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THERMOGRAVIMETRIC ASSESSMENT OF SERVICE PERFORMANCE OF MARINOL CB SAE-30 LUBE OILS

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ABSTRACT

On the example of analysis of 106 samples of Marinol CB SAE-30 lube oil the usefulness of thermoanalytical techniques has been estimated, considering the possibility of re-using the oil for further service. The existence of a strong linear relationship has been found between the values of kinematic viscosity at 323 and 373 K, the flash point and the temperature values for onset of thermal degradation and for successive mass losses as registered under a static atmosphere of air. The possibility of practical application of regression line equations for the assessment of service performance of lubricating oils has been indicated.

INTRODUCTION

Differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG) and derivative TG (DTG) are more and more frequently being used for the examination of fuel and lubricating oils [1–7].

DTA has been acknowledged to be a rapid and precise method for defining the thermal stability of lubricating oils, both petroleum based and synthetic [8]. It enables the effectiveness of lubricant oil additives to be defined, and the ageing of oils to be monitored during use.

The temperature ranges, shape and characteristic heats of transitions, as determined on the basis of DSC effects, can be employed for the quality assessment of trade oils. It has been pointed out that with progressive use of the lubricating oil, the onset and range of crystallization of the used oil are shifted towards lower temperatures [9]. Based on the heat of fusion value of a fuel oil, the amount of gas oil contained in it can be estimated. The heat of fusion [10] and the latent heat of phase transition [11] for paraffin wax have been employed for defining its content in lube and spindle oils. The information obtained on the basis of DSC effects also allows us to determine the tendency of gear oils and hydraulic fluids to age and, moreover, it enables the maximum temperature for their service to be determined [12].

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The usefulness of TG as an industrial method for defining the chemical composition of lubricating oils consists in the possibility of carrying out microdistillation and determining the asphalt content of oils [13]. The usefulness of TG and DTG as fast analytical techniques, which allow the chemical composition and service performance of fuel and lube oils to be assessed in a technological context, has also been indicated [14–17]. By varying the heating rate of an oil sample and the type and amount of gas passing through the measuring cell, the conditions of laboratory work can be adapted for operational needs giving it great practical significance.

From literature data it follows that the shape of thermoanalytical curves is conditioned by the chemical composition of the oil being degraded. By analysing the relationship between the change in chemical composition of lube oils due to use and the shape of their thermal degradation curves, it was considered pertinent to examine the possibility of applying the DTA, TG and DTG techniques for assessing the usefulness of used Marinol CB SAE-30 lube oils for further service.

EXPERIMENTAL

Materials

In this study Marinol CB SAE-30 lube oils were employed, both new and used, which were taken directly from the oil system of marine engines after having run a few to a few thousand hours.

Test samples were taken in accordance with Polish Standard PN-66/C-04000 [18]. 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.

Test procedure

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 [19]. For the determination of kinematic viscosity of used oils at 323 and 373 $\pm$ 0.02 K, the Pinkevitch viscometer was used in accordance with Polish Standard PN-73/C-04011 [20]. The flash point of lube oils was measured by the Pensky–Martens method according to Polish Standard PN-75/C-04009 [21]. The procedure for carrying out the determinations has been exactly described in a previous paper [22].

The content of foreign solids in Marinol CB SAE-30 lube oils was determined by the centrifuging method. A sample of 1 g oil was placed in a centrifuge tube heated to constant weight and thereafter 9 ml of a diluent solution was added. After thorough mixing, the contents of the tube were allowed to stand for 24 h to completely dissolve all soluble components of

the oil. Next, the tube and its contents were centrifuged to entirely deposit the foreign solids. The clear supernatant solution was poured off and the centrifuge tube was dried in an oven at 378 K 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 mass of centrifuge tube and foreign solids (g), m_2 is the mass of the centrifuge tube (g) and m_3 is the weighed amount of oil (g).

The content of oxide ash was determined by weighing a sample of 2 g Marinol CB SAE-30 lube oil into a porcelain crucible which had been pickled with hydrochloric acid and ignited to constant weight. After placing the crucible on a sand-bath, the oil was evaporated without allowing it to creep out over the edge of the crucible or its vapours to ignite. The oil sample was heated until a dry residue was obtained, which is ignited over a Meker-type burner until complete ashing of the residue. The crucible was weighed after cooling. These operations were repeated until the difference between two successive weighings was not greater than 0.0004 g. The amount of oxide ash was calculated according to the formula

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

where m_1 is the mass of crucible and ash (g), m_2 is the mass of crucible (g) and m_3 is the weighed amount of oil (g).

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

Determination of thermal parameters

The DTA, TG and DTG curves of thermal degradation of Marinol CB SAE-30 lube oils were recorded using a OD-103 derivatograph (MOM, Budapest). All measurements were made under identical conditions. A weighed amount (200 mg) of oil in a platinum crucible (9.5 mm diameter) was heated under the furnace atmosphere at a heating rate of 5 K min^{-1} up to a final temperature of 973 K. α-Al_2O_3 was used as reference material. Each thermogram was registered at least three times. The temperatures for the onset (T_0) and end (T_{100}) of thermal degradation were read from the TG and DTG curves, whereas the temperatures for 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 investigation

The most important parameters, which define the usefulness of lube oils for further service, are the content of water, kinematic viscosity at 323 and

TABLE 1

Values of the water content, the kinematic viscosity at 323 and 373 K, flash point, contents of foreign solids and oxide ash for the used Marinol CB SAE-30 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			
C-1	3,00	Trace	48.0	9.5	452	0.27	0.86
C-2	15,00	Trace	55.7	10.3	455	0.63	0.72
C-3	15,00	Trace	65.0	11.8	478	0.50	0.93
C-4	40,25	Trace	64.9	11.8	484	0.20	0.98
C-5	43,25	Trace	51.2	9.7	453	0.54	0.86
C-6	45,55	ND	56.9	10.6	464	0.42	0.84
C-7	50,00	0.05	64.4	11.6	476	0.41	0.84
C-8	50,00	Trace	68.8	11.6	491	0.51	0.84
C-9	52,00	Trace	65.9	11.8	478	0.32	0.80
C-10	52,43	Trace	66.7	11.9	488	0.40	1.10
C-11	60,25	Trace	63.9	11.6	482	0.16	1.01
C-12	73,30	Trace	62.5	11.3	471	0.52	0.95
C-13	93,32	Trace	69.3	12.1	487	0.33	0.93
C-14	94,26	Trace	63.6	11.7	480	0.27	0.91
C-15	98,00	Trace	64.7	11.5	478	0.26	0.93
C-16	98,50	Trace	62.4	11.4	468	0.36	1.01
C-17	99,00	0.6	28.5	6.6	453	0.42	0.64
C-18	101,25	Trace	41.5	8.8	441	0.11	0.89
C-19	104,00	ND	61.7	11.0	484	0.39	0.77
C-20	107,15	Trace	53.2	9.9	453	0.28	0.72
C-21	108,00	Trace	62.9	11.1	467	0.19	0.83
C-22	108,00	Trace	65.6	11.7	464	0.31	0.96
C-23	109,00	Trace	67.8	12.1	486	0.22	1.00
C-24	112,00	Trace	63.8	11.4	458	0.46	1.07
C-25	112,25	Trace	63.4	11.5	485	0.08	0.97
C-26	113,00	Trace	66.1	11.9	473	0.59	1.03
C-27	116,11	Trace	68.2	12.2	494	4.82	1.02
C-28	118,00	Trace	59.0	10.8	458	0.25	0.61
C-29	120,00	Trace	60.2	11.0	470	0.13	0.83
C-30	126,20	Trace	53.3	9.9	452	0.27	0.73
C-31	128,00	Trace	66.1	11.9	471	0.22	0.86
C-32	129,23	Trace	67.1	11.5	465	0.46	0.89
C-33	130,00	0.1	61.1	10.9	477	0.53	0.84
C-34	130,00	Trace	68.3	12.1	478	0.21	0.84
C-35	139,46	Trace	68.8	12.1	475	0.32	0.87
C-36	157,30	Trace	51.4	9.8	461	0.71	0.85
C-37	159,55	0.06	45.6	9.0	443	0.34	0.77
C-38	160,00	0.2	52.9	10.3	461	0.42	0.75
C-39	160,00	Trace	55.2	10.3	455	0.27	0.81
C-40	172,25	0.6	60.7	11.0	475	0.55	0.76
C-41	172,45	Trace	58.5	11.0	468	0.48	0.84
C-42	189,00	Trace	62.9	11.3	462	0.67	0.88

TABLE 1 (continued)

Sample No.	Running time (h, min)	Water content (%)	Kinematic viscosity (cSt) at		Flash point (K)	Foreign solids content (%)	Oxide ash (%)
			323 K	373 K			
C-43	194,00	Trace	62.7	11.2	469	0.74	0.90
C-44	200,10	Trace	65.4	11.8	482	0.36	0.85
C-45	204,36	Trace	56.8	10.5	451	0.54	0.86
C-46	208,45	Trace	56.9	10.6	453	0.92	0.88
C-47	210,46	ND	64.5	11.3	481	1.16	0.94
C-48	211,41	0.2	36.8	8.0	418	0.05	0.89
C-49	217,40	0.2	33.9	7.4	415	0.12	0.90
C-50	218,27	Trace	70.1	12.2	491	0.14	0.90
C-51	253,32	Trace	57.1	10.6	467	0.21	1.07
C-52	254,10	Trace	75.4	13.0	497	0.30	0.94
C-53	258,00	Trace	60.3	11.1	461	1.05	1.04
C-54	264,57	Trace	71.3	12.4	487	2.49	1.11
C-55	267,00	Trace	53.2	10.2	463	0.33	0.84
C-56	278,20	Trace	40.4	8.6	445	0.96	0.86
C-57	280,00	0.1	79.2	13.1	471	1.89	0.89
C-58	281,48	Trace	34.1	7.6	413	0.80	0.88
C-59	286,03	0.06	29.9	7.0	415	0.72	0.84
C-60	297,40	Trace	55.8	10.2	452	0.53	0.87
C-61	297,45	Trace	69.5	12.0	487	0.39	0.92
C-62	300,00	Trace	50.7	9.6	444	0.89	0.93
C-63	300,00	Trace	50.8	9.7	451	0.73	0.90
C-64	301,29	Trace	73.1	12.4	479	0.36	1.12
C-65	303,00	Trace	52.2	9.9	442	0.21	0.84
C-66	304,22	Trace	58.5	10.6	420	0.37	0.88
C-67	306,25	Trace	66.0	11.8	475	0.97	1.03
C-68	314,22	Trace	58.0	11.9	461	0.61	0.77
C-69	314,50	Trace	71.3	12.7	463	1.80	1.03
C-70	316,00	Trace	52.1	9.8	441	0.82	0.85
C-71	316,05	Trace	57.0	10.4	453	0.77	0.78
C-72	324,03	0.1	68.8	11.9	487	0.67	0.99
C-73	325,45	Trace	78.3	13.0	491	1.41	1.05
C-74	332,50	Trace	66.6	11.9	467	0.76	1.04
C-75	347,27	0.2	54.6	10.1	453	0.61	0.77
C-76	348,00	0.2	44.1	9.1	423	0.57	0.74
C-77	350,00	Trace	69.3	12.1	488	0.42	1.21
C-78	350,17	Trace	56.1	10.4	455	0.64	0.82
C-79	353,00	Trace	65.1	11.7	470	1.02	1.01
C-80	361,09	Trace	59.7	11.2	468	0.39	1.03
C-81	376,00	0.2	43.3	8.7	418	1.18	0.76
C-82	390,55	Trace	47.3	9.4	442	0.98	0.88
C-83	420,00	Trace	72.4	12.7	487	0.95	1.08
C-84	424,45	Trace	41.8	8.6	445	0.27	0.78
C-85	435,51	Trace	51.7	10.0	447	0.48	0.78
C-86	438,05	Trace	51.5	9.9	447	0.21	0.78

TABLE 1 (continued)

Sample No.	Running time (h, min)	Water content (%)	Kinematic viscosity (cSt) at		Flash point (K)	Foreign solids content (%)	Oxide ash (%)
			323 K	373 K			
C-87	453,00	0.06	53.5	9.9	453	0.17	0.70
C-88	576,15	Trace	69.3	12.0	486	0.61	0.87
C-89	626,05	Trace	61.5	11.2	463	0.91	0.96
C-90	702,40	Trace	87.9	14.8	465	3.69	0.95
C-91	1497,45	Trace	87.1	15.0	468	2.89	1.23
C-92	1539,40	Trace	68.0	12.2	496	0.22	0.96
C-93	1543,45	Trace	68.6	12.4	493	0.17	0.98
C-94	1759,10	Trace	80.1	14.3	475	2.26	1.18
C-95	2571,35	0.15	70.7	12.1	492	0.40	0.80
C-96	2572,45	Trace	70.9	12.1	498	0.35	0.85
C-97	3153,55	Trace	68.8	12.1	488	0.08	1.04
C-98	3158,40	Trace	66.8	11.8	481	0.21	1.03
C-99	3335,40	Trace	68.9	12.1	485	0.19	1.05
C-100	3341,25	Trace	71.2	12.4	497	0.21	1.07
C-101	3864,00	Trace	70.3	12.1	480	0.13	1.24
C-102	4094,05	0.1	69.6	12.0	468	0.22	1.22
C-103	4818,40	0.06	68.9	11.8	493	0.08	0.92
C-104	4921,15	0.1	63.6	11.5	477	0.65	1.03
C-105	5142,45	Trace	69.0	11.9	485	0.57	1.03
C-106	5537,30	Trace	67.1	11.9	488	0.18	0.96

ND = Not detected.

373 K, flash point and the content of foreign solids and oxide ash. Within the framework of this work the values of these parameters for samples of used Marinol CB SAE-30 lube oil were determined. The results obtained are listed in Table 1.

The presence of water in lubricating oil is always undesirable. It effects acceleration of an oil's ageing process, reduces the lubricating ability of the oil, and furthers corrosion and formation of oil sludge. Viscosity is one of the many properties of lubricating oil, which is decisive for its application. It considerably affects the volatility, pumpability and proper progress of cleaning of an oil. The viscosity of lubricating oils displays a strong dependence on temperature and pressure. Next, learning the flash point is important in view of safety of transportation, storage and service of an oil. The foreign solids present in a lubricating oil, of dimensions in excess of the oil layer thickness forming during lubrication, give rise to an increase in friction between the mating parts and to their scratching and premature wear. On the other hand, the content of oxide ash is a measure of how well the lube oil was refined, and of its purity. It is a specific indicator of the content of lubricant additives in the oil.

From the analysis of data contained in Table 1 it follows that the poorer quality of a Marinol CB SAE-30 lube oil is reflected by an excessive variation of kinematic viscosity. The changes in viscosity are to be considered in connection with changes in the remaining parameters of physicochemical assessment of a lubricating oil. The oxidation products, which arise as a result of an oil's ageing, effect an increase in its kinematic viscosity. On the other hand, the penetration of fuel into a lube oil lowers its viscosity and flash point. In this connection, contamination of fuel by a high content of foreign solids such as black, coke and ash (which appear in crank-case lubricants as a result of incomplete fuel combustion, coking and combustion of oil on engine parts warmed up to high temperatures) causes the kinematic viscosity of a lube oil, which was used over a longer period of time, to differ only slightly from the standard. Nevertheless, the oil will be unfit for further service. This is one of the reasons that no relationship has been found between the service time of a lubricating oil in the oil system of a marine engine and the above-mentioned parameters of physicochemical quality assessment of lubricating oils.

Thermal investigation

Marinol CB SAE-30 lube oil is a product relatively resistant to temperatures. This is a result of its chemical composition, which alters with the service time of the oil. Contamination of a lubricating oil, by its oxidation products and products of incomplete fuel combustion, causes the shapes of DTA, TG and DTG thermal degradation curves of sample under test to alter. This is due to the fact that the degradation curves are plots of resultant physicochemical and thermochemical phenomena which occur in the product during its heating.

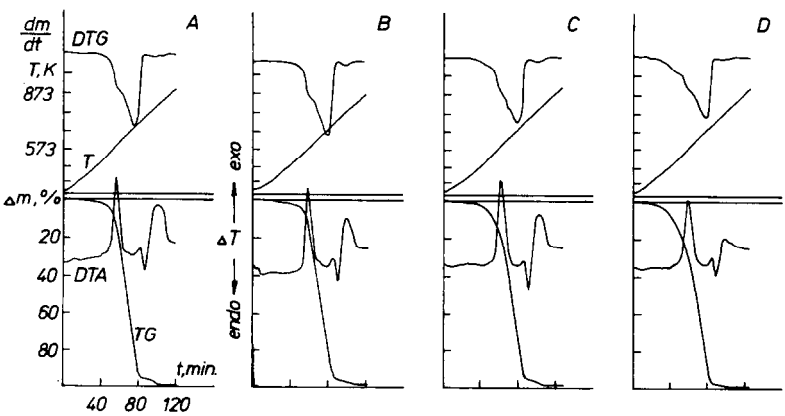

Fig. 1. DTA, TG and DTG curves of the thermal degradation of Marinol CB SAE-30 lube oils worn to various degrees: (A) C-73, (B) C-77, (C) C-36 and (D) C-17. The classical and thermal parameters for these oils are listed in Tables 1 and 2.

In Fig. 1 the degradation curves of lube oil samples are presented, which are arranged according to decreasing values of kinematic viscosity and flash point. The lowering of these values is well reflected by the shape of the DTA, TG and DTG thermal degradation curves of successive oil samples. This is particularly characterized by the TG and DTG curves, from which it follows that with lowering a lube oil's quality, the onset of deviation of the TG curve from the baseline is shifted towards lower temperatures and, in addition, the curve displays a less steep course. The same relationship is observed for temperatures related to successive mass losses. The observations made are confirmed by the shape of DTG curves. In this connection, in a further study, the temperature values for the onset, end and successive mass losses of Marinol CB SAE-30 lube oils were used, which were determined on the basis of the TG (DTG) curves. They are listed in Table 2.

Correlation analysis

In order to express the strength of the relationship between temperature values for the onset, end, successive mass losses and kinematic viscosity, flash point, the content of foreign solids and oxide ash, values of linear correlation coefficients for these parameters were calculated by the least-squares method.

The results of calculations made for Marinol CB SAE-30 lube oil are listed in Table 3. With the exception of the correlation coefficient for T_{100} and the flash point, in all remaining cases the correlation coefficients assume positive values. In the case of the kinematic viscosity the correlation coefficients are characterized over the entire range of temperatures by values higher than the critical value at a probability of 0.01 [23]. On the other hand, for flash point and oxide ash the correlation coefficients do not assume values higher than the critical one only for T_{75} and T_{100}. In the case of foreign solids, however, it is to be acknowledged as an incidental fact that the linear correlation coefficients assume higher values than the critical one for T_{30}, T_{50}, T_{75} and T_{100}. No correlations exist for the temperature of thermal degradation onset and for T_1, T_5 and T_{15}.

The linear relationship between T_0 and kinematic viscosity and flash point for used lube oils is graphically presented in Figs. 2–4. The diagrams reflect the existence of a strong linear relationship between both variables throughout the range of their values. The standard deviations of regression lines are characterized by the lowest kinematic viscosity values, which is reflected by the scatter of points about the regression line. For some T_0 values a fairly large scatter of points has been observed, however. For instance, for $T_0 = 453$ K, 14 kinematic viscosity results were stated at a temperature of 323 K within the range of values from 59.0 to 71.3 cSt, whereas for $T_0 = 398$ K, only 6 viscosity results, but over a considerably wider range of values, from 40.4 to 56.9 cSt.

TABLE 2

Results of the thermogravimetric analysis of the used Marinol CB SAE-30 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}
C-1	408	448	508	563	618	658	683	798
C-2	423	473	533	593	628	658	688	828
C-3	453	498	558	603	633	663	688	818
C-4	443	498	553	588	628	658	683	808
C-5	393	448	503	558	593	628	663	813
C-6	398	448	513	558	603	633	663	813
C-7	453	498	568	613	648	683	728	858
C-8	458	498	553	583	623	648	678	813
C-9	438	483	543	588	618	648	678	808
C-10	453	503	553	593	623	653	683	823
C-11	453	488	553	583	623	658	693	823
C-12	448	488	543	583	623	653	678	818
C-13	453	493	553	593	633	653	683	813
C-14	458	498	543	583	618	643	673	818
C-15	418	478	538	578	608	638	673	813
C-16	436	481	541	583	621	648	676	823
C-17	363	413	476	536	588	638	673	818
C-18	373	423	488	553	603	648	683	803
C-19	438	483	543	578	613	648	673	823
C-20	421	461	526	576	613	648	678	828
C-21	448	478	538	573	608	643	668	818
C-22	448	498	563	598	643	673	698	833
C-23	453	493	548	593	623	653	678	818
C-24	423	463	533	578	623	658	678	803
C-25	448	488	543	583	623	653	678	803
C-26	438	483	541	586	628	658	683	823
C-27	453	493	548	583	623	653	683	818
C-28	453	493	553	593	633	663	703	828
C-29	438	478	533	573	608	643	673	818
C-30	402	456	524	576	612	651	682	837
C-31	451	501	561	606	636	668	696	838
C-32	453	498	548	583	623	653	683	823
C-33	433	473	533	573	613	643	673	818
C-34	450	498	560	605	636	666	691	828
C-35	453	498	553	588	628	658	683	828
C-36	418	473	528	578	613	653	683	833
C-37	408	453	513	573	618	653	683	828
C-38	423	468	538	583	623	658	688	828
C-39	433	483	548	593	628	663	688	818
C-40	433	486	541	576	613	648	683	818
C-41	428	468	528	573	613	643	673	818
C-42	438	483	553	593	633	663	693	833
C-43	438	488	548	588	623	653	683	818
C-44	453	503	563	603	633	658	688	813
C-45	398	458	518	573	608	633	663	808

TABLE 2 (continued)

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}
C-46	393	448	518	563	603	633	663	828
C-47	413	473	533	578	613	643	673	813
C-48	353	398	473	548	593	633	668	818
C-49	343	388	473	543	593	633	673	818
C-50	478	518	568	603	643	673	693	843
C-51	413	473	528	573	613	653	683	813
C-52	473	518	568	603	633	663	693	833
C-53	438	473	533	573	618	648	678	823
C-54	453	498	553	583	618	648	678	843
C-55	433	478	528	583	623	653	678	813
C-56	398	443	498	563	603	643	673	808
C-57	448	478	543	588	623	658	688	868
C-58	368	408	478	568	603	653	688	828
C-59	363	408	478	553	613	658	688	843
C-60	428	473	538	588	623	658	688	838
C-61	451	498	556	588	623	658	686	831
C-62	403	451	521	576	618	648	678	828
C-63	386	443	516	573	603	648	678	836
C-64	461	501	561	591	628	663	688	831
C-65	393	448	521	576	618	651	678	831
C-66	428	453	518	568	603	633	668	813
C-67	438	483	543	578	618	653	683	808
C-68	433	463	533	583	623	653	683	833
C-69	443	488	558	593	633	663	693	863
C-70	393	443	513	576	613	646	673	833
C-71	418	463	533	578	618	648	678	823
C-72	458	508	558	593	628	658	683	833
C-73	463	508	563	596	633	663	693	851
C-74	438	488	546	586	621	656	683	826
C-75	428	461	526	576	613	646	676	818
C-76	373	423	498	563	603	643	678	828
C-77	453	503	553	588	623	653	683	823
C-78	413	466	531	578	616	646	676	823
C-79	423	458	533	583	613	648	678	823
C-80	433	473	533	578	613	653	683	823
C-81	398	438	501	563	603	638	668	813
C-82	408	458	518	583	618	653	683	833
C-83	456	503	556	588	623	656	683	813
C-84	398	438	493	553	593	633	668	818
C-85	403	448	521	578	618	653	680	828
C-86	421	463	526	583	623	656	683	836
C-87	398	438	508	563	593	623	658	818
C-88	453	493	548	583	623	648	673	813
C-89	423	473	543	578	613	653	683	838
C-90	478	523	583	623	663	693	708	868
C-91	476	511	563	608	646	676	703	886
C-92	458	503	568	608	638	663	693	828

TABLE 2 (continued)

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}
C-93	458	503	558	603	628	663	688	813
C-94	481	516	573	616	651	678	703	866
C-95	471	511	561	593	628	656	681	813
C-96	468	511	556	583	621	648	676	821
C-97	446	496	551	581	628	658	683	813
C-98	451	486	543	581	623	656	681	816
C-99	433	493	543	578	618	648	668	778
C-100	458	498	548	583	623	653	678	808
C-101	473	508	558	593	628	663	688	808
C-102	468	513	563	593	628	658	688	818
C-103	433	483	538	573	613	638	668	798
C-104	428	478	518	578	603	638	668	833
C-105	443	498	548	578	613	643	673	838
C-106	448	498	558	593	638	668	693	823

The relationship between some parameters of physicochemical assessment of oils and the results of thermoanalytical tests has been stated by other authors, too. Noel [24,25] has pointed out the existence of a linear relationship between the onset of an exothermic DSC effect associated with the crystallization of waxes contained in fuel and lube oils and the cloud point as determined by the ASTM rotary bomb method. A similar relationship has been determined between the temperature of the extremum DSC effect and the pour point. Casellato et al. [26] have come to the same conclusions when analysing the crystallization process of waxes contained in the middle distillates from crude oil and in diesel fuels. When studying the degradation of lube oils under oxidizing conditions, Noel [24] pointed out that in the presence of antioxidants, the onset temperature of the exothermic DSC effect shifts towards higher temperatures and its temperature range reduces.

TABLE 3

Correlation coefficients between the values of the temperature for the onset, end, successive mass losses and the values of the kinematic viscosity, flash point, the content of foreign solids and oxide ash for the used Marinol CB SAE-30 lube oils ($n = 106$)

Physicochemical parameter	T_0	T_1	T_5	T_{15}	T_{30}	T_{50}	T_{75}	T_{100}
Kinematic viscosity at 323 K	0.90	0.91	0.91	0.79	0.71	0.52	0.38	0.26
Kinematic viscosity at 373 K	0.90	0.90	0.91	0.81	0.74	0.55	0.41	0.29
Flash point	0.81	0.86	0.80	0.60	0.52	0.28	0.21	−0.07
Foreign solids content	0.18	0.15	0.18	0.23	0.26	0.26	0.24	0.51
Oxide ash	0.46	0.48	0.44	0.36	0.35	0.32	0.21	0.09

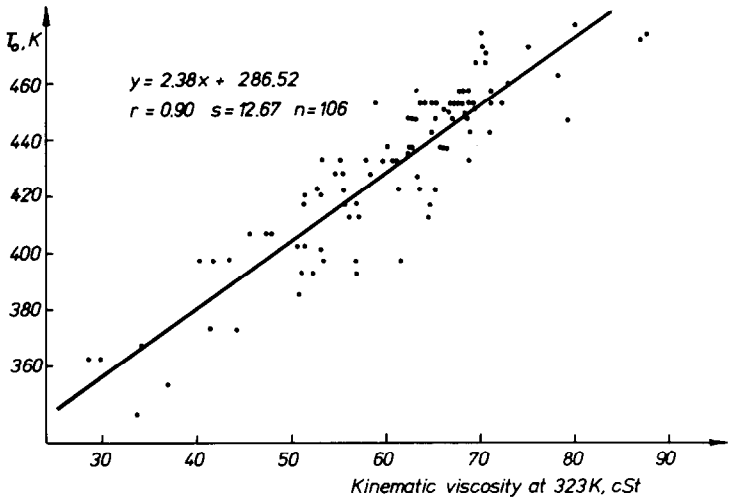

Fig. 2. Relationship between the onset temperature of the thermal degradation and the kinematic viscosity at 323 K for the used Marinol CB SAE-30 lube oils.

This shift increases linearly with increasing concentration of antioxidant over a range of its concentrations, displaying a relatively good agreement with the data as obtained by the ASTM rotary bomb method.

From the practical point of view the correlation between kinematic viscosity, flash point and T_0, T_1, T_5, T_{15} are of utmost importance. Starting from the linear equation $y = ax + b$ the temperature ranges have been determined which the thermal degradation onset of Marinol CB SAE-30 lube

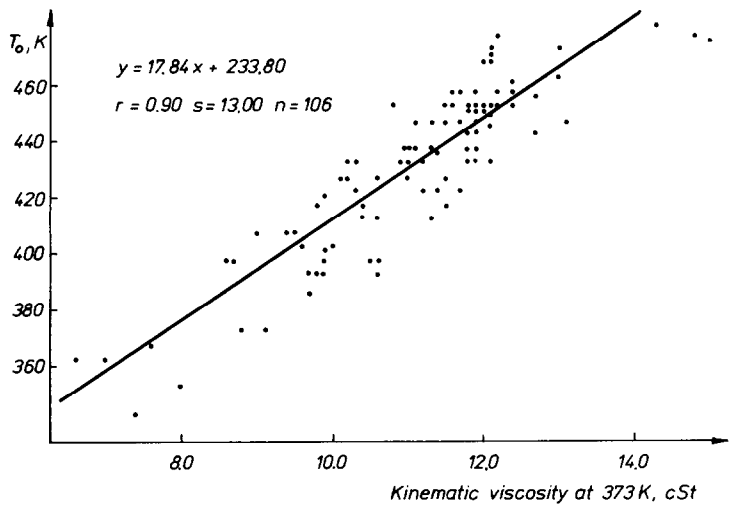

Fig. 3. Relationship between the onset temperature of the thermal degradation and the kinematic viscosity at 373 K for the used Marinol CB SAE-30 lube oils.

TABLE 4

Temperature ranges of the thermal degradation onset and of the 1, 5 and 15% mass losses for the Marinol CB SAE-30 lube oil meeting 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	66–70	444–453(12.7)	488–497(11.7)	547–554(9.6)	587–591(9.3)
Viscosity at 373 K	$\leqslant 12.5$	$\leqslant 457(13.0)$	$\leqslant 501(12.3)$	$\leqslant 557(9.9)$	$\leqslant 594(8.9)$
Flash point	$\geqslant 463$	$\geqslant 427(17.0)$	$\geqslant 472(14.4)$	$\geqslant 533(14.0)$	$\geqslant 580(12.0)$

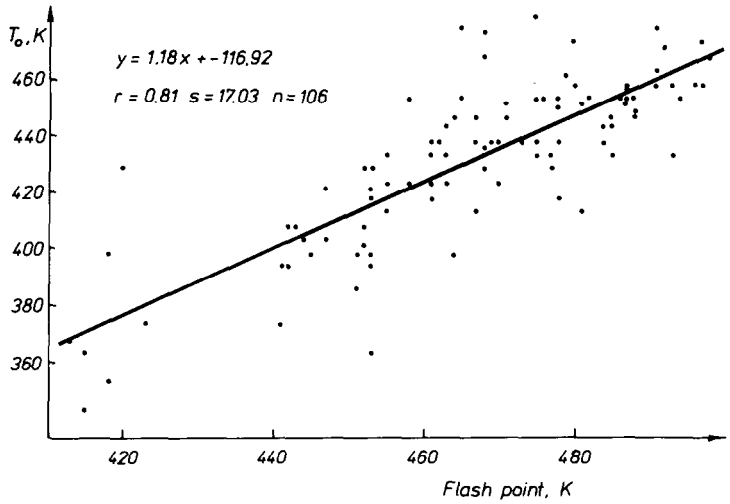

Fig. 4. Relationship between the onset temperature of the thermal degradation and the flash point for the used Marinol CB SAE-30 lube oils.

oil and the 1, 5 and 15% mass loss should correspond to, so that it can be estimated whether the oil under test meets the requirements of Polish Standard PN-75/C-96089 [27] and is suitable for further service. The thermal degradation temperature ranges obtained as a result of appropriate calculations are listed in Table 4.

On account of the nature of the relationship between both variables it is causatively justified to evaluate the independent variable x on the basis of values of the dependent variable y. Based on the equation $x = ay + b$ the

TABLE 5

Regression line equations for the thermal degradation onset and for the 5% mass loss for the Marinol CB SAE-30 lube oil

Physico-chemical parameter	Regression line equations	Standard deviations of regression lines
Viscosity at 323 K	$0.34T_0 + -86.44$	4.80
	$0.43T_5 + -170.86$	4.55
Viscosity at 373 K	$4.50 \times 10^{-2} T_0 + -8.33$	0.65
	$5.69 \times 10^{-2} T_5 + -19.46$	0.62
Flash point	$0.56T_0 + 223.87$	11.79
	$0.69T_5 + 94.75$	12.12
Oxide ash	$2.00 \times 10^{-3} T_0 + 0.05$	0.11
	$2.37 \times 10^{-3} T_5 + -0.36$	0.11

values of kinematic viscosity and flash point can be determined after determining from the thermogram the temperatures which correspond to the onset and to mass losses of a few or a dozen or so per cent. In Table 5 the regression line equations for T_0 and T_5 are listed.

CONCLUSIONS

Based on the investigation performed it has been stated that thermoanalytical techniques can be applied for defining the usefulness of used Marinol CB SAE-30 lube oils for further service. A general assessment of their service performance is to be most advantageously carried out based on simultaneously registered DTA, TG and DTG curves of thermal degradation of the oil. The quantitative assessment, however, can be carried out only based on the TG and DTG curves.

The values of linear correlation coefficients indicate that the assessment of the degree of use of the product examined is to be most advantageously carried out based on the temperatures for thermal degradation onset or for 1, 5 or 15% mass loss. By making use of appropriate regression line equations the kinematic viscosity values at temperatures of 323 and 373 K and flash points for the oil examined can be estimated.

Application of thermoanalytical techniques eliminates the necessity of using chemical reagents and laboratory equipment, which reduces the costs of analysis. By automatically recording the thermal degradation curves the time-consumption for the determination is also reduced. When using these methods it is not possible, however, to determine the content of foreign solids in the products examined.

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