

## **THERMOGRAVIMETRIC ASSESSMENT OF SERVICE PERFORMANCE OF M-20 Bp AND MS-20 p LUBRICATING OILS**

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### **ABSTRACT**

On the example of used engine lubricants an evaluation of the applicability of thermoanalytical methods to the assessment of the service performance of oils was made. As part of the study, the water content, kinematic viscosity at 323 and 373 K, the flash point and the content of foreign solids and oxide ash in the oils were determined. On correlating the data obtained to the temperatures of successive weight losses, as determined on the basis of the TG and DTG curves of thermal decomposition of the same oils under dynamic conditions, the existence of strong relationships was found between the viscosity, flash point and the temperatures of the initial weight losses. The possibility of a practical utilization of the regression equation for the assessment of the service performance of lubricating oils was indicated.

### **INTRODUCTION**

Thermal studies on fuel and lubricating oils indicate that a real possibility exists for replacing a number of expensive and time-consuming chemical determinations in the control industry laboratories by rapid thermal methods requiring small sample sizes, viz. thermogravimetry (TG) and derivative thermogravimetry (DTG). Adonyi [1], when performing a detailed TG study of the carbon residue formation process under conditions defined by the Conradson carbon residue test, found that the classical method failed to provide the complete coking of lubricating oils. Voelker and Fischer [2] have proposed utilizing the TG technique as an industrial method for the control of the chemical composition of lubricating oils. Masek [3] has pointed to the usefulness of TG and DTG methods for the fast assessment of the composition and properties of commercial fuel and lubricating oils. In his opinion the TG and DTG curves of the thermal decomposition are relatively clear and sufficiently characteristic to distinguish the particular fuel oils. On the other hand, Sobańska and Wachal [4] made an attempt to utilize the DTA,

TG and DTG curves as measures of the service performance of lubricating oils.

The aim of this work is to define the applicability of used engine lubricants for further service on the basis of the analysis of their thermal decomposition. It is known from common experience that the most important parameters in defining the service performance of oils at present are: the content of water and its origin, viscosity, flash point, acid number, the water-extract reaction, the total base number and the content of foreign solids. Performing these determinations requires a few dozen hours of work, significant amounts of product to be tested, various chemical reagents and laboratory equipment. In addition, the analytical results obtained in different laboratories differ greatly from each other in spite of the fact that the testing technique is based on the same standards. In this connexion it can be supposed that the application of the TG and DTG methods will be helpful in partially overcoming these difficulties.

It has been decided to realize the aim of this work as follows. To determine, based on the standards as used in control industry laboratories, the most substantial parameters which define the degree of wear of used lubricating oils, viz. the content of water, the kinematic viscosity at 323 and 373 K, the flash point and the content of foreign solids and of oxide ash. Furthermore, to carry out the thermal decomposition of the same used lubricating oils under dynamic conditions. To define these from among the thermal parameters taken from the TG and DTG curves, which reflect changes in the physico-chemical properties and in the chemical composition of oils due to their wear. Based on the data obtained, to define the correlations between the classical and thermal parameters of assessment of the service performance of oils. This would provide information on the possibility of replacing the more troublesome classical methods by thermo-analytical ones.

## EXPERIMENTAL

### *Materials*

In the study, M-20 Bp and MS-20 p lubricating oils were used, both new and used ones, sampled from the oil system of marine engines after a few to a few thousand hours of work.

The samples for these studies were collected according to Polish Standard PN-66/C-04000 [5]. The oils were thoroughly mixed; a shaking period of 5 min is necessary to uniformly suspend the sludge throughout the sample. Thereafter, the oils were strained through a metal screen and the filtrate was protected against dustiness.

## Testing technique

### *Determination of classical parameters*

The water content in the lubricating oils under study was determined by the distillation method according to Polish Standard PN-66/C-04523 [6]. Solvent-carrier liquid (100 ml) was poured into a 500-ml distillation flask containing the weighed sample of 100 g oil. Extraction gasoline III was used as solvent-carrier liquid. On thoroughly mixing the contents of the flask until the soluble products were dissolved, the flask was connected to the distillation assembly and the distillation was performed so as to obtain the condensation rate of 2 to 4 drops of distillate per second. The distillation was completed after reaching full clarity of the solvent-carrier liquid, which was overflowing from the receiver into the distillation flask and when the water level in the receiving trap remained constant. The time of distillation should not exceed 1 h. On cooling the distillate to  $293 \pm 2$  K the volume of water accumulated was read with accuracy to the nearest scale division above the surface of the water level. The water content of the oil under test was calculated from the formula

$$\text{Water content (\%)} = \frac{Vd}{m} \times 100$$

where  $V$  is the volume of water in the trap (ml),  $d$  is the density of water at  $293 \pm 2$  K ( $\text{g ml}^{-1}$ ) and  $m$  is the weight of the oil sample (g).

The kinematic viscosity of oils was determined according to Polish Standard PN-73/C-04011 [7] by means of the Pinkevitch viscometer, which had been thoroughly rinsed several times with a mixture of benzene and ethyl alcohol (4 + 1) before each measurement and then dried with a stream of clean dry air. The reservoir part of the viscometer was filled with a sample of oil and then the viscometer was placed in a vertical position in a thermostat at  $323$  or  $373 \pm 2$  K and left for a period of 30 min. After obtaining a constant temperature of the sample it was sucked by means of a pump through a capillary so that its level was over the upper mark of the measuring reservoir. Next, the flow time of oil flowing freely between the upper and the lower mark of the measuring reservoir was measured, the lower meniscus being taken as the level of the liquid. The flow time was determined two times at least. The kinematic viscosity of the oil under test was defined according to the formula

$$\gamma = kt$$

where  $\gamma$  is the kinematic viscosity (cSt),  $k$  is the capillary constant ( $\text{cSt s}^{-1}$ ) and  $t$  is the arithmetic mean of the flow time (s).

The flash point of the used lubricating oils was determined by the Pensky-Martens closed-tester method according to Polish Standard PN-75/C-04009 [8]. The product to be tested was placed in the clean, dry cup

equipped with a cover and a suitable thermometer and then placed in a thermostat. The heating of the cup was controlled so that the rate of the temperature increase was  $5\text{--}6\text{ K min}^{-1}$ , and the speed of the stirrer  $90\text{--}120$  rpm. The first measurement of the flash point was taken at a temperature  $17\text{ K}$  lower than that of the expected flash point. The subsequent measurements were made at each temperature step of  $3\text{ K}$ . As the flash point of oil, the temperature at which the first sudden ignition of its vapours occurred was taken. The ignition is as a rule accompanied by a slight explosion and extinction of the burner flame.

For the determination of foreign solids in lubricating oils, Polish Standard PN-58/C-04089 [9] was employed. A sample ( $50\text{ g}$ ) of oil was placed in a 3- to 6-fold amount of benzene and the contents of the beaker were lightly heated over a water bath. The hot solution obtained was filtered through an ashless filter paper, which had been formerly rinsed with benzene and heated in a drying oven at  $378\text{ K}$  to constant weight. The filter paper with the insoluble fraction was then extracted in an extraction apparatus with the same solvent which had been used for the dissolution of the oil. The extraction was run until the solvent flowing down was colourless and a drop of it placed on blotting paper did not leave a trace upon its evaporation. After the filter paper had been removed from the extraction apparatus it was dried in a drying oven to constant weight. The content of foreign solids was calculated from the formula

$$\text{Foreign solids (\%)} = \frac{m_1 - m_2}{m_3} \times 100$$

where  $m_1$  is the weight of the weighing bottle with filter paper containing foreign solids (g),  $m_2$  is the weight of the weighing bottle with filter paper (g) and  $m_3$  is the weight of the oil sample (g).

The content of oxide ash was determined by weighing a sample of  $2\text{ g}$  lubricating oil into a porcelain crucible pickled with hydrochloric acid, ignited and burnt to constant weight. After placing the crucible over a sand bath, the oil was evaporated without allowing either the oil to flow out over the edge of the crucible or the vapours to ignite. The sample of oil was heated so as to obtain the dry residue which was ignited over a Meker burner until the ashing of the residue was complete. The crucible was weighed on cooling. These operations were repeated until the difference between two successive weighings was not greater than  $0.0004\text{ g}$ . The amount of the oxide ash was calculated from the formula

$$\text{Oxide ash (\%)} = \frac{m_1 - m_2}{m_3} \times 100$$

where  $m_1$  is the weight of the crucible with ash (g),  $m_2$  is the weight of the crucible (g) and  $m_3$  is the weight of oil sample (g).

The arithmetic mean of at least two test results was assumed as the results of the determinations performed.

### *Determination of thermal parameters*

The DTA, TG and DTG curves of the thermal decomposition of lubricating oils, both new and used ones, were recorded on an OD-130 derivatograph (MOM, Hungary). All measurements were accomplished under identical conditions. A 200-mg sample of oil in a platinum crucible was heated under an atmosphere of air at a heating rate of  $5 \text{ K min}^{-1}$  up to the final temperature of 973 K. As reference material,  $\alpha\text{-Al}_2\text{O}_3$  was used. Each thermogram was recorded at least three times.

The temperatures at the beginning ( $T_0$ ) and end ( $T_{100}$ ) of thermal decomposition of the oils were read from the TG and DTG curves, whereas the temperatures at 1, 5, 15, 30, 50 and 75% loss in weight ( $T_1$ ,  $T_5$ ,  $T_{15}$ ,  $T_{30}$ ,  $T_{50}$  and  $T_{75}$ ) were read solely from the TG curves.

## RESULTS AND DISCUSSION

### *Significance of classical parameters*

The following were determined in this work from the parameters defining the performance of used lubricating oils: the content of water, the kinematic viscosity at 323 and 373 K, flash point and the content of foreign solids and oxide ash.

The values of water-extract reaction, the acid number and the total base number were not determined, however. The water-extract reaction and the acid number allow the correct conclusions to be drawn on the content of acids in the used oil only with regard to untreated oils which contain no lubricant additives. On the other hand, the total base number serves to estimate the content of active basic additives in additive-treated oils. They thus fail to provide substantial indications on the degree of wear of used lubricating oils.

The majority of components of oxide ash are metal oxides originating from the combustion of lubricating oil. In principle, the content of oxide ash is determined for straight mineral oils and for these additive-type oils whose additives do not form solid residues after combustion. This value is a measure of accuracy of the oil refining and its purity. In the case of additive-type lubricating oils the content of ash is proportional to the amount of the additives. It is thus a specific indicator of their content in the additive-treated oil.

When analysing the numerical values listed in Tables 1 and 2 for used M-20 Bp and MS-20 p lubricating oils as a function of the running time of a particular oil in the oil system of a marine engine, no correlation was found between these parameters. A few or a dozen or so times longer running time of oil does not always influence the change in its water content, kinematic viscosity and flash point. This is due to filling up, i.e., making up for the loss

TABLE 1

Values of the water content, kinematic viscosity at 373 K, flash point, foreign solids content and oxide ash for the used M-20 Bp lubricating oils

Sample No.	Running time (h.min)	Water content (%)	Kinematic viscosity at 373 K (cSt)	Flash point (K)	Foreign solids content (%)	Oxide ash (%)
A-1	0.20	trace	19.6	486	0.017	0.605
A-2	0.40	0.05	18.8	481	0.038	0.672
A-3	2.15	trace	19.2	486	0.004	0.640
A-4	2.25	trace	19.2	491	0.141	0.635
A-5	2.30	trace	18.9	484	0.032	0.636
A-6	12.09	trace	11.5	381	0.040	0.195
A-7	18.40	trace	17.9	462	0.021	0.671
A-8	22.00	trace	18.0	460	0.029	0.673
A-9	24.50	trace	19.3	463	0.049	0.665
A-10	25.45	0.06	18.9	470	0.039	0.649
A-11	27.20	trace	19.7	471	0.050	0.734
A-12	27.20	trace	19.3	477	0.040	0.769
A-13	28.55	trace	19.3	472	0.018	0.687
A-14	30.00	0.3	17.8	458	0.036	0.483
A-15	31.55	trace	18.8	466	0.033	0.736
A-16	32.40	trace	18.9	469	0.030	0.712
A-17	33.45	trace	18.8	467	0.022	0.629
A-18	40.10	trace	18.7	462	0.050	0.753
A-19	42.25	trace	18.9	461	0.055	0.718
A-20	42.35	trace	18.9	483	0.084	0.774
A-21	44.15	trace	19.6	471	0.052	0.748
A-22	44.50	trace	19.1	471	0.045	0.764
A-23	47.10	trace	18.3	467	0.102	0.718
A-24	47.13	trace	19.2	476	0.052	0.677
A-25	64.15	trace	19.0	477	0.149	0.773
A-26	66.50	trace	19.3	475	0.042	0.700
A-27	91.40	trace	19.3	471	0.063	0.765
A-28	94.49	trace	18.8	474	0.036	0.489
A-29	97.00	trace	19.0	460	0.042	0.720
A-30	97.55	trace	19.4	473	0.031	0.731
A-31	98.10	trace	18.7	477	0.060	0.741
A-32	99.00	trace	18.4	461	0.034	0.712
A-33	99.00	trace	19.3	475	0.043	0.716
A-34	100.0	trace	16.4	448	0.052	0.672
A-35	102.43	trace	19.8	491	0.028	0.622

of oil in the oil system of an engine with new oil, as well as to different operating conditions of the engine.

#### *Choice of conditions for thermal measurements*

The shape of DTA, TG and DTG curves of the thermal decomposition is conditioned by a number of factors and in particular by the parameters of

TABLE 2

Values of the water content, kinematic viscosity at 323 and 373 K, flash point, foreign solids content and oxide ash for the used MS-20 p lubricating 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			
B-1	15.20	ND	145.6	19.5	484	0.020	0.281
B-2	28.40	ND	137.8	19.1	470	0.023	0.314
B-3	34.00	ND	131.2	18.3	456	0.023	0.210
B-4	35.30	ND	28.7	6.8	398	0.026	0.177
B-5	35.40	ND	89.2	14.2	424	0.031	0.218
B-6	47.00	ND	155.6	20.2	505	0.014	0.273
B-7	50.35	trace	152.3	19.8	487	0.015	0.323
B-8	50.40	ND	129.8	18.3	462	0.023	0.232
B-9	52.05	ND	132.8	18.3	465	0.016	0.274
B-10	53.40	trace	152.8	20.1	487	0.009	0.302
B-11	54.05	trace	152.8	20.1	484	0.030	0.314
B-12	54.50	trace	57.9	10.9	420	0.034	0.209
B-13	55.40	trace	108.2	16.4	438	0.005	0.298
B-14	67.00	ND	38.2	8.2	420	0.018	0.185
B-15	77.05	ND	147.2	19.0	478	0.069	0.328
B-16	91.25	0.1	149.0	19.3	456	0.142	0.278
B-17	95.36	ND	154.8	20.3	484	0.59 <sup>a</sup>	0.379
B-18	98.42	ND	151.4	19.9	482	0.59 <sup>a</sup>	0.385
B-19	99.06	ND	153.6	20.2	483	1.28 <sup>a</sup>	0.378
B-20	100.00	trace	132.7	18.5	468	0.013	0.279
B-21	100.20	ND	124.3	17.5	454	0.054	0.265
B-22	105.20	ND	33.2	7.7	411	0.005	0.216
B-23	105.20	trace	85.7	14.1	433	0.014	0.238
B-24	108.10	ND	150.8	20.2	502	0.016	0.285
B-25	113.10	ND	152.2	20.3	493	0.002	0.306
B-26	119.25	ND	155.3	20.3	474	0.048	0.353
B-27	119.45	trace	156.4	20.4	477	0.058	0.317

<sup>a</sup> The content of the foreign solids was determined by the centrifuge method. ND, not detected.

the sample being decomposed and by the variable instrument parameters. In the case of lubricating oils the instrument parameters are of substantial significance. Their influence was determined on the example of a random sample of the used M-20 Bp lubricating oil A-7.

#### *Influence of the sample size*

Measurements were accomplished by using the sizes of 50, 100, 200 and 500 mg of the A-7 sample. The changes in the shape of DTA, TG and DTG curves of its thermal decomposition at unaltered remaining instrument parameters are displayed in Fig. 1.

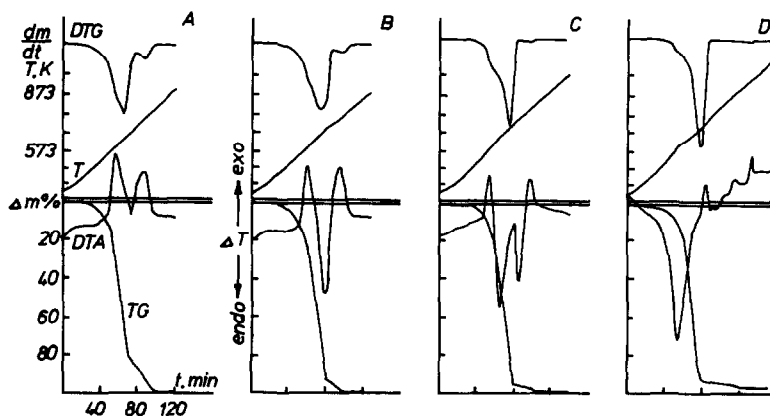


Fig. 1. DTA, TG and DTG curves of the thermal decomposition of the A-7 sample for the sizes: (A) 50, (B) 100, (C) 200 and (D) 500 mg. Heating rate,  $5 \text{ K min}^{-1}$ ; DTA and DTG sensitivity,  $1/5$ .

The analysis of the shape of the curves has shown that the double-stage course of the oil decomposition process decays with an increase in the size of the sample. This is depicted by the TG and DTG curves. In the case of the 50-mg sample the temperatures of both the beginning of decomposition and the 75% loss in weight have lower values as compared to the same temperatures for the sample sizes of 100 and 200 mg. For the 500-mg sample the temperature of the beginning of the weight loss is significantly shifted to lower temperatures.

Essential changes are also observed on the DTA curves. Two distinctly parted exothermic effects for the 50-mg sample are separated by endothermic effects as the size of the sample increases. A correlation is also evident between the areas of these effects and the size of the sample. In the case of the 500-mg sample, however, only a high and broad endothermic peak and a following pointed exothermic effect are related to the decomposition of the lubricating oil. A number of exothermic effects in the temperature range beyond 773 K reflects the burning up of the rest of the oil distilling from the crucible onto the lower part of the thermocouple sheath. On cooling the furnace, large drops of pale-yellow oil were also found in the lower part of the thermocouple sheath. This is an analytical residue of a few percent as registered by the TG curve.

The differences in the shape of DTA, TG and DTG curves of thermal decomposition of the A-7 sample depict the influence of sample size on the mechanism of oil decomposition. The combustion process is predominant in the case of smaller sample sizes, whereas the distillation process dominates for the larger ones. The causes for this phenomenon lie, among others, in the temperature gradient between the crucible wall and the inside of the sample, and also in its chemical composition. For this reason it was decided to employ sample sizes of 200 mg in further research.



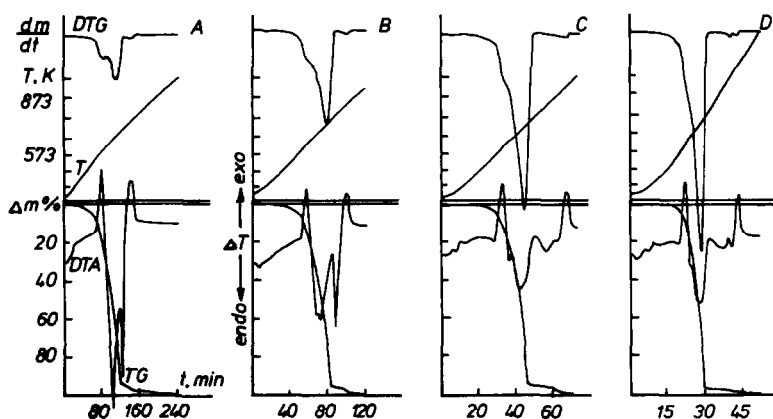


Fig. 2. DTA, TG and DTG curves of the thermal decomposition of the A-7 sample at the heating rates: (A) 2.5, (B) 5, (C) 10 and (D) 15 K min<sup>-1</sup>. Sample size, 200 mg; DTA and DTG sensitivity, 1/5.

#### *Influence of heating rate*

In Fig. 2 the DTA, TG and DTG curves of thermal decomposition of the 200-mg A-7 sample are presented as recorded at heating rates of 2.5, 5, 10 and 15 K min<sup>-1</sup>. It was found that increasing the heating rate leads to the shifting of the particular thermal processes to higher temperatures. This is reflected in the most characteristic way by the DTA and DTG curves.

At higher heating rates an overlapping of endothermic DTA peaks is observed, since their parameters (the height and width at half-height of the effect) are increased. This results from the increase in the extent of over-reacting the substances in the time unit and from the formation of a greater spatial temperature gradient inside the sample under test. In addition, the TG curve runs more steeply under the same conditions.

The unfavourable influence of higher heating rates on the shape of two decomposition curves under study has caused the heating rate of 5 K min<sup>-1</sup> to be employed in further measurements.

#### *Thermal decomposition of lubricating oils*

Owing to the fact that lubricating oils are, in chemical respect, a mixture of a great variety of different, hydrocarbon-type compounds with approximate physico-chemical properties, it is understandable that the DTA, TG and DTG curves of their thermal decomposition are plots of resultant physico-chemical and thermochemical phenomena occurring in the test sample during the course of its heating. Thermal effects on the DTA curves result from the overlapping of the endothermic and exothermic effects due to the transitions of individual components. In this connexion difficulties are encountered in identifying the reaction responsible for the appearance of a thermal process. Moreover, the recognition of the mechanism of the thermal

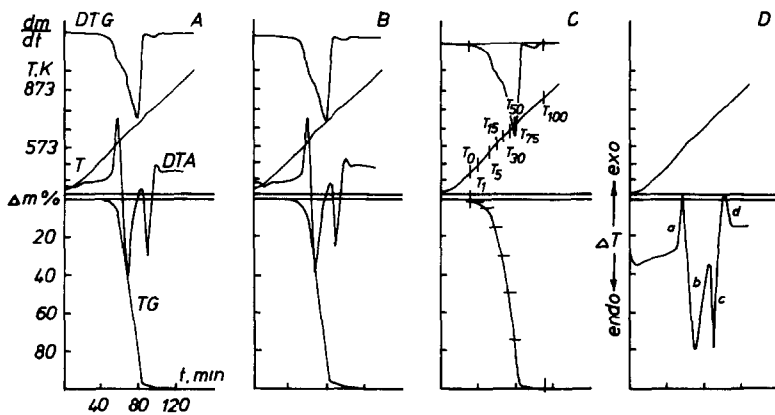


Fig. 3. DTA, TG and DTG curves of the thermal decomposition of the new lubricating oils: (A) M-20 Bp and (B) MS-20 p. (C) The graphical method of determination of the temperatures of successive weight losses on the TG (DTG) curves. (D) The method of defining the effects on the DTA curves.

decomposition is additionally hindered by the dependence of the chemical composition of an oil on the crude oil type, from which it was obtained.

This is graphically shown in Figs. 3A and B, where the decomposition curves of new M-20 Bp and MS-20 p lubricating oils are presented.

The thermal decomposition of oils is preceded by the phase transitions of their components. Taking into consideration that the instrument used in this study has been equipped with Pt/Pt–Rh thermocouples with their thermo-electrical voltage curve running very flatly below 473 K, it is not possible for these processes to be investigated in more detail. The endothermic effect reflecting them is shallow and broad, and, in addition, it occurs over a temperature range of a few dozen degrees.

It can be stated in general that the thermal decomposition of lubricating oils proceeds in the two stages. In the first stage the thermal degradation of oil components takes place. This process is confirmed on the DTA curve by a narrow and sharp exothermic peak. The subsequent two overlapping endothermic effects are related to the distilling of more-volatile oil fractions and to desorbing the gaseous decomposition products out of the system. The analysis of the shape of the TG and DTG curves has shown that it is impossible to determine the boundary between both endothermic processes. In addition, a coking process is observed in the final sector of this stage. It must be pointed out, however, that the release of volatile oil fractions and decomposition products is characterized by an almost rectilinear segment of weight loss on the TG curve over the temperature range 523–673 K. This suggests that the rate of weight loss over this range is approximately constant.

The coke originating from coking the products formed during the course of the thermal decomposition of lubricating oils is burned in the second

stage of the decomposition. This process is distinctly separated from the preceding stage. This is confirmed by a not too large, rounded exothermic DTA effect and a flat DTG curve peak. On the TG curve, however, a plateau is observed, which makes the determination of the amount of coke formed possible.

A great similarity of the shape of the DTA, TG and DTG curves of the thermal decomposition of lubricating oils, the approximate temperature ranges of particular thermal processes and comparable values of energy effects indicate a close similarity of their chemical composition and the resulting similar character of the chemical transitions occurring.

### *Interpretation of TG and DTG curves*

A thorough analysis of the shape of TG and DTG curves of the thermal decomposition of used lubricating oils has shown that the less contaminated the oil, the more steep is the deviation of its TG decomposition curve from the baseline. On the other hand, with the increase in the degree of oil wear and with resulting oil contamination by its decomposition products, the temperature at the onset of decomposition is shifted to lower temperatures. These conclusions are confirmed by the analysis of temperatures of successive weight losses on the TG curves.

The graphical way of determination of temperatures of successive weight

TABLE 3

Statistical evaluation of the determination of the temperatures of successive weight losses and of the ratio of peak height to its width at half-height on the example of a random sample of the used M-20 Bp lubricating oil A-7 (the temperatures of the successive weight losses are given in Kelvin; the calculations were based on 21 determinations. The peak height and its width at half-height are in mm; the calculations were based on 14 determinations)

Thermal parameters	Arithmetic mean, $\bar{x}$	Standard deviation		Confidence interval $t_{0.95}$	Coefficient of variation (%)
		$s$	$s_{\bar{x}}$		
$T_0$	430.9	5.61	1.22	$430.9 \pm 2.6$	1.30
$T_1$	483.0	6.12	1.34	$483.0 \pm 2.8$	1.27
$T_5$	551.8	6.50	1.42	$551.8 \pm 3.0$	1.18
$T_{15}$	606.6	6.74	1.47	$606.6 \pm 3.1$	1.11
$T_{30}$	645.6	7.18	1.57	$645.6 \pm 3.3$	1.11
$T_{50}$	676.6	7.10	1.55	$676.6 \pm 3.2$	1.05
$T_{75}$	703.2	6.42	1.40	$703.2 \pm 2.9$	0.91
$T_{100}$	836.3	5.55	1.21	$836.3 \pm 2.5$	0.66
Peak a	9.48	0.76	0.20	$9.48 \pm 0.44$	8.05
Peak b	8.35	2.33	0.62	$8.35 \pm 1.35$	27.93
Peak c	29.74	2.49	0.67	$29.74 \pm 1.44$	8.37
Peak d	4.38	0.53	0.14	$4.38 \pm 0.30$	12.02

losses on the TG and DTG curves is presented in Fig. 3C, whereas a statistical evaluation of this method of determination of temperatures is demonstrated in Table 3. It follows that the results being obtained are accurate. They characterize the TG (DTG) approach as precise, and particular determinations as repeatable to a great extent. The values of the coefficients of variation qualify them into the class of less-accurate scientific measurements.

TABLE 4

Results of the thermogravimetric analysis of the used M-20 Bp lubricating oils

Sample No.	Temperatures of successive weight losses (K)							
	$T_0$	$T_1$	$T_5$	$T_{15}$	$T_{30}$	$T_{50}$	$T_{75}$	$T_{100}$
A-1	466	521	576	616	666	691	708	828
A-2	453	513	566	613	658	686	710	826
A-3	458	513	571	613	656	686	703	828
A-4	463	518	566	618	661	686	706	831
A-5	453	513	563	611	658	688	708	816
A-6	358	413	471	528	601	653	691	836
A-7	431	483	552	607	646	677	703	836
A-8	428	468	548	588	638	673	698	821
A-9	446	499	565	616	655	683	705	825
A-10	453	503	563	613	658	693	713	833
A-11	451	506	571	618	666	693	716	843
A-12	456	511	571	618	666	693	716	848
A-13	451	498	563	616	656	683	706	838
A-14	428	473	546	598	646	678	701	823
A-15	440	475	560	608	655	685	708	831
A-16	453	500	566	611	656	688	715	845
A-17	453	503	568	613	653	683	708	835
A-18	438	488	561	611	656	686	711	846
A-19	446	493	561	608	653	683	708	843
A-20	450	498	561	601	651	680	701	831
A-21	453	505	566	611	656	683	710	845
A-22	446	506	565	620	665	698	720	845
A-23	442	496	561	609	651	681	706	832
A-24	448	495	563	613	656	685	713	846
A-25	458	513	565	618	666	696	718	851
A-26	446	500	570	621	656	690	711	845
A-27	458	503	566	616	661	688	716	851
A-28	441	491	556	606	653	681	708	836
A-29	443	495	560	615	668	696	718	843
A-30	446	501	566	618	658	688	713	851
A-31	448	496	558	608	658	688	713	843
A-32	443	488	551	603	661	693	715	855
A-33	451	493	563	618	663	690	708	843
A-34	423	468	536	596	653	693	713	836
A-35	453	513	568	618	646	676	701	831

TABLE 5

Results of the thermogravimetric analysis of the used MS-20 p lubricating oils

Sample No.	Temperatures of successive weight losses (K)							
	$T_0$	$T_1$	$T_5$	$T_{15}$	$T_{30}$	$T_{50}$	$T_{75}$	$T_{100}$
B-1	453	505	563	603	646	675	696	836
B-2	458	501	563	608	651	681	706	836
B-3	438	498	568	618	653	683	711	843
B-4	358	408	453	501	571	646	693	838
B-5	398	443	508	583	628	663	693	826
B-6	470	520	568	605	643	670	696	816
B-7	470	518	578	616	655	678	700	840
B-8	428	481	551	601	643	676	701	826
B-9	426	481	553	601	643	668	696	836
B-10	473	521	573	616	648	678	706	831
B-11	468	513	576	618	651	681	708	833
B-12	400	441	493	563	628	673	703	833
B-13	423	478	548	616	653	688	716	841
B-14	373	418	468	523	591	658	698	826
B-15	443	495	555	596	631	660	688	821
B-16	443	486	556	603	636	670	698	833
B-17	458	513	573	623	646	676	703	836
B-18	458	498	561	601	636	671	691	828
B-19	468	521	586	626	661	688	713	838
B-20	431	481	556	608	646	678	703	831
B-21	428	476	543	598	641	671	698	841
B-22	358	403	456	506	568	633	676	816
B-23	393	443	518	593	638	668	698	833
B-24	493	533	583	621	656	683	711	833
B-25	465	508	563	601	641	670	695	833
B-26	453	498	563	598	638	668	698	833
B-27	460	503	568	615	651	676	700	845

The temperatures of the beginning and the end of decomposition and the temperatures of successive weight losses as determined based on the TG and DTG curves of thermal decomposition of used M-20 Bp and MS-20 p engine lubricants are listed in Tables 4 and 5. By comparing their values with the data contained in Tables 1 and 2 it has been found that the change in kinematic viscosity, the decreased flash point or increased content of water and foreign solids testify to the greater wear of the lubricating oil, and this is reflected in the course of their thermal decomposition under dynamic conditions.

The most characteristic changes in the shape of DTA, TG and DTG curves of the thermal decomposition of M-20 Bp and MS-20 p lubricating oils are presented in Figs. 4 and 5. It is of interest that with shifting the onset temperature for the decomposition to lower values the area of the narrow and sharp exothermic DTA peak undergoes great changes. This results from

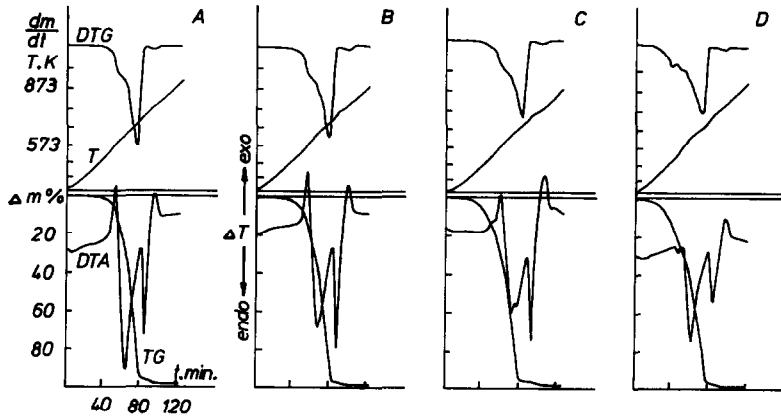


Fig. 4. DTA, TG and DTG curves of the thermal decomposition of the M-20 Bp lubricating oils worn to various degrees: (A) A-35, (B) A-28, (C) A-8 and (D) A-6.

overlapping the endothermic process of distillation of volatile impurities such as fuel and the exothermic process of thermal degradation of oil components. Both processes differentiate the DTG curves to reflect the increasing oil contamination in the form of shaping an additional minimum.

The presence of chemically unbound water is also reflected by the shape of the curves of the thermal decomposition of used lubricating oils. This is presented in Fig. 6 for an M-20 Bp oil sample. As the content of water increases, the effects on the DTA and DTG curves associated with its release are elongated. The narrow temperature range of this process is also reflected by the TG curve. It should be remembered, however, that the accurate determination of the water content is problematic, particularly when it amounts to declining by parts of a percent. For this reason, based on the TG curves, it is neither possible to read the content of foreign solids contained in

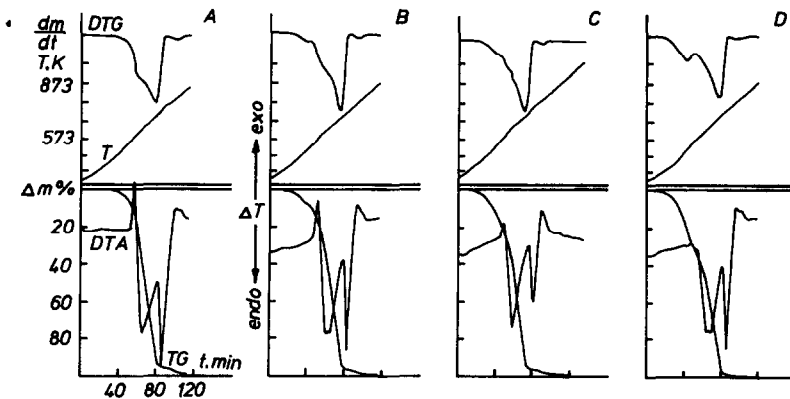


Fig. 5. DTA, TG and DTG curves of the thermal decomposition of the MS-20 p lubricating oils worn to various degrees: (A) B-6, (B) B-5, (C) B-12 and (D) B-4.

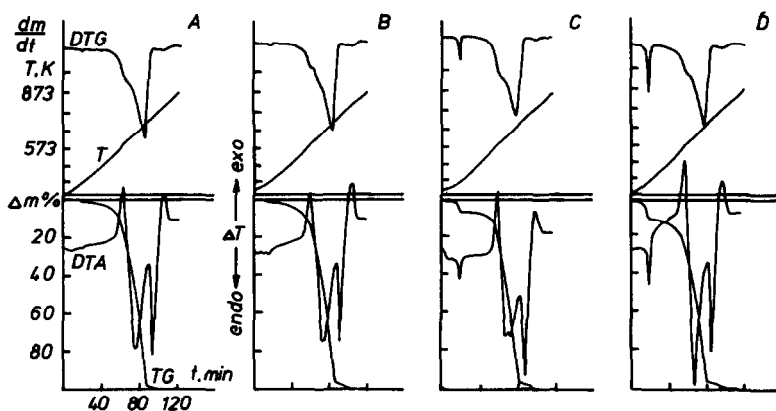


Fig. 6. DTA, TG and DTG curves of the thermal decomposition of the M-20 Bp lubricating oils containing chemically unbound water: (A) 0.3, (B) 0.6, (C) 4.0 and (D) 9.5%.

the lubricating oil nor the amount of oxide ash. This value can be determined as the difference between the weight of the crucible with residue and the weight of the empty crucible.

#### Correlation analysis

To express the strength of the relationship between the values of kinematic viscosity, flash point, foreign solids content, oxide ash and the values of the temperatures of successive weight losses, the values of linear correlation coefficients for these parameters were calculated by the method of least squares.

The results of calculations performed for the M-20 Bp and MS-20 p lubricating oils are listed in Table 6. The correlation coefficients assume positive values. This means that with decreasing values of the independent variable  $x$  the values of the dependent variable  $y$  trend downwards as well. In the case of kinematic viscosity and flash point for temperatures of successive weight losses together with  $T_{50}$ , the correlation coefficients are characterized by higher values than the critical ones at the probability of 0.01 [10]. Correlation coefficients assume critical values for the given number,  $n$ , of results being worked out, even at the full independence of both variables. In this connexion it can be stated that no correlations exist for  $T_{75}$  and  $T_{100}$ . The same can be said about the correlations between the foreign solids content and the temperatures of successive weight losses. As with the oxide ash, however, the correlation coefficients are characterized by higher values than the critical ones even for  $T_{75}$  in the case of M-20 Bp lubricating oil and  $T_{50}$  in the case of MS-20 p lubricating oil, these values not being satisfactory at that. For the higher weight losses, no correlation exists.

In Figs. 7–11 the linear relationship between  $T_0$  and the kinematic viscosity, and flash point for used M-20 Bp and MS-20 p lubricating oils is

TABLE 6

Correlation coefficients between the values of kinematic viscosity, flash point, foreign solids content, oxide ash and the values of the temperatures of successive weight losses for the used M-20 Bp and MS-20 p lubricating oils (the calculations for M-20 Bp lubricating oil were based on 35 determinations, whereas for MS-20 p lubricating oil were based on 27 determinations)

<i>x</i>	<i>y</i>							
	<i>T</i> <sub>0</sub>	<i>T</i> <sub>1</sub>	<i>T</i> <sub>5</sub>	<i>T</i> <sub>15</sub>	<i>T</i> <sub>30</sub>	<i>T</i> <sub>50</sub>	<i>T</i> <sub>75</sub>	<i>T</i> <sub>100</sub>
<i>(A) M-20 Bp lubricating oil</i>								
Kinematic viscosity at 373 K	0.94	0.88	0.98	0.95	0.85	0.66	0.51	0.12
Flash point	0.94	0.91	0.92	0.88	0.77	0.58	0.36	-0.06
Foreign solids content	0.14	0.16	0.04	0.09	0.16	0.15	0.18	0.19
Oxide ash	0.71	0.61	0.75	0.76	0.78	0.72	0.66	0.21
<i>(B) MS-20 p lubricating oil</i>								
Kinematic viscosity at 323 K	0.95	0.96	0.98	0.90	0.85	0.68	0.36	0.22
Kinematic viscosity at 373 K	0.94	0.95	0.98	0.93	0.88	0.72	0.40	0.25
Flash point	0.96	0.96	0.91	0.80	0.75	0.60	0.30	0.06
Foreign solids content	0.25	0.27	0.28	0.25	0.21	0.26	0.21	0.12
Oxide ash	0.76	0.75	0.75	0.68	0.60	0.48	0.22	0.18

presented. The plots reflect the existence of a strong relationship between both variables over the full range of their values. The standard deviations of regression lines are characterized by lower values for the M-20 Bp oils. For these oils none of the values being determined exceeds the limit of two standard deviations. In the case of MS-20 p oils, however, the scatter of

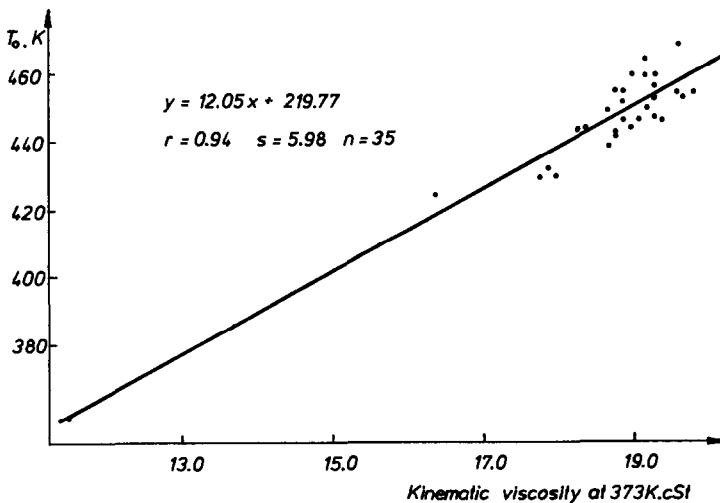


Fig. 7. Relationship between the temperature of the beginning of the thermal decomposition and the kinematic viscosity at 373K of the M-20 Bp lubricating oils.



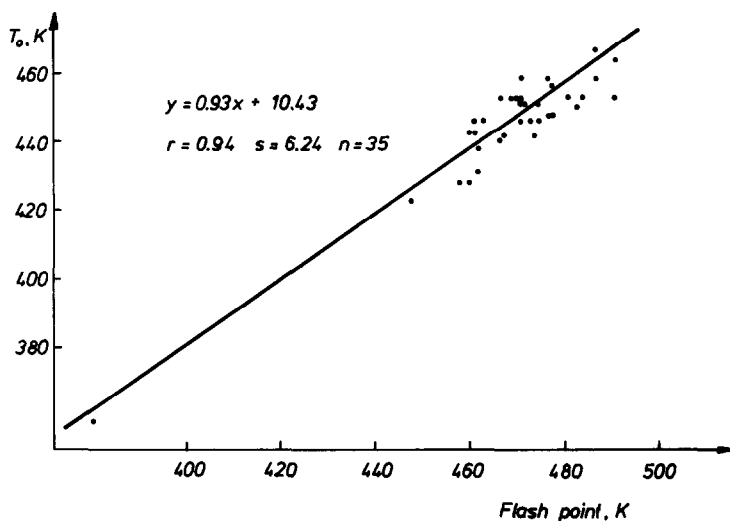


Fig. 8. Relationship between the temperature of the beginning of the thermal decomposition and the flash point of the M-20 Bp lubricating oils.

points around the regression line is greater, particularly in the case of the relationship between  $T_0$  and the kinematic viscosity. One of the values being determined lies on the limit of two standard deviations of the regression line.

From the practical point of view the correlations between the kinematic viscosity, flash point and  $T_0$ ,  $T_1$ ,  $T_5$  and  $T_{15}$  are of most significance. From the linear equation  $y = ax + b$  the temperature ranges were determined to

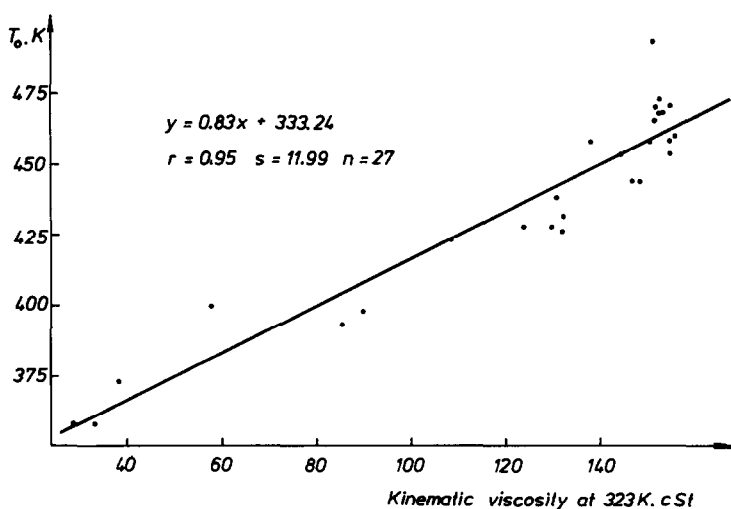


Fig. 9. Relationship between the temperature of the beginning of the thermal decomposition and the kinematic viscosity at 323 K of the MS-20 p lubricating oils.

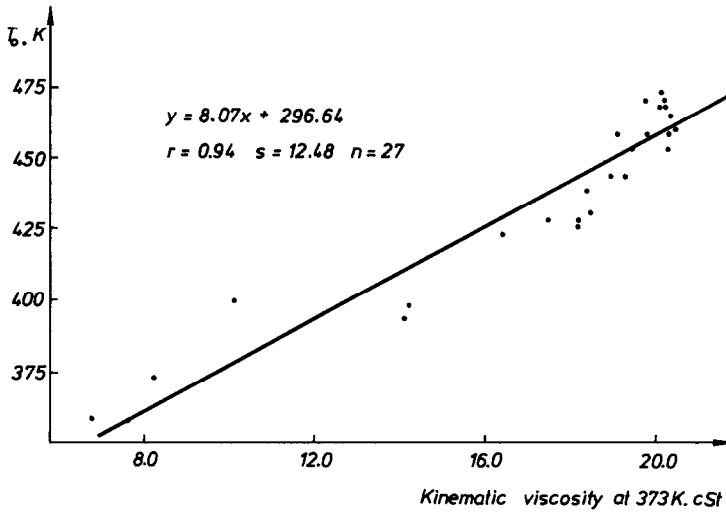


Fig. 10. Relationship between the temperature of the beginning of the thermal decomposition and the kinematic viscosity at 373 K of the MS-20 p lubricating oils.

which the beginning of thermal decomposition of the lubricating oil and the 1, 5 and 15% weight loss should correspond so that it could be estimated whether the oil under study met the standard and was suitable for further use. The temperature ranges of the thermal decomposition of M-20 Bp and MS-20 p lubricating oils obtained as a result of adequate calculations are listed in Table 7.

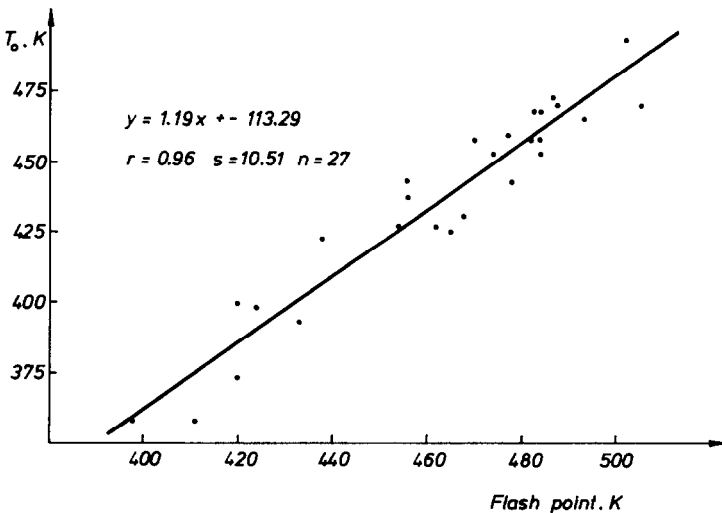


Fig. 11. Relationship between the temperature of the beginning of the thermal decomposition and the flash point of the MS-20 p lubricating oils.

TABLE 7

Temperature ranges of the beginning of thermal decomposition and of the 1, 5 and 15% weight loss for the M-20 Bp and MS-20 p lubricating oils which met the standard (the standard deviations of the regression lines are indicated in parentheses)

Physico-chemical parameters	Requirement according to the standard	Temperature ranges (K)			
		$T_0$	$T_1$	$T_5$	$T_{15}$
<i>(A) M-20 Bp lubricating oil</i>					
Viscosity at 373 K	19.5–21.5	455–479 (6.0)	506–531 (9.3)	569–594 (3.6)	618–639 (4.9)
Flash point	> 493	> 467 (6.2)	> 519 (8.1)	> 581 (6.9)	> 627 (7.7)
<i>(B) MS-20 p lubricating oil</i>					
Viscosity at 323 K	> 150	> 458 (12.0)	> 506 (10.8)	> 569 (8.7)	> 614 (14.6)
Viscosity at 373 K	> 20	> 458 (12.5)	> 506 (11.2)	> 570 (7.3)	> 615 (12.4)
Flash point	> 498	> 478 (10.5)	> 526 (10.7)	> 588 (15.7)	> 627 (20.7)

From the point of view of the relation character of both variables the estimation of the independent variable  $x$  on the basis of the values of the dependent variable  $y$  is causatively justified. Based on the equation  $x = ay$

TABLE 8

Equations of the regression lines of the beginning of thermal decomposition and of the 5% weight loss for the M-20 Bp and MS-20 p lubricating oils

Physico-chemical parameters	Equations of regression lines	Standard deviations of regression lines
<i>(A) M-20 Bp lubricating oil</i>		
Viscosity at 373 K	$7.40 \times 10^{-2} T_0 + -14.25$	0.47
	$7.95 \times 10^{-2} T_5 + -25.80$	0.29
Flash point	$0.95 T_0 + -45.25$	6.33
	$0.97 T_5 + -72.00$	7.22
Oxide ash	$4.28 \times 10^{-3} T_0 + -1.23$	$7.75 \times 10^{-2}$
	$4.70 \times 10^{-3} T_5 + -1.95$	$7.25 \times 10^{-2}$
<i>(B) MS-20 p lubricating oil</i>		
Viscosity at 323 K	$1.08 T_0 + -345.21$	13.64
	$1.05 T_5 + -450.13$	9.36
Viscosity at 373 K	$0.11 T_0 + -30.49$	1.45
	$0.11 T_5 + -41.93$	0.80
Flash point	$0.77 T_0 + -125.49$	8.48
	$0.70 T_5 + -80.85$	11.98
Oxide ash	$1.22 \times 10^{-3} T_0 + -0.25$	$3.86 \times 10^{-2}$
	$1.15 \times 10^{-3} T_5 + -0.35$	$3.87 \times 10^{-2}$

+  $b$  the value of the kinematic viscosity, flash point and oxide ash can be determined after determining  $T_0$ ,  $T_1$ ,  $T_5$  or  $T_{15}$  from the thermograms. In Table 8 the equations of the regression line for  $T_0$  and  $T_5$  for the M-20 Bp and MS-20 p lubricating oils are listed.

#### *Problem of the interpretation of the DTA curve*

Differences in the shape of the DTA curves of thermal decomposition of M-20 Bp and MS-20 p lubricating oils used to a different degree are essential, particularly over the range 573–823 K. This is illustrated in Figs. 4 and 5. Significant changes of the area of the exothermic DTA peak ( $T_{\max} \approx 573$  K) and of two subsequent endothermic effects occur, which appear as narrow and high effects. A similar situation is observed in the case of the exothermic DTA peak ( $T_{\max} \approx 773$  K) related to the final stage of the oil decomposition.

To examine the possibility of utilising these effects in the assessment of the degree of use of lubricating oil, the DTA thermal decomposition curves of the A-7 sample were repeatedly recorded at unaltered parameters of the instrument. The changes observed in their shape are illustrated in Fig. 12 and the method of determination of the effects on the DTA curve is presented in Fig. 3D. The data contained in Table 3 indicate that the ratio of peak height to its width at half-height varies over a broad range. The values of the standard deviations and of the variation coefficients qualify the DTA measurements into the class of technical or approximate measurements. This excludes the application of thermal parameters based on the measurement of any quantity related directly or indirectly to the area of the endothermic or exothermic DTA peak in the assessment of the usefulness of lubricating oils for further service.

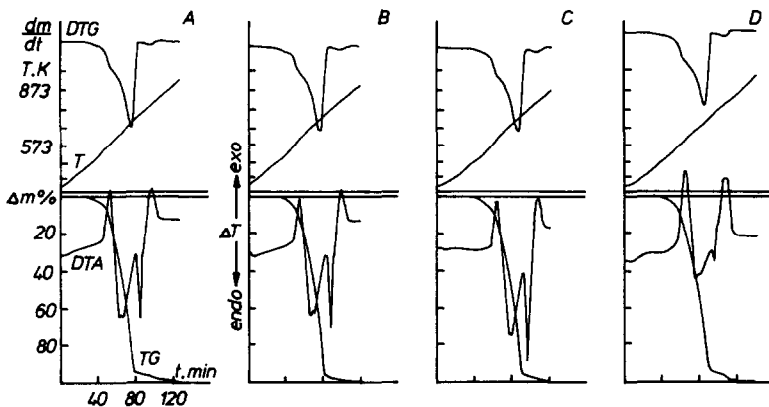


Fig. 12. DTA, TG and DTG curves of the thermal decomposition of the A-7 sample recorded at unaltered instrument parameters.

## CONCLUSIONS

Based on the investigations performed, it was found that the thermoanalytical methods can be utilised for the assessment of the service performance of used M-20 Bp and MS-20 p lubricating oils. It is most advisable to carry out the performance assessment on the basis of simultaneously recorded DTA, TG and DTG curves of their thermal decomposition. The TG and DTG curves provide the most useful parameters.

The results of the thermal analysis cannot be assumed indiscriminately, however. The method of interpretation of the thermograms makes only an experimental analysis of tribological ageing of the oil being used possible and also the forecasting of its effective running time. For further estimation it would be advisable to introduce the thermal parameters proposed in industrial control laboratories. It is obvious that during the course of time, experience will be enriched and the measuring methods improved. This would make the introduction of thermal parameters into the group of conventionally employed parameters possible.

Despite a number of stipulations the thermoanalytical methods can be of great service. Omitting the troublesome procedure of determining the classical parameters they eliminate the necessity of using chemical reagents and laboratory equipment, which decreases the cost of analysis considerably. Automatic recording of the thermal decomposition curves also decreases the labour consumption for the determination. Despite the long recording time of a thermogram (at a heating rate of  $5 \text{ K min}^{-1}$  up to 973 K it amounts to 130 min) as compared to classical analytical methods, there is a possible significant reduction of time needed for performing a defined determination. Thermoanalytical methods are particularly advisable when a singular control analysis is needed every now and then. Moreover, most significantly, a record remains after each analysis, which can be made use of at any desired time.

Recording the DTA, TG and DTG curves of thermal decomposition of lubricating oils affords no greater difficulties. It should be remembered, however, that their shape depends to a great extent on the homogeneity of the sample and on the variable parameters of the instrument. In this connexion, when not preserving the constant measurement conditions, an analysis repeated many times may sometimes show some changes in the shape of the DTA, TG and DTG curves of its decomposition.

Incidentally, to the problem discussed, it should be mentioned that information obtained from the decomposition curves may find application in the work of blending lubricating oils and in the assessment of the influence of lubricant additives on oil performance.

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