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THERMOGRAVIMETRIC ASSESSMENT OF SERVICE PERFORMANCE OF DS-11 LUBE OILS

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ABSTRACT

On the example of analysing used DS-11 engine oils the usefulness of thermoanalytical techniques for assessing the performance of lubricating oils has been confirmed. Correlations between onset temperatures and a few per cent mass loss and the kinematic viscosity at 323 and 373 K have been found. The possibility of practical utilization of regression lines for assessing the performance of lubricating oils has been indicated.

INTRODUCTION

Thermogravimetry (TG) ensures a relatively simple quantitative interpretation of results and for this reason it is the most frequently used thermoanalytical method. It has proved to be more advisable, however, to employ TG simultaneously with derivative TG (DTG) and differential thermal analysis (DTA), because the results obtained by each method mutually facilitate their interpretation.

The derivatograph is a commonly used instrument which allows simultaneous recording of TG, DTG and DTA curves. It can be employed for recording approximate distillation and cracking distillation curves, for determining the temperature range of first-order phase transitions, and for examining the thermal stability of commercial oils, both crude and refined, under standard conditions [1–3]. The derivatograph enables the evaporated oil portion of mineral oils to be distinctly separated from the decomposed resinous material [4] and, moreover, it facilitates identification of the chemical composition of distilling and non-distilling portions of fuel oils [5]. It was also employed for laboratory quality inspection tests of commercial lubricating oils, based on easily determinable ranges of the boiling and decomposition temperatures of an oil and on its coking point [6]. Furthermore, an attempt was made to use the derivatograph as a means for fast determination of the chemical composition and performance of fuel and lubricating oils [7] as well as the service performance of lubricating oils [8].

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The examples presented do not exhaust the wide range of possibilities of employing the derivatograph for examining physicochemical properties and the chemical composition of fuel and lubricating oils. In previous reports, it was found possible to employ the derivatograph for qualitative and quantitative assessments of ageing processes of M-20 Bp, MS-20 p [9] and Marinol CB SAE-30 [10] lubricating oils, which were sampled from the marine engines during service. The present work is a continuation of these studies with regard to samples of used DS-11 lubricating oils.

EXPERIMENTAL

Samples for testing

In this study DS-11 lube oils were employed both new and used, which were taken directly from the oil system of marine engines after having run a few dozen to a few hundred hours.

Test samples were taken in accordance with Polish Standard PN-66/C-04000 [11]. They were thoroughly mixed prior to each analysis. A shaking period of 5 min is necessary for the sludge to be homogeneously suspended in the oil.

Testing technique

Determination of classical parameters

The content of water in lubricating oils was determined by the distillation method in accordance with Polish Standard PN-66/C-04523 [12]. For the determination of kinematic viscosity of used oils at 323 and 373 ± 0.02 K the Pinkevitch viscometer was used in accordance with Polish Standard PN-73/C-04011 [13]. The flash point of lube oils was measured by the Pensky–Martens method according to Polish Standard PN-75/C-04009 [14]. For the determination of foreign solids in lubricating oils, Polish Standard PN-58/C-04089 [15] was employed. The procedure for carrying out determinations of the content of oxide ash has been exactly described in previous papers [9,10].

Determination of thermal parameters

The TG, DTG and DTA curves of thermal decomposition of DS-11 lube oils were recorded using an OD-103 derivatograph (MOM, Budapest). All measurements were made under identical conditions. A sample of 200 mg oil in a platinum crucible was heated under an air atmosphere at a heating rate of 5 K min^{-1} up to the final temperature of 973 K. As reference material, α-Al_2O_3 was used. Each thermogram was recorded at least three times.

The temperatures of the onset (T_0) and of the end (T_{100}) of the thermal decomposition of oils were read from the TG and DTG curves, whereas the temperatures of 1, 5, 15, 30, 50 and 75% mass losses (T_1, T_5, T_{15}, T_{30}, T_{50} and T_{75}) were read solely from the TG curves.

RESULTS AND DISCUSSION

Physicochemical assessment of lubricating oils

Assessment of the usefulness of lubricating oils is carried out based on the knowledge of their general physicochemical properties and those of certain characteristic indicators. It follows from common practice that the most important parameters for defining the service performance of lubricating oils are the content and origin of water, kinematic viscosity, flash point and the content of foreign solids and oxide ash. The values obtained as a result of carrying out the above determinations are confronted with the requirements specified by appropriate standards, the lube oil quality thus being checked both at the oil's acceptance on board and during its service. This latter is particularly important, because the usage of a lubricating oil over a longer period of time generally effects changes in its physicochemical properties and may determine the further service of this product.

TABLE 1

Values of the water content, kinematic viscosity at 323 and 373 K, flash point, foreign solids content and oxide ash for the used DS-11 lube oils

Sample No.	Running time (h, min)	Water content (%)	Kinematic viscosity (cSt) at		Flash point (K)	Foreign solids content (%)	Oxide ash (%)
			323 K	373 K			
D-1	30,55	ND	72.8	12.2	477	0.019	0.552
D-2	39,10	Trace	72.6	12.1	481	0.068 [a]	0.639
D-3	40,50	ND	70.0	11.9	476	0.005	0.521
D-4	60,40	Trace	71.9	12.1	475	0.190 [a]	0.648
D-5	115,50	ND	69.1	11.5	472	0.155 [a]	0.491
D-6	120,25	ND	69.1	11.8	474	0.130 [a]	0.519
D-7	230,15	Trace	70.0	11.6	471	0.013	0.511
D-8	453,50	Trace	75.0	12.3	471	0.50 [b]	0.595
D-9	479,30	Trace	73.3	12.1	470	1.07 [b]	0.576
D-10	486,15	Trace	70.9	11.9	474	0.020	0.580
D-11	503,15	Trace	71.5	12.3	475	0.033	0.586

[a] Extraction naphtha II was used as a solvent of lube oil.

[b] Content of the foreign solids was determined by the centrifuging method.

ND = not detected.

In Table 1 the results of determinations are listed, carried out for DS-11 lubricating oil. Comparing their values with the requirements laid down for this product in the appropriate standard, the degree of use of the lube oil tested can be defined. It is known from previous studies [9,10] that the shape of TG, DTG and DTA thermal decomposition curves of a lubricating oil is conditioned by its chemical composition. In this connection analyses have been made of the relationship between the chemical composition change of DS-11 lube oil due to use and the shape of its thermal degradation curves.

Thermal decomposition of lubricating oils

The analysis of the shape of TG, DTG and DTA thermal decomposition curves of used DS-11 oils has shown that the onset of mass loss is observed in the temperature range 436–456 K. This process is accompanied by a moderate exothermic effect, followed by two overlapping endothermic effects. They are associated with the evaporation of volatile oil fractions and with the desorption of gaseous degradation products from the crucible. On the TG curve this process is accompanied by an almost rectilinear segment of mass loss within the temperature range 523–673 K.

Adonyi [16–18] has stated that when using the appropriate kinetic equations a lube oil's evaporation process can be distinguished from its thermal decomposition. He pointed out that up to 558 K the mass loss is effected by evaporation, which is reflected by the linear dependence of evaporation rate on the temperature and surface area of evaporation. Above this temperature, decomposition occurs. Adonyi and Körösi [19,20] have stated, furthermore, that at lower temperatures the volatile component evaporates from the mixture at a higher rate as compared with its evaporation as a pure substance, although the effective surface of evaporation from the mixture is smaller. Thus, it follows that the non-volatile components act as accelerators of the evaporation process. Along with the reduction of volatile component concentration in the mixture the DTG peak undergoes a slight shift towards higher temperatures, whereas the evaporation temperature range is widened by the upper temperature limit shifting towards higher values.

The change in a lube oil's chemical composition due to use is reflected both by the evaporation process and that of thermal decomposition of the product under test. This is particularly markedly depicted by a temperature interval of about 100 K, which is found between the onset of mass loss and the beginning of the rectilinear segment of mass loss. It is accompanied by a mass loss of about 5%. The analysis of the temperature values for this interval in connection with classical parameter values of the physicochemical assessment of DS-11 lube oil's use has pointed out that the less used the oil, the more the temperature interval is shifted towards higher values. The value of the obtuse angle at the intersection point of the baseline produced on the TG curve and the tangent to the rectilinear segment of mass loss on the TG

TABLE 2

Results of the thermogravimetric analysis of the used DS-11 lube oils

Sample No.	Temperatures of the successive mass losses (K)							
	T_0	T_1	T_5	T_{15}	T_{30}	T_{50}	T_{75}	T_{100}
D-1	453	493	548	593	623	658	688	833
D-2	446	483	538	586	621	658	691	831
D-3	443	483	533	578	613	648	681	818
D-4	441	478	531	588	626	661	688	833
D-5	441	476	536	588	626	658	688	838
D-6	436	478	541	583	628	653	686	833
D-7	443	483	538	593	633	658	693	838
D-8	456	508	563	608	643	673	706	841
D-9	446	483	543	593	628	663	693	833
D-10	441	481	543	606	641	678	708	846
D-11	446	493	551	606	643	653	683	821

curve is approximately 90°. On the other hand, considerable use of a lubricating oil manifests itself by the shift of T_0 and T_5 towards lower values. Similar relationships hold also for the temperatures of successive mass losses, which are reflected by the data listed in Table 2.

On the TG (DTG) thermal decomposition curves of used lubricating oils no mass gain associated with the oxidation processes of the product under study has been found, which is a result of carrying out the analyses in a static air atmosphere. The crude oil's mass gain starting at 477 K, as observed by Bae [21], is a result of applying a dynamic air atmosphere during analysis.

Correlation analysis

The coefficient values of the linear correlation between the temperatures for onset, end, successive mass losses and the kinematic viscosity, flash point, the content of foreign solids and oxide ash were calculated by the least-squares method. They are listed in Table 3. It has been stated that with the exception of correlation coefficients for T_{100} and the kinematic viscosity at 373 K, as well as for T_1, T_5, T_{15}, T_{30}, T_{50}, T_{75}, T_{100} and the flash point, the correlation coefficient values for all remaining cases assume positive values. At a probability of 0.05 [22] only the correlation coefficients for T_0, T_1, T_5 and the kinematic viscosity assume higher values than the critical one. In all remaining cases no correlations exist.

In Figs. 1 and 2 the scatter of points about the regression lines for the relationship between T_0 and the kinematic viscosity at 323 and 373 K is presented. It is greater for the viscosity at 373 K. The same situation was also observed in the case of MS-20 p [9] and Marinol CB SAE-30 [10] lube

TABLE 3

Correlation coefficients between the temperature values for the onset, end, successive mass losses and the values of the kinematic viscosity, flash point, foreign solids content and oxide ash for the used DS-11 lube oils ($n = 11$)

Physicochemical parameter	T_0	T_1	T_5	T_{15}	T_{30}	T_{50}	T_{75}	T_{100}
Kinematic viscosity at 323 K	0.84	0.74	0.65	0.50	0.28	0.48	0.45	0.14
Kinematic viscosity at 373 K	0.67	0.69	0.59	0.45	0.26	0.18	0.11	−0.26
Flash point	0.01	−0.10	−0.25	−0.33	−0.46	−0.33	−0.34	−0.41
Foreign solids content	0.26	0.17	0.27	0.15	0.12	0.30	0.26	0.16
Oxide ash	0.29	0.23	0.14	0.29	0.18	0.36	0.26	0.01

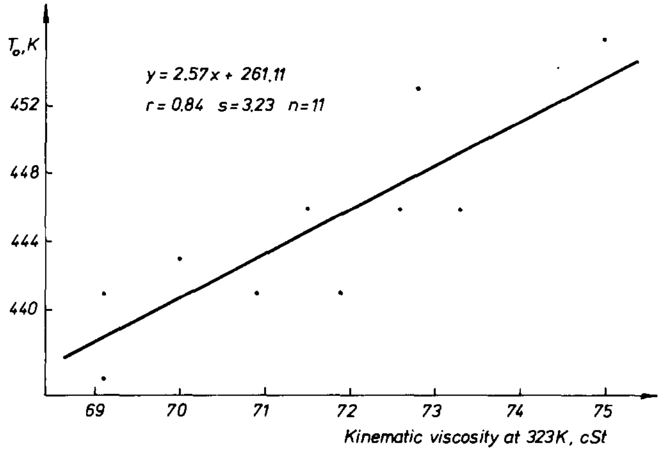

Fig. 1. Relationship between the onset temperature of the thermal decomposition and the kinematic viscosity at 323 K for the used DS-11 lube oils.

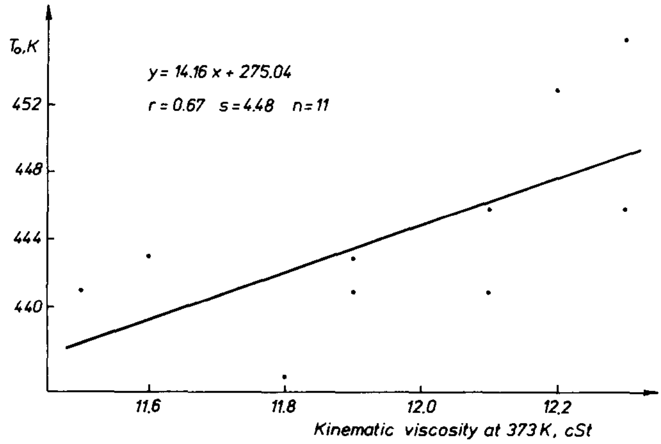

Fig. 2. Relationship between the onset temperature of the thermal decomposition and the kinematic viscosity at 373 K for the used DS-11 lube oils.

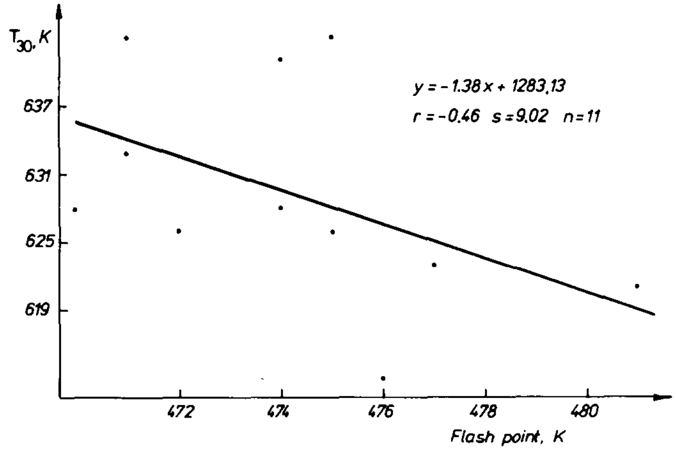

Fig. 3. Relationship between the 30% mass loss temperature of the thermal decomposition and the flash point for the used DS-11 lube oils.

oil analyses. From Fig. 3, a negative relationship between T_{30} and the flash point is evident. It is incompatible with the results obtained for M-20 Bp and MS-20 p [9] and for Marinol CB SAE-30 [10] lubricating oils. The insufficient number of results for DS-11 lube oil makes it impossible to explain this fact.

Using the linear equation $y = ax + b$ the temperature ranges were determined, which the onset of thermal decomposition and 1, 5 and 15% mass loss of DS-11 lube oil should correspond to, so that it could be estimated whether or not the kinematic viscosity at 323 and 373 K of the sample examined met the requirements of the standard. The results obtained are presented in Table 4, whereas in Table 5 the regression line equations for T_0 and T_5 of DS-11 lube oils are listed, based on which the kinematic viscosity value can be estimated after determining T_0 or T_5 from the thermogram. From the nature of both variables it is causatively justified to use the

TABLE 4

Temperature ranges of the thermal decomposition onset and of the 1, 5 and 15% mass losses for the DS-11 lube oil met the standard (standard deviations of the regression lines are indicated in parentheses)

Physico-chemical parameter	Requirements according to the standard	Temperature ranges (K)			
		T_0	T_1	T_5	T_{15}
Viscosity at 323 K	65.0 ± 2.5 [a]	428 ± 6 (3.2)	461 ± 9 (6.6)	522 ± 8 (7.3)	576 ± 7 (9.1)
Viscosity at 373 K	11.0 ± 0.5	431 ± 7 (4.5)	462 ± 12 (7.1)	523 ± 10 (7.7)	577 ± 8 (9.4)

[a] Values of the kinematic viscosity at 323 K were calculated based on the regression equation $x = ay + b$.

TABLE 5

Regression line equations for the thermal decomposition onset and for the 5% mass loss for the DS-11 lube oils

Physicochemical parameter	Regression line equation	Standard deviation of regression line
Viscosity at 323 K	$0.28T_0 + -51.61$	1.06
	$0.13T_5 + -0.43$	1.50
Viscosity at 373 K	$3.13\times10^{-2}T_0 + -1.94$	0.21
	$1.74\times10^{-2}T_5 + -2.54$	0.23

equation $x = ay + b$ and to estimate the independent variable x on the basis of the dependent variable y.

Based on an analysis of the shape of TG, DTG and DTA curves, Sobańska and Wachal [8] have determined the characteristic parameters, which can measure the service performance of a lubricating oil. Among these parameters are the temperature and time of an oil's fractional stability, the temperature, time and mass of an oil's chemical stability, of thermal ageing and of coking of an oil. The experimental material presented in this work is very poor and, moreover, the results obtained by thermoanalytical techniques have not been compared with the results of classical determinations.

CONCLUSIONS

The investigation performed on used DS-11 engine oils confirms the results obtained for M-20 Bp, MS-20 p [9] and Marinol CB SAE-30 [10] lubricating oils. The values of linear correlation coefficients indicate that assessment of the service performance of the product examined is most advantageously carried out based on the temperature values for the onset and a few per cent of mass loss. The low values of correlation coefficients and lack of correlation for flash point and the content of oxide ash are to be explained by the small number of test samples, for objective reasons, and by small differences in the degree of use.

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