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Title of retracted article: Developments of Multifunctional Additives for High Quality Lube Oil
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Email: dr.n.almehbad@hotmail.com
Journal: Journal of Power and Energy Engineering
Year: 2013
Volume: 1
Number: 5
Pages (from - to): 84 - 89
DOI (to PDF): https://doi.org/10.4236/jpee.2013.15014
Paper ID at SCIRP: 40183
Article page: https://www.scirp.org/journal/paperinformation.aspx?paperid=40183
Retraction date: 2020-1-3

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□ Editor with hints from
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Developments of Multifunctional Additives for High Quality Lube Oil

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Received October 2013

ABSTRACT

In most lubrication systems, the oil is mixed with air, in contact with air, in contact with metals and at high temperature. This is mean cause of premature lubricant deterioration which can result in oxidation products, which are mainly acid. Hydrocarbon oxidation in the liquid phase proceeds by a radical chain reaction. In the present paper polyalkyphenol formaldehyde sulphonate and its ethoxylate were synthesized and evaluated as pour point depressant, viscosity improver and antioxidant. The efficiency of these additives depends on their chemical structure and degree of mixing (mole fraction). Values of surface tension of these additives were measured in oil phase and consequently CMC was determined for all additives and their mixtures. A novel method of inhibiting oxidation was proposed. The author suggests the mechanism of inhibiting oxidation according to surface activity of additive in oil phase. More confirmations for suggested mechanism were investigated by measuring the area occupied per molecule of additive at oil phase. The results indicate that the compatibility of sulphonate with ethoxylate group and forming stable micelle which acts as wax dispersant and improver viscosity.

Keywords: Lubrication Oil; Polymers; Additives of Base Oil; Micelles

1. Introduction

Paraffin wax deposition from middle distillate fuel low temperature is one of the serious and long standing problems in petroleum industry. At low temperature, the crystals of wax easily form impermeable cakes, which can block filters and eventually lead to engine failure. Many methods have been attempted for the prevention of the crystals mating together. Some anionic surfactants had been applied as pour point depressant by Omar et al. [1]. It is found that the surface parameters and free energies of micellization and adsorption confirm the decreasing and improving of pour point. Also it is found that there is a good relation between surface properties especially interfacial tension of the surfactants and their efficiency in depressing the pour point.

Cacium octadecyl benzene sulphonate and octadecyl phenol ethoxylate with 6 units of ethylene oxide were synthesized and evaluated as pour, cloud points depressant by Omar et al. [1]. It is found that the surface parameters and free energies of micellization and adsorption confirm the decreasing and improving of pour point. Also it is found that there is a good relation between surface properties especially interfacial tension of the surfactants and their efficiency in depressing the pour point.

Calcium octadecyl benzene sulphonate and octadecyl phenol ethoxylate with 6 units of ethylene oxide were synthesized and evaluated as pour, cloud points depressant and viscosity index improvers. These additives were compared with imported natural wax dispersing agent. The surface tensions of these additives were measured in oil phase. The values of critical micelle concentration, CMC, minimum area per molecule and surface excess were determined. It is found that increasing concentration of these additives is accompanied by an increase in the minimum area occupied per molecule and surface excess concentration. There is a good relationship between the structure of hydrophilic group of the additive and its efficiency. Mixing the binary additives enhances its efficiency. The results were discussed according to surface excess concentration at oil/air interface [2]. On the other hand the physical properties of the mixed system of cationic/nonionic surfactant and its efficiency in pour point depression were studied elsewhere [3]. It is found that the pour point depressing depends on CMC. The Widespread applications of surfactants originate from the intrinsic duality in their molecular characteristics namely; they are composed of a polar head group (hydrophilic) part and nonpolar tail group (hydrophobic) part. The modification of the lyophobic and lyophilic groups, in the structure of the surfactant, may become necessary to maintain surface activity at a suitable level.

The tribochemical reactions of n-hexadecane proceeding in a tribosystem lubricated was studied elsewhere [4]. It is hypothesized that at ambient temperature reactions are mostly initiated by the mechanical action of the system and elevated temperature (200°C) thermochemical reactions should be dominant. One of the most important modes of lubricant degradation is oxidation, which is the primary cause of increase in viscosity, pour point, sludge,
acidic component formation. The author studied new antioxidant for lube oil. This antioxidant dibenzyl-s-phenyl thio glyconitrile and other derivatives were prepared phase transfer catalysts. These compounds were added to oil in different concentrations. The antioxidants activities of different dosages were evaluated and suggested mechanism according to micelle and their thermodynamic. The oxidation stability of lubricating oil has a critical influence on the oil performance during service. In this paper dibenzyl-s-phenyl thioglyconitrile and other derivative were prepared by phase transfer catalysts and investigated as antioxidants. These compounds were added to oil in different concentrations. The antioxidants activities of different dosages were evaluated and suggested mechanism according to micelle and their thermodynamics. The oxidation of the oil has been carried for different time intervals. The degradation of the oil has been monitored by total acid formation. Oxidation stability of lube oil was largely affected by sulphur and aromatic hydrocarbons concentration in oil, with increased sulphur content increase oxidation stability. The prepared compounds gave higher oxidation stability than imported compound (IRCANOX L 135-CIBA) [5].

The structural effect of polymeric sodium nonyl phenol formaldehyde sulphonate and its mixture with poly-nonyl phenol formaldehyde ethoxylate with 12 ethoxylate units was prepared and evaluated for metal working fluid at different interface by Omar 2004 [6]. Suitable detergents are alcohols and ammonium salts, these applications encouraged us to initiate the symmetric studies on the physico-chemical behavior of ammonium soaps and different captions salts. The purpose of the present work was to characterize ammonium poly alkylphenol formaldehyde sulphonate and its ethoxylate on pour point and oxidation stability of the paraffinic gas oil.

2. Experimental

Raw Materials

The physicochemical properties of lubricating were carried out using ASTM and IP standard test methods (Table 1).

Synthesis of the additive (ammonium poly dodecyl phenol sulphonate).

The polymeric surfactant utilized in this study was prepared by sulphonation of dodecyl phenol which prepared elsewhere by alkylation of phenol with chlorododecane in the presence of mixture of catalysts (benzyl triethyl ammonium chloride as phase transfer catalysts and zinc chloride) The prepared dodecyl phenol was sulphonated with fuming sulphonic acid and neutralized with ammonium solution. The result compound is ammonium dodecyl phenol sulphonate which are dected by IR and elementary analysis (carbon, hydrogen, oxygen, sulphur and nitrogen). The then product was condensed with paraformaldehyde to obtain polymeric dodecyl phenol formaldehyde sulphonate (PAS). The purity of the polymer was about 92.5% [6-8] and average molecular weight 4000.

The polymeric dodecyl phenol formaldehyde was ethoxylated which has on an average 12 moles of ethylene oxide per mol of polymeric dodecyl phenol formaldehyde polymer (non ionic polymer PAN).

Surface and interfacial tension measurement.

Surface tension of different concentrations for 10⁻⁷ to 0.1 mol/L of the synthesized additives was measured by using Kruss Model 8451 in petroleum ether at 30°C according to omar et al. [9].

3. Results and Discussions

Detailed physico-chemical characteristics of the paraffinic oil are reported in Table 1. The data reveal that the oil is rich in n-paraffin and has low carbon residue content and total acid number. The above lube oil analyzed by gas chromatography as shown in Figure 1. From this figure the band represents different carbon number of paraffin and a lower frequency of sulphonate just below 1575 - 1544 cm⁻¹.
The variation of surface tension with concentration is shown in Figure 3. It is clear that the surface tension decreases more with increasing the polymer concentrations. The difference between them is attributed to functional group of each molecule (hydrophilic group). The action of additive of oil phase can be calculated using Gibbs adsorption Equation (6). Comparing the data in Table 3 shows that the CMC value for the polymer PAS was lower than that of the polymer PAN, which indicates that the former PAS favors micellization processes at a lower concentration than the latter compound. Studying the results in Table 3 shows that, the synthesized polymer PAS has large values of surface excess and minimum surface area, indicating the PAS is the most efficient and gives a greater lowering in surface tension of oil. Thus the change in head group of polymer (hydrophilic part) affect of degree of micellization which will be reflect of efficiency of the additive of its activity in oil phase. This concept is clearly observed in Figure 3. From this figure, as concentration increase, the surface excess concentration increase to reach a constant value at CMC, while the additive PAS has large value than PAN as shown in Table 3. This is due to area occupied of sulphonate group. These results confirm sulphonate more solublize and more active in oil phase while ethoxylate group less soluble in oil phase depend on its hydrophilic and hydrophobic balance (HLB). The author prefers number of exylene oxide units about 12 to give the best solubility in oil phase according the above mention HLB. These results are compatible by Omar et al. [6].

In addition, the variation of mixing ratios of nonionic at constant concentration of PAS (10^{-5} mol/L) shows reduction in surface tension and decrease in CMC. At the same time, the best surface tension reduction with minimum total concentration obtained at mole 0.7 of PAS/PAN is shown in Table 4. The addition of PAN to PAS reduces the surface tension due to formation stable micelle in oil phase, which act as trap for wax and disperse
Figure 2. IR spectrum of the anionic polymer.

Table 2. Characteristic absorption frequencies (cm⁻¹) of PAS polymer.

| Assignment                     | Frequencies  |
|--------------------------------|--------------|
| CH₂, C-H antisymmetrical stretching | 2918 cm⁻¹   |
| CH₃, C-H symmetrical stretching  | 2860 cm⁻¹   |
| CH₂, deformation                | 1467 cm⁻¹   |
| C-O, symmetrical stretching     | 1408 cm⁻¹   |
| CH₃, symmetric deformation      | 1330 cm⁻¹   |

Figure 3. Effect of additive concentration on surface tension reduction of oil.

Table 3. Surface properties of additives.

| Conc mol/L | Anionic additive | Nonionic additive |
|------------|------------------|-------------------|
| CMC mol/L  | 3.5 × 10⁻⁶       | 2.4 × 10⁻⁶        |
| Surface area nm² | 2.9 | 2.5 |
| Surface excess mol/m² | 7.11 × 10⁻⁷ | 6.3 × 10⁻⁷ |

Table 4. Surface properties of additives at different mole fractions Nonionic/Anionic.

| Mole fraction | CMC mol/L.10⁶ | Surface tension at CMC mN/m² | Area occupied per molecule nm² |
|---------------|---------------|-------------------------------|--------------------------------|
| 0.2           | 3.5           | 22                            | 2.9                            |
| 0.4           | 3.1           | 20                            | 3.3                            |
| 0.6           | 2.9           | 18                            | 6.5                            |
| 0.7           | 1.6           | 12                            | 8.6                            |
| 0.8           | 2.2           | 15                            | 5.5                            |

in oil phase. It can be conclude that, the activity of additive PAS in oil phase enhances by degree of mixing with nonionic additive PAN. This is due to the fact the moiety of large ethelene oxide units act as shield between sulphonate groups of PAS, as results decrease repulsion...
between them giving stable micelle. These results are depicted on Table 4.

The investigation of the ability of additives and their mixtures as pour point depressant and viscosity improver are shown in Tables 5 and 6. It is clear that, the pour point and kinematic viscosity are improved by increasing the additive concentration. The optimum value for reduction pour and kinematic viscosity appear at the critical micelle concentration of additive and at mole fraction of PAN/PAS equal 0.7. These results can be discussed according the surface activity of the additive and according the stability of micelle. From the structure of additive, it has lyophilic part like the paraffinic wax which completely miscible with wax molecule, while the lyophobic group (sulphonate, or ethylene group) arrange in geometrical shape act as micelle. These micelles disperse wax crystal lattice to small sizes. As the results, the pour point decrease and viscosity improve. The addition of PAN to pas form mixture exhibiting pettier performance in reduction pour point and enhancing viscosity (Table 6). The author confirms degree of mixing has predominant factor in enhance property of oil. This is due to stability of micelle increase with increasing ratio of PAN and CMC decrease until mole fraction equal 0.7 of PAN/PAS. As the results more dispersion of wax crystal by micelle core, consequently improve viscosity of oil, i.e these additive have multifunction purposes, which act by lyophilic portion of each molecule and lyophobic part (sulphonate, chelen oxide group). Moreover, these results are more confirmed by increasing the activity of each additive in oil phase which has surface property depend on CMC and degree of mixing (Table 4).

The effect of these additive on the oxidation stability of oil is given in Figure 4 and 5. The data show the additive retards the oxidation of oil by phenol group in each additive, which act as trap for free radical of R-O. From Figures 4 and 5, the total acid decrease by increasing the additive concentrations and reach the optimum value at CMC each additive and their mixtures. Further increase concentration of the additive, the oxidation stability decrease due to the additive tend to adsorption rather than forming micelle and reverse its orientation at oil phase as confirmed by omar et al. [6]. Comparing between two additives in increasing oil stability, the additive PAS is the best, due to it has the best surface properties. The mole fraction 0.7 of PAN/PAS is the best in its oxidation stability. The author concludes that the ability and stability of micelle is predominant factor for increase oxidation stability of oil. The micelle and inhibit propagation of free radicals and terminate reaction processes of free radicals. More confirmation, the increasing surface area occupied per molecule of mixture attend at mole fraction 0.7 PAN/PAS (Table 4). these prevent contact the free radicals R-O With other hydrocarbon molecules and terminate it as R-O-R.

4. Conclusions

1) The oxidation stability of oil as measured by total acid number indicates that, the oxidation inhibitor efficiency follows the order.

PAN/PAS > PAS > PAN and the mole fraction affect on degree of oil stability. These results depend on value of CMC and area occupied per molecule at oil phase.

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**Table 5. Effect of different additives on pour point at different concentration.**

| Additive            | Cone mol/L | Pour point, °C | Kinematics viscosity, cSt at different temperatures |
|---------------------|------------|----------------|----------------------------------------------------|
|                     |            |                | 40°C | 60°C | 17 | 26.14 | 12 | 5.5 | 10 | 4.5 | 7 | 5.1 | 3 | 5.5 |
| Anionic additive    |            |                |      |      | 6.6 | 12 |      |      | 5.5 | 7 | 4.5 | 3 | 5.1 | 3 | 5.5 |
|                     | 0.000002   | 0.000025       |      |      | 0.00003  | 0.000035 |      |      | 0.00004 | 0.00002   | 0.0000035 | 0.000004 |      |
|                     |            |                | 10   | 7    | 12 | 6.5 | 3.5 | 5.5 | 2.5 | 6.5 | 6.5 | 7 | 7 |
| Nonionic additive   |            |                |      |      | 0.000025 | 0.0000025 |      |      | 0.0000035 | 0.000004 |      |
|                     | 0.0000025  | 0.00003       | 0.000035 | 0.000004 |      |      |      |      |      |      |      |
|                     | 6          | 7              | 6.5  | 6.5  | 2  | 3.5 | 6.5 | 3.5 | 2.5 | 2.5 | 5 | 4.5 | 2.5 | 2.5 |

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**Table 6. Effect of different mole fraction Nonionic/Anionic on pour point at different concentration.**

| Additive           | Mole fraction | Pour point, °C | Kinematics viscosity, cSt at different temperatures |
|--------------------|---------------|----------------|----------------------------------------------------|
|                    |               |                | 40°C | 60°C | 6.1 | 5.14 | 5.5 | 3.5 | 4.8 | 3.5 | 3.8 | 2.1 | 5 | 4.5 |
| Nonionic/Anionic    |               |                | 0.2  | 2.6  | 40°C | 6.1 | 5.14 | 5.5 | 3.5 | 4.8 | 3.5 | 3.8 | 2.1 | 5 | 4.5 |
|                     | 0.2           | 0.4            | 2.5  | 5.5  | 3.5 | 3.5 | 3.5 | 3.8 | 2.1 | 5 | 4.5 | 3.5 | 3.5 | 3.8 | 2.1 | 5 | 4.5 |
|                     | 0.6           | 0.7            | 2    | 4.8  | 3.5 | 3.5 | 3.5 | 3.8 | 2.1 | 5 | 4.5 | 3.5 | 3.5 | 3.8 | 2.1 | 5 | 4.5 |
|                     | 0.8           | 0.7            | 1.8  | 3.8  | 2.1 | 2.1 | 2.1 | 3.8 | 2.1 | 5 | 4.5 | 3.5 | 3.5 | 3.8 | 2.1 | 5 | 4.5 |

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2) The synthesized additives and their mixtures have a multifunction for pour point depressant, improving viscosity and enhance oxidation stability of oil. These results depend on activity of additives and their mixtures at oil phase. Further work will study the composition of mixed micelles and measure the hydrophilic and hydrophobic balance of additives HLB.

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