Acid-Neutralizing of Marine Cylinder Lubricants: Measurements and Effects of Dispersants

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Considerable amounts of sulfuric acid are produced in marine diesel engines during the combustion of high-level sulfur fuels, thus causing corrosive wear. The acid-neutralizing ability of marine cylinder lubricants (MCLs) is therefore a "measuring stick" of their quality. A new experimental protocol was previously published to qualitatively test the acid-neutralizing ability of marine cylinder lubricants. Using a capillary video-microscopy technique and measuring the shrinking rate of the size of nitric-acid drops in MCL, the acid-neutralizing ability of commercial MCLs, as well as model lubricants, can be determined quantitatively. The shrinking rate of the nitric-acid drop size in MCL was constant during the reaction period and independent of the initial drop size. Analysis of the experimental results, following an interfacial neutralization reaction mechanism, suggests that the adsorption of overbased reverse micelles on acid-oil interface is the controlling step in the reaction process. The presence of small amounts of dispersant (1 wt. %) in a model MCL on the neutralization reaction decreased the reaction rate for both nitric and sulfuric acid, while further increase in dispersant concentration (up to about 4%) did not reduce the acid-neutralizing ability further. For sulfuric acid, dispersants act also to effectively disperse the hydrated calcium sulfate crystals produced by the neutralization reaction with sulfuric acid.

Introduction

The fuel oil used in slow-speed marine diesel engines contains very high levels of sulfur (2–5%), which results in the formation of highly corrosive acids, mainly sulfuric, during the combustion process (Mitsutake et al., 1987; Wilbur and Wight, 1984). Sulfuric acid condenses inside the engine, leading to corrosive wear of the cylinder liners and/or piston rings. The piston and cylinders in crosshead engines are lubricated by an injection system which provides lubricant through the cylinder liner during each piston stroke such that the lubricant is only used once (Wilbur and Wight, 1984). The lubricants used in crosshead engines are of the general class called marine cylinder lubricants (MCLs), and one of their most important functions is to neutralize the acids formed during combustion and thus help prevent corrosive wear (Carter, 1992). The corrosive wear problem in crosshead engines is particularly important, and, over the years, a large number of studies have been reported on various aspects of this problem ranging from the mechanism of sulfuric acid formation and metal corrosion (Forsund, 1957; Shott and MacDonald, 1988; Vinogradov, 1967) to means of controlling corrosive wear (Groth and Behens, 1990; Inouye and Mitou, 1988; McGeehan and Kulkarni, 1987).

Commercial MCLs are typically formulated with overbased detergent additives, and it is these detergent additives which provide a source of oil-soluble base to neutralize the acids formed during combustion. The overbased detergents used to formulate MCLs are normally Group-II metal (usually calcium or magnesium) organo-metallic colloid complexes, most notably sulfonates, salicylates, and phenates. When these complexes contain a large excess of base, they are commonly referred to as overbased detergents. The generally accepted

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structure of these overbased sulfonates is that of reverse micelles (Benfaremo and Liu, 1996; Inoue and Watanabe, 1981; Jao and Kreuz, 1988; Krasin et al., 1989; Mansot et al., 1993a,b; Martin et al., 1986, 1989), with a mixed metal hydroxide/carbonate core stabilized by an outer alkyl-aryl shell which makes the detergent oil soluble. The calcium carbonate core of a typical overbased sulfonate reverse micelle has a diameter of between 4 and 14 nm and, including the stabilizing surfactant layer, the overall diameter is between 8–18 nm (Lewis, 1991). Overbased sulfonates may also contain between 5 and 15 wt. % metal noncarbonate (mainly hydroxylic) base, which surrounds the carbonate core (Marsh, 1987; Papke, 1988). Unlike commonly studied reverse micelles, which are dynamic structures and have very short relaxation times (Eicke and Zinsli, 1978), the surrounding alkylaryl sulfonyl groups in overbased sulfonates are tightly bonded chemically to the mineral core, which causes the micelles to remain stable even after being separated out from their original medium and redispersed in model solvent systems (Mansot et al., 1993a,b). Another structural aspect of the overbased sulfonate detergents is the apparent presence of free surfactant molecules in the compositions (Lewis, 1991).

Though overbased calcium detergents form the backbone in the majority of MCL formulation, other types of additives, such as ashless dispersants, antioxidants, corrosion inhibitors, and pour-point depressants, may also be used to formulate an MCL (Colyer and Gergel, 1992). Among these other additives used, the dispersants are of great importance because they can improve engine cleanliness by suspending harmful soot contaminants. Most dispersants are of the polyisobutylene-succinimide or polyisobutylene-succinate ester type (Colyer and Gergel, 1992). In this study, we investigated the effects of dispersants on the acid-neutralizing ability of model MCLs.

In a previous article, we presented a new experimental protocol, using a capillary video-microscopy technique, which qualitatively ranked the acid-neutralizing ability of model MCLs (Wu et al., 1999). In this study, by using nitric acid and measuring the shrinkage rate of acid drops in an MCL, the acid-neutralizing ability could be quantitatively determined. Furthermore, the quantitative results allow us to support the interfacial neutralization reaction mechanism proposed in our previous work and to study the reaction kinetics.

Materials and Methods

Materials

Six MCL samples were obtained through Chevron Chemical, Oronite Additives Division. The basicity of an additive or an oil is expressed in terms of the total base number (TBN), which is defined as the milligrams of KOH that have the equivalent acid-neutralizing ability as that of the base present in one gram of the sample. The commercial MCLs had TBN values of about 70.

The model MCLs were prepared by dissolving an overbased calcium alkylbenzene sulfonate (C_{20-24}-C_6H_5 based; TBN = 325; Ca = 12.9 wt. %, S = 1.9 wt. %) in dodecane (anhydrous, 99+%, Aldrich Inc.) followed by centrifugation of the resulting model oil at 5,000 rpm to eliminate solid particles and then filtration through a syringe filter (Gelman acrodisc, HT Tuffryn, 0.2 μm pore size). In some formulations, a commercial polyisobutylene-succinimide (provided by Oronite) was then added to the model lubricant. Both nitric acid and sulfuric acid were used as received from Aldrich, Inc. Water was deionized and ultrafiltered by means of a Barnstead E-pure system. Microcapillaries and micropipettes were pulled from Microcaps (Drummond Scientific).

Methods

The capillary video-microscopy technique used to monitor the neutralization reaction was the same as described previously (Wu et al., 1999). A specially pulled micropipette was used to inject an acid drop into the lubricant-filled microcapillary with an inner diameter of 80–100 μm. Drop size was measured as the longest axial dimension L since it did not have a perfect spherical shape. The fate of the acid drop and the surrounding oil phase were monitored visually. To suc-

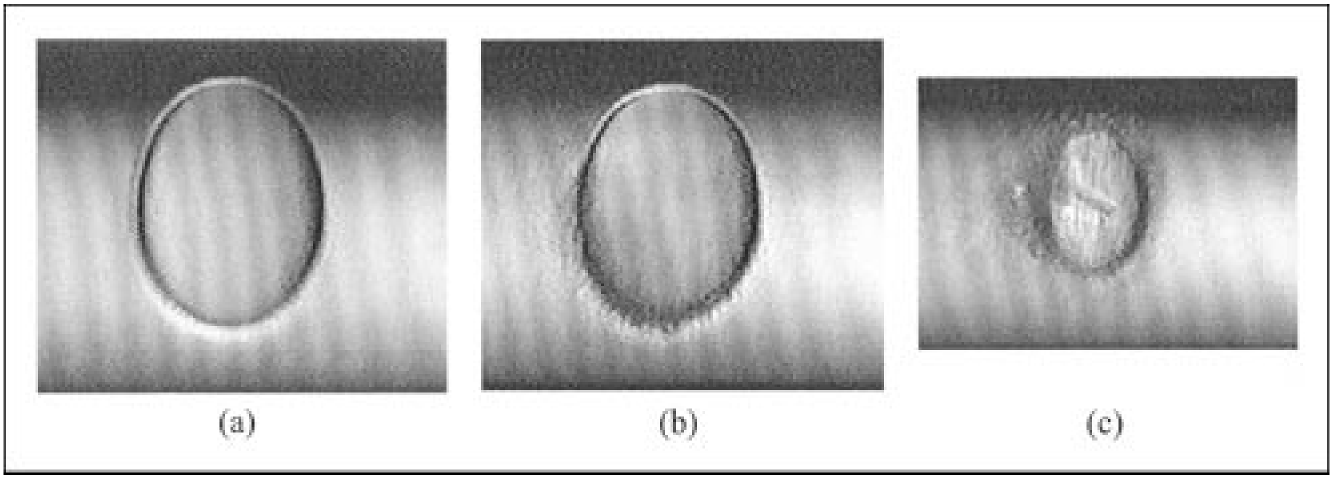

Figure 1. Fate of a 15.6 mol/L nitric-acid drop in commercial MCL E: (a) right after injection; (b) after 8 min; (c) after 60 min.

cessfully produce an acid drop, which did not wet and spread on the wall of an oil-filled capillary, both the internal wall of the microcapillary and the external surface of the injection micropipette were hydrophobically treated (Hou and Papadopoulos, 1997). The microscopic experiments were carried out at ambient temperature.

Results and Discussion

Quantitative neutralization ability measurement

The most intuitive method to study the neutralization reaction in an MCL is to observe the shrinking of an acid drop as the acid is consumed. Unfortunately, it is impossible to quantitatively measure the size of a sulfuric-acid drop during the neutralization reaction in an MCL, because the neutralization reaction between sulfuric acid and the overbasing present in the detergent produces hydrated calcium sulfate, which forms crystals on the acid-oil interface. These crystals make the drop boundary unclear, so that the acid drop size cannot be accurately determined. In addition, crystal growth leads to the eventual breakup of the acid drop (Wu et al., 1999). In order to avoid these problems, nitric acid was used instead of sulfuric acid because the calcium nitrate formed is more water soluble than calcium sulfate and does not form crystals. Although this is not the real situation in the marine crosshead diesel engines, it is reasonable to believe that the neutralization reaction between nitric acid and overbased detergents would provide correct information on the acid-neutralizing ability of MCLs.

The six commercial MCLs (*A* through *F*) all have a TBN of 70. Figure 1 shows a typical example of the fate of a 15.6 mol/L nitric-acid drop in oil E. Bubbles of carbon dioxide were seen forming at the acid-oil interface on the oil-side of the interface, that is, outside the nitric-acid drop (Figure 1b). No crystals were seen because calcium nitrate, a product of the neutralization reaction, is apparently solubilized by the MCL and dispersed in the oil phase. During the neutralization reaction, the acid drop was observed to shrink in size as the carbon dioxide bubbles formed and moved away from the oil-acid interface (Figure 1b). Initially, small CO_2 bubbles are formed which aggregate and coalesce and eventually become invisible, possibly due to their adsorption on the capillary wall followed by immediate spreading along the wall. After 60 min (Figure 1c), the drop size decreases from 90.9 μm to 53.5 μm, which corresponds to an 80% volume decrease. Considering that a 15.6 mol/L nitric-acid drop contains about 60 vol. % nitric acid, not only acid, but also water, has been consumed by the reaction process and solubilized by the MCL.

During the neutralization reaction, the shrinkage of the nitric-acid drop was clear enough to be accurately measured. Figure 2 shows the size decrease of three nitric-acid drops with time for oil *E*. The drop size, measured as the longest axial dimension *L*, decreased linearly with time during the period the reaction was observed. The shrinkage rate $-dL/dt$, which is proportional to the volume change per unit area as $-(1/A)(dV/dt)$, can be regarded as a good indication of the neutralization reaction rate. Figure 2 and all other experiments indicate that this rate is independent of the initial drop size for a given MCL.

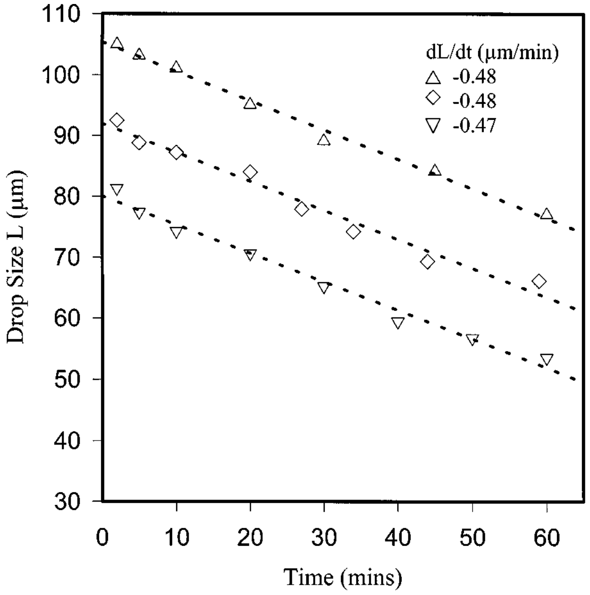

Figure 2. Shrinkage of three nitric-acid drops in commercial MCL E.

Although the initial acid drop size did not affect the drop shrinkage rate, in all rate-test experiments with the commercial oils, the initial size of a nitric-acid drop was controlled to between 80–100 μm. The final shrinkage rate used to rank the commercial oils was the average value of at least two measurements and is shown in Figure 3. The figure clearly indicates that oil *C* has the greatest acid-neutralizing ability, while oil *A* had the worst. As far as the acid-neutralizing ability is concerned, the oils can be ranked as $C > B > (D = F) > E > A$. Noting that the six commercial oils tested here have the same TBN value, this result shows that some

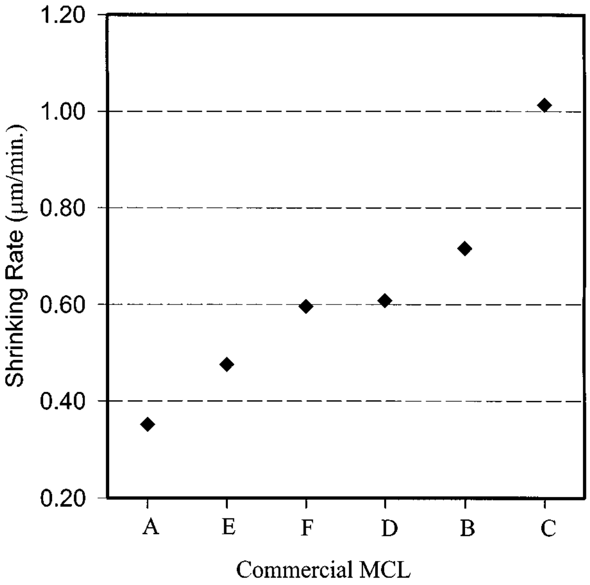

Figure 3. Comparisons on the acid-neutralizing ability of commercial MCLs.

MCL formulations are much more efficient than others from the point of view of acid neutralization.

Mechanism of neutralization reaction

In previous work, we proposed the interfacial neutralization-reaction mechanism shown in Figure 4. This mechanism of the neutralization reaction between an overbased detergent reverse micelle and the acid drop in the MCL is similar, although on a different size scale, to the classic gas-solid surface-reaction (Fogler, 1992). Since any free surfactant molecules in the oil phase will form a surfactant monolayer at the oil-acid interface once the acid phase is introduced, the first step in the reaction mechanism is the "adsorption" of an overbased detergent reverse micelle M_1 on the acid-oil interface S. Following a successful (sticky) collision with the interface, a channel can form which allows the water and acid to move into M_1 (Plucinski and Nitsch, 1994). Once the acid and water get into the alkaline core, the next step is the neutralization reaction between calcium carbonate and acid, which happens immediately. Following the neutralization reaction, the overbased detergent reverse micelle M_1 becomes M_2, where water as well as reaction products are solubilized in the reverse micelle. The last step in the mechanism is the "desorption" of reverse micelle M_2 from the interface, which generates vacant interface space for more reverse micelles M_1 to "adsorb." The kinetic description of this three step mechanism is shown in Eqs. 1–3 in which κ_i, κ_{-i} are specific reaction constants $K_i = \kappa_i/\kappa_{-i}$, C_i is the concentration of species i, $C_{M_1\cdot S}$ is the surface concentration of sites occupied by i, and C_t, C_v are total surface concentration of sites and vacant surface concentration, respectively

$$M_1 + S \underset{k_{-A}}{\overset{k_A}{\longleftrightarrow}} M_1\cdot S \quad r_{AD} = k_A\left(C_{M_1}C_v - \frac{C_{M_1\cdot S}}{K_A}\right) \tag{1}$$

$$M_1\cdot S \xrightarrow{k_S} M_2\cdot S \quad r_S = k_S C_{M_1\cdot S} \tag{2}$$

$$M_2\cdot S \underset{k_{-D}}{\overset{k_D}{\longleftrightarrow}} M_2 + S \quad r_D = k_D\left(C_{M_2\cdot S} - \frac{C_{M_2}C_v}{K_D}\right) \tag{3}$$

The total surface concentration is constant during the reaction

$$C_t = C_{M_1\cdot S} + C_{M_2\cdot S} + C_v \tag{4}$$

The surface reaction step II occurs very rapidly and irreversibly, and is likely not rate limiting in the process. Beginning with Eqs. 1 through 4, and noting that initially no M_2 is present, that is, $C_{M_2} = 0$, if the reaction is adsorption-limited

$$-r_0' = k_A C_{M_1} C_t \tag{5}$$

and if the reaction is desorption-limited

$$-r_0' = k_D C_t \tag{6}$$

where $-r_0'$ is the initial reaction rate. Equations 5 and 6 indicate that if the process is "adsorption" controlled, the initial reaction rate is proportional to the initial concentration of M_1, while if it is "desorption" controlled, it should be independent of the initial concentration of M_1.

The TBN of an MCL is proportional to the amount of calcium in one gram of lubricant and, assuming that the overbased reverse micelles are reasonably monodisperse and contain the same amount of alkaline in the core, the TBN can be viewed as an indicator of reverse micelle concentration. Three model MCLs were blended with different TBN values, and the reaction rates, or shrinkage rate of the nitric-acid drop in the model oils, are shown in Figure 5. The measured reaction rate was constant throughout and Figure 5 shows that the initial rate increases with TBN, that is, the initial concentration of overbased reverse micelles. This observation suggests that in the proposed interfacial neutralization mechanism, the "adsorption" of overbased reverse micelles is the rate-limited step. It is noteworthy to point out that with the model MCL,

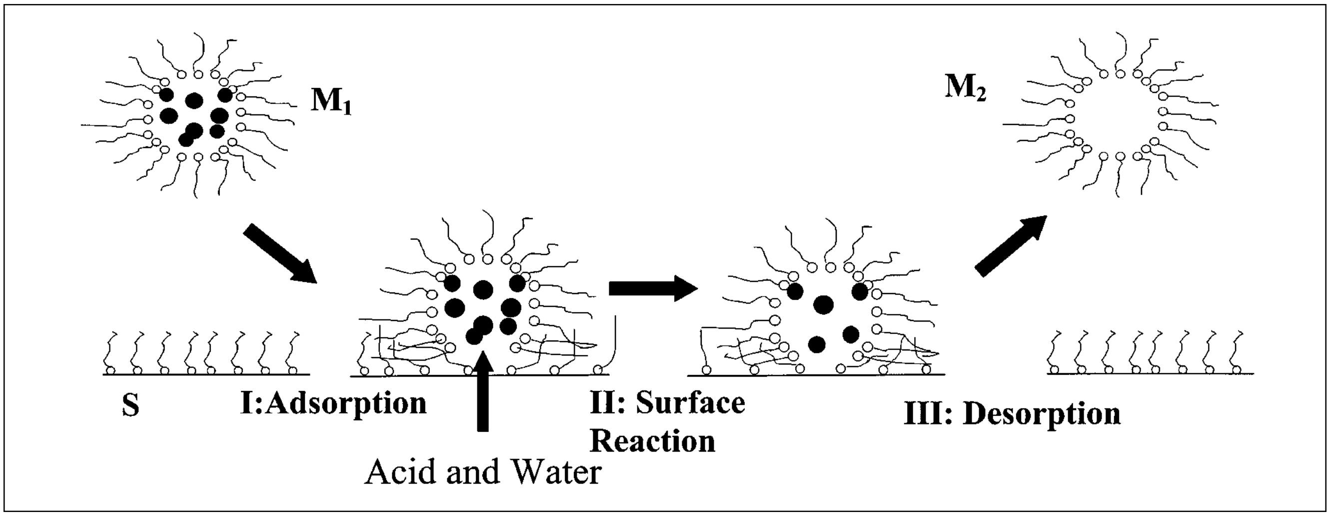

Figure 4. Interfacial neutralization mechanism.

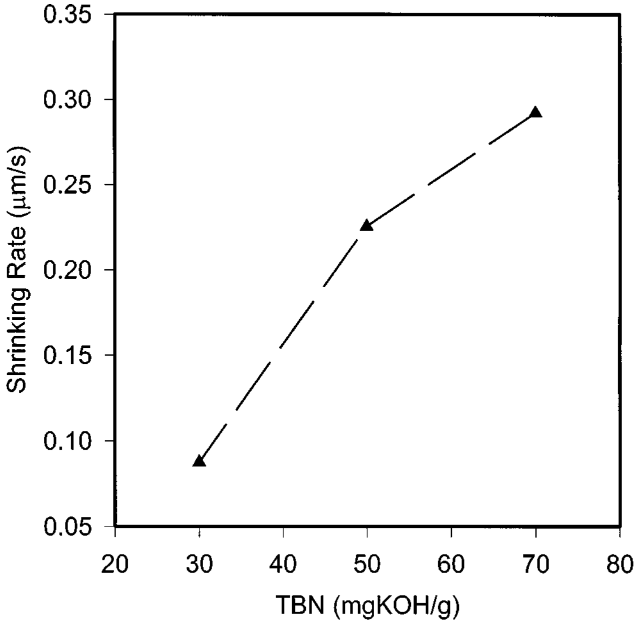

Figure 5. Shrinkage rate of nitric-acid drop in model MCL vs. lubricant TBN.

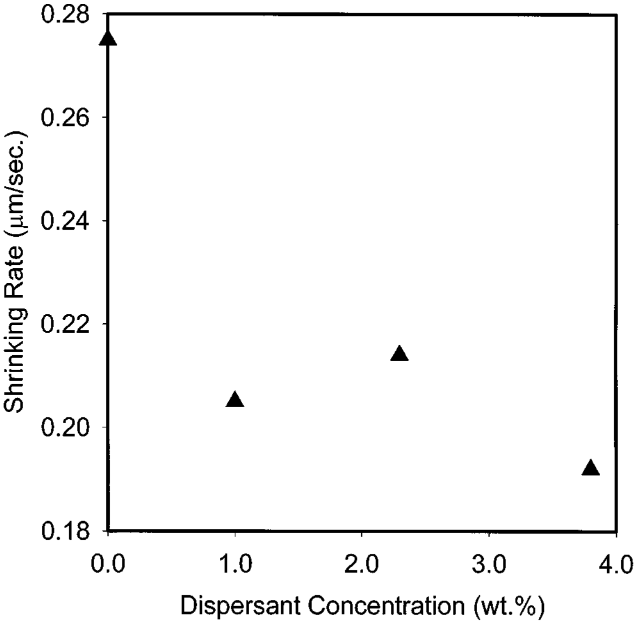

Figure 6. Shrinkage rate of nitric-acid drop in model MCL vs. dispersant concentration.

the reaction rate is about an order of magnitude greater than those found for any of the commercial MCLs. The more complex composition of commercial MCLs probably accounts for this observation. For example, the presence of dispersants in commercial MCLs can decrease the rate of acid-neutralization, as shown in the next section.

Assuming the "adsorption" step is rate-limiting in the neutralization mechanism, one can further understand the size-reduction behavior of an acid drop in a MCL. The decrease of the acid/water volume in the aqueous phase should be equal to the amount transported into the reverse micelles. Considering a spherical acid drop of radius r with a fraction f_m of its interface vacant at time t, the number of overbased reverse micelles adsorbing onto the interface per unit time is proportional to the vacant space $4\pi r^2 f_m$. If the proportionality constant is k and it is assumed that the adsorption of one reverse micelle results in the transport of M grams of acid and water, during the time dt the volume decrease of acid drop will be

$$dV = \frac{k \cdot 4\pi r^2 f_m \cdot dt \cdot M}{\rho} \tag{7}$$

where ρ is the density of the acid drop. The volume decrease can also be expressed as

$$dV = -4\pi r^2 dr \tag{8}$$

Combining Eq. 7 and Eq. 8, gives

$$-\frac{dr}{dt} = \frac{k f_m M}{\rho} = \text{const.} \tag{9}$$

Equation 9 implies that the shrinkage rate of an acid drop is a constant, as observed experimentally.

Effects of dispersants

The effect of dispersants on the neutralization reaction cannot be determined in commercial MCLs, due to the complexity and number of other additives present in the commercial oils. Consequently, we blended model MCLs with and without dispersants, and at different dispersant concentrations and compared their rate of acid-neutralization to determine more accurately the effects of dispersants on the neutralization reaction.

The nitric-acid drop shrinkage rate was measured in four model oils containing a dispersant at concentrations of 0, 1.0, 2.3, and 3.8 wt. %, respectively. The results are shown in Figure 6. The presence of only 1.0% dispersant dramatically decreases the shrinking rate from about 0.27 μm/s to about 0.20 μm/s. Further increases in dispersant concentration did not additionally reduce the acid-neutralizing ability. The explanation for this observation is shown in Figure 7, which envisions the dispersant molecules as having longer hydrophobic tails than the detergent sulfonate surfactants. Small amounts of dispersants (1%) may adsorb on the interface, and present an adsorption barrier to the approaching detergent reverse micelles. The observed leveling of the shrinkage rate shown in Figure 6 also suggests that the adsorption behavior of dispersants follows the Langmuir adsorption isotherm, which means that above a certain bulk concentration of dispersant, there may be no further adsorption on the acid-oil interface.

The effects of dispersants were also studied by observing the fate of a sulfuric-acid drop in a model lubricant. Without a dispersant present, needle-like crystals form immediately after the acid drop is injected into the oil, as previously de-

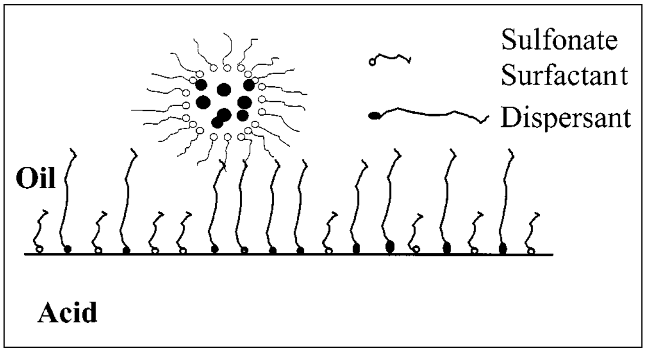

Figure 7. Effects of dispersants in neutralization reaction.

scribed (Wu et al., 1999) and shown in Figure 8a. Progressively, more crystals form with time, as shown in Figure 8b. The drop may also break apart after additional time. With 1 wt. % dispersant present, the behavior of the sulfuric acid drop is significantly different, as shown in Figure 9. No crystals formed until after 8 min (Figure 9b), and, when they did form, they did so very slowly. Since the amount of crystals was not large enough to cover the surface, in this case, the shrinkage of sulfuric acid drop could be accurately measured (Figure 9c) and a shrinkage rate, $-dL/dt$, of about 0.7 μm/min was measured, about an order of magnitude slower than that of a nitric-acid drop in the same oil. The effects of dispersants on the sulfuric acid neutralization appears to be twofold: first, as in the nitric-acid drop shrinkage experiments, the presence of a dispersant decreases the neutralization reaction rate and, hence, the crystal-formation rate, and second, once the crystals are formed, they appear to be dispersed into the ‘‘bulk’’ oil by the dispersant.

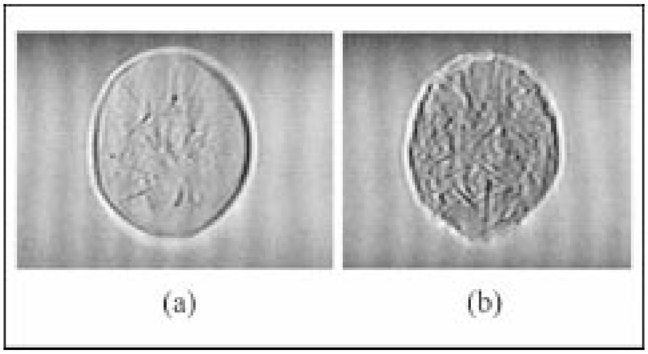

Figure 8. Sulfuric-acid drop in model MCL without a dispersant: (a) 10 s after injection; (b) 2 min after injection.

Since dispersants may be able to disperse acid as well as the crystals, ‘‘blank’’ oils were blended which contained only 1 wt. % dispersant in dodecane. The shrinkage rate of a pure water drop or an acid drop, that is, the solubilization rate, was on the order of 10^{-3} μm/s for the dispersant only oils, compared to a reaction rate of approximately 10^{-1} μm/s for the acid drop for the model MCLs. It is therefore concluded that solubilization of the acid drop by dispersants does not play a role in the neutralization process.

While our results indicate that dispersants may reduce the acid-neutralizing ability of an MCL to some extent, they do not necessarily make an MCL ‘‘bad.’’ In marine crosshead diesel engines where sulfuric acid is a primary concern, dispersants will effectively disperse the crystals generated by the neutralization reaction, which could otherwise deposit on the sulfuric acid drop interface and inhibit further neutralization. In fact, considering the hostile environment in which commercial MCLs are used, dispersants are indispensable for effectively dispersing harmful contaminants.

Acknowledgments

We would like to thank Chevron Chemical Company, Oronite Division, for supporting this work. Financial support was also provided by the Louisiana Board of Regents under grant LEQSF-RD-B-14.

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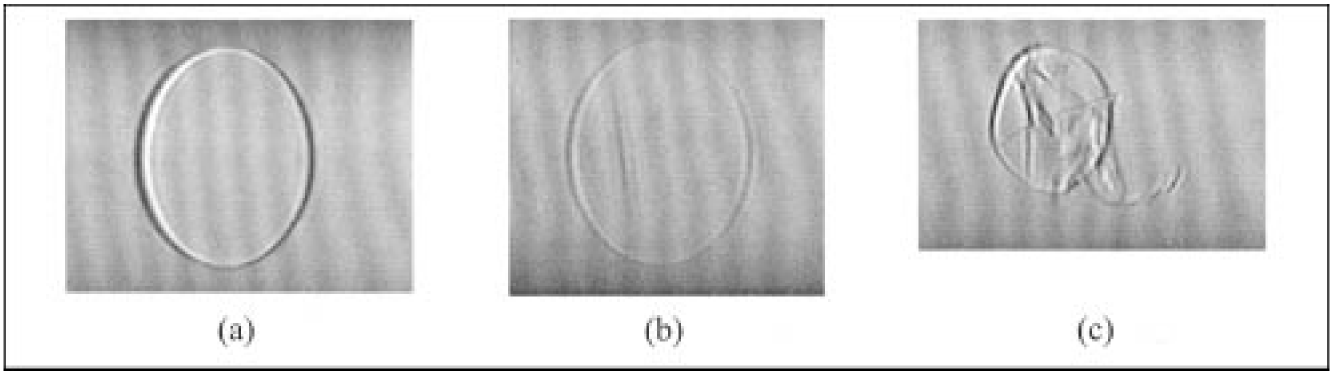

Figure 9. Sulfuric-acid drop in model MCL with 1.0 wt. % dispersant: (a) right after injection; (b) 8 min after injection; (c) 30 min after injection.

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Manuscript received Aug. 13, 1999, and revision received Jan. 11, 2000.