Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Laboratory of fuels, oils and lubricants

Laboratory exercise

Flash point measurement in an open cup (Marcusson's method) and a closed cup (Martens-Pensky method)

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Szczecin

EXERCISE SHEET

<table>
<tr><td>1</td><td colspan="3">Relation to subjects: Marine Power Plant Operation/28</td></tr>
<tr><td></td><td>Specialty/Subject</td><td>Learning outcomes for the subject</td><td>Detailed learning outcomes for the subject</td></tr>
<tr><td></td><td>MPPO – Chemistry of fuels and lubricants.</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP12 – Determination of selected quality indicators of petroleum products;</td></tr>
<tr><td>2</td><td colspan="3">Purpose of the exercise:
teaching the student how to independently measure the flash point using the Marcusson method in an open cup and the Martens-Pensky method in a closed cup;</td></tr>
<tr><td>3</td><td colspan="3">Prerequisites:
the student is trained in the health and safety regulations in a laboratory position, which he confirms with his signature on the appropriate form, knows the terms: ignition, burning and self-ignition temperature, lower explosive limit and upper explosive limit as well as the explosive range for a mixture of flammable substances with air, methods of measuring the ignition temperature for fresh and used oil, knows the operational meaning and method of diagnostic conclusions based on changes in the ignition temperature of used oil and operational reasons for these changes, flash point limits for used engine oils;</td></tr>
<tr><td>4</td><td colspan="3">Description of the laboratory workplace:
Marcusson apparatus for testing the flash point in an open cup, Martens-Pensky apparatus for testing the flash point in a closed cup, metal cup forceps, a stand for washing cups of measuring apparatus, extraction gasoline, samples of lubricating oils and other petroleum products;</td></tr>
<tr><td>5</td><td colspan="3">Risk assessment*:
heating lubricating oils (or other petroleum products) to a temperature of up to 260°C, contact with hot oil, extraction gasoline used to wash measuring devices – probability of thermal burn with hot oil and fire hazard due to the presence of flammable gasoline vapour.
Final assessment – CONSIDERABLE THREAT, EFFECTS - SERIOUS
Safety measures required:
a. lab coats, safety glasses, metal tongs for hot cups,
b. health and safety cleaning products, cleaning cloths, paper towels,
c. petroleum products waste container (for disposal),
d. container for waste gasoline beakers (for regeneration);</td></tr>
<tr><td>6</td><td colspan="3">The course of the exercise:
a. Read the workplace manual (appendix 1) and familiarize with the laboratory kit for the exercise,
b. Take flash point measurements in an open and closed cup for lubricating oil (or other petroleum product);</td></tr>
<tr><td>7</td><td colspan="3">Exercise report:
a. Develop the exercise in accordance with the instructions contained in the workplace manual;
b. On the basis of the obtained measurement results, evaluate the quality and operational suitability of the tested lubricating oil by comparing the determined ignition temperature with its limit value;</td></tr>
</table>

	c. On the basis of the obtained results, determine the operational causes of the changes in the oil ignition temperature, and therefore make a diagnostic conclusion about the condition of the engine. If necessary, propose appropriate corrective actions.
8	**Archiving of research results:** Submit a written report on the performed exercise to the academic teacher.
9	**Assessment method and criteria:** a. EKP1, EKP2 – tasks given for independent solution and development: mark 2.0 – the student has no basic physicochemical and operational knowledge concerning the temperatures: ignition, burning, self-ignition and explosion ranges of petroleum products, as well as the ability to solve simple tasks in this field; mark 3.0 – has basic physicochemical and operational knowledge regarding the temperatures: ignition, burning, self-ignition and explosion ranges of petroleum products, as well as the ability to calculate and solve simple tasks in this field; mark 3.5 – 4.0 – has extended physicochemical and operational knowledge of the above-mentioned performance parameters of petroleum products and the ability to solve complex tasks in this field; mark 4.5 – 5.0 – has the ability to apply complex physicochemical and operational knowledge to partial evaluation of the quality and operational suitability of the analysed petroleum products due to the determined operational parameters and the ability to make operational decisions on this basis. b. EKP3 – control works: mark 2.0 – does not have the ability to analyse and evaluate the results of the performed analyses and determinations, and to draw conclusions; mark 3.0 – has the ability to analyse the obtained results, interpret the laws and phenomena, transform formulas, and interpret charts and tables; mark 3.5 – 4.0 – has the ability to broaden the analysis of results, apply laws, construct monograms and charts; mark 4.5 – 5.0 – has the ability to comprehensively analyse the obtained results, make generalizations, detect cause-effect relationships and make the right operational decisions.
10	**Literature:** 1. Krupowies J., Wiznerowicz Cz.: Pomiar temperatury zapłonu w tyglu otwartym (metodą Marcussona) i w tyglu zamkniętym (metodą Martensa-Pensky'ego). Instrukcja stanowiskowa do ćwiczenia, AM, Szczecin 2013. 2. Barcewicz K.: Ćwiczenia laboratoryjne z chemii wody, paliw i smarów. Wyd. AM w Gdyni, Gdynia 2006. 3. Podniało A.: Paliwa oleje i smary w ekologicznej eksploatacji. WNT, Warsaw 2002. 4. Przemysłowe środki smarne. Poradnik. TOTAL Polska Sp. z o.o., Warsaw 2003. 5. Urbański P.: Paliwa i smary. Wyd. FRWSzM w Gdyni, Gdańsk 1999. 6. Krupowies J.: Badania zmian parametrów fizykochemicznych silnikowych olejów smarowych eksploatowanych na statkach Polskiej Żeglugi Morskiej. WSM w Szczecinie, Studia nr 27, Szczecin 1996. 7. Krupowies J.: Badania zmian właściwości oleju obiegowego okrętowych silników pomocniczych. WSM w Szczecinie, Studia nr 40, Szczecin 2002. 8. PN/EN/ISO standards for the testing of petroleum products. 9. Oil product catalogs of oil companies. 10. Dudek A.: Oleje smarowe Rafinerii Gdańskiej. „MET-PRESS", Gdańsk 1997. 11. Baczewski K., Biernat K., Machel M.: Samochodowe paliwa, oleje i smary. Leksykon, Wydawnictwa Komunikacji i Łączności, Warsaw 1993.

	12. Herdzik J.: Poradnik motorzysty okrętowego. Wydawnictwo TRADEMAR, Gdynia 1995.
10	Notes

APPENDIX 1 – MANUAL

1. SCOPE OF THE EXERCISE

- getting acquainted with the workplace instructions for the exercise,
- independent measurement of the ignition temperature in an open and closed cup,
- assessment of the quality of fresh oil on the basis of the determined ignition temperature of the open cup and the catalogue value,
- evaluation of the usability of the tested oil on the basis of the determined ignition temperature in a closed cup and the ignition temperature limit.

2. THEORETICAL INTRODUCTION TO THE EXERCISE

2.1. Flash-point

The flash point of a lubricating oil characterizes its ability to evaporate. The flash point is the lowest temperature at which the oil, heated in a specific manner and under certain conditions (pressure 1013.25 hPa), releases vapours, which with the surrounding air create a mixture which ignites when the flame is approached. The flash points of fresh engine oils range from 190º to 220ºC. The flash point of the oils used is an indirect measure of the presence of fuel in them, which is very important for operation. It is assumed that lowering the flash point, determined in a closed cup, to about 180°C, makes the used oil unusable. The presence of fuel in the oil deteriorates its viscosity and lubricating properties, anti-corrosive properties, resistance to oxidation, and poses a threat to the safety of the crew and the ship (risk of fire and explosion of fuel vapours in the engine start-up).

The flash point is determined by a number of methods which give different results. The most commonly used is the Marcusson open cup method, used to measure the flash point of fresh oils, and the Martens-Pensky closed cup method - to measure the flash point of all petroleum products, especially used oils.

When giving the measurement results, always indicate the method by which they were performed. When assessing the quality and suitability of the lubricating oil, the method of determination must be stated. This is important because the correlations between the two methods are not known.

Warning values for used oils from companies: Elf, Castrol and Mobil as well as values specified by marine engine manufacturers are listed in the auxiliary tables at the end of the manual.

The flash point makes it possible to evaluate the formation of mixtures of explosive vapours of a flammable substance with air. This mixture becomes explosive after reaching certain values of the concentration of vapours of this substance under the influence of an external initiating factor (e.g. flame, sparks). A distinction is made between a lower LEL and an upper UEL explosive limit. If the concentration of the vapours of the flammable substance is lower than the lower explosive limit, the explosion will not occur, because there is an excess of air that absorbs the heat generated at the moment of explosion and prevents the remaining part of the substance from igniting. If the concentration of the vapours of the flammable substance is higher than the upper explosive limit, the explosion will not take place either due to the insufficient amount of oxygen in the mixture. Thus, an explosion only occurs in the area between the lower and upper explosive limits. As the temperature of the mixture increases,

its explosive range is slightly narrowed. The presence of inert gases (e.g. CO_2, N_2, exhaust gases - the so-called inert gases) in the vapor mixture of a combustible substance with air also narrows its explosive limits. On the other hand, the increase in pressure causes an increase in the upper explosion limit. Examples of explosive limits for some flammable substances are given in Table 1.

Table 1

Lower and upper explosion limits for some flammable gases and vapours

Flammable liquid vapours and gases	Explosion limits [% vol.]	
	lower	upper
Hydrogen	4.0	75.0
Carbon monoxide	12.5	74.0
Methane	5.3	14.0
Ethane	3.0	12.5
Propane	2.2	9.5
Butane	1.9	8.5
Pentane	1.4	7.8
Natural gas	4.3	15.0
Acetylene	2.3	82.0
Car gasoline	0.76	7.6
Extraction gasoline	1.1	1.5
Petroleum	1.4	7.5
Diesel	1.3	6.0

3. PERFORMING THE EXERCISE

3.1. Determination of flash point in an open cup using the Marcusson method

Cup – 1 (fig. 1), washed with gasoline and dried in a jet of warm air, fill the test sample to the mark. When filling the cup, make sure that the tested sample does not remain air bubbles and that the walls of the cup are not wetted above the mark.

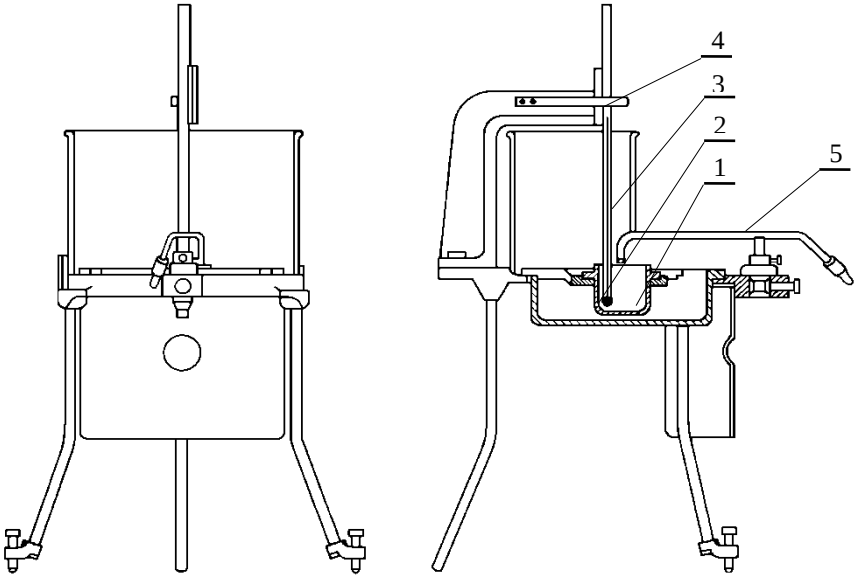

Fig. 1. Apparatus for determining the flash point by Marcusson's method:
1 – cup, 2 – cup socket, 3 – thermometer, 4 – thermometer holder, 5 – burner

Insert the cup – 1 into the cup socket – 2 and place the thermometer – 3 in it so that it touches the bottom of the cup and then lift it in the holder – 4 by 2 mm. Check that the burner – 5 does not touch the cup when moving it and that the centre of the flame, 10 mm long, is in its axis. Then, start heating the apparatus by setting the temperature regulator knob in such a position that in the initial period the temperature increase of the tested product is 6 ± 1°C per minute. After reaching a temperature 30°C lower than the expected flash point, for an oil with a flash point below 250°C, the heating rate shall be reduced so that the temperature rise is 3 ± 0,5°C per minute and this heating rate shall be maintained, and for oil with a flash point above 250°C, reduce the heating speed after reaching a temperature 50°C lower than expected.

Simultaneously with the temperature reaching 30ºC or 50ºC lower than the anticipated flashpoint, move the flame of the burner back and forth over the cup with a steady motion. The retention of the flame above the cup is a mistake. Repeat ignition attempts at intervals of 1ºC.

The ignition temperature of the tested product will be that at which the first flame appears above the cup and goes out.

If you do not know the expected ignition temperature of the analysed petroleum product, the first measurement should be made as the so-called indicative measurement, using a heating speed within 5 ± 1°C per minute and taking measurements every 5°C increase in temperature until ignition is achieved. Then the oil should be changed and the normative measurement should be performed, knowing the expected ignition temperature of the petroleum product.

Note!

If ignition occurred when the temperature was checked for the first time, the measurement should be considered incorrect and repeated, starting the determination at a lower temperature.

Elaboration of the results

If the determination is made at atmospheric pressure different from 101.3 kPa, more than 2.0 kPa, the read ignition temperature should be corrected according to the formula:

$$\Delta t = 0.25(101.3 - p)$$

where:

Δt – correction in °C according to table 2,

p – pressure measured during the measurement, in kPa.

Table 2

The value of the Δt corrections for the measured pressures

Atmospheric pressure p [kPa]	Correction Δt [ºC]	Atmospheric pressure p [kPa]	Correction Δt [ºC]
84.0 ÷ 87.7	+ 4	95.7÷ 99.3	+1
87.8 ÷ 91.6	+ 3	103.3 ÷ 107.0	– 1
91.7 ÷ 95.6	+ 2		

The final result should be the arithmetic mean of at least two determinations differing not more than that specified in Table 3.

Table 3

Acceptable measurement error

Flash-point [ºC]	Acceptable measurement error [ºC]
up to 250	6
250 ÷ 300	7
over 300	9

Note!

It should be noted that the measurement of the flash point in an open cup must not be used to assess the operational suitability of the marine oils used, but only to assess fresh oils.

3.2. Determination of flash point in a closed cup using the Martens-Pensky method

Cup – 1 (fig. 2) wash with petroleum ether, dry with a stream of warm air and fill to the mark with the tested sample.

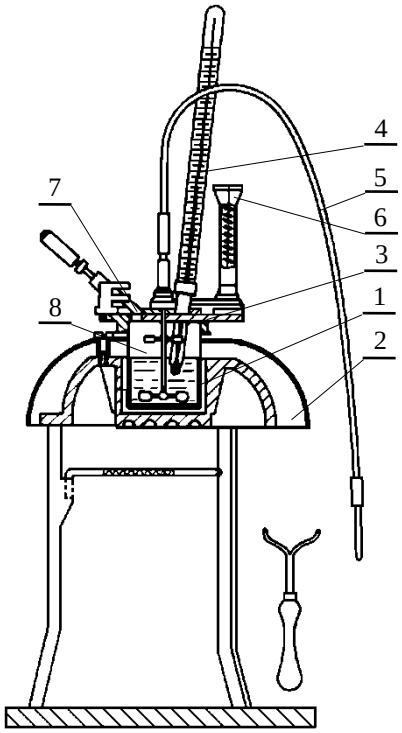

Fig. 2. Apparatus for determining the flash point using the Martens-Pensky method:
1 – cup, 2 – mantle, 3 – cover, 4 – thermometer, 5 – stirrer, 6 – knob, 7 – burner, 8 – chamber

If the tested petroleum product contains water (interfering with determination), it should be dehydrated by shaking with anhydrous sodium sulphate, and then filtered through a filter paper. Put the cup in the mantle – 2, cover with the lid – 3 and start heating by adjusting the temperature rise on the thermostat – 4 so that it amounts to 5 – 6°C per minute. During the measurement, stir the sample using the stirrer – 5. Check the ignition temperature by turning the knob – 6 and introducing the burner – 7 to the chamber – 8, simultaneously stopping mixing. The burner flame should be ball-shaped with a diameter of 4 mm.

The first flash point measurement should be made at a temperature 17°C below the expected temperature. Perform the next tests with a temperature increase of 1°C for a petroleum product with the expected flash point lower than 104°C, and for a flash point higher than 104°C – after each increase by 3°C.

The ignition temperature of the test sample should be taken as the temperature at which the first sudden ignition of the product vapours (blue flame) inside the cup occurs. Ignition is usually accompanied by a slight explosion and the extinction of the burner flame.

If you do not know the expected ignition temperature of the analysed petroleum product, the first measurement should be made as the so-called indicative measurement, using a heating speed within 5 ± 1°C per minute and taking measurements every 5°C increase in temperature until ignition is achieved. Then the oil should be changed and the normative measurement should be performed, knowing the expected ignition temperature of the petroleum product.

Note!

If ignition occurs when the temperature is checked for the first time, the measurement should be considered incorrect and the determination repeated at a lower temperature.

If the measurement was performed at a pressure different from 101.3 kPa, the correction should be calculated

$$\Delta t = 0.25(101.3 - p)$$

where:

Δt – correction in ºC,

p – pressure measured during the measurement, in kPa.

Elaboration of the results

The final result should be the arithmetic mean of at least two determinations differing not more than that specified in Table 4.

Table 4

Acceptable measurement error

Flash-point [ºC]	Acceptable measurement error [ºC]
up to104	2
over 104	6

4. DEVELOPMENT OF THE EXERCISE

1. Compare the obtained results with the catalogue values.
2. Compare the obtained results with warning values for the tested oil.
3. On the basis of the measured ignition temperature, evaluate the operational suitability of the tested oil.
4. State the risk of operating oil containing fuel.
5. In auxiliary tables 5 – 8 at the end of the manual, warning values of oils from the following companies are given: Elf, Castrol, Mobil and limit values recommended by manufacturers of marine engines.

5. THE FORM AND CONDITIONS FOR PASSING THE LABORATORY EXERCISE

1. passing the so-called "entry" before starting the exercise.
2. submission of a correct written report on the completed exercise, which should contain:

   – short theoretical introduction,
   – operational significance of the measured parameter,
   – processing of the obtained results according to the position manual.

3. final credit for the test at the end of the semester.

Tasks and questions to be completed by the student

1. The viscosity and flash point of Marinol RG 2040 oil from the auxiliary engine circuit were determined. The following results were obtained: the kinematic viscosity of the oil was 118.25 mm^2/s, and the flash point in a closed cup was 155°C. Fresh oil viscosity at 40°C is within 158 – 170 mm^2/s. Determine the operational suitability of this oil and give reasons for changes in its parameters.
2. The viscosity and flash point of Marinol RG 4030 oil from the auxiliary engine circuit were determined. The following results were obtained: the kinematic viscosity of the oil was 120.68 mm^2/s, and the flash point in a closed cup was 168°C. The viscosity of fresh oil at the temperature of 40°C is within the limits of 110 – 112 mm^2/s. Determine the operational suitability of this oil and give reasons for changes in its parameters.
3. The viscosity and flash point of Marinol RG 1530 oil from the auxiliary engine circuit were determined. The following results were obtained: kinematic viscosity of oil 132.28 mm^2/s, flash point in a closed cup 205°C. The viscosity of fresh oil at the temperature of 40°C is within the limits of 110 – 112 mm^2/s. Determine the operational suitability of this oil and give reasons for changes in its parameters.

Questions

1. Define the terms: flash point and self-ignition temperature and ignition temperature. What external factor influences the flash point value?
2. For what purpose are the flash point measurements of fuels and lubricating oils used on ships performed?
3. By what methods is the flash point of fresh lubricating oils and used oils determined and why?
4. Explain why the flash point of the same lubricating oil, measured in open and closed cup, is different? What does the magnitude of this difference depend on?
5. What is the reduction of the flash point of the used engine oil in relation to the flash point of the same fresh oil as evidenced by?
6. What is the flash point value for oils used in trunk piston engines? What operating decisions should be made when this value is exceeded?
7. What are the fire safety requirements in relation to the petroleum products used in the ship's power plant?
8. What is the upper and lower explosive limits of a mixture of flammable vapours with air? Why is there no explosion outside these boundaries?

Auxiliary tables

Table 5

Warning values for the basic physicochemical parameters of some Elf oils

Markings	Disola M3015 Disola M4015	Aurelia XT4040
Kinematic viscosity at 40°C [mm^2/s]	+30% –20%	+30% – 20%
Base number [mg KOH/g]	> 8	> 15
Flash point in a closed cup [ºC]	> 180	> 180
Water content [%]	< 0.3	< 0.3
Content of impurities insoluble in n-pentane [%]	< 2	< 2

Table 6

Warning values for the basic physicochemical parameters of some Castrol oils

Markings	Castrol MPX 40 Castrol MLC 40	Castrol MXD 303
Kinematic viscosity at 40°C [mm^2/s]	± 25%	± 25%
Base number [mg KOH/g]	– 50%	–50%
Flash point in a closed cup [ºC]	> 180	> 180
Water content [%]	< 0.2	< 0.2
Content of impurities insoluble in n-pentane [%]	< 2	< 4

Table 7

Warning values for the basic physicochemical parameters of some Mobil oils

Markings	Mobil 312	Mobil 412	Mobil 442
Kinematic viscosity at 40°C [mm^2/s]	min mm^2/s max 143 mm^2/s	min 102 mm^2/s max 218 mm^2/s	min 102 mm^2/s max 218 mm^2/s
Base number [mg KOH/g]	– 50%	– 50%	– 50%
Flash point in a closed cup [ºC]	> 190	> 190	> 190
Water content [%]	< 0.2	< 0.2	< 0.2
Content of impurities insoluble in n-pentane [%]	< 2	< 2	< 2

Table 8

Limits for the basic physicochemical parameters of lubricating oils recommended by Western manufacturers of marine engines

Compression ignition engines			Kinematic viscosity [mm^2/s] ~~w~~ at 100°C		Flash-point FP	Water content max	Contaminant content	BN
producer	type	model	min	max	[°C]	[% wt.]	[% wt.]	[mgKOH/g]
1	2	3	4	5	6	7	8	9
Daihatsu	four-stroke	all	–20%	+30%	180	0.1% obj.	2.5	3.0 for fuel (MDO) 5.0 for fuel (LMFO) 10.0 for fuel (HFO)
Deutz-MWM	four-stroke	D/TBD 234 TBD 604 B S/BAM 816	9 (SAE 30) 11 (SAE 40)	+25%	190	0.2	2.0	min 50%
	four-stroke	D/TBD 440 S/BAM 628 TBD 645 R/S/BVM 640	9 (SAE 30) 11 (SAE 40)	+25%	190	0.2	2.0	min 60%
Krupp MaK	four-stroke	all	80 at 40°C (SAE 30) 130 at 40°C(SAE 40)		180	0.2	2.0	min 15* min 18**,*** min 50% for fuels MDO/MGO
MAN B&W	four-stroke two-stroke	20/27 to 58/64	±1 SAE degree		185	0.5	1.5	min 50%* min 70%**
MTU	four-stroke	all	9,0 (SAE 30) 10,5 (SAE 40)	+25%	190	0.2	2.5	min 50%
Wartsila	four-stroke	VASA 46	11,5 for 40°C 95	19 for 40°C 212	170	0.3 (0.5)	2.0	50% min 15
Sulzer	two-stroke (oil cooling of the pistons)	RTA 84 C/M/T 72, 62, 52 48, 38	–10%	+20%	180	0.5	0.5	min 5
	two-stroke (water cooling of the pistons)	RTA 84, 76, 68, 58 and all RND, RLA i RLB	–10%	+20%	180	0.5	0,5	min 5
	four-stroke	Z40, ZA40, ZA40S	–20%	+30%	180	0.5	2.5	min 60%
	four-stroke	type-A and S20	–20%	+30%	180	0.5	2.5	min 50%
Yanmar	four-stroke	all	–20%	+30%	180	0.3% obj.	2.0	4 (for fuel MDO) 15 (for fuel HFO)

* engines with separate cylinder oil circuit, fuelled by HFO,
** HFO-fuelled engines without separate circulation of cylinder oil,
*** applies to the MaK 453 C engine.