Research results of makeup influence on semi-synthetic motor oils thermal oxidation stability

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Abstract. During the running motor oil quality determination oil makeup has a big influence on thermal oxidation mechanism, however there is a problem of insufficient examination of makeup influence on motor oil conditions. Main goal of these researches is to determine how makeup effects on motor oil’s thermal oxidation stability. For the research Lube oil Lukoil Super 10W-40 SG/CD has been chosen. Thermal oxidation stability results assessment was conducted basing on obtained values of: light stream absorption criteria, volatility and thermal oxidation stability criteria in cases of research with makeup and without it. There was offered a criteria of makeup influence on thermal oxidation stability values, which identified as change of light stream absorption rate proportion and thermal oxidation stability criteria in case of research with and without makeup. Research methodology involved motor oil test on thermostating device consequently under temperatures 180, 170 and 160 °C with makeup and without it in condition when quantity of makeup oil corresponded to vaporized oil quantity. Research results demonstrated that oil makeup decrease thermal oxidation intensity on the whole temperature test rate.

1. Introduction

The most important operating features of motor oils are lubricity, viscosity, thermal oxidation stability, anticorrosion and protection features, foaming resistance. However, in case of motor oil thermal oxidation viscosity, foaming and corrosion activities are increase while extreme pressure quality decreases. Rate and depth of thermal oxidation depend on process duration, oil temperature, metal catalytic influence and oxygen concentration. The greatest impact on oxidation rate has a temperature. Since in thermal oxidation appear products affecting on lubricity, viscosity, corrosion activity, protection features and foaming resistance, thermal oxidation stability value which estimated by light stream absorption quantity, volatility, thermal oxidation stability criteria and relative viscosity gives certain representation of the oil quality [1-4].

Along with the running lube oil quality determination big influence on thermal oxidation mechanism has oil makeup [5-6]. However, there is no common opinion about the makeup impact in case of oil fumes and leaks in the system. Some think, that makeup does not effect on oil quality due to antiwear properties stability, other suppose, that makeup influences on optical features and provides high concentration of additives.

Objective of these experimental researches is makeup evaluation on thermal oxidation stability values.
For examination was chosen semi-synthetic motor oil Lukoil Super 10W-40 SG/CD which is all-season and multipurpose motor oil applied in the high-forced both gasoline and diesel engines.

2. Methodology
Research methodology involved oil thermostating device usage, developed on the basis of a patented method for determining the thermal oxidation stability, photometer for optical properties evaluation and electronic scale for vaporized oil mass establishing [7].

Thermal oxidation stability semi-synthetic motor oil Lukoil Super 10W-40 SG/CD was investigated at temperatures 160, 170 and 180 °C during the time of light stream absorption criteria was increasing up to 0.7-0.8. Makeup influence was taken into account by comparing the tests results with oil makeup and without it.

Oil sample with weight 100±0.1g was poured into the device glass for thermostating and oxidized under the certain temperature during the certain period of time with mixing at rotation speed 300 rpm. During the thermostating process temperature and mixer rotation frequency was automatically maintained. After each period of time oxidized oil sample was weight up and mass of vaporized oil \( V \) was calculated. After that 2 grams of sample was used for direct photometring and light stream absorption coefficient \( K_A \) evaluation at 2 mm thickness of photometric layer.

After each measurement oil from cuvet poured to device glass for thermostating, which weight up again. In case of test with makeup oil sample in glass was increased with new oil up to 100±0.1 g.

In oxidation process coefficient \( K_A \) and volatility \( V \) are changing, that’s why thermal oxidation stability coefficient can be founded as a summary:

\[
\text{ТОС} = K_A + K_V
\]

where \( K_V \) – coefficient of motor oil volatility, which can be found:

\[
K_V = \frac{m}{M}
\]

where \( m \) – vaporized oil mass (g) for the period of time \( t \). \( M \) – initial mass (g).

Figure 1 shows the dependence of the light stream absorption coefficient \( K_A \) on the test time \( t \), expressed by the second order polynomials. Oil makeup in the interval from 160 to 180 °C diminishes oxidation intensity. It was established, that in temperatures from 160 to 180 °C makeup strongly affects the oxidation process in case of high values \( K_A \) than at the beginning of test.

\[K_A = 7.79 \cdot 10^{-4}t^2 + 0.0027t + 0.0059\]
\[ K_A = 1.31 \cdot 10^{-5} t^2 + 0.0028 t - 0.0058 \]  
\[ K_A = 7.46 \cdot 10^{-6} t^2 + 6.4 \cdot 10^{-4} t - 0.015 \]  

Correlation coefficients of equations (3 – 5) are respectively equal 0.997, 0.997 and 0.998.

Oxidation processes regression equations with oil makeup at temperatures 180 °C, 170 °C and 160 °C:

\[ K_A = 2.69 \cdot 10^{-5} t^2 + 0.0044 t - 0.031 \]  
\[ K_A = 2.06 \cdot 10^{-5} t^2 + 0.0013 t - 0.0017 \]  
\[ K_A = 2.90 \cdot 10^{-6} t^2 + 0.0014 t - 0.049 \]  

Correlation coefficients of equations (6 – 8) are respectively equal 0.997, 0.994 and 0.991.

In figure 2 represented the dependence of volatility \( V \) of semi-synthetic motor oil Lukoil Super 10W-40 SG/CD on the test time \( t \), expressed by second-order polynomials. It has been established that oil makeup has an ambiguous effect on the evaporation process. Makeup decreases evaporation intensity in temperature 180 °C (curve 1'), but it increases intensity in 160 and 170 °C (curves 2' and 3').

![Figure 2](image)

**Figure 2.** Dependence of the volatility on the test time and temperature for semi-synthetic motor oil Lukoil Super 10W-40 SG/CD: 1 – 180 °C; 2 – 170 °C; 3 – 160 °C; 1, 2, 3 – no makeup; 1’, 2’, 3’ – makeup.

Oxidation processes regression equations without oil makeup at temperatures 180 °C, 170 °C and 160 °C:

\[ V = -2.74 \cdot 10^{-4} t^2 + 0.1680 t + 0.6366, \]  
\[ V = -1.60 \cdot 10^{-4} t^2 + 0.0907 t + 0.4147, \]  
\[ V = -4.22 \cdot 10^{-5} t^2 + 0.0528 t + 0.4567. \]  

Correlation coefficients of equations (9 – 11) are respectively equal 0.994, 0.996 and 0.998.

Oxidation processes regression equations with oil makeup at temperatures 180 °C, 170 °C and 160 °C:

\[ V = -2.52 \cdot 10^{-4} t^2 + 0.1337 t + 0.4497, \]  
\[ V = -1.21 \cdot 10^{-4} t^2 + 0.0888 t + 0.4491, \]
\[ V = -6,91 \times 10^{-5} t^2 + 0,0613t + 0,6650. \] (14)

Correlation coefficients of equations (12 – 14) are respectively equal 0.997, 0.997 and 0.994.

In figure 3 represented dependences thermal oxidation stability coefficient \( K_{TOS} \) on the test time \( t \), expressed by second-order polynomials. This coefficient takes into account the combined influence of oxidation and evaporation. It has been established, that oil makeup in temperature interval from 160 to 180 °C decreases thermal oxidation intensity. At a test temperature of 180 °C, makeup affects already at the initial stages of the process and is enhanced at high values of the \( K_{TOS} \) coefficient, at a temperature of 170 °C, makeup slow down the thermal oxidation proportionally during the all-time, and at 160 °C makeup effect observed only after 120 h of oil test.

Figure 3. Dependence of the thermal oxidation stability coefficient on test time for semi-synthetic motor oil Lukoil Super 10W-40 SG/CD: 1 – 180 °C; 2 – 170 °C; 3 – 160 °C; 1', 2', 3' – no makeup; 1', 2', 3' – makeup.

Oxidation processes regression equations without oil makeup at temperatures 180 °C, 170 °C and 160 °C:

\[ K_{TOS} = 7,63 \times 10^{-5} t^2 + 0,0046t + 0,0097, \] (15)
\[ K_{TOS} = 1,22 \times 10^{-5} t^2 + 0,0037t + 0,00039, \] (16)
\[ K_{TOS} = 7,40 \times 10^{-6} t^2 + 0,0011t - 0,0072. \] (17)

Correlation coefficients of equations (15 – 17) are respectively equal 0.997, 0.998 and 0.998.

Oxidation processes regression equations with oil makeup at temperatures 180 °C, 170 °C and 160 °C:

\[ K_{TOS} = 2,90 \times 10^{-5} t^2 + 0,0052t - 0,0122, \] (18)
\[ K_{TOS} = 1,99 \times 10^{-5} t^2 + 0,0022t + 0,0033, \] (19)
\[ K_{TOS} = 2,76 \times 10^{-6} t^2 + 0,0018t - 0,0223. \] (20)

Correlation coefficients of equations (18 – 20) are respectively equal 0.998, 0.996 and 0.995.

The amount of oil makeup effects on thermal oxidation stability semi-synthetic motor oil Lukoil Super 10W-40 SG/CD, expressed the light stream absorption, volatility and thermal oxidation stability coefficient, was estimated by the makeup influence criteria \( CM \) at a test time of 60 h.

The makeup influence criteria on light stream absorption \( K_A \) is determined by the ratio:

\[ C_{M(A)} = \frac{R_{K_A}}{R_{K,M}} \] (21)
where \( R_{K_A} \) and \( R_{K_AM} \) – rates of light stream absorption \( K_A \) values change with oil makeup and without it (h\(^{-1}\)).

The makeup influence criteria on volatility \( V \) is determined by the ratio:

\[
C_{M(V)} = \frac{R_V}{R_{VM}}
\]

(22)

where \( R_V \) and \( R_{VM} \) – rates of evaporation \( G \) with oil makeup and without it (g/h).

The makeup influence criteria on thermal oxidation stability coefficient \( K_{TOS} \) is determined by the ratio:

\[
C_{M(S)} = \frac{R_{K_{TOS}}}{R_{K_{TOS,M}}}
\]

(23)

where \( R_{K_{TOS}} \) and \( R_{K_{TOS,M}} \) – rates of thermal oxidation stability coefficient \( K_{TOS} \) with oil makeup and without it (h\(^{-1}\)).

Rates of light stream absorption, volatility and thermal oxidation stability values change were determined by finding the derivatives of equations (3 – 20) and are summarized in table 1.

**Table 1.** Results of light stream absorption, volatility and thermal oxidation stability values calculation for semi-synthetic motor oil Lukoil Super 10W-40 SG/CD.

| Test temperature, °C | Values of light stream absorption rate change during the test time \( t = 60 \) h |  |
|----------------------|--------------------------------------------------|-----|
|                      | no makeup, \( R_{K_A} \), h\(^{-1}\) | makeup, \( R_{K_AM} \), h\(^{-1}\) |  |
| 180                  | 0.0120                                          | 0.0076 |  |
| 170                  | 0.0044                                          | 0.0038 |  |
| 160                  | 0.0015                                          | 0.0017 |  |

| Test temperature, °C | Values of evaporation rate change during the test time \( t = 60 \) h |  |
|----------------------|----------------------------------|-----|
|                      | no makeup, \( R_V \), g/h | makeup, \( R_{VM} \), g/h |  |
| 180                  | 0.1351                          | 0.1035 |  |
| 170                  | 0.0715                          | 0.0743 |  |
| 160                  | 0.0477                          | 0.0530 |  |

| Test temperature, °C | Values of thermal oxidation stability rate change during the test time \( t = 60 \) h |  |
|----------------------|----------------------------------|-----|
|                      | no makeup, \( R_{K_{TOS}} \), h\(^{-1}\) | makeup, \( R_{K_{TOS,M}} \), h\(^{-1}\) |  |
| 180                  | 0.0138                          | 0.0087 |  |
| 170                  | 0.0052                          | 0.0046 |  |
| 160                  | 0.0020                          | 0.0021 |  |

Values of makeup effect on light stream absorption \( K_A \), volatility \( V \) and thermal oxidation stability \( K_{TOS} \) are represented in table 2.
Table 2. Values calculation results of the makeup influence criteria on the light stream absorption coefficient, the volatility and thermal oxidation stability coefficient of semi-synthetic motor oil Lukoil Super 10W-40 SG / CD.

| Test temperature, °C | The value of the makeup influence criteria on light stream absorption $C_{M(A)}$ |
|----------------------|----------------------------------------------------------------------------------|
| 180                  | 1.58                                                                             |
| 170                  | 1.16                                                                             |
| 160                  | 0.88                                                                             |

| Test temperature, °C | The value of the makeup influence criteria on volatility $C_{M(V)}$ |
|----------------------|---------------------------------------------------------------------|
| 180                  | 1.31                                                                 |
| 170                  | 0.96                                                                 |
| 160                  | 0.90                                                                 |

| Test temperature, °C | The value of the makeup influence criteria on thermal oxidation stability $C_{M(S)}$ |
|----------------------|------------------------------------------------------------------------------------------|
| 180                  | 1.59                                                                                   |
| 170                  | 1.13                                                                                   |
| 160                  | 0.95                                                                                   |

The value of the makeup influence criteria less than 1 indicates acceleration of oil thermal oxidation processes in case of makeup, more than 1 – indicates processes deceleration. Based on table 2 data it’s can be concluded that during the test time $t = 60$ h makeup strongly decreases oil oxidation intensity at temperatures 180, 170 and 160 °C and evaporation intensity at 180°C.

In general makeup effect of semi-synthetic motor oil Lukoil Super 10W-40 SG/CD on thermal oxidation stability is positive.

3. Conclusion
During the motor oil Lukoil Super 10W-40 SG/CD tests was established, that offered estimating method application allows to find makeup influence on oxidation processes, evaporation and thermal oxidation stability changes.

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