Wiesław ZWIERZYCKI*, Kasper GÓRNY**

TRENDS IN THE PROCESS OF GREENING LUBRICANTS

TENDENCJE W PROCESIE EKOLOGIZACJI ŚRODKÓW SMAROWYCH

Key words:	lubricants, environmental impacts, biodegradation, non-toxicity, refrigeration compressor oils.
Summary:	In this article, the authors have characterized the main activities that reduce the impact of lubricants on the environment. To begin with, new solutions in the area of engine oils that reduce the emission of harmful substances in exhaust gases ("Low SAPS" oils) were discussed. Next, the activities concerning the improvement of biodegradability of lubricating oils used in devices in Nature Reserves, as well as in all of the "open lubrication systems" were characterized. Another problem was related to the non-toxicity (and other derivative features) of lubricants that may have incidental contact with a sensitive technological medium in production processes (in the food, pharmaceutical, and cosmetics industries). The last issue that was discussed concerns the compatibility of compressor oils with refrigerants in connection with the global exchange program of Freon for more environmentally friendly substances (currently, mainly affecting global warming to a lesser extent).
Słowa kluczowe:	środki smarne, oddziaływania środowiskowe, biodegradacja, nietoksyczność, oleje do sprężarek chłodniczych.
Streszczenie:	W tym artykule scharakteryzowali autorzy główne działania zmniejszające oddziaływania środków smarowych na środowisko. Najpierw omówione zostały nowe rozwiązania w obszarze olejów silnikowych zmniejszające emisję szkodliwych substancji w spalinach (tzw. oleje „Low SAPS"). Następnie scharakteryzowano działania związane z poprawą biodegradowalności olejów smarowych, stosowanych w urządzeniach w rezerwatach przyrody, ale również we wszystkich tzw. otwartych układach smarowania. Kolejny problem dotyczył nietoksyczności (i innych cech pochodnych) środków smarowych, które w procesach produkcyjnych mogą mieć incydentalny kontakt z wrażliwym medium technologicznym (w przemyśle spożywczym, farmaceutycznym, kosmetycznym). Ostatnie omówione zagadnienie związane jest z kompatybilnością olejów sprężarkowych z czynnikami chłodniczymi w związku z ogólnoświatowym programem wymiany tzw. freonów na substancje bardziej przyjazne środowisku (obecnie głównie mniej wpływające na ocieplenie klimatu).

INTRODUCTION

For many years, efforts have been made to reduce the negative impact of industry and transport on the environment. In both of these activities, the general point is to reduce the amount of fuel burned (lower CO_2 emissions) and to increase the purity of the exhaust gases emitted to the atmosphere. In the automotive aspect, technologies for the production of conventional fuels that are more environmentally friendly than before have been developed. Gasoline is a sulphur-free fuel,

with almost zero benzene content and a limited content of combined aromatic hydrocarbons. The progress in the production of diesel oils also resulted in sulphur-free fuels, with a slightly different density and the final distillation temperature (this reduces the amount of solid particles in the exhaust gases). Further versions of alternative fuels as well as more and more perfect versions of hybrid and electric drives are also being developed.

Ecological requirements also apply to lubricating oils, both the automotive and industrial ones. Some issues

* ORCID: 0000-0002-9950-4799. Poznan University of Technology, Faculty of Working Machines and Motor Vehicles, Institute of Working Machines and Motor Vehicles, Piotrowo 3 Street, 60-965 Poznań, Poland.
** ORCID: 0000-0002-5551-2690. Poznan University of Technology, Faculty of Working Machines and Motor Vehicles, Institute of Working Machines and Motor Vehicles, Piotrowo 3 Street, 60-965 Poznań, Poland.

in this area have been addressed in this article. First, new solutions in the field of engine oils reducing the emission of harmful substances in the exhaust gases ("Low SAPS" oils) were discussed. Next, the activities related to the improvement of the biodegradability of lubricating oils used in devices in nature reserves, as well as in all of "open lubrication systems" were characterized. Another problem concerned the non-toxicity (and other derivative features) of lubricants that may have incidental contact with a sensitive technological medium in production processes (in the food, pharmaceutical, and cosmetics industries). The last issue discussed is related to the compatibility of compressor oils with refrigerants in connection with the global exchange program of Freon for more environmentally friendly substances (currently, mainly affecting global warming to a lesser extent).

NEW ENGINE OILS AND ATMOSPHERIC CLEANNESS

In the last dozen or so years, new classes of engine oils have appeared that meet subsequent, increasingly stringent exhaust purity standards (this applies to qualitative classification) and allow the engine to reduce fuel consumption (the new viscosity classes).

In the first aspect, attention should be paid to the new ACEA classifications, in which new classes of ecological oils marked "Cx" – low ash and with low content of phosphorus and sulphur were introduced, with the year 2004 being the starting point. They were called "Low SAPS" oils, where SA is sulphated ash, P is phosphorus, and S is sulphur, of course.

Phosphorus and sulphur in the previous generation oils are components of effective anti-wear and anti-seize additives. But because these elements negatively affect the work of "catalysts" in the exhaust system reducing the content of CO, HC and NOx in the exhaust gases, in the new generation oils of the "Cx" type (according to ACEA), their concentration has been significantly reduced.

The additives in the older generation engine oils are metal compounds which emit a certain amount of ash after combustion and on molecules of which solid particles (PM) are formed. In order to reduce the scale of this phenomenon, refining additives based on organic compounds were developed which do not contain metals, and thus "giving off" much less ash after combustion.

To sum up the advantages of "Low SAPS" oils, it can be stated that the reduced amount of phosphorus and sulphur affects the correct work (and increased durability) of catalysts in the exhaust system, and the reduced overall content of ash coming from refining additives increases the durability of particulate filters, especially in the systems with EGR (Exhaust Gas Recirculation). The "breakthrough" ACEA classification with "Cx" oils is shown in **Table 1**, and **Table 2** presents the concise characteristics of oils from the "Cx" group.

Table 1. General diagram of the new ACEA 2004 classification [L. 1]
Tabela 1. Ogólny schemat nowej klasyfikacji ACEA 2004 [L. 1]

Engines		
Gasoline and diesel passenger cars and vans with catalytic converters and particle filters		Diesel in trucks
A1/B1	C1	E2
A3/B3	C2	E4
A3/B4	C3	E6
A5/B5	(low ash oils)	E7

Table 2. Classification of Cx oils ACEA 2004 [L. 1]
Tabela 2. Klasyfikacja ACEA 2004 – oleje Cx **[L. 1]**

Class	Oil characteristics
C1	Very low ash level. Low friction, low viscosity oils, i.e. fuel-efficient. HT / HS 2.9 mPa s They meet the requirement of a significant service life of DPF (Diesel Particulate Filter) and TWC (Three Way Catalyst) catalysts. "Low SAPS" designation (Sulphated Ash, Phosphorus, Sulphur – sulphated ash, phosphorus, sulphur). Synthetic and semi-synthetic oils: 0W-30, 5W-30.
C2	HT / HS 2.9 mPa s; medium ash level.
C3	No HT / HS requirement; medium ash level.

It should be noted that similar properties to Cx oils from the ACEA 2004 classification (and the subsequent ones) are possessed by API grade CI-4, and mainly CJ-4 oil, designed for modern catalytic systems, oriented to the latest exhaust emission standards.

In **Table 2**, in the characteristics of C1 class oils with low ash levels, there is a note that they are low-friction, low-viscosity or fuel-efficient oils, in the synthetic or semi-synthetic version, multi-grade, e.g., 0 W/30, 5 W/30.

The newer trends in the classification of viscosity of engine oils are XX/20 or even XX/16 (13) classes. These means lower viscosity at operating temperatures, lower friction losses, and thus lower fuel consumption.

Figures 1 and **2** compare the viscosities of oils of previously recommended grades (e.g., 15 W/40 and 10 W/40), currently 0 W/30 and 5 W/30 (e.g., C1 and C2 oils from the ACEA classification) and the recently introduced – 0 W / 20. It can be seen in **Figure 1** that the cold engine starting resistance with the use of multi-grade oil 0 W / XX or (5 W/XX) is significantly lower than it is in the case of the previously recommended 15 W/40 and 10 W/40 oils. In turn, **Figure 2** compares oil viscosities at operating temperatures including the following:
– The viscosity at 100°C when switching from class 30 to class 20 in SAE is reduced by about 30%; whereas,

– The viscosity measured in the HT / HS test (High Temperature = 150°C and High Shear – intensive shear 10^6 s^{-1}) simulating the "operation" of the system: oil film on the cylinder bearing surface – piston rings – the reduction by approx. 10%.

Therefore, in real conditions when driving a car in road conditions, one can expect savings in the fuel consumption of a few (maybe a dozen) percentage points.
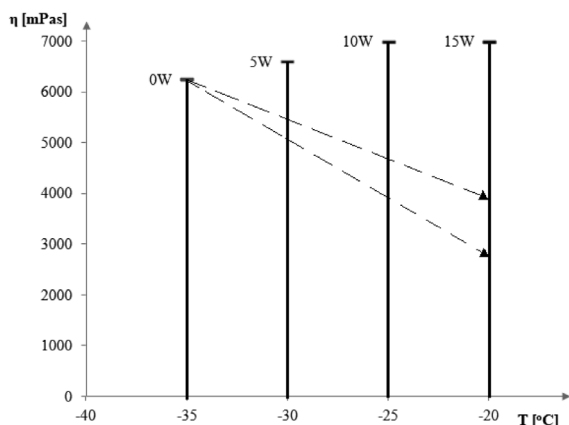

Fig. 1.   Starting viscosity at negative temperatures
Rys. 1.   Lepkość rozruchowa w ujemnej temperaturze

Fig. 2.   Comparison of viscosity at the operating temperature: a) 100°C, b) 150°C – HT/HS test
Rys. 2.   Porównanie lepkości w temperaturze roboczej: a) 100 °C, b) 150°C – test HT/HS

On the other hand, lower viscosity at the operating temperature means a thinner hydrodynamic film in the bearings and on the cylinder bearing surface. Therefore, along with the lowering of classes 30 (40) to the level of class 20 (possibly "16" or even "13"), it would be necessary to "strengthen" the boundary layers, which are the "last protection" against direct metal-metal contact. This was done with the help of a new generation of additives – friction modifiers.

In other words, the efforts of engine oil manufacturers for the reduction of toxins from internal combustion engines are mainly the following:

a) A reduction of friction losses by reducing viscosity at the operating temperature (the change of viscosity classes from 40 (30) to "20" (possibly 16, 13?), which is reflected in a lower fuel consumption by the engine and lower CO_2 emissions into the atmosphere;

b) The development of "Low SAPS" oils with a lower AS ash content (fewer PM particulates) and reduced phosphorus (P) and sulphur (S) contents (the reduction of the negative effect on the efficiency of "catalysts" in the engine exhaust system); the examples are C1, C2, and C3 oils according to ACEA (2004 and subsequent) and API CJ-4 class.

BIODEGRADABILITY OF LUBRICATING OILS

It is estimated that approximately 13 to 15% of the oils produced annually are exploited in open lubrication systems from where they pass into the natural environment, mainly soil and water **[L. 2]**. Open lubrication systems occur, inter alia, in chain saws, two-stroke engines, in rail transport to lubricate the wheel and rail contact point when driving on curves, etc. Generally, it can also be considered that biodegradable oils should be used in all vehicles used in nature reserves, e.g., in forestry tractors, motorboat engines, and in the chainsaws already mentioned above. The requirement of biodegradability also applies to hydraulic oils, which often (in emergency) may be "released" into the environment due to the high pressures prevailing in the systems.

The biodegradability of lubricating oils is determined by the properties of the base oils used for their production. By chance, the share of base oils in mineral engine oils fluctuates within 70–90%, but in turbine and transformer oils, the share amounts to over 99%, while, in hydraulic or compressor oils, it is 98–99%. The remaining part of the lubricating oil are the enriching additives, i.e. the basic ones – oxidation and corrosion inhibitors, frequently also anti-wear and anti-seize additives and others, depending on the specificity of the lubricated device.

Over the past forty years, the quality of base oils has changed significantly for the better, which resulted from the technical progress, but also due to the environmental protection requirements.
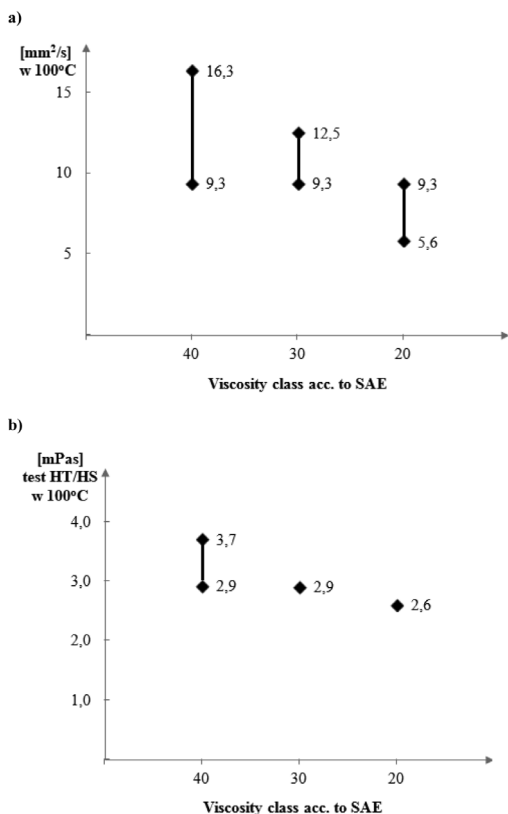
Contemporary base oils are still mostly obtained from crude oil, and apart from the conventional method, new methods have developed with the presence of hydrogen processes, allowing one to obtain products with useful properties similar to synthetic hydrocarbons of the PAO type (polyalphaolefins). The classification in this aspect is provided by the API 1509W.1.3 classification, dividing the base oils into the following five groups (**Table 3**):

– In Group I, there are conventional mineral oils, designated as SN (Solvent Natural) obtained (approx. 75% of world production) by conventional refining of hydrocarbon fractions obtained in the vacuum distillation process, where there are there are three stages of refining: solvent refining – removing aromatic hydrocarbons and parts of heterocyclic compounds, deparaffinization – reducing the amount of normal paraffin with high solidification point, low pressure hydro-cracking – removing sulphur, nitrogen and oxygen compounds.

– Groups II and III include unconventional mineral oils obtained with the use of hydrogen catalytic processes, such as hydro-treating, hydrocracking, hydroisomerization, which allows the reconstruction of the structure of hydrocarbons separated from crude oil by fractional distillation. "Structure reconstruction" refers to aromatic hydrocarbons and n-paraffins, and the final products are isoparaffins with increased viscosity indexes and low solidification temperatures. this represents around 15% of world production [**L. 2**].

– Group IV are synthetic hydrocarbons – polyalphaolefins (PAO).

– In Group V, other synthetic oils, and vegetable oils (usually after structure modification) were included, except PAO. The most important in this group are ester oils, polyalkylglycols (PAG), silicone oils, and hydrocarbon oils (e.g., polybutene and alkylaromatic).

One should also mention the future technology of GTL (gas to liquid), the synthesis of "artificial" crude oil, where the raw material is used to produce synthesized gas (CO and H2), e.g., from methane. Methane is found, among others, in natural gas, whose resources are much larger than those of crude oil. The properties of GTL base oils – in comparison to the oils from Groups I and II and PAO – are presented in **Table 4**.

Table 3. **Division of base oils into groups according to API [L. 2]**
Tabela 3. Podział olejów bazowych na grupy wg API **[L. 2]**

Parameter	Mineral oils			Synthetic oils PAO
	Group I	Group II	Group III	Group IV
Viscosity index	95	95–100	120–130	123
Sulphur content [ppm m/m]	200-400	<20	<10	0
Content of PAH polycyclic aromatic hydrocarbons % m/m	>10	1-10	<1	0
Evaporation losses (Noack) % m/m	28	26–28	13–15	13

Note – **Group V** includes all base oils which do not belong to Groups I – IV, i.e. the remaining ones, except for PAO, synthetic oils, and vegetable oils (after modification). The most common in this group are ester oils, polyalkylglycols (PAG), silicone oils, and hydrocarbon oils (polybutene and alkylaromatic).

Table 4. **Comparison of GTL base oil properties with oils in Groups I and II and PAO [L. 1]**
Tabela 4. Porównanie właściwości olejów bazowych GTL z olejami grup I i II oraz PAO **[L. 1]**

Characteristic	Mineral (Group I)	Group II	PAO	GTL
Viscosity 100°C [cSt]	4.1	4.1	4.0	4.1
Viscosity index	99	104	120	136
Sulphur content [ppm]	2000	<20	0	0
Aromatic hydrocarbons content [%]	22	1–10	0	0

Table 5 shows approximate biodegradability values of various base oils. It shows that the biodegradability of vegetable oils is high, as expected, and low for mineral oils. In the group of synthetic oils, polyethylene glycol – 90 to 100% (PAG oils) and most ester oils are the most biodegradable. For example, some carboxylic acid esters achieve 100% biodegradability. In Group IV (according to API), biodegradability is average and the effect of viscosity is evident, i.e. PAO2 and PAO4 oils are biodegradable, and PAO6 and the more viscous ones are less biodegradable [**L. 3**].

Table 5.　Typical biodegradability values of selected operating fluids [L. 3]
Tabela 5.　Typowe wartości biodegradowalności wybranych cieczy eksploatacyjnych **[L. 3]**

Oil base type	Biodegradability, %
Mineral bases	15 ... 30
Vegetable oils	70 ... 100
PAO 4	60
PAO 6	10 ... 20
Polyethylene: **Polyethylene glycol** **Polyethylene glycol / propylene glycol (1:1)**	90 ... 100 10 ... 60
Fatty and neopentyl esters	20 ... 100
Adipic ester	>90
Phthalic ester	10 ... 75

Extensive literature and studies on the relationship between chemical structure and biodegradability (and other operational properties) of base oils from various groups (according to API) are presented in the dissertation **[L. 2]**. Important observations from these studies are given below:

– Some ester oils have a chemical structure that makes their rapid biodegradability possible, while others are hardly biodegradable; an example from **Table 5** – fatty acid esters and neopentyls – the biodegradability range is from 20 to 100%; the attribute of quickly biodegradable ester oils are ester bonds in the structure of compounds forming the oil composition available for microorganisms (bacteria and enzymes). Ester degradation begins with an ester bond hydrolysis reaction catalysed by microbial hydrolases, which allows subsequent decomposition steps. The availability of ester bonds for microorganisms is different for different chemical compounds that make up the oil composition, because it depends on their characteristic structure, hence the wide range of the biodegradation index, e.g., fatty acid esters – from 20 to 100%;

– In the group of hydrocarbon oils, both mineral and synthetic ones (e.g., PAO), their lower susceptibility to degradation than in the group of ester oils depends mainly on the initial mechanism of their biodegradation; in ester oils, due to hydrolysis, smaller "structures" are created, which are more easily accessible to microorganisms which trigger the further stages of decomposition.

– The first phase of metabolic changes in hydrocarbon oils occurs mainly at the ends of the paraffin, naphthenic and aromatic hydrocarbon chains, which does not cause a significant molar change in the resulting metabolites. Therefore, it is the size of the oil-forming hydrocarbons that determines the further progress of decomposition processes. Oils with lower viscosity classes, i.e. smaller particle sizes, characterized by a high proportion of paraffin structures and a very high viscosity index (such as oils from Group III as well as PAO4) may undergo preliminary biodegradation even above 50% **[L. 2]**. It can be assumed that, along with the increase in the share of paraffinic carbon in the carbon structure of the average oil molecule, there is an increase in the susceptibility to biodegrade; therefore, unconventional oils from Group III with a high viscosity index will be characterized by greater biodegradability compared to mineral oils (from Group I), in which cyclic naphthenic and aromatic hydrocarbons are responsible for the lower viscosity index and lower biodegradability.

– Oils from the polyalkyl glycol group (PAG) are more biodegradable than hydrocarbon oils if there are alcohol groups -OH or ester groups at the end of the PAG chain (see **Table 5** – polyethylene glycol (OH-CH_2-CH_2-OH) – 90 to 100% biodegradability); this note applies to oils with the viscosity of 30 to 250 mm^2/s **[L. 2]**.

NON-TOXICITY AND BIODEGRADABILITY REQUIRED COMBINED

Modern ecological requirements force the replacement of oil derivative lubricants with biodegradable and / or non-toxic products, especially when there is a risk of their getting into the natural environment. This is very important in the case of open lubrication systems, where soil, groundwater, and surface water may be contaminated.

The development of new technologies is based on non-toxic ingredients. Special requirements have been formulated for lubricants for the food and pharmaceutical industries (including cosmetics). It is absolutely essential for them both to meet the requirements of non-toxicity in the event of incidental contact in the production process

with food (pharmaceuticals) and not to pose a threat to the ecosystem after the loss of operational properties. The requirement of non-toxicity and biodegradation also applies to lubricants operated in conditions where their penetration into soil and water is inevitable (agriculture, forestry).

In addition to having basic lubricating properties, lubricants for the food industry must be non-toxic, physiologically natural, and should not change the organoleptic properties of food (appearance, smell, taste). According to the international USDA nomenclature (United States Department of Agriculture), these lubricants are divided into the following three categories:
– H1 which includes lubricating materials for accidental, or incidental contact with food items;
– H2 which consists of lubricants for the food industry, but in conditions preventing any contact with food; and,
– H3 which applies to cleaning and corrosion protection agents for machine parts being in direct contact with food.

In the food industry, white mineral oils are most often used as lubricating oils; however, in more demanding operating conditions, synthetic oils and lubricants are also used. The requirements for the food and pharmaceutical industry are met, among others, by synthetic oils, such as PAO, polyalphaolefins, ester, polyglycol, and silicone, and based on natural and synthetic esters [L. 4].

The design process for lubricant grease obtained by thickening the base oil with various substances is complex. The composition is supplemented with functional additives for various purposes. There is about 70% of the base oil, and the remaining ones are a thickener and additives. Therefore, there are three components, i.e. the base oil, the thickener, and the improvers, for which ecological requirements should be formulated.

An important element in the selection of a base oil for a lubricant grease for the food industry is non-toxicity and biodegradability. In hydrocarbon oils, the primarily toxic ones are polycyclic aromatic hydrocarbons (PAHs) with carcinogenic and mutagenic effects (benzene is the main building block in these compounds). PAHs with more than three benzene rings in the molecule, e.g., benzo (a) pyrene – B (A) P, contribute to the strongest carcinogenic effect. White oils are thoroughly purified paraffin oils. They are non-toxic, because they do not contain aromatic hydrocarbons. They also do not contain synthetic oil bases from Groups IV and V according to API. When assessing the level of biodegradation of base oils for the production of lubricants for the food industry, it was assumed that the level of biological degradation within 28 days should be equal to or higher than 40%. If the oil meets this condition and is included in the FDA (Food and Drug Administration) inventory of raw materials for the production of lubricants for the food

industry, it can be used as the base oil for the production of lubricant grease.

As thickeners, according to the PN-EN1672-2: 1999 machinery standard [L. 4, 5], the acceptable ones are simple and complex calcium soaps, complex aluminium, lithium soaps, inorganic siliceous, and siliceous aluminium Si-Al thickeners. Simple soaps of other metals (Al, Na, Ba, and Li), inorganic thickeners or graphite, polymethanes, and metallic fillers (Ag, Cu, Mo, Zn) are unacceptable.

As improvers, lead, antimony and other heavy metals must not be present in any category of "food" lubricants. At the H1 level, calcium, phosphorus, silicon, and sulphur are acceptable. At the H2 level, barium, magnesium, molybdenum, sodium, and heavy metals are not allowed.

A comprehensive methodology for designing ecological lubricant greases for the food and pharmaceutical industry (including cosmetics) is presented in [L. 4]. That work also presented extensive research concerning the stage of developing new (Polish) ecological lubricants and at the stage of implementation operation.

OILS FOR NEW, ECOLOGICAL REFRIGERATION AGENTS

For over twenty years, there has been a worldwide process of exchanging refrigerants such as "Freons", i.e. chlorine, bromine and fluorine compounds from the CFC (chloro-fluoro-carbons) and HCFC (Hydro-chloro-fluoro-carbons) groups for more environmentally friendly cooling agents. The chlorine contained in these compounds destroys the ozone contained in the stratosphere, causing the ozone holes, through which more ultraviolet UVB radiation has reached the Earth's surface, adversely affecting plant, animal, and human organisms. Chlorine (i.e. CFC and HCFC) groups were abandoned first, fluoride (HFC hydro-fluoro-carbons) agents with the ozone depletion potential of ODP = 0 (ozone depletion potential) were left for a transitional period. However, their main environmental disadvantage is the impact on the intensification of the greenhouse effect expressed sometimes with significant values of the GWP index (global warming potential, for carbon dioxide GWP = 1).

The introduction of new, more ecological refrigerants currently means a relatively low value of the GWP indicator, at ODP = 0. There is a phase-out program for HFC (fluorine) agents, and new combinations of agents are created in the form of azeotropic or zeotropic mixtures. Each new refrigerant requires the selection of a suitable compressor oil.

There are natural agents with ODP = 0 and low GWPs like CO_2 with GWP = 1, NH_3 with GWP = 0, hydrocarbons also with GWP = 0; however, they cause

some problems with the safety of the installation. Hydrocarbons and ammonia, for example, are flammable.

A compressor oil should not only have typical lubrication functions, but it should also properly "interact" with the refrigerant. This additional specific requirement is the demand for the solubility of the lubricating oil in the refrigerant over the entire pressure range and operating temperatures. Why is this so important? This is due to the pumping action of the piston rings in the compressor when some, initially small, amount of lubricating oil is pumped to the refrigeration part of the installation together with the refrigerant. The process of wear during operation means that the amount of oil pump is gradually increased. After the initial "saturation" of the installation with oil, the stream of oil "entrained" from the compressor is balanced with its stream returning to it from the refrigeration part (through the oil separator). A properly designed refrigeration system should ensure that this condition is established at the lowest oil content in the refrigerant in the evaporator (oil dissolved in the refrigerant worsens its thermodynamic properties).

This phenomenon of oil dissolving in the refrigerant is very beneficial, because it prevents oil from accumulating in the heat exchangers (the evaporator and condenser), which facilitates a long-term operation of the installation. If oil layers were deposited on the walls of the exchangers, they would worsen the heat transfer and cause a decrease in efficiency, until the operation of the refrigeration system stopped working. The solubility for many combinations of "refrigerant – compressor oil" is partial (**Figures 3** and **4**).
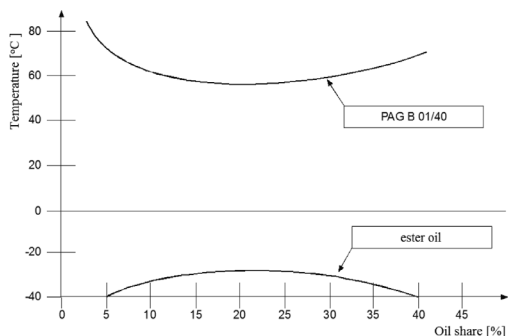
Fig. 3. Solubility limits of exemplary polyglycol (PAG) and ester (POE) oil with R134a [L. 6]

Rys. 3. Granice rozpuszczalności przykładowego oleju poliglikolowego (PAG) i estrowego (POE) z czynnikiem R134a **[L. 6]**

Given below are the examples of oil – refrigerant "solubility": selected cases of agents operating in transport refrigeration units. Currently used factors are mainly – R134a (aggregates in refrigerated delivery vans and semitrailers used in transport conditions from 0°C to +12°C), R404A, and R452A (the main replacement for R404A) meeting the requirements of Regulation 517/2014 – low- and medium-temperature refrigeration systems **[L. 7, 8]**.
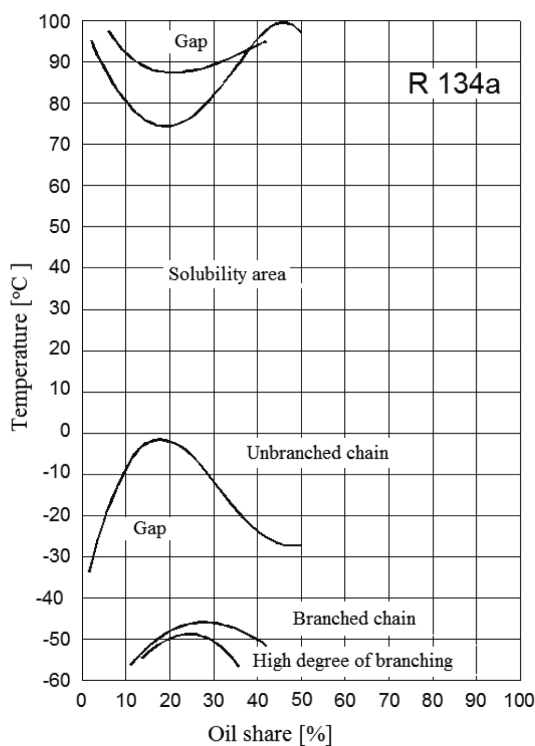
Fig. 4. The influence of branching of the acid group in the structure of polyester oil with ISO viscosity 46 on the size of solubility gaps with R134a factor [L. 6]

Rys. 4. Wpływ na rozgałęzienia grupy kwasowej w strukturze oleju poliestrowego o lepkości ISO 46 na wielkość luk rozpuszczalności z czynnikiem R134a **[L. 6]**

Figure 3 presents the limits of solubility of polyalkylglycol (PAG) and ester (POE) oil with R134a. The combination of R134a with polyester oil (POE) seems better. The solubility of polyester oils can be significantly improved during the production of POE base oil, with the important thing being the degree of branching of the acid group in the structure of the lubricant. The high degree of POE branching "shifts" the solubility area in R134a in the favourable direction of low temperatures (**Fig. 4**).

It should be mentioned that the "refrigerant – lubricating oil" interactions also occurs in the lubricating part of the compressor. The refrigerant mixing with the compressor oil in various concentrations, depending on the operating conditions, deteriorates its lubricating properties. These phenomena are researched by the team from the Division of Food Processing and Food Transport Poznan University of Technology **[L. 9–12]**.

CONCLUSIONS

Generally, it can be said that the basis for "fighting" global warming is reducing the emission of CO_2 and other greenhouse gases (such as Freon, methane, etc.) into the atmosphere. Air cleanliness is improved by "clean" combustion technologies, environmentally

friendly fuels, and industrial and automotive exhaust gas treatment.

Regarding the problems characterized in this article, the following comments can be made:

1. Due to their lower viscosity at operating temperature, a new generation environmentally friendly oils reduce frictional resistance and thus reduce fuel consumption by the engine. This is the correct tendency, but doubts can only be raised by whether sufficiently effective friction modifiers "strengthening" the boundary layers have already been developed.

   New "Low SAPS" oils should slightly contribute to improving the cleanliness of engine exhaust gases, which is a favourable solution from an ecological point of view.

2. A lot has been achieved in the area of assessing and shaping the biodegradability of lubricating oils, or actually the base oils used in their production:

   – Some carboxylic acid esters and some polyalphagglycols are most susceptible to biodegradation (the index reaches 100%).
   – Hydrocarbon oils are moderately biodegradable, greater in Classes II and III according to API, the least in Class I of mineral oils. For PAO synthetic hydrocarbons, the impact of viscosity is observed (the lower the viscosity, the greater the biodegradability).

3. It is recognized that oil bases without aromatic hydrocarbons are non-toxic, i.e. white oils (very pure paraffin oils), synthetic hydrocarbons (isoparaffins), vegetable and animal oils, and ester and polyalphagglycol oils.

4. The development of oils for refrigeration compressors that are compatible with new ecological refrigerants (with ozone destruction index ODP = 0 and the lowest possible GWP) is a big challenge. The relatively best "polyester" in this section are polyester oils.

LITERATURE

1. Zwierzycki W.: Płyny eksploatacyjne do środków transportu drogowego. Charakterystyka funkcjonalna i ekologiczna. Wyd. Politechniki Poznańskiej, Poznań 2006.
2. Beran E.: Wpływ budowy chemicznej bazowych olejów smarowych na ich biodegradowalność i wybrane właściwości eksploatacyjne. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2008.
3. Gawrońska H., Górski W.: Biodegradowalne ciecze eksploatacyjne a środowisko. Paliwa, Oleje i Smary w Eksploatacji, 1999, nr 65, pp. 25–27.
4. Drabik J.: Ekologiczne smary plastyczne w eksploatacji maszyn. Projektowanie, metodyka oceny oraz problemy stosowania. Wyd. ITeE – PIB, Radom 2015.
5. PN-EN 1672-2:1999 Maszyny dla przemysłu spożywczego. Pojęcia podstawowe i wymagania z zakresu higieny.
6. Bonca Z. (red.): Nowe czynniki chłodnicze i nośniki ciepła. IPPU MASTA Gdańsk 2004.
7. Rozporządzenie Parlamentu Europejskiego i Rady nr 517/2014 w sprawie fluorowanych gazów cieplarnianych (i uchylenia rozporządzenia WE nr 842/2006).
8. Bitzer – Czynniki chłodnicze. Raport, Wyd. 19.
9. Górny K., Tyczewski P., Zwierzycki W.: Wear tests of sliding surfaces in the environment of mixtures of lubricating oils and refrigerants. Advances in Science and Technology – Research Journal, Vol. 8, No. 21, March 2014, pp. 49–53.
10. Górny K., Stachowiak A., Tyczewski P., Zwierzycki W.: Lubricity evaluation of oil-refrigerant mixtures with R134a and R290, International Journal of Refrigeration 69, 2016, pp. 261–271.
11. Górny K., Stachowiak A., Tyczewski P., Zwierzycki W.: Lubricity of selected oils in mixtures with the refrigerants R452A, R404A, and R600a, Tribology International 134, 2019, pp. 50–59.
12. Tyczewski P.: Problemy modelowania eksploatacyjnych stanów węzłów tarcia tłokowych sprężarek chłodniczych. Biblioteka Budowy i Eksploatacji Maszyn, Wyd. ITeE – PIB w Radomiu, Poznań – Radom 2019.