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SPECTROSCOPIC STUDY AND ANALYSIS OF THE CONTENT OF RESIDUE ELEMENTS IN MARINOL RG 1240 OIL AFTER WORKING IN VARIOUS TYPES OF ENGINES

ANALIZA ZAWARTOŚCI PIERWIASTKÓW ŚLADOWYCH W OLEJU SILNIKOWYM MARINOL RG 1240 PO RÓŻNYM CZASIE PRZEPRACOWANIA W RÓŻNEGO TYPU SILNIKACH

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Abstract: During exploitation, the engine oil undergoes the irreversible aging process that is – degradation. The speed of this process is affected by many factors such as high temperature, pressure, power output, oxygen from the air, mechanical shear forces, type, structure, and technical condition of the engine, time and conditions of work and also used fuel. In the article, the author shows that also the purpose of the engine influences the degradation of the engine oil. Using the method of optical emission spectrometry in accordance with ASTM D 6595 standard, the concentration of trace elements like: Ag, Al, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, V, Zn, was determined. The samples of engine oil – Marinol RG 1240 were checked after various periods of use in three different engine types Cegielski – Sulzer.

Keywords: engine oil, marine oil, degradation process, spectrometry, trace elements, oil analysis, contamination.

Streszczenie: Oleje silnikowe podczas eksploatacji ulegają nieodwracalnemu procesowi starzenia. Intensywność wspomnianego procesu jest uzależniona od wielu czynników, takich jak: wysoka temperatura oraz ciśnienie, obecność tlenu z powietrza, wielkość występujących sił ścinających, typ, struktura i stan techniczny silnika, stosowane paliwa, a także czas i warunki pracy silnika. W artykule podkreślono wpływ przeznaczenia silnika na zanieczyszczenia występujące w oleju obiegowym. Do badań wykorzystano metodę optycznej spektrometrii emisyjnej zgodnie z normą ASTM D 6595 i oznaczono obecność następujących pierwiastków: Ag, Al, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, V, Zn. Próbki przepracowanych olejów obiegowych typu Marinol RG 1240 były pobierane z trzech różnych typów silników.

Słowa klucze: olej silnikowy, zanieczyszczenia, proces zużycia, spektrometria, pierwiastki śladowe, analiza oleju.

1. INTRODUCTION

Lubricating oils are used in engines to minimize friction, heating and wearing by preventing metal to metal contact between moving parts, especially in internal combustion engines [Pelitli, Doğan and Köroğlu 2017]. In the literature, it can be found that "Lubricants are the life blood of oil wetted machinery" [Henning et al. 2014]. Therefore, proper in-service oil analysis can provide users of various types of machines and devices with information about quality of lubrication, presence of contaminants, and wear of components (Fig. 1), for example engine. Basing on obtained results, operators and maintenance specialists may plan further work, maintenance methods, and repair work. "Immediate benefits of oil analysis include avoiding oil mixing, pollution control, maintenance, and failure analysis" [Henning et al. 2014]. There are many parameters enabling the estimation of the oils condition, for example viscosity, alkalinity, flash point, etc. In the paper, the author focused on the presence of elements in oil using spectrometry. "The determination of wear metals in used lubricating oils is of great interest in preventive maintenance of engines" [Sanz-Segundo et. al 1999].

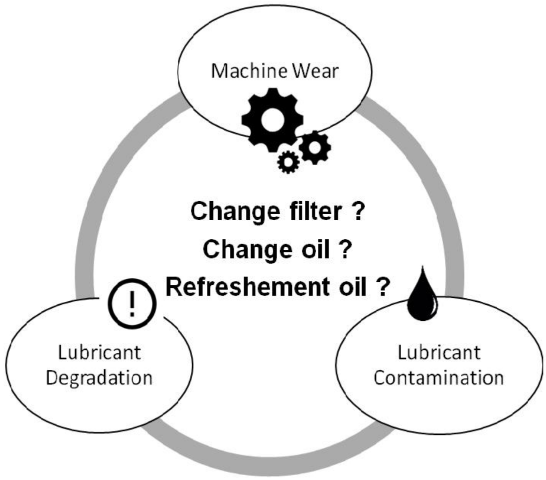

Fig. 1. *Information provided by in service oil analysis [Henning et al. 2014]*

Rys. 1. Informacje uzyskane za pomocą analizy oleju [Henning i in. 2014]

2. DEGRADATION OF ENGINE OIL

Normal operation of engine leads to increased oil aging, which consists of two processes: oxidation and contamination (Fig. 2). During aging, the oil properties change, which is affected by high temperature, high power output and oxygen from the air, in the presence of catalytically interacting metals and mechanical shear forces. The effect of oil aging results most often in changes of color, viscosity, total basic number, flash point, sediment and lacquer formation and an increase in solids content. It is worth pointing out that this process is random and may depend on the technical condition and type of the engine, the original base oil, type of combusted fuel, oil cleaning methods, refreshing frequencies, and supply systems for example fuel or cooling water [Ludema 1996; Krupowies 2002, 2006; Jakóbiec and Budzik 2007; Wolak and Janocha 2015; Pelitli, Doğan and Köroğlu 2017].

The oxidation of oil takes place with atmospheric oxygen at a temperature above the ambient temperature. The first result of this reaction consists of unstable peroxides, which then decompose into, dangerous for the correct operation of the engine, new compounds: asphaltenes, carbides, carbon black and organic acids. Oil-soluble oxidation products circulate with it, while insoluble solids settle on the engine components [Rose 1991; Kastelik 2011].

Oil contamination is defined as "Every substance that is not oil or an integrated part of oil but occurs in oil" [Malinowska 2016]. All contamination can be divided into two groups: inside and outside (Fig. 2).

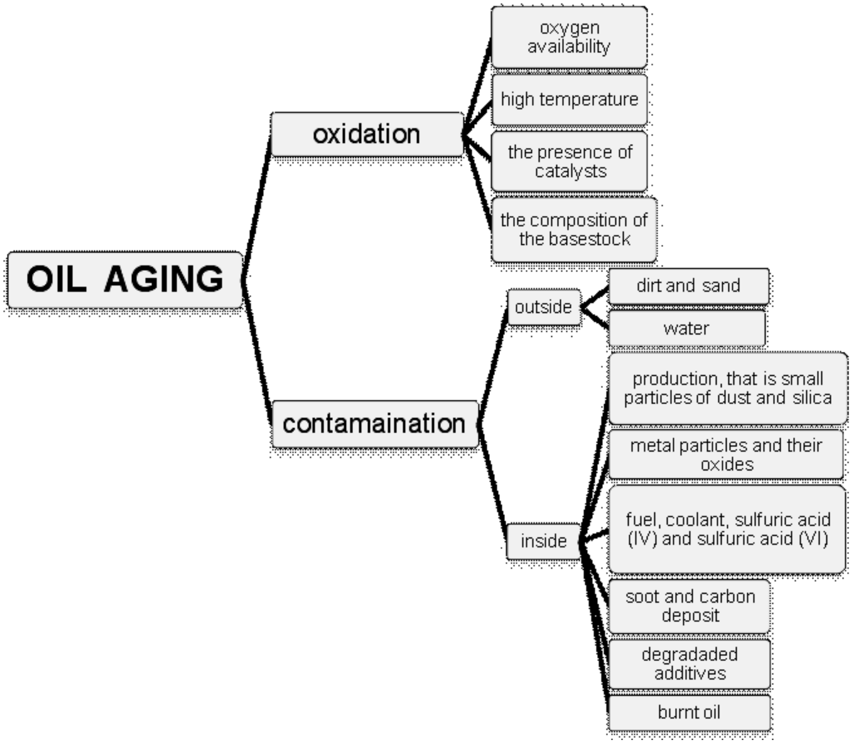

Fig. 2. *Elements influence on aging process of engine oil*

Rys. 2. Czynniki wpływające na proces zużycia oleju silnikowego

The most common source of contamination problems in engine oils are degraded additives, engine blow-by, burnt oil, dirt, sand, soot, carbon deposit, dust, coolant, sulfuric acid, wear metals from engine components and incomplete combustion of fuels. Wear metals are important waste oil components. Heavy metal particles are introduced into the oil of the engine as a result of wear, corrosion or external particles from the surrounding environment [Pelitli, Doğan and Köroğlu 2017].

3. CONCENTRATION TRENDS OF WEAR METALS

The analysis of new and used motor oil for concentration trends of wear metals has been known for many years, because during exploitation of engine, the operators have always been interested to determine levels of pollution of lubricating oil. In engine oil one can find, in general, three types of elements sources [Krupowies 2001; Aucelio 2007; Al-Ghouti and Al-Atoum 2009; Henning et al. 2014; Zali et al. 2015]:

- wear metals: Aluminum, Cadmium, Chromium, Copper, Iron, Lead, Magnesium, Molybdenum, Manganese, Nickel, Silver, Tin, Titanium, Vanadium, Zinc which may indicate wear in engine or devices of lubricating system;
- contaminants: Boron, Calcium, Potassium, Silicone, and Sodium may identify contamination issues such as coolant leaks, sea water contamination, ingested dirt, dust, fuel etc.;
- additives elements: Barium, Boron, Calcium, Chromium, Copper, Magnesium, Molybdenum, Phosphorus, Silicone and Zinc were blended with oil for metallic detergents, ashless dispersants, anti-oxidant, anti-wear, friction modifier, anti-foam purposes etc.

The modern method of determining the content of trace elements in oil is optical emission spectroscopy. “Spectroscopy utilizes the fact that each element has a unique atomic structure. When subjected to the addition of energy, each element emits light of specific wavelengths or colors. (…) The intensity of the emitted light is proportional to the quantity of the element present in the sample allowing the concentration of that element to be determined” [Henning et al. 2014]. Since many transitions of different energy are possible for complicated atoms which have many electrons, light of many different wavelengths is emitted. “If this light is dispersed by using a dispersing element such as a prism, a line spectrum will occur. (…) These spectral lines are unique to the atomic structure of only one element. (…) Table 1 shows typical metal elements that can be analyzed by spectroscopy and their sources” [Henning et al. 2014].

Table 1. *Typical source of elements analyzed with spectroscopy in oil*
Tabela 1. Źródła pochodzenia pierwiastków śladowych w oleju silnikowym

Metal	Engine, Transmission, Gears	Metal	Engine, Transmission, Gears
Aluminum Al	pistons or crankcases on reciprocating engines, housings, bearing surfaces, pumps, thrust washers	Manganese (Mn)	shafts, valves, anti-friction bearings, dirt entry, anti-wear additive
Barium Ba	synthetic oil additive, dust, dirt, grease	Nickel Ni	alloy from bearing metal, valve trains, turbine blades
Boron B	oil additives, internal coolant leak	Phosphorous P	anti-wear additive
Calcium Ca	detergent, dispersant additive, water containment, airborne contamination	Potassium K	coolant leak, airborne contaminant, fuel
Chromium Cr	pistons, cylinder liners, exhaust valves, coolant leak from Cr corrosion inhibitor	Silicon Si	airborne dusts, seals, coolant leak, additive
Copper Cu	either brass or bronze alloy detected in conjunction with zinc for brass alloys and tin for brass alloys, bearings, bushing, thrust plates, oil coolers, oil additive	Silver Ag	bearing cages (silver plating), wrist pin bushing on EMD engines, piping with silver solder joints from oil coolers
Iron Fe	most common of wear metals, cylinder liners, piston rings, valve guides, rocker arms, bearing, crankshaft, camshaft, wrist pins, housing, engine nuts, pins	Sodium Na	coolant leak, salt water and grease in marine equipment, additive, fuel
Lead Pb	bearing metal, bushings, seals, solder, grease, leaded gasoline	Tin Sn	bearing metal, piston rings, seals, solder
Magnesium Mg	housing on aircraft and marine systems, oil additive	Titanium Ti	gas turbine bearing hub wear, turbine blades, compressor discs
Molybdenum Mo	piston rings, additive, coolant contamination	Zinc Zn	anti-wear additive
		Vanadium	turbine blades, valves, fuel contaminant (bunker fuel)

The testing the content of trace elements in oil samples was conducted using the spectrometer Spectroil Q100 (Fig. 3) in accordance with ASTM D 6595 standard. This method was chosen as the most appropriate experimental procedure since it does not require any dilution or preparation. Therefore, analyses were carried out faster and the contaminant losses caused by sample preparation were minimized.

Fig. 3. Spectrometer Spectroil Q100 in laboratory
Rys. 3. Spektrometr Spectroil Q100 w laboratorium

4. SAMPLES

The research was conducted using motor oil samples of Lotos Company – Marinol RG 1240. The trials differed in terms of overwork in three different engines:

- Laboratory engine Cegielski-Sulzer 3AL25/30 of 396 kW;
- Main engine Cegielski-Sulzer 8AL20/24 of 552 kW placed on the sailing vessel "Dar Młodzieży";
- Auxiliary engine Cegielski-Sulzer 6AL20/24 of 410 kW placed on the sailing vessel "Dar Młodzieży".

In all cases, engine oil was collected using a drain valve mounted on the oil supply system.

The operating hours are shown in Table 2.

Table 2. *Operating hours of tested oils*
Tabela 2. Liczba godzin pracy badanych próbek olejów

Samples	Source	Hours of operation
1	Fresh oil	0
2	3AL25/30	600
3	3AL25/30	750
4	8AL20/24	1000
5	6AL20/24	650
6	6AL20/24	1030

Marine motor oil Marinol RG 1240 is TPEO (Trunk Piston Engine Oil) and it is designed for lubrication of marine anhydride light fuel engines. It is formulated on the base of deeply refined, solvent dewaxed and hydrorefined oil distillates received from crude oil. They contain a properly selected package of washing and dispersing additives as well as auto-oxidising, anti-corrosion, anti-rust and anti-wear attributes.

Parameters of Marinol are presented in Table 3. The oil fulfills the API CD requirements (American Petroleum Institute, category CD) for marine engines.

Table 3. *Parameters of engine oil – MARINOL RG 1240*

Tabela 3. Parametry oleju silnikowego – MARINOL RG 1240

No.	Requirements	Research methods by	Unit	RG 1240
1	Kinematic viscosity at 100°C	ASTM D-445	mm^2/s	14,3
2	Pour point	ASTM D-5950	°C	–24
3	Flash point	PN-EN ISO 2592	°C	260
4	Base number	ASTM D-2896	mgKOH/g	12,5
5	Viscosity index	ASTM D-270		96
6	Corrosion effect at 100°C, 3h, Cu	PN-EN ISO 2160 ASTM D-130	degree	1

5. RESULTS

During the first phase of research, every sample series of collected oil was tested three times on Spectroil Q100 and then the content of each element was averaged. The concentration of elements was presented in ppm (parts per million). After averaging, the results were put into the table, which enables conducting the analysis (Table 4). The elements which quantity decreased in comparing to fresh oil are indicated by arrows. It means consumption of oil additive.

Fifteen from the received elements can be divided into three characteristic groups:

- the first group contains elements that have not changed (or in the amount of < 0.2 ppm) in relation to fresh oil. They are Silver, Aluminum, Nickel and Titanium;
- in the second group are wear metals, which trend very similarly for oil samples from all types of engines, they are: Copper (increase 3.5–8.3 ppm), Iron (increase 9.9–12.4 ppm), Magnesium (increase 2.2–5.6 ppm) Lead (increase 3–7.5 ppm), Chromium (increase 1.3–2.4 ppm). These may indicate wear of bearings, piston rings, cylinder liners and other engine components. It is worth mentioning one metalloid in this group - silicon, which occurs about 19–23.3 ppm for all samples. Silicon is listed in the group of contaminations, but it is used in seals, so it can also determine wear of components of engine;
- the third group consists of the elements characteristic only for marine engines:
  - Due to the presence of seawater, they are Sodium, Boron and Molybdenum (Mo is also a lubricate additives, in fresh oil 4.535 ppm). The Sodium is the most important indication of an internal coolant leak. The amount of Sodium increase for marine engines is about 87–130 ppm;
  - From the bunker fuel leaks come: Sodium, Potassium and Vanadium.

Table 4. *Test results of concentration of elements*

Tabela 4. Uzyskane wyniki zawartości pierwiastków śladowych w próbkach olejów

	Ag	Al	B	Ba	Ca	Cr	Cu
sample 1	0.171	2.060	0.346	0.290	4779.400	0.000	0.000
sample 2	0.193	2.946	0.388	13.988	4999.750	2.253	3.530
sample 3	0.287	3.499	0.344	14.084	5190.429	2.033	3.863
sample 4	0.138 ↓	2.482	2.954	1.548	4643.000 ↓	1.275	8.264
sample 5	0.188	3.203	1.175	0.573	5524.333	2.350	5.065
sample 6	0.210	2.720	1.173	0.577	5450.667	2.410	5.460
	Fe	**K**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**
sample 1	1.922	0.757	16.977	3.081	4.535	3.941	0.649
sample 2	13.515	0.945	19.204	3.110	4.010 ↓	5.704	0.680
sample 3	13.747	1.132	19.548	3.874	4.443 ↓	5.773	1.168
sample 4	14.238	9.164	20.276	2.578 ↓	5.838	90.762	0.430 ↓
sample 5	14.293	4.513	22.655	2.010 ↓	6.075	133.898	0.546 ↓
sample 6	11.860	3.820	22.404	1.930 ↓	5.770	125.648	0.563 ↓
	P	**Pb**	**Si**	**Ti**	**V**	**Zn**	
sample 1	415.886	0.908	15.367	0.991	0.265	631.147	
sample 2	444.183	7.830	19.887	1.106	0.030 ↓	676.427	
sample 3	442.663	7.030	19.022	1.689	0.007 ↓	678.652	
sample 4	393.216 ↓	3.934	20.652	0.966	0.370	579.724 ↓	
sample 5	886.763	5.430	23.252	1.110	1.188	634.820	
sample 6	655.800	8.363	19.660	1.173	1.523	657.777	

Unfortunately, the rest of the designated elements cannot qualify for the mentioned groups.

- Barium is very interesting, increases significantly for the oil from laboratory engine (almost 50 times as much than fresh oil) it can originate from dust or contact with other greases;
- the quantity of Calcium grows for oil samples from the auxiliary engine (increase 671–744 ppm) and laboratory engine (increase 220–411 ppm), but decreases for a sample from main engine (decrease 136 ppm). Increased Calcium suggests the presence of water or airborne contamination. The Calcium is also a detergent and dispersant additive, so losing it in case of the main engine indicates a loss of ability to keep the engine clean and to maintain washed out residues in a dispersed state;
- Manganese, which decreases in samples from all types of marine engines, about 0.5–1 ppm (in laboratory engine-unchanged), is an anti-wear additive, used to protect valves and valve seats, its loss suggests reduced protection of mentioned parts of the engine;

- Phosphorus is a corrosion inhibitor and lubricant additive. Its quantity decreases for sample from main marine engine (22.7 ppm), but increases for the other engines, for auxiliary engine more than twice, which means the wear bronze components;
- Zinc is found in chemicals used to make anti-wear, anti-oxidant, detergent and corrosion inhibitor additives. Zinc is alloyed with copper to make brass so it can be evident as a wear metal. Its trend is similar to phosphorous, decreasing for oil from main engine (about 50 ppm) and increasing for oil samples from other engines.

6. CONCLUSIONS

The paper analyzes the effect of the purpose of engine on the content of trace elements in circulating engine oil. Three engines from Cegielski-Sulzer were compared: laboratory 3AL25/30, main marine engine 8AL20/24 and auxiliary marine engine 6AL20/24. The number of working hours of oil samples was within limits of 600 to 1030 hours.

In engine oil, it is possible to find two types of pollution sources, they are wear metals and contaminants. In all of the studied samples of oil, similar amount of elements derived from wear, ie.: Fe, Pb, Cu, Mg, Cr was found. However, the bigger problem is a second group – contaminants. The most significant pollution of marine engine oils is caused by Na, which is an indicator of seawater content. The second ones are K and V, whose source is the bunker fuel, which proves that the marine engines are burning fuel of inferior quality. In case of the laboratory engine 3AL25/30 there is an increase in Ba, Ca, Si content, which source can be dust. This engine works very little hours during the year and most of the time it is unused, which results in an increased participation of oil contaminations – air pollution. All external particles (dust, dirt, smoke) are sucked together with air into the crankcase and contaminate the oil.

The analysis of fresh oil allows for an identification of oil additives. Producer of motor oil uses detergents and dispersants (Ca, Mg), oxidation and corrosion inhibitors (P, Zn) and lubricate additives (P, Mo). The important information is that the marine main engine used most of oil additives, which may indicate its worst condition and the highest load.

By using optical emission spectrometry it was possible to obtain results for twenty different elements simultaneously, which give a whole picture of the technical condition of the engines, their components and supply systems. Analysis of single elements does not give such possibilities.

Next step, focuses on gathering more numbers of oil samples and determination of correlations between the concentration of elements and hours of engine oil operations.

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