including the control, showed a small second phase at the top of the mixture. At room temperature, ethanol has a lower density (0.789 g/ml) compared to the lubricating oil (ca. 0.89 g/ml) and is expected to be in the top phase of separated oils. FTIR analysis confirmed that the top phase was mostly ethanol. The emulsion made with Oil 2, which contains styrene-isoprene VII, was observed to have a small amount of an opaque, white top phase rather than the clear top phase observed in the other oils

As seen in [Figure 1b](#), increasing the ethanol content by using E85 in the fuel/oil mixture leads to a larger top layer, which is opaque in the control oil and Oils 1 and 2. Oil 3 shows a