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A Possibility to Use a Batch of Ashless Additives for Production of Commercial Transmission and Motor Oil

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1. Introduction

The aim of the present chapter is to study the possibility to use PSA synthesized by the authors for production of commercial transmission and motor oil.

The practically used compounds are usually surfactants, which must be soluble in a medium of non-polar petroleum hydrocarbons. This required the optimal length of the hydrocarbon radical of the main hydrocarbon chain guarantees property. The polar group of the additive, which determines its main function, has certain electron effect. As a result, significant static and dynamic dipole moments are generated, as it has been discussed in the previous chapters. These effects stipulate the affinity of the additives to different border surfaces, especially in their intermolecular interactions when used within a batch [2].

In our previous investigations, the methods for synthesis of PSA by sulphonation, nitration and oxidation have been reported [3, 4,5].

2. Experimental

Taking into account our earlier studies [6,7] on the optimization of the composition of the additives synthesized by us, a batch of petroleum soluble additives was composed on the basis of an oil component and the most effective of them was found to be the composition containing PSA-SK-N-H: PSA-SK-S-U: PSA-SK-O-U = 10:50:40 referred to further as batch P-1. The denotations and the most important values for additives preparation have been published earlier [6]. With the selected batch of additives, the possibility to prepare operation-conserving lubricants of transmission and motor type was investigated. For this purpose, basic lubricant mixtures were taken from fractions of the corresponding class of viscosity and the batch P-1 was added to them. The standard physicochemical and performance properties of the alloyed lubricants were then determined to estimate their performance quality. The results obtained from the analysis are presented in Table 1.

Table 2 shows the general technical characteristics of the transmission lubricants after the tests carried out. Tests were performed also by the method PPA-2 [8] for fuller assessment of the protective coatings formed by the transmission lubricant. The tests were carried out in
presence of copper disks (alloy M-5) since, as it is well known, this metal catalyzes the oxidation of petroleum hydrocarbons especially in presence of air and at higher temperature. Fig.1 illustrates the depositions of acidic products in lubricant samples depending on the oxidation time at three temperature regimes (100, 200 and 300 °C).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Basic fraction TM-5/90</th>
<th>Standard regulations TM-5/90 BSS 9797</th>
<th>Parameters at different concentrations in % of P-1</th>
<th>Method of analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4 5 6 7 8 9 10</td>
<td></td>
</tr>
<tr>
<td>1. Kinematic viscosity at 100 °C, mm²/s</td>
<td>18,5</td>
<td>20.0 ± 2</td>
<td>20.0 20.2 20.5 20.9 21.4</td>
<td>BSS EN ISO 3104</td>
</tr>
<tr>
<td>2. Viscosity index</td>
<td>50</td>
<td>95</td>
<td>97 99 103 109 115 116</td>
<td>BSS ISO 2909</td>
</tr>
<tr>
<td>3. Pour point, °C</td>
<td>-6</td>
<td>-15</td>
<td>-8 -10 -14 -16 -18 -20</td>
<td>BSS ISO 3016</td>
</tr>
<tr>
<td>5. Marten-Penski temperature in open spot, °C</td>
<td>210</td>
<td>210</td>
<td>210 210 210 210 210 210</td>
<td>BSS EN ISO 2592</td>
</tr>
<tr>
<td>6. foamforming, cm³</td>
<td></td>
<td></td>
<td></td>
<td>BSS ISO</td>
</tr>
<tr>
<td>-ability toward foamforming</td>
<td>80/80/80</td>
<td>90/40/90</td>
<td>90/40/90 95/45/90 97/47/97 98/48/98 100/50/100 110/55/110</td>
<td>6247</td>
</tr>
<tr>
<td>-stability of foam</td>
<td>10/10/10</td>
<td>0/0/0</td>
<td>0/0/0 0/0/0 0/0/0 0/0/0 0/0/0 0/0/0 2/2/2</td>
<td></td>
</tr>
<tr>
<td>7. Stablility of oxidation:</td>
<td></td>
<td></td>
<td></td>
<td>DIN 51394</td>
</tr>
<tr>
<td>-increasing of viscosity at 100 °C, %</td>
<td>31</td>
<td>20</td>
<td>28 25 23 20 18 17</td>
<td></td>
</tr>
<tr>
<td>-lose of mass, %</td>
<td>7</td>
<td>5</td>
<td>7 6 6 5 4</td>
<td></td>
</tr>
<tr>
<td>-insoluble in n-pentan, %</td>
<td>4</td>
<td>1</td>
<td>4 4 3 2 1 1</td>
<td></td>
</tr>
<tr>
<td>8. Acid number, mg KOH/ g</td>
<td>0.01</td>
<td>0.04</td>
<td>0.09 0.08 0.07 0.05 0.03 0.02</td>
<td>BSS 1752</td>
</tr>
</tbody>
</table>

Table 1. Physicochemical and exploration characteristics of transmission oil from viscosity class 90.
A Possibility to Use a Batch of Ashless Additives for Production of Commercial Transmission and Motor Oil

Property | Value at the test temperature
---|---
| TM-5/90 – commercial | TM-5/90 – basic fraction + 0,005 % P-1 |
| 100 °C | 200 °C | 300 °C | 100 °C | 200 °C | 300 °C |
1. Ignition temperature in open pot, °C | 204 | 200 | 190 | 204 | 204 | 196 |
2. Kinematic viscosity at 100 °C, mm²/s | 21,6 | 22,4 | 23,8 | 22,3 | 22,7 | 23,0 |
3. Freezing temperature, °C | -19 | -20 | -22 | -23 | -26 | -26 |
4. Mechanical contaminants, % | 0,08 | 0,12 | 0,17 | 0,03 | 0,05 | 0,09 |
5. Corrosion tests
- by „Salt fog”, g/m² | 77,13 | 75,24 | 72,15 | 35,24 | 31,18 | 30,71 |
- by „Aggressive media”, mg | 2838 | 2809 | 2759 | 1838 | 1724 | 1656 |
- by “Humidity”, g/m² | 0,2235 | 0,2178 | 0,2101 | 0,1754 | 0,1621 | 0,1537 |
- by “Condensed moisture”, g/m²
- Steel 08 grade, rimming, pcs, g/m² | 10 | 11 | 12 | >12 | >12 | >12 |
- copper, degree (Cu, bal) | 2 | 3 | 4 | 1 | 1 | 1 |

Table 2. General technical characteristics of transmission lubricants after the tests.

Fig. 1. Depositions of acidic products in lubricant samples depending on the oxidation time at three temperature regimes.

During the proved optimal induction period of oxidation (4 hours), the processes giving acidic products depending on experiment temperature were studied (Fig.2). Simultaneously, the accumulation of carbonyl containing compounds in the oxidized lubricants was
established by the intensity of the absorption band at 1720 cm\(^{-1}\) in the IR spectra of their 10% solutions in tetrachloromethane.

![Graph showing adsorption at 1720 cm\(^{-1}\) in the IR spectra of their 10% solutions in tetra chloromethane.](image)

Fig. 2. The intensity of the adsorption band at 1720 cm\(^{-1}\) in the IR spectra of their 10% solutions in tetra chloromethane.

To find the quantity of metal dissolved in the exhaust lubricant as a result of their interaction with the products obtained from their oxidation, analyses of their composition were carried out by atomic absorption spectroscopy (Fig.3).

![Graph showing concentration of metal dissolved in the exhaust lubricant.](image)

Fig. 3. Quantity of metal dissolved in the exhaust lubricant as a result of their interaction with the products obtained from their oxidation.

As can be seen from Table 1, the use of the batch P-1 in the optimal concentration established to be 0,005 %, the requirements of the Bulgarian national standard can be fulfilled by the transmission lubricant at performance level TM-5. According to BSS 14368-
02, this lubricant can be used to lubricate gears and its properties are like these of the commercial product “Ulita ER”. The studies showed that the lubricant obtained has very good anticorrosion and antiwearing properties. As general conclusion it can be stated that the batch of ashless PSA gives the lubricant alloyed polyfunctional properties. The antioxidative stability of the alloyed lubricant is especially important since the transmission oils in the process of operation are subjected to intense stirring under atmospheric medium and in presence of ferrous and non-ferrous metals and alloys. The surfactant properties of the additive affect the amount of foam formed and its stability. The presence of air in the lubricants did not enhance the accumulation of oxidized products in them. All the physicochemical and performance properties measured at the recommended concentration of the additive showed that the transmission lubricant obtained is of the operation-conserving type and possessed enhanced resistance to oxidation. At the same time, it did not change significantly its performance properties during the experiments carried out (table 2).

The studies carried out showed (Fig.1) that the presence of the additive P-1 did not have significant effect on the duration of the induction period of oxidation of the experimental samples. The positive effect observed after the fourth hour of operation was that the intensity of the oxidation processes decreased and the accumulation of acidic products in the exhausted lubricants was almost constant. This resulted from the exhaustion of the easily oxidizable hydrocarbons and, probably, the antioxidative effect of some of the products obtained. Positive effect on the antioxidative protection of the hydrocarbons in the lubricants studied had also the chemiadsorption properties of the ashless PSA participating in the composition of P-1 towards the metal surfaces. When adsorbed on the metal surface, they could impede the catalytic effect they have on the oxidation of the petroleum products.

As can be seen from Fig.2, the most intense oxidation processes were observed at temperatures up to 200 °C. Above this temperature, the acid number remained almost the same. The use of the additive P-1 slowed down the acid number increase rate and limited the accumulation of acidic products (Fig.3).

The studies carried out showed that, without the additive, processes of corrosion-mechanical wearing of all the metals contacting with the lubricant actively occur during the tests according to the PPA-2 method. In the presence of the additive P-1 these processes almost stopped after the fourth hour of operation. Probably, the additive formed chemiadsorption compounds on the metal surfaces which protect them from the interaction with the corrosion aggressive products. As a result, the concentration of metals in the exhausted lubricant sharply decreased and remained almost the same after the induction period.

After 2 months of operation of the lubricant with P-1 and the commercial additive, it was found that probably strong enough chemiadsorption film was formed on the metal surface, which decreased the intensity of their corrosion-mechanical wearing. This effect is much more pronounced with the batch of ashless PSA P-1 at low concentration, compared to the metal containing additives of the previous generation. Due to the good lubricating characteristics of the more viscous lubricant usually used only in summer, the results on the corrosion-mechanical wearing were worse and the protection of the lubricated surfaces was better. (Figs.4 - 7).
Fig. 4. The wearing of the parts of the piston-cylinder system was monitored by measuring the concentrations of iron.

Fig. 5. The wearing of the parts of the piston-cylinder system was monitored by measuring the concentrations of aluminium.
Fig. 6. The wearing of the parts of the piston-cylinder system was monitored by measuring the concentrations of tin.

Fig. 7. The wearing of the parts of the piston-cylinder system was monitored by measuring the concentrations of lead.
The results illustrated in figs. 8 and 9 confirmed the higher effectiveness with regard to the anti-wearing properties possessed by the ashless additives included in the combined batch P-1. The wearing in the individual cylinders of the motor was found to be different. Probably, in this case, the liquid film formed in the combustion chamber due to the over-fractioning of the fuel during the formation of the fuel-air mixture in the cylinders exerted some influence. In the middle cylinders (II) and (III) the wearing was slightly more intense.

Fig. 8. The results on the relative wearing of the first segment of the pistons of the individual cylinders of the motor „Ch 10,5/13“.

Fig. 9. The results on the relative wearing of the first segment of the pistons of the individual cylinders of the motor „Ch 10,5/13“.
It is well known that this type of wearing in presence of a liquid film is of the so called type “corrosion mechanical wearing”. The main reason for its occurrence is the washing out of the lubricating film and disturbance of the laws of hydrodynamic friction, as well as decrease of the lubricating film thickness. Nevertheless, this effect of wearing in the presence of the batch P-1 was significantly weaker.

The experiments carried out showed that the nature of the compounds from which the PSA were prepared gives them surface active properties and improve the protective and other properties of the fuels and lubricants alloyed with them. This is especially important for the use of fuels with high sulphur content used more widely for ship engines. In this case, an important problem arises since the sulphur containing compounds and the products of their combustion accelerate the corrosion-mechanical wearing of the aggregates and, of course, have adverse effect on the environment. In this respect, it appeared to be interesting to study the anti-wearing properties of the motor oils M 6W 8 C2/D1 and M 16 D2/E1 alloyed with the batch additive P-1. Simultaneously, experiments were carried out also with the magnesium-containing additives synthesized by the authors and implements in the industry in the prescribed concentration of 6% [5]. The experiments were carried out with four-cycle four-cylinder motor „Ch 10,5/13” mounted in many lightweight sea vessels. These motors use ship diesel fuel LK produced according to Bulgarian national standard BSS 12833-82 and contains up to 1.4% sulphur. The wearing of the parts of the piston-cylinder system was monitored by measuring the concentrations of iron, aluminium, tin and lead found in the lubricant according to BSS ISO 9778-00 and BSS ISO 15430-02. These are the main metals used to manufacture the parts of the motors. This method is widely used practically both for determination of the moment to replace the lubricants and oils and establishing of emergency cases of accelerated wearing of some units in the motors. The results obtained from the studies of the operation-conserving lubricants are shown in Figs.4-7.

Figs.8 and 9 show the results on the relative wearing of the first segment of the pistons of the individual cylinders of the motor „Ch 10,5/13” determined by their weight after 1 year service using different lubricants.

3. Conclusion

The studies on the use of the batch of ashless petroleum soluble additives P-1 for the production of transmission lubricant carried out showed that the addition of 0.005% P-1 to basic lubricant mixtures gave transmission lubricant complying with BDS 14368-02. The transmission lubricant obtained can be used to lubricate gears and is fully comparable to the commercial product “Ulita ER”. The results obtained from the physicochemical analyses showed that the operation-conserving motor lubricants alloyed with the batch mentioned above fully comply with the requirements of BSS 15021 and BSS 9797. It was found that the optimal concentration of the batch P-1 is 0.010%. The ashless PSA included in the batch impart depressing and very good protective properties of the alloyed lubricants.

4. References

The petrochemical industry is an important constituent in our pursuit of economic growth, employment generation and basic needs. It is a huge field that encompasses many commercial chemicals and polymers. This book is designed to help the reader, particularly students and researchers of petroleum science and engineering, understand the mechanics and techniques. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at the petroleum science and engineering technologist. This book is must-read material for students, engineers, and researchers working in the petrochemical and petroleum area. It gives a valuable and cost-effective insight into the relevant mechanisms and chemical reactions. The book aims to be concise, self-explanatory and informative.

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