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Modern Automotive Gear Oils - Classification, Characteristics, Market Analysis, and Some Aspects of Lubrication

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1. Introduction

1.1 Classification of automotive gear oils

Modern gear oils can be divided into three main groups (Chwaja, Marko, 2010):

- manual transmission fluids (MTF) intended for lubrication of automotive manual gear boxes, transaxles, axles, and differentials,
- automatic transmission fluids (ATF) which lubricate: step-type automatic transmissions (AT), double clutch transmissions (DCT), and continuously variable transmissions (CVT),
- oils for lubrication of gears in off-road vehicles (e.g. tractors).

In European automotive market manual transmission fluids (MTF) are predominant with over 75% of the market compared to only 25% of ATFs. However, in USA and Japan the situation is reversed: ATFs take respectively 92% and 75% of the market, leaving 8% and 25% to MTFs.

This chapter concerns solely the first group of oils, i.e. manual transmission fluids (MTF); for simplification, the equivalent name “automotive gear oils” will be used throughout the text.

There are two different classifications of automotive gear oils.

The first one specifies lubricant service designations or the so-called performance levels of automotive gear oils. It has been provided by the American Petroleum Institute (API) in the API Publication 1560, 7th Edition, published in July, 1995. The API classification divides automotive gear oils into 7 performance levels. Four performance levels are in current use, three are not. The reason for the performance level not to be in current use results from the unavailability of test equipment and does not mean that such products have been withdrawn from the market.

The API classification has been described in Tab. 1 (API designations in current use) and Tab. 2 (designations not in current use).

Apart from the designations from Tabs. 1 and 2, there is also a class denoted as API GL-5(LS) or GL-5+. Gear oils that meet the requirements of this class contain special friction modifiers (FM) preventing from the *stick-slip* occurrence under conditions of limited slip (LS). As such, GL-5(LS) oils are intended for lubrication of limited slip differentials.

To reduce the number of various gear oils in the market and in turn simplify oil selection, many lubricant manufacturers implement more universal (multi grade) gear oils. In this group gear oils denoted as API GL-4/GL-5 or GL-4+ predominate.

API service designation (performance level)	Application and short characterisation
GL-1	Manual transmissions operating under such mild conditions that straight petroleum or refined petroleum oil may be used satisfactorily. Not satisfactory for many passenger car manual transmissions. GL-1 oils may contain oxidation and rust inhibitors, defoamers, and pour depressants. Friction modifiers (FM) and extreme pressure (EP) additives shall not be used.
GL-4	Axles with spiral bevel gears operating under moderate to severe conditions of speed and load or axles with hypoid gears operating under moderate speeds and loads. GL-4 oils may be used in selected manual transmission and transaxle applications where MT-1 lubricants are unsuitable. GL-4 oils contain up to 4% of extreme pressure (EP) additives.
GL-5	Gears, particularly hypoid gears, in axles operating under various combinations of high-speed/shock load and low-speed/high-torque conditions. GL-5 oils contain up to 6.5% of extreme pressure (EP) additives.
MT-1	Nonsynchronised manual transmissions used in buses and heavy-duty trucks. API MT-1 does not address the performance requirements of synchronized transmissions and transaxles in passenger cars and heavy-duty applications. API MT-1 oils provide protection against the combination of thermal degradation, component wear, and oil-seal deterioration, which is not provided by lubricants in current use meeting only the requirements of API GL-1, 4, or 5.

Table 1. API service designations of automotive gear oils in current use, according to API Publication 1560

The second classification is the SAE viscosity classification according to SAE J306:2005 standard. It divides automotive gear oils into 11 grades basing on their rheological properties - tab. 3.

For lubrication of automotive gears the most often multiviscosity-grade oils are employed, e.g. SAE 80W-90. This designation means that such an oil meets the requirements of both a low-temperature (SAE 80W) and a high-temperature grade (SAE 90).

1.2 Characteristics of automotive gear oils on the base of the „market analysis”

The authors have performed a comprehensive „market analysis” of the automotive gear oils. The analysis was related to a search for commercial automotive gear oils offered (mainly in the European market) by the most recognised lubricant manufacturers, including Polish companies. On the base of the up-to-date information presented on the webpages a database has been collected including the manufacturer name, trade name of the oil, API GL performance level, SAE viscosity grade, kind of the base oil, application, fulfilled

API service designation (performance level)	Application and short characterisation
GL-2	Automotive worm-gear axles operating under such conditions of load, temperature, and sliding velocities that lubricants satisfactory for API GL-1 service will not suffice. GL-2 oils contain anti-wear or film-strength improvers specifically designed to protect worm gears.
GL-3	Manual transmissions operating under moderate to severe conditions and spiral-bevel axles operating under mild to moderate conditions of speed and load. GL-3 oils provide load-carrying capacities exceeding those satisfying API GL-1 but below the requirements of API GL-4 oils. GL-3 oils are not intended for axles with hypoid gears. Contain up to about 3% of antiwear (AW) additives.
GL-6	Hypoid gears designed with a very high pinion offset. EP properties typically better than of GL-5 oils. GL-6 oils contain up to 10% of extreme pressure (EP) additives.

Table 2. API service designations of automotive gear oils not in current use, according to API Publication 1560

SAE viscosity grade	Maximum temperature for viscosity of 150 000 cP, °C	Kinematic viscosity at 100°C, cSt (mm ² /s) Minimum	Kinematic viscosity at 100°C, cSt (mm ² /s) Maximum
70W	-55	4.1	-
75W	-40	4.1	-
80W	-26	7.0	-
85W	-12	11.0	-
80	-	7.0	<11.0
85	-	11.0	<13.5
90	-	13.5	<18.5
110	-	18.5	<24.0
140	-	24.0	<32.5
190	-	32.5	<41.0
250	-	41.0	-

Table 3. Automotive gear oil viscosity classification, according to SAE J306:2005

requirements, certificates achieved, recommendations, etc. The collected database includes information on over 330 automotive gear oils. The offer of the following 35 lubricant manufacturers (given in an alphabetical order) has been analysed: Agip (Eni Group), Amsoil, Aral, BP Lubricants, Carlube, Castrol, ChevronTexaco, Comma, Exxon Mobil Corporation, FL Selenia Poland, Fuchs Oil Corporation, Gulf Oil International, Kager Products, Kroon-Oil, Liqui Moly, Lotos Oil S.A., Lukoil-Permnefteorgsintez, Magna Industrial Co. Ltd, Motul, Naftochem,

Neste Oil, Oel Brack A.G., Orlen Oil, PPHTU Adwa, Quaker State, Red Line Synthetic Oil Corp., Royal Dutch Shell Group, Silesia Oil, Specol Lubricants, Statoil, Sunoco, Tedex Production, Total SA, Valvoline (Ashland Inc.), Zakl. Chem. Organika S.A. It is worth to add that among the analysed offers the widest offer of automotive gear oils proposes Exxon Mobil, followed by the offer of ChevronTexaco, Orlen Oil (Poland), Fuchs, Aral, Gulf, Neste Oil, Kroon-Oil, Agip, and Castrol.

The database enabled the authors to identify the most often used and popular API GL performance levels of the automotive gear oils, and their percentage in the general offer - Fig. 1.

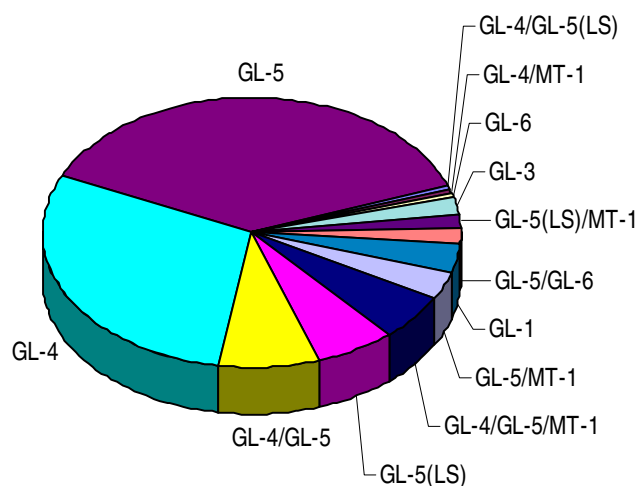


Fig. 1. The percentage of gear oils of particular API GL performance levels (including universal - multi grade oils) in the general offer of automotive gear oils in the market

From Fig. 1 it is apparent that automotive gear oils denoted as API GL-5 and GL-4 definitely predominate. There is also a considerable offer of API GL-5(LS) gear oils, known also as GL-5+ oils.

As concerns universal (multi grade) gear oils, for some time they have been constituting a substantial part of the market. In this group oils denoted as API GL-4/GL-5 or GL-4+, as well as API GL-4/GL-5/MT-1 predominate.

Regarding API MT-1, the authors have not found any products labelled with only this designation. It is used complementarily with other designations of the universal oils, e.g. API GL-4/GL-5/MT-1.

The designations API GL-2 and GL-6 may be treated as obsolete. There are very few manufacturers of GL-6 gear oils. The GL-2 designation is practically no longer used at present; the lubricant manufacturers tend to use the ISO VG classification instead to identify oils for worm gears.

The next step of the analysis of the database was to identify the most often used and popular SAE viscosity grades of the automotive gear oils, and their percentage in the general offer - Fig. 2.

From Fig. 2 it can be seen that multiviscosity-grade oils definitely predominate. In this group SAE 80W-90, 75W-90 and 85W-140 oils constitute the most substantial part.

As concerns single-grade oils, the biggest segment of the market belongs to SAE 80W oils.

The last step of the analysis of the database was to identify the percentage of the types of base oils used for formulation of modern automotive gear oils - Fig. 3.

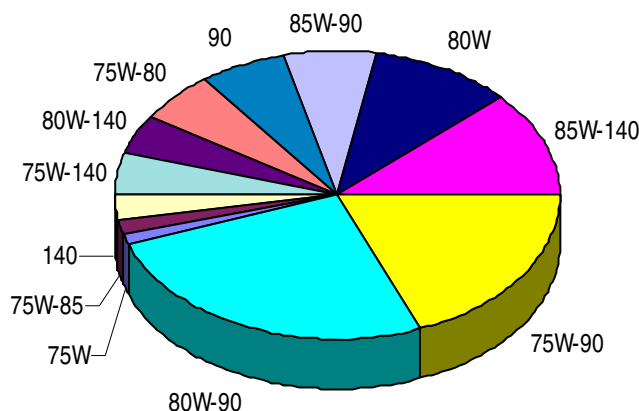


Fig. 2. The percentage of gear oils of particular SAE viscosity grades (including multiviscosity-grade oils) in the general offer of automotive gear oils in the market; only those grades of which percentage was at least 1% are considered

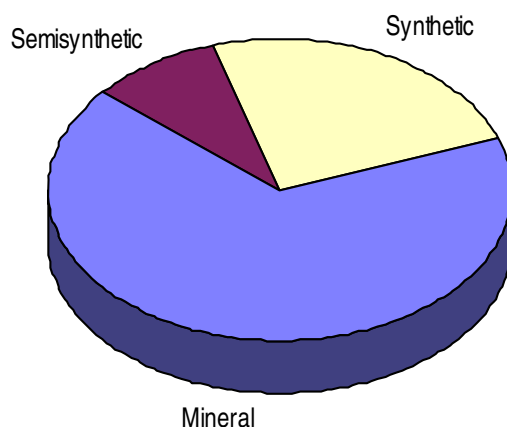


Fig. 3. The percentage of the types of base oils used for formulation of automotive gear oils

From Fig. 3 it is apparent that mineral, automotive gear oils still definitely predominate in the market, followed by synthetic oils. The smallest segment of the market is occupied by gear oils with semisynthetic bases. It is interesting that some lubricant manufacturers, e.g. American firms like Amsoil and Red Line Synthetic Oil Corp. use exclusively synthetic base oils to formulate automotive gear oils.

1.3 Some aspects of degradation of automotive gear oils

During exploitation of lubricating oils in machines significant changes of oil physico-chemical properties take part due to ageing. The ageing rate depends on the working temperature, load, speed and environment. They lead to oil degradation which causes deterioration of oil performance and may even result in a necessity for the oil change.

The following processes in the bulk of the aged oil can be identified: oxidation and polymerisation of hydrocarbons, production of acids and resins, decrease in the content of additives due to precipitation of their oxidised products, mechanical destruction of viscosity improvers leading to a drop in the viscosity index, rise in the concentration of solid contaminants coming from mating components (particles of steel, bronze, metal oxides, rubber), increase in the concentration of contaminants coming from the environment (dust,

soil, water), and contamination with products of bacteria activity (Baczewski & Hebda, 1991/92), (Luksa, 1990). The technical systems like transmissions of road vehicles are especially exposed to an adverse influence of the environment.

1.4 Example of gear oil degradation in a car

The authors investigated physico-chemical changes in the commercial API GL-3 gear oil lubricating the transmission of a small car at the mileage of 50 000 km. The following measures were determined: kinematic viscosity (ν) measured at 40 and 100°C, viscosity index (VI), total acid number (TAN), contamination with water (H₂O), and contamination with solid particles (SP). The comparison of the fresh and used oil is presented in Tab. 4.


	State of gear oil	ν_{40} mm s ⁻²	ν_{100} mm s ⁻²	VI	TAN mg KOH g ⁻¹	H ₂ O ppm	SP vol. %
	Fresh	164	15	90	0.8	23	≈0.0
	Used	126	12	85	1.1	129	0.2

Table 4. Changes of measures of physico-chemical properties of the API GL-3 gear oil due to deterioration during lubrication of the car transmission

As could be expected, in the used oil at the mileage of 50 000 km a significant increase in the content of solid particles and water was identified; TAN rose as well. Both kinematic viscosity and viscosity index significantly decreased due to mechanical degradation of polymer chains in the viscosity improvers and/or hydrocarbon chains in the oil at the contact zone of mating components (gears, rolling bearings, synchronizers). These adverse processes have an influence on wear of components of automotive transmissions.

1.5 Wear of transmissions components - gears and rolling bearings

One of the dominating forms of wear of toothed gears is scuffing. Scuffing is a form of wear typical of highly-loaded surfaces working at high relative speeds. Another form of wear is rolling contact fatigue (pitting). Pitting is a form of wear typical of highly-loaded surfaces working at a sliding-rolling and rolling contact, e.g. such components in transmissions like toothed gears and rolling bearings. It is caused by the cyclic contact stress, which leads to cracks initiation. The lubricant is pressed into the cracks at a very high pressure (elastohydrodynamic lubrication), making them propagate. Finally, cyclic stress results in breaking a piece of material off the surface (Pytko & Szczerek, 1993), (Lawrowski, 2008). The mentioned forms of wear are shown in Fig. 4.

The resistance to scuffing and pitting depends on many various factors. They are: material properties, surface machining, geometry of the tribosystem, working conditions, as well as physico-chemical properties of the lubricant which significantly change due to ageing. Although an effect of the aged oil degradation on its performance has been described in the literature (Yamada et al., 1993), (Hohn et al., 2001), few data concern differentiation between behaviour of automotive gear oils having different API GL performance levels, particularly in the aspect of the oil-surface interactions.

In the further part of this chapter the authors compare two different automotive gear oils of different chemistry and performance levels - API GL-3 and GL-5. The aim is to find an effect of their ageing on deterioration of their properties, and in turn on scuffing and pitting prevention. To simulate oil deterioration taking part during exploitation of machines (e.g. cars), laboratory ageing of the oils was performed.

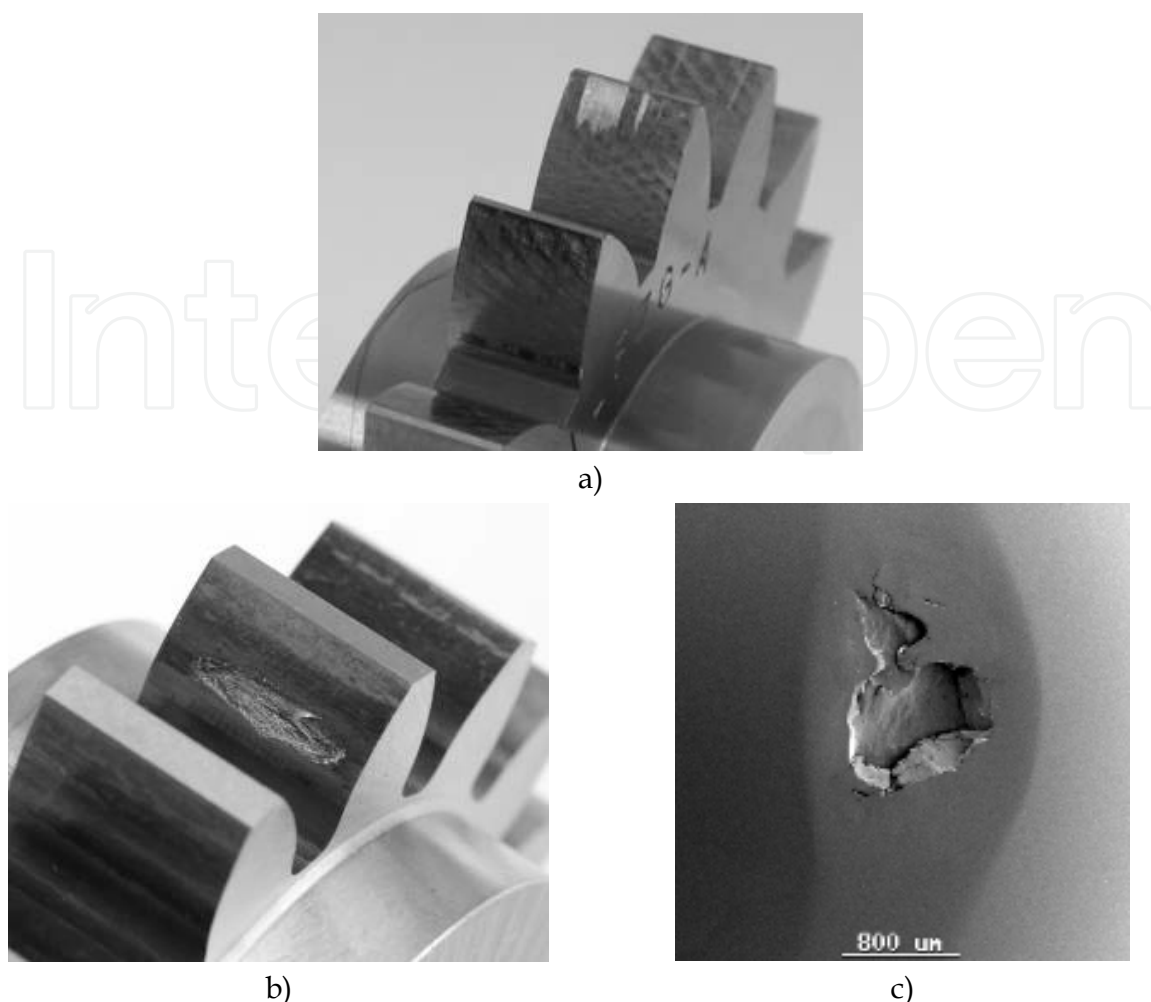


Fig. 4. Most dangerous forms of wear of transmission components: a) scuffing of a gear, b) pitting of a gear, c) pitting of a bearing ball

2. Research equipment

2.1 Scuffing tests

The scuffing tests were performed using a four-ball testing machine, denoted as T-02, designed and manufactured by ITeE-PIB - Fig. 5.

Test specimens were bearing balls made of chrome alloy bearing steel, with diameter of 12.7 mm. Surface roughness was $R_a = 0.032 \mu\text{m}$ and hardness between 60 and 65 HRC. The sliding four-ball tribosystem and some its important dimensions are shown in Fig. 6.

The tribosystem consists of the three stationary balls (2) fixed in the ball pot (4) and pressed at the required load P against the top ball (1). The top ball is fixed in the ball chuck (3) and rotates at the defined speed n . So, between the balls pure sliding appeared, which created conditions for investigation of scuffing. The contact zone of the balls was immersed in the tested oil.

After tribological experiments the worn surface of the bottom balls was analysed using a scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). EDS analyses were performed at the accelerating voltage of 15 kV. Prior to analyses test balls were washed for 5 mins in n-hexane using an ultrasonic washer.



Fig. 5. T-02 Four-ball testing machine

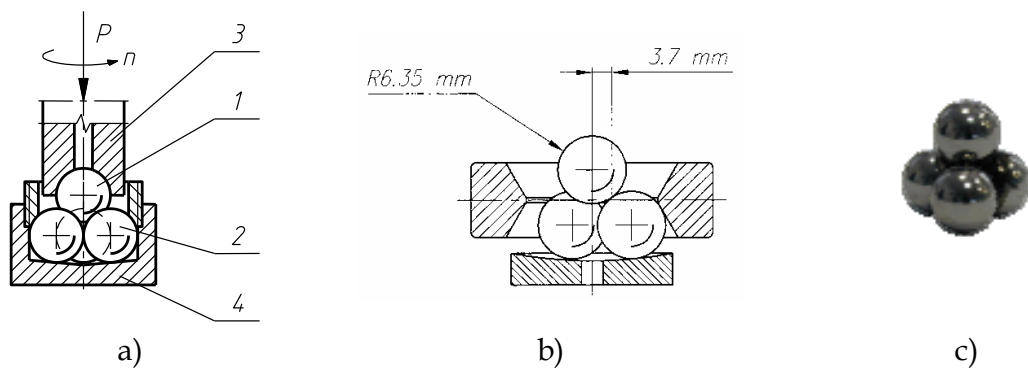


Fig. 6. Sliding four-ball tribosystem: a) drawing (1 - top ball, 2- stationary balls, 3 - ball chuck, 4 - ball pot), b) some important dimensions (wear track radius and ball radius), c) photograph

2.2 Pitting tests

The surface fatigue (pitting) tests were performed using a four-ball rolling tester, also designed and manufactured by ITeE-PIB, denoted as T-03 - Fig. 7.

The rolling four-ball tribosystem and some its important dimensions are shown in Fig. 8.

The tribosystem consists of the three bottom balls (2), free to rotate in the special race (3), and pressed at the required load P against the top ball (1). The bottom balls are driven by the top ball which is fixed in the ball chuck and rotates at the defined speed n . The contact zone of the balls was immersed in the tested oil.

The test balls were the same as used in the scuffing tests.

The T-03 tester was equipped with a vibration monitoring system. At the onset of the fatigue failure, when vibrations increased sharply, the system turned the rig down.



Fig. 7. T-03 Four-ball pitting tester

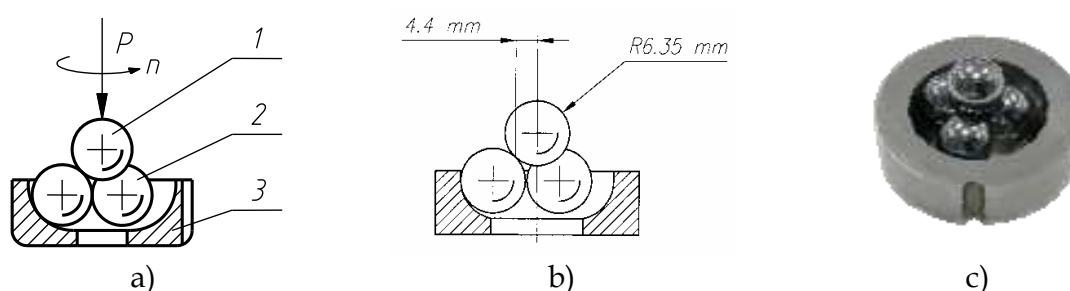


Fig. 8. Rolling four-ball tribosystem: a) drawing (1- top ball, 2 - bottom balls, 3 - race), b) some important dimensions (wear track radius and ball radius), c) photograph

The worn surface on the upper ball was analyzed using a scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and atomic force microscope (AFM). EDS analyses were performed at the accelerating voltage of 15 kV. Prior to analyses the test balls were washed for 5 mins in n-hexane using an ultrasonic washer.

3. Test methods

3.1 Scuffing tests

The properties of the tested lubricants related to prevention of scuffing are called the extreme pressure (EP) properties. In this work the extreme pressure properties of the tested oils are characterised by the so-called limiting pressure of seizure, denoted as p_{oz} . This measure is determined according to a test method developed in the Tribology Dept. of ITeE-PIB, having been presented in the literature (Piekoszewski et al., 2001), (Szczerek & Tuszynski, 2002), (Burakowski et al., 2004). A unique feature of the test method is related to continuously increasing load until scuffing and then seizure occurs, and analysis of scuffing propagation.

Test conditions are: load increase 409 N s^{-1} , initial load 0, maximum load about 7400 N, load increase time approximately 18 s (until the highest load is reached), rotational speed 500 rpm (sliding speed 0.19 m s^{-1}).

It is assumed that the test finishes when seizure takes place, i.e. at the time of exceeding 10 N m friction torque (this quantity is calculated on the base of measurements from a force transducer located at the distance 0.15 m from the test shaft axis). When seizure is not detected, the attaining of maximum load (about 7400 N) finishes the test.

For the tested lubricant the limiting pressure of seizure (p_{oz}) is calculated from the equation (1):

$$p_{oz} = 0.52 \frac{P_{oz}}{d^2} \quad (\text{N mm}^{-2}) \quad (1)$$

where:

P_{oz} - load that causes seizure (or maximum load when seizure does not appear), the so-called seizure load, N,

d - average wear scar diameter, from the measurements on the three bottom balls in the direction parallel and perpendicular to the "striations", mm.

The rounded value 0.52 results from the four-ball geometry.

So, the limiting pressure of seizure (p_{oz}) is a nominal pressure at the time of seizure (or at the end of a run) exerted on the wear scar area between two contacting balls. The bigger p_{oz} value, the better extreme pressure properties of the tested lubricant.

For each tested oil at least 3 runs were performed and the results averaged. The outliers were rejected on the base of Dixon test, for the significance level $\alpha = 5\%$.

3.2 Pitting tests

The resistance to pitting was characterised by the so-called 10% fatigue life, denoted as L_{10} . The procedure of its determination is presented in IP 300 standard. The value of L_{10} represents the life at which 10% of a large number of test balls, lubricated with the tested oil, would be expected to have failed.

Test conditions, adopted from IP 300, were as follows: rotational speed 1450 rpm, applied load 5886 N (600 kgf), run duration until pitting occurs, number of runs 24. Only those runs were accepted for which pitting occurred on the top ball (requirement of IP 300 standard). In each run the time to pitting failure occurrence was measured.

After test completion the 24 values (failure times) were plotted in the Weibull co-ordinates, i.e. the estimated cumulative percentage failed against the failure time. Then, a straight line was fitted to the points. From the line the 10% life L_{10} was read off.

4. Gear oils tested and their ageing

Two mineral, automotive gear oils of API GL-3 and GL-5 performance levels were used. The oils were formulated and delivered by the Central Petroleum Laboratory (CLN) in Warsaw, Poland.

In the GL-3 oil the commercial package of lubricating additives was based on zinc dialkyldithiophosphate (ZDDP), classified as antiwear (AW) and partly extreme pressure (EP) additives. GL-5 oil contained a package of EP additives based on organic sulfur-phosphorus (S-P) compounds.

The gear oils were contaminated with a special test dust (3 samples with various dust concentrations), distilled water (3 samples with various water concentrations) and were laboratory oxidised at 150°C (3 samples oxidised at various times) - Fig. 9.

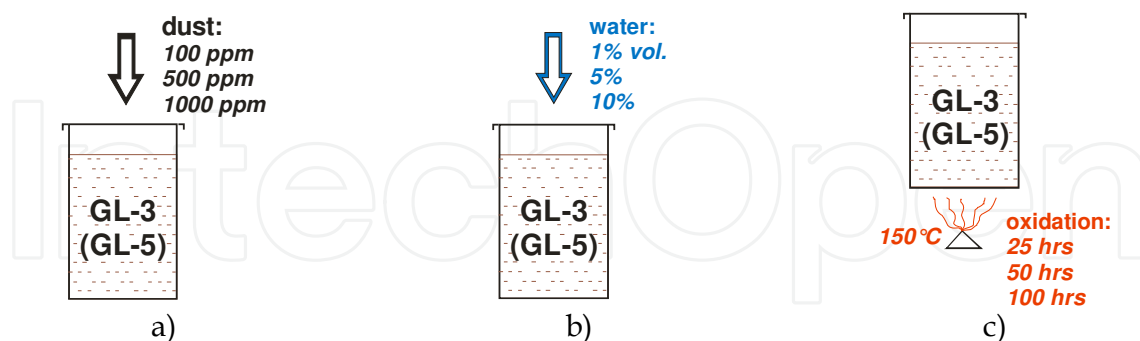


Fig. 9. Laboratory ageing of the API GL-3 and GL-5 gear oils: a) contamination with dust, b) contamination with water, c) oxidation

The main components of the test dust were SiO₂ grains (72.4% wt.) and Al₂O₃ (14.2% wt.). Maximum grain size did not exceed 0.08 μm. The granulometric composition of the test dust is given in Tab. 5.

Grain size, μm	Grain share, wt. %
0.08 - 0.04	9.1
0.04 - 0.02	19.5
0.02 - 0.01	14.7
0.01 - 0.005	19.7
0.005 - 0	37.0

Table 5. The granulometric composition of the test dust

Prior to pouring in the oils, the dust had been dried at 100°C for 6 hrs.

Oxidation of the oils was performed using a special oil bath at 150°C, without air flow, nor a catalyst. After oxidation for a given time, basic physico-chemical properties of the oil sample were determined, for example total acid number (TAN) and changes in infrared (IR) spectra, i.e. changes of areas under peaks characteristic for interesting chemical bonds in the lubricating additives. IR spectra were obtained using Fourier transform infrared microspectrophotometry (FTIRM). It is worth mentioning that TAN is the quantity (expressed in mg) of potassium hydroxide (KOH) needed to neutralize the acid in 1 g of oil. So, TAN indicates the amount of oxidation that the oil has undergone.

Before tribological tests each oil sample was stirred for 30 mins to equalise their bulk composition. In case of water contamination, oil-water emulsions were obtained.

5. Results and discussion - scuffing tests

5.1 Testing of dust-contaminated gear oils

Fig. 10 presents the values of the limiting pressure of seizure (p_{oz}) obtained for the gear oils of API GL-3 and GL-5 performance levels - pure and contaminated with the test dust at increasing concentrations. Interval bars reflecting the repeatability of the used test method have been added to the graphs.

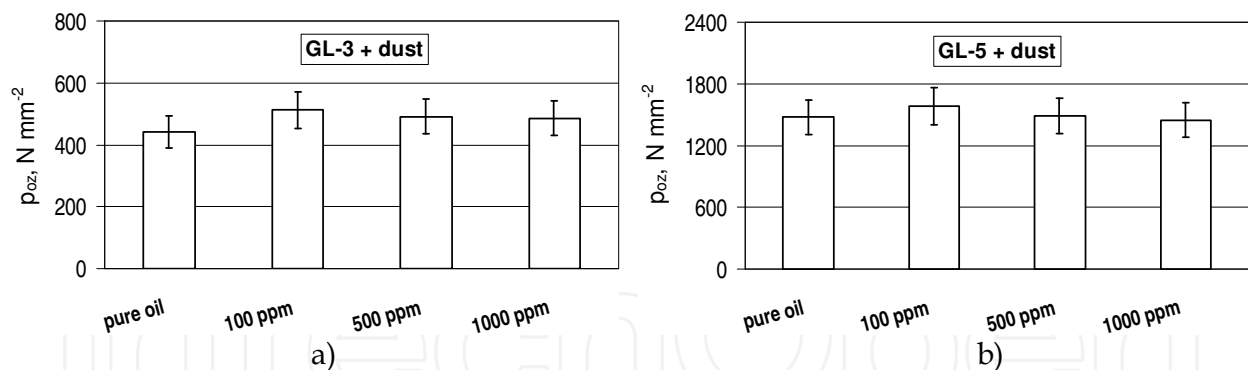


Fig. 10. Limiting pressure of seizure (p_{oz}) obtained for the gear oils - pure and contaminated with the test dust: a) GL-3 oil, b) GL-5 oil

From Fig. 10 it can be observed that the contamination of the oil with the dust practically does not affect the oil extreme pressure properties. The reason is that under severe friction conditions wear is so intensive that abrasive action of the dust does not matter.

It should also be noted that the GL-3 gear oil gives about threefold lower values of p_{oz} than GL-5. This much less efficiency of the GL-3 oil under severe friction conditions can be attributed to action of AW type lubricating additives (ZDDP) which are used in such oils. It is known that AW additives shows much poorer performance under severe conditions than EP ones (S-P compounds) which are used in GL-5 gear oils.

5.2 Testing of water-contaminated gear oils

Fig. 11 presents the values of the limiting pressure of seizure (p_{oz}) obtained for the gear oils of API GL-3 and GL-5 performance levels - pure and contaminated with water at increasing concentrations.

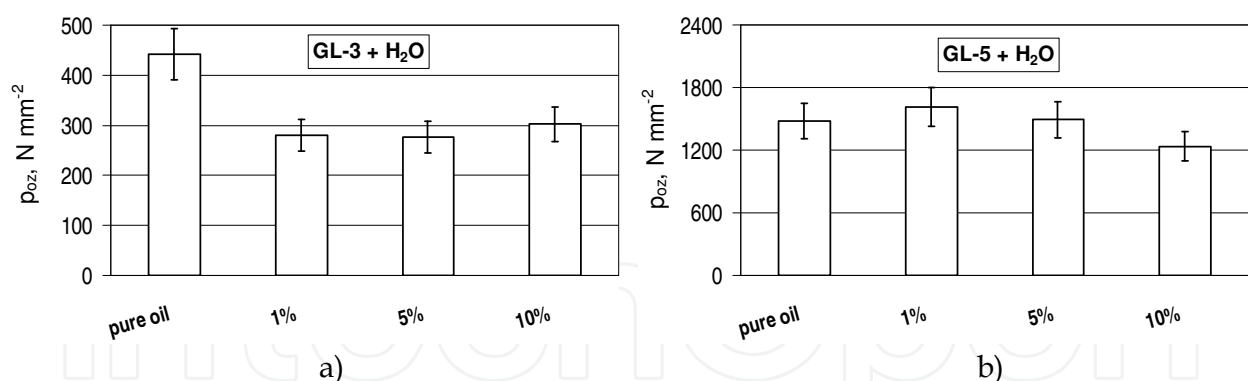


Fig. 11. Limiting pressure of seizure (p_{oz}) obtained for the gear oils - pure and contaminated with the water: a) GL-3 oil, b) GL-5 oil

The contamination of the GL-3 gear oil by water at the concentration of 1% has a significant, deleterious effect on the oil extreme pressure properties. Further increasing the water contamination has no effect on p_{oz} values. In comparison, GL-5 gear oil shows less "sensitivity" to water contamination - lower concentrations of water do not exert any effect and a drop in the extreme pressure properties is visible only when 10% of water is added to the oil.

For interpretation of the obtained results the wear scars on the bottom balls were analysed using SEM/EDS. SEM images of the worn surface and EDS maps for sulfur and phosphorus

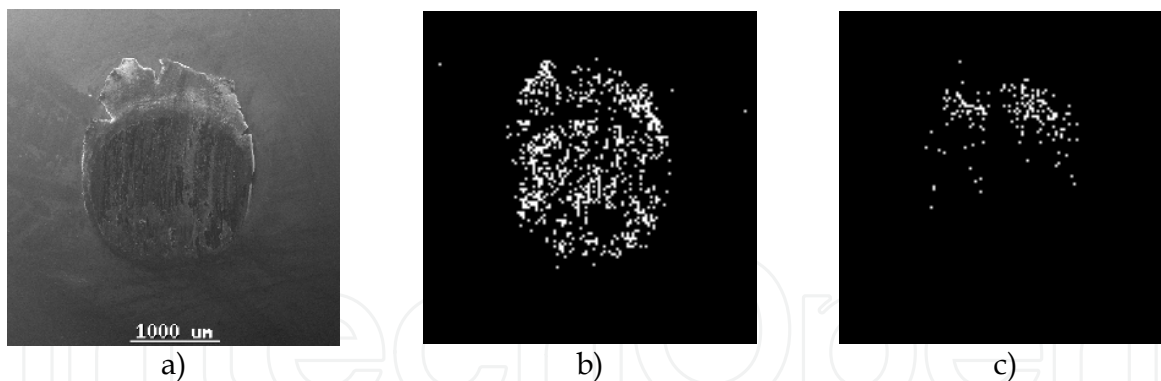


Fig. 12. Pure GL-5 oil - SEM image of the wear scar (a) and EDS maps for: b) sulfur, c) phosphorus

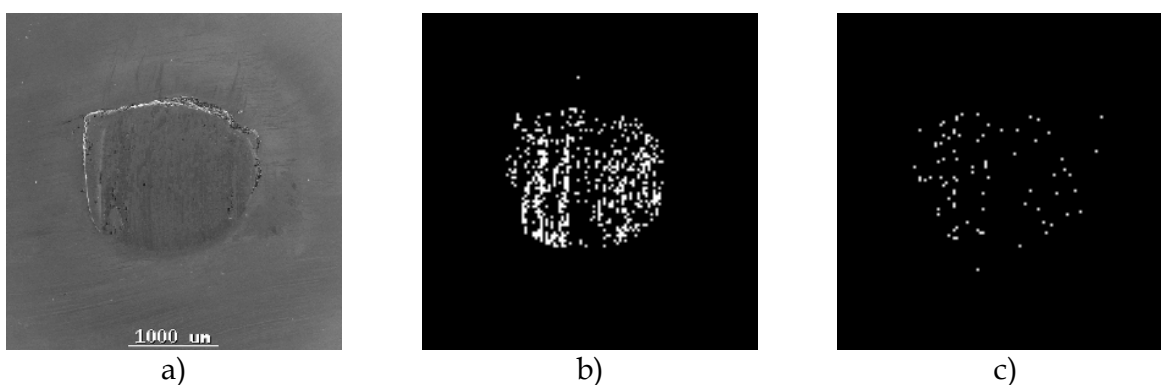


Fig. 13. GL-5 oil contaminated with water at 10% concentration - SEM image of the wear scar (a) and EDS maps for: b) sulfur, c) phosphorus

in the surface layer are shown in Figs. 12 and 13 for pure GL-5 oil and this oil contaminated with 10% water.

From Figs. 12 and 13 it is evident that water contamination affects the oil-surface interactions - one can observe a decrease in phosphorus content in the tribochemically modified surface layer of the wear scar.

The next step of analysis was to quantitatively examine the wear scar surface layer using EDS. Fig. 14 shows the weight concentration of sulfur and phosphorus in the surface layer for both the gear oils contaminated with water. The analyses were performed at three different points of the wear scar. The graphs present the average values of elemental concentration.

From Fig. 14 it is apparent that for GL-3 gear oil contaminated with 1% or more water a significant decrease in the concentration of sulfur and phosphorus takes place. For the contaminated GL-5 oil the concentration of sulfur remains practically constant but a drop in phosphorus concentration occurs in case of the highest rates of water contamination.

It is well known that prevention of scuffing is realised by sulfur and phosphorus compounds (Godfrey, 1968), (Forbes, 1970), (Stachowiak & Batchelor, 2001). These compounds are formed owing to physical and chemical adsorption, followed by chemical reactions of active lubricating additives with the steel surface. The sulfur and phosphorus compounds prevent creation of adhesive bonds or enable their shearing. A great role is played here particularly by inorganic compounds like FeS.

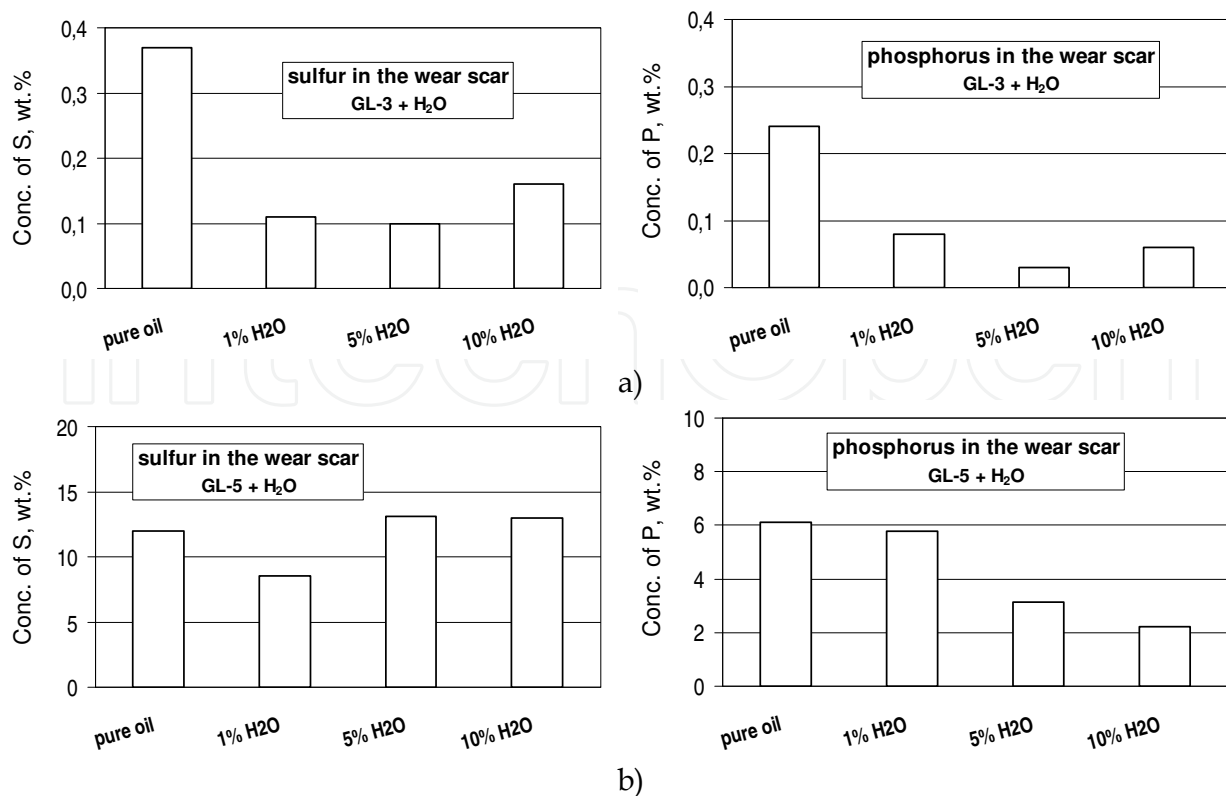


Fig. 14. Average concentration of sulfur and phosphorus in the surface layer of the wear scar for the gear oils contaminated with water: a) GL-3 oil, b) GL-5 oil

So, a significant decrease in the concentration of sulfur and phosphorus in the surface layer of the wear scar for GL-3 gear oil contaminated with 1% or more water is responsible for a dramatic deterioration of its extreme pressure properties (Fig. 11 a). For GL-5 gear oil poorer scuffing performance observed not sooner than for 10% water contamination (Fig. 11 b) can be attributed to a drop of phosphorous visible in case of the highest water content.

It should also be noted that for all samples of GL-5 gear oil incomparably higher concentration of sulfur and phosphorus can be found in the wear scar surface layer than for GL-3 oil. This is a result of more effective action of EP additives in GL-5 oils than AW additives in GL-3 oil, hence much better extreme pressure properties of the sooner.

5.3 Testing of oxidative degradation of gear oils

Fig. 15 presents the values of the limiting pressure of seizure (p_{oz}) obtained for the gear oils of API GL-3 and GL-5 performance levels - pure ("fresh") and oxidised for longer and longer time.

Fig. 15 shows that the oil oxidation exerts in general a positive effect on extreme pressure properties of both the tested gear oils. For GL-3 oil the values of p_{oz} increase with extending oxidation time. Only after the longest oxidation time a sudden drop in the oil performance occurs. For GL-5 oil its oxidation also exerts a rather positive effect on extreme pressure properties - a slow but sustained rise in the values of p_{oz} is observed with extending oxidation time. The only exception is GL-5 oil oxidised for 50 hrs, giving an unexpected, noticeable drop in its performance.

For interpretation of the obtained results the wear scars on the bottom balls were analysed using SEM/EDS. SEM images of the worn surface and EDS maps for sulfur and phosphorus

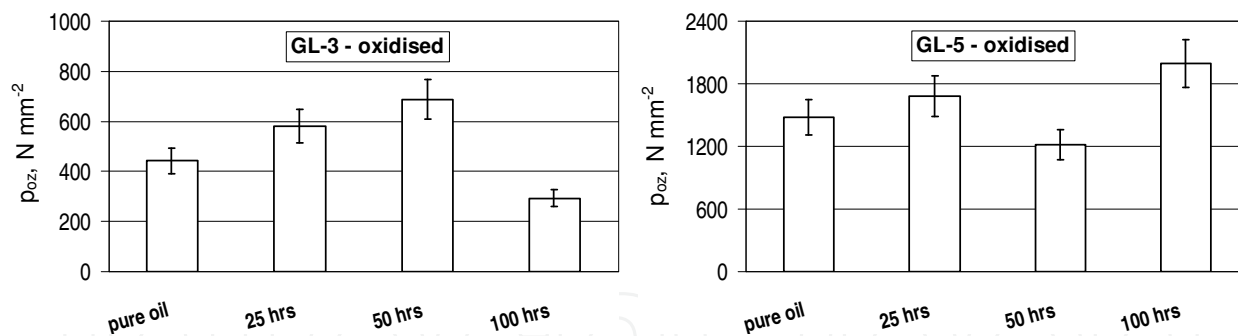


Fig. 15. Limiting pressure of seizure (p_{oz}) obtained for the pure and oxidised gear oils: a) GL-3 oil, b) GL-5 oil

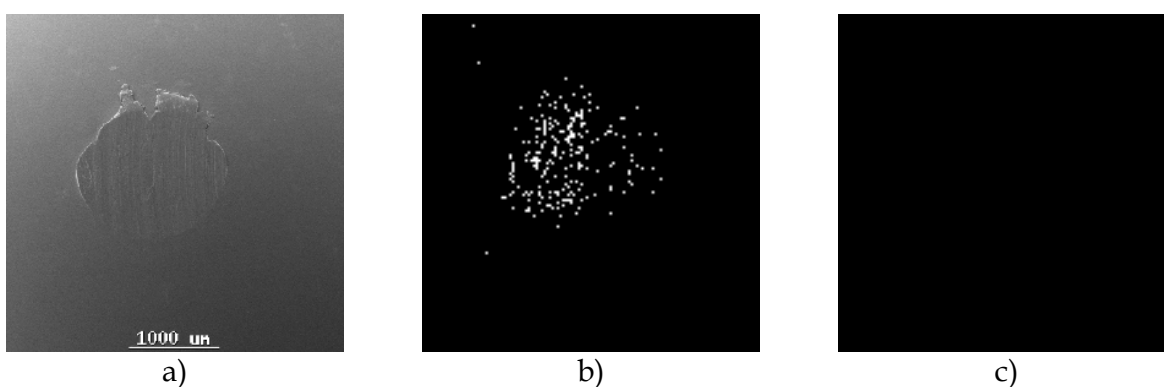


Fig. 16. GL-5 oil oxidised for 100 hrs - SEM image of the wear scar (a) and EDS maps for: b) sulfur, c) phosphorus

in the surface layer are shown in Fig. 16 for GL-5 oil oxidised for 100 hrs. Respective images obtained for the pure GL-5 oil have been shown earlier in Fig. 12.

From Figs. 12 and 16 it is evident that oil 100 hrs-long oxidation affects the oil-surface interactions - one can observe a noticeable decrease in phosphorus content in the tribochemically modified surface layer of the wear scar. The map of phosphorus is 'empty' for the reason of its very little concentration in the surface layer, less than 1% wt. (a sensitivity threshold of EDS mapping is in practice about 1% wt.).

The next step of analysis was to examine the wear scar surface layer quantitatively using EDS. Fig. 17 shows the weight concentration of sulfur and phosphorus in the surface layer for the both oxidised gear oils.

From Fig. 17 it can be seen that for GL-3 gear oil oxidised for 25 and 50 hrs the concentration of sulfur and phosphorus in the surface layer of the wear scar is much higher than for the pure oil. A dramatic drop in their concentration, down to unidentifiable values is noticed not sooner than for the longest time of oxidation (100 hrs). So, the concentration of these elements in the surface layer in some way correlates with the tribological results (Fig. 15 a). One can thus infer that their concentration increase is beneficial to the extreme pressure properties of the oxidised oil and the respective mechanisms of such an action have been described earlier.

In case of GL-5 gear oil irrespective of the oxidation time the concentration of sulfur in the surface layer of the wear scar is high and does not change. A small drop in sulfur concentration is noticed only for the middle time of oxidation (50 hrs). The concentration of phosphorus significantly decreases for the longest oxidation times. It is the decrease in

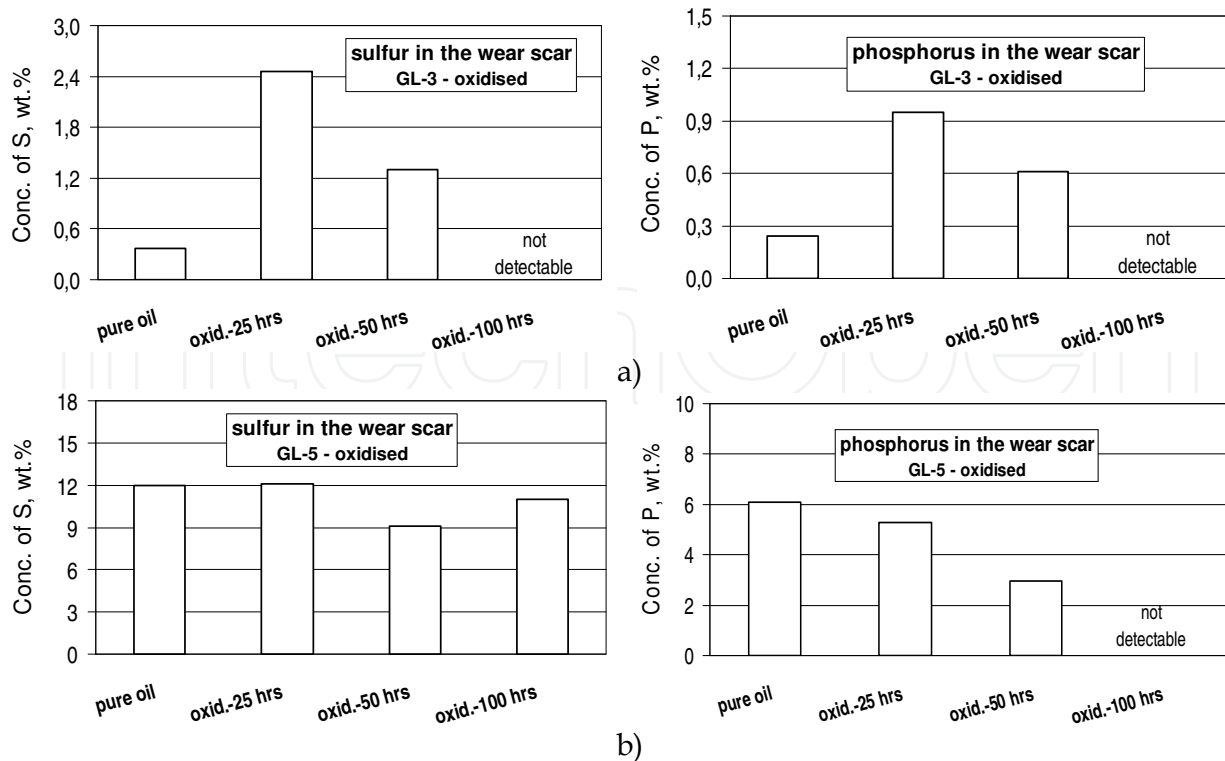


Fig. 17. Average concentration of sulfur and phosphorus in the surface layer of the wear scar for the oxidised gear oils: a) GL-3 oil, b) GL-5 oil

sulfur that may be a reason for an unexpected drop in the extreme pressure properties observed for GL-5 oils oxidised for 50 hrs (Fig. 15 b).

A dramatic drop in the concentration of sulfur and phosphorus in the wear scar surface layer in case of GL-3 oil oxidised for 100 hrs, accompanied by deterioration of its extreme pressure properties (Fig. 15 a) comes from a decrease in the lubricating additives in the oil due to precipitation of their oxidised products in the form of sludge, which has been postulated in the literature (Yamada et al., 1993), (Makowska & Gradkowski, 1999).

The changes in the physico-chemical properties due to oxidation were investigated by determination of TAN and FTIRM analysis of the tested oils. The values of TAN for the pure and oxidised oils are shown in Fig. 18, and the IR spectra - in Figs. 19 and 20.

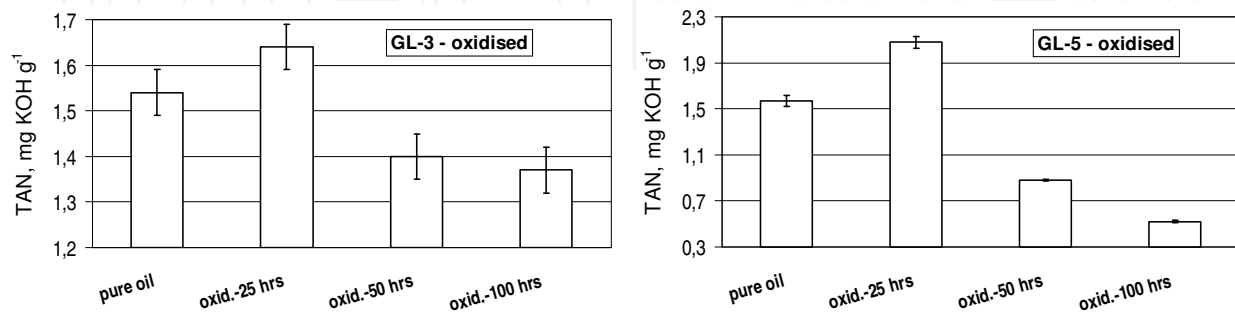


Fig. 18. TAN for the pure and oxidised gear oils: a) GL-3 oil, b) GL-5 oil

From Figs. 18 to 20 it is apparent that the symptoms of additives decrease in the oxidised GL-3 oil are: 10% drop in TAN and a very big decrease in the area under the peak at 965 cm^{-1}

in the IR spectrum; such a peak is typical of P-O-C bonds in the lubricating additives (ZDDP) used in GL-3 oils.

A decrease in the content of lubricating additives due to precipitation was also noticed for the oxidised GL-5 oil, which was identified by threefold drop in TAN of the oil oxidised for the longest time in comparison with the pure oil (Fig. 18 b). This much reduced the content of phosphorus in the worn surface, but because the concentration of sulfur (which is the most important element in the EP additives) practically did not change (Fig. 17 b) the extreme pressure properties of the oil oxidised for 100 hrs did not deteriorate.

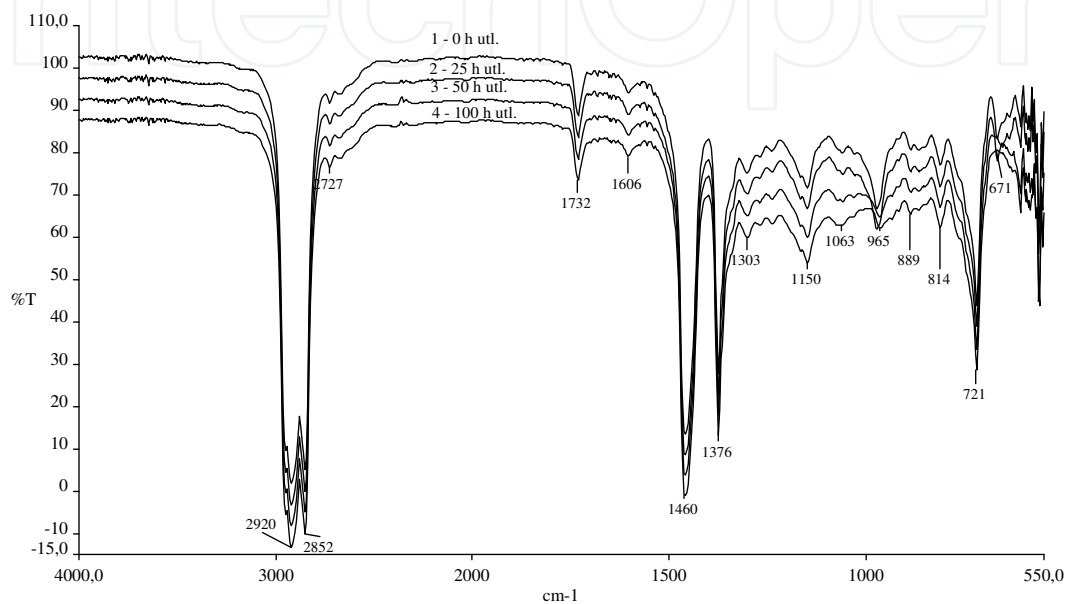


Fig. 19. IR spectrum for the pure and oxidised GL-3 oil; 1 - pure oil, 2 - oxidation for 25 hrs, 3 - 50 hrs, 4 - 100 hrs

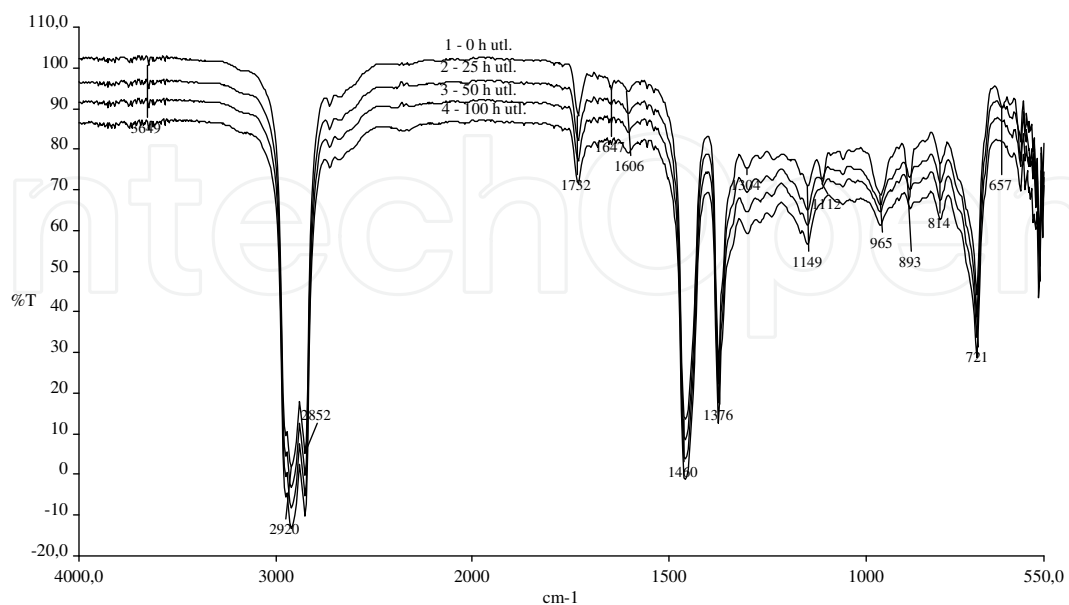


Fig. 20. IR spectrum for the pure and oxidised GL-5 oil; 1 - pure oil, 2 - oxidation for 25 hrs, 3 - 50 hrs, 4 - 100 hrs

6. Results and discussion - pitting tests

6.1 EHD oil film thickness during pitting tests - calculations

Because knowledge of the conditions in rolling contact will be helpful for further analyses, the authors have calculated the oil film thickness during pitting tests.

In the first approach the authors adopted a purely elastic model of the point contact for calculation. The calculated minimum film thickness was about 0.02 μm . However, the load between the balls gave unrealistic maximum Hertzian pressure 8.5 GPa, which would much exceed the yield strength of the material of the bearing balls (roughly assumed to be about 3 GPa, i.e. about one third of the average hardness expressed in GPa).

Because inspection of the wear track surface on the upper ball using profilometry revealed that the material was plastically deformed, the assumption of the point contact was no longer justified. So, an elastic model of the line contact of rolling elements was adopted for calculations with the well-known Dowson and Higginson's formulae compiled in the book (Winer & Cheng, 1980). It should be emphasized here that the contact of the four balls creates a circular wear track on the upper ball (plastically deformed), while the three bottom balls contact with the upper one randomly - over their entire surfaces.

The input data used for calculation of the minimum oil film thickness are given in Tab. 6 and some important dimensions of the four-ball rolling tribosystem are shown in Fig. 8 b.

In Tab. 6 the length L denotes the width of the plastically deformed zone between two mating balls and was averaged from measurements of the wear track profile on the upper ball made by a profilometer. As concerns rheological properties of the oils, they were determined at the temperature of 80°C, typical of relatively long (a few hours) tests in rolling movement. Pressure-viscosity coefficient was adopted from (Wang et al., 1996) for a mineral oil.

Quantity, unit	GL-3 oil	GL-5 oil
Radius R_1 , mm	6.35	
Radius R_2 , mm	6.35	
Length L , mm	1.3	
Load w , N	2649	
Velocity u_1 , m s ⁻¹	0.67	
Velocity u_2 , m s ⁻¹	0.67	
Modulus of elasticity E_1 , GPa	210	
Modulus of elasticity E_2 , GPa	210	
Poisson's ratio ν_1	0.3	
Poisson's ratio ν_2	0.3	
Oil viscosity (at 80°C) μ_0 , Pa·s	0.0203	0.0199
Pressure viscosity coefficient (at 80°C) a , Pa ⁻¹	1.1 · 10 ⁻⁸	

Table 6. Input data for calculation of the oil film thickness during pitting tests; symbols taken from (Winer & Cheng, 1980).

The calculated minimum lubricating film thickness h_{min} formed during the pitting tests for the pure gear oils is about 0.04 μm and is similar to values obtained by other authors for this kind of the tribosystem, e.g. (Libera et al., 2005). It should be noticed that the calculated film thickness is much thinner than occurring in service of machines. It is a result of relatively low velocity as well as disregarding an effect of viscosity improvers in the oil on the pressure-viscosity coefficient.

6.2 Testing of dust-contaminated gear oils

Fig. 21 presents the values of the 10% fatigue life (L_{10}) obtained for the gear oils of API GL-3 and GL-5 performance levels - pure and contaminated with the test dust at increasing concentrations. Confidence intervals calculated for the probability 90% have been added to the graphs.

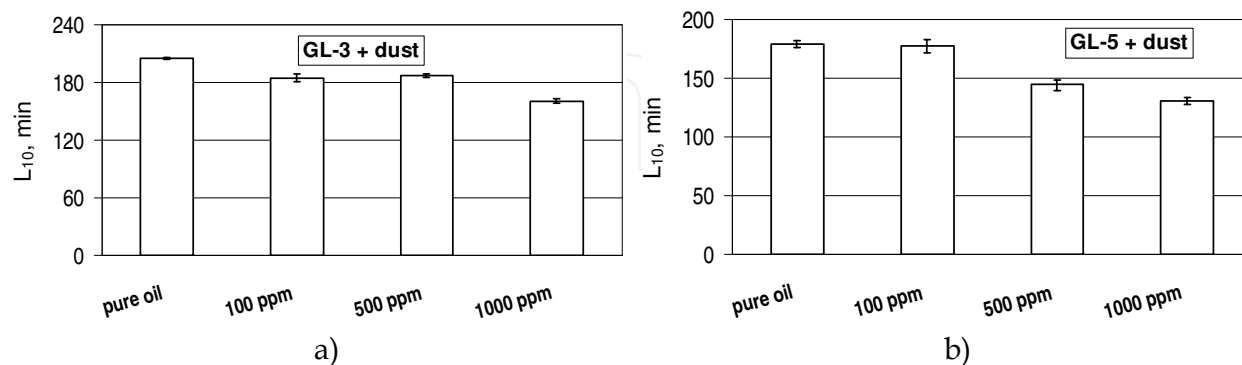


Fig. 21. Values of 10% fatigue lives (L_{10}) obtained for the gear oils - pure and contaminated with the test dust: a) GL-3 oil, b) GL-5 oil

From Fig. 21 it is apparent that the both contaminated gear oils give shorter fatigue lives with increasing concentration of the test dust.

The micro/nanotopography of the wear track surface on the top ball for the pure and dust contaminated GL-5 oil was inspected using AFM - Fig. 22.

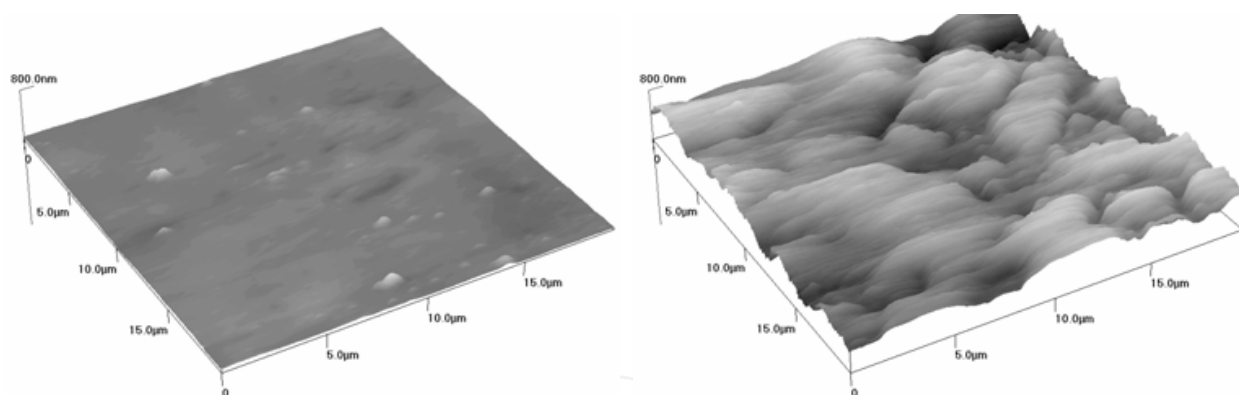


Fig. 22. AFM images of the wear track: a) pure GL-5 oil, b) GL-5 oil contaminated with the test dust at a concentration of 1000 ppm

It can be seen that the dust in the oil due to its abrasive action makes the worn surface rough and produces numerous surface defects. These defects act like stress raisers and accelerate initiation of surface fatigue cracks in this way. The abrasive action of dust particles resulted from their maximum size of $0.08 \mu\text{m}$, which was much bigger than the minimum oil film thickness ($0.04 \mu\text{m}$).

6.3 Testing of water-contaminated gear oils

Fig. 23 presents the values of the 10% fatigue life (L_{10}) obtained for the gear oils of API GL-3 and GL-5 performance levels - pure and contaminated with water at increasing concentrations.

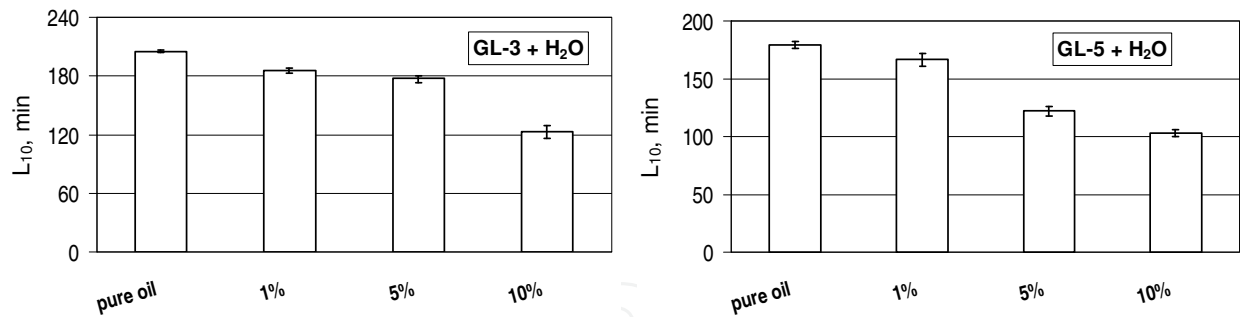


Fig. 23. Values of 10% fatigue lives (L_{10}) obtained for the gear oils - pure and contaminated with water: a) GL-3 oil, b) GL-5 oil

From Fig. 23 it is apparent that the both contaminated gear oils give shorter fatigue lives with increasing concentration of water. This is particularly noticeable for 10% water contamination in GL-3 oil as well as 5% and higher water content in GL-5 oil.

For interpretation of the obtained results the wear tracks on the top balls were analysed using SEM/EDS. SEM images of the worn surface and EDS maps for sulfur, phosphorus and zinc in the surface layer are shown in Figs. 24 and 25 for pure GL-3 oil and this oil contaminated with 10% water.

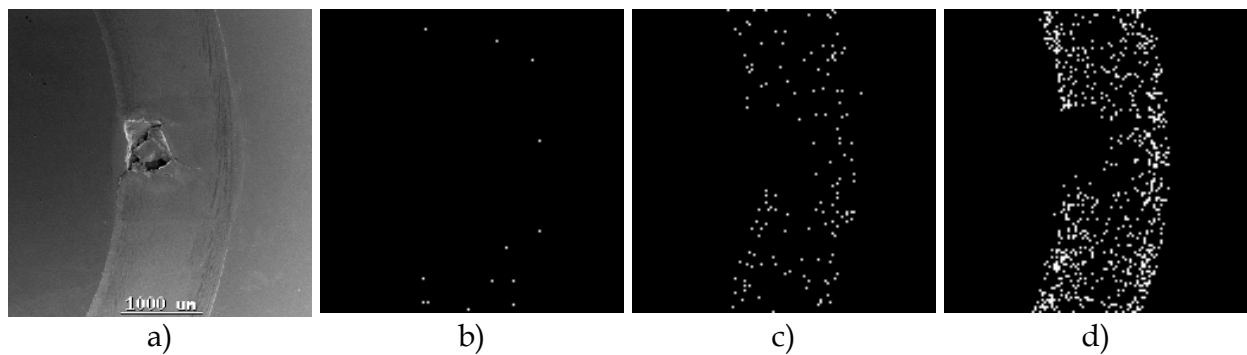


Fig. 24. Pure GL-3 oil - SEM image of the wear track (a) and EDS maps for: b) sulfur, c) phosphorus, d) zinc

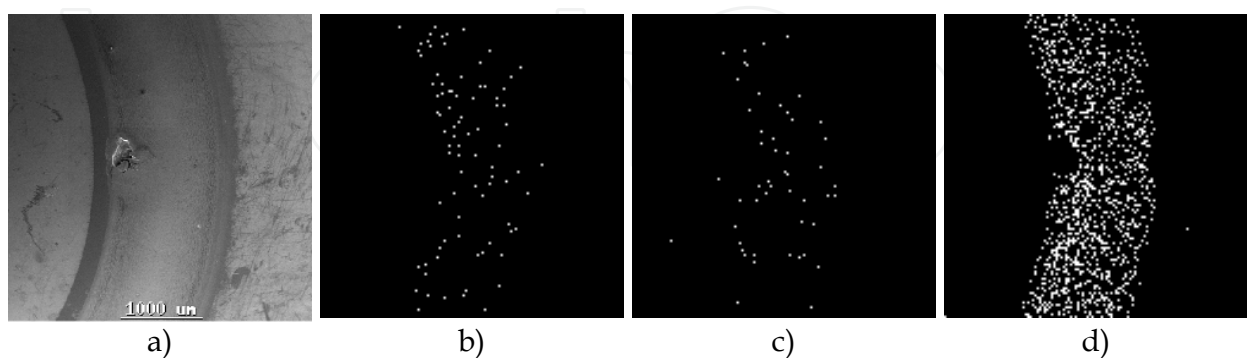


Fig. 25. GL-3 oil contaminated with water at 10% concentration - SEM image of the wear track (a) and EDS maps for: b) sulfur, c) phosphorus, d) zinc

From Figs. 24 and 25 it is evident that water contamination affects the oil-surface interactions - one can observe a rise in sulfur and zinc content in the tribochemically modified surface layer of the wear track.

The next step of analysis was to quantitatively examine the wear track surface layer using EDS. Fig. 26 shows the weight concentration of sulfur and zinc (GL-3 oil) as well as sulfur and phosphorus (GL-5 oil) in the surface layer for both the gear oils contaminated with water. The analyses were performed at three different points of the wear track. The graphs present the average values of elemental concentration.

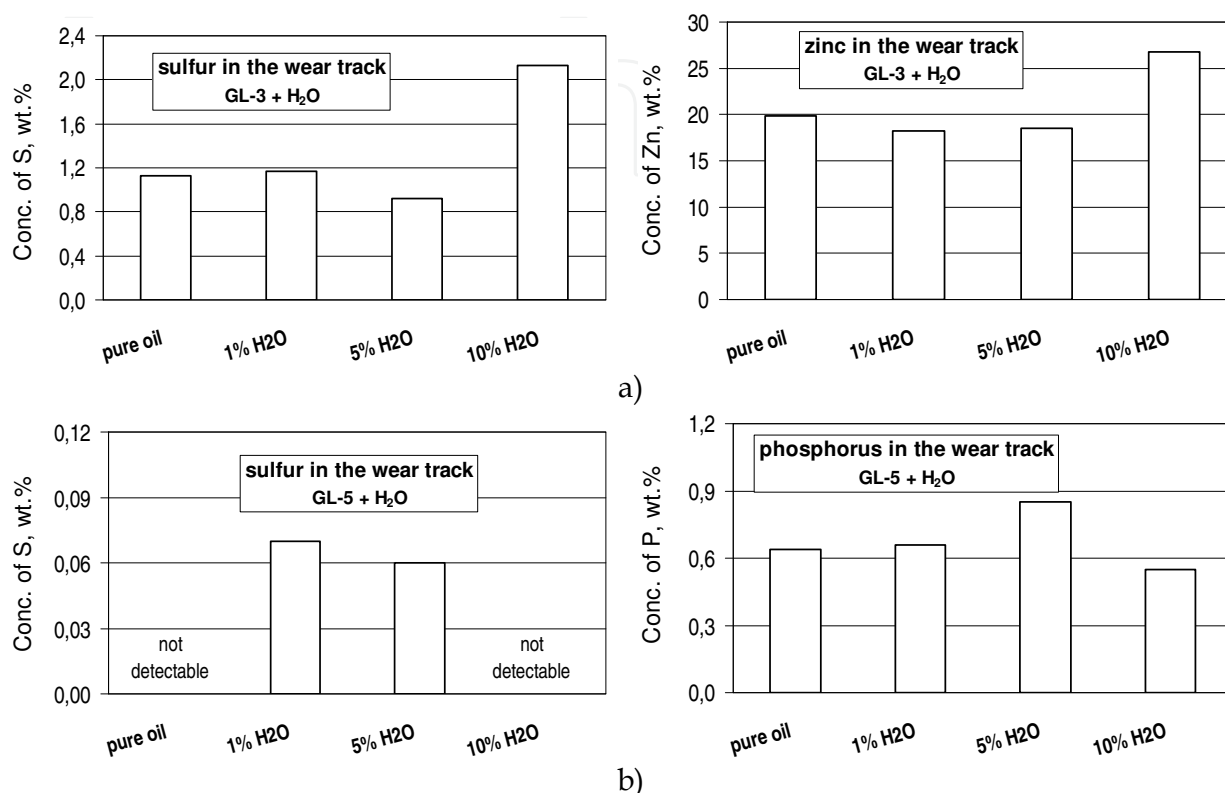


Fig. 26. Average concentration of sulfur, zinc, and phosphorus in the wear track surface layer for the gear oils contaminated with water: a) GL-3 oil, b) GL-5 oil

From Fig. 26 it is apparent that AW additives in GL-3 oil, having relatively low temperature of thermal decomposition, i.e. 200-300°C (Kawamura, 1982) under mild test conditions of rolling movement incomparably better tribochemically modify the wear track surface layer than EP ones. EP additives, present in GL-5 oil, with their much higher temperature of thermal decomposition, i.e. 400-500°C (Wachal & Kulczycki, 1988), have an incomparably lower chemical impact on the surface.

As can also be seen from Fig. 26, only for GL-3 gear oil contaminated with 10% water a significant change in the concentration of sulfur and zinc takes place in the wear track surface layer. For the contaminated GL-5 oil the concentration of sulfur is very low, within the limit of the sensitivity of the EDS technique. The content of phosphorus is also small and changes insignificantly. So, there is no evident correlation between the fatigue lives given by the water contaminated gear oils and elemental concentration of the tribochemically modified surface of the wear track.

Thus, for the oils contaminated with water a mechanism responsible for the drop in the fatigue life must be related to a decrease in the oil viscosity. This is followed by a drop in the thickness of EHL film leading to more frequent action of surface asperities; almost all of the load is carried in the plastically deformed tracks by asperity contact. More frequent cyclic

stress results in a shorter fatigue life. Hypothetically, hydrogen embrittlement may also be at stake in case of oils contaminated with water, which is postulated elsewhere (Rowe & Armstrong, 1982), (Magalhaes et al., 1999).

6.4 Testing of oxidative degradation of gear oils

Fig. 27 presents the values of the 10% fatigue life (L_{10}) obtained for the gear oils of API GL-3 and GL-5 performance levels - pure ("fresh") and oxidised for longer and longer time.

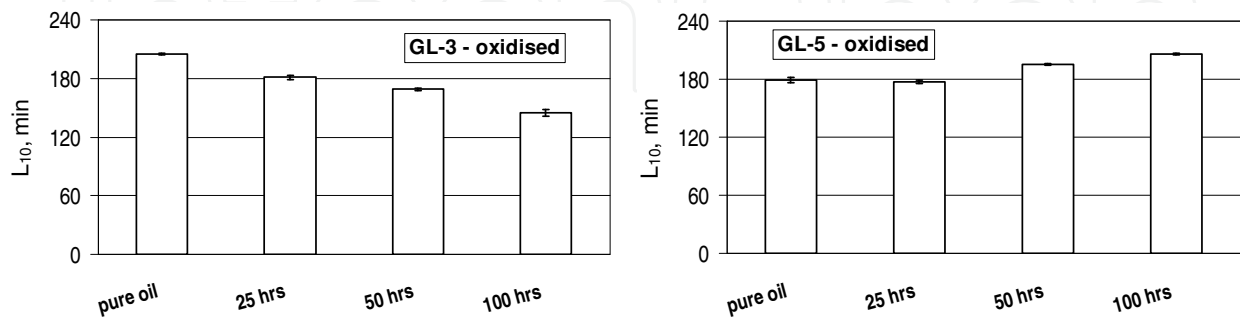


Fig. 27. Values of 10% fatigue lives (L_{10}) obtained for the pure and oxidised gear oils: a) GL-3 oil, b) GL-5 oil

From Fig. 27 it can be seen that the oil oxidation of GL-3 oil has an adverse effect on the fatigue life - its values steadily drop with increasing oxidation time. An opposite trend is shown by the oxidised GL-5 oil - the values of L_{10} increase with extending oxidation time, which is especially noticeable for the longest times.

For interpretation of the obtained results the wear tracks on the top balls were analysed quantitatively using EDS. Fig. 28 shows the weight concentration of sulfur and oxygen in the surface layer for the both oxidised gear oils.

From Fig. 28 it is apparent that for the oxidised GL-3 gear oil the concentration of sulfur in the surface layer of the wear track is much lower than for the pure oil. It comes from a decrease in the lubricating additives in the oil due to precipitation of their oxidised products in the form of sludge, which has been postulated in the literature (Yamada et al., 1993).

The changes in the physico-chemical properties due to oxidation were investigated by determination of TAN and FTIRM analysis of the tested oils. The values of TAN for the pure and oxidised oils are shown earlier in Fig. 18, and the IR spectra - in Figs. 19 and 20.

It has been already mentioned that the symptom of additives decrease in the oxidised GL-3 oil is a dramatic, several-fold drop in the area under the peak at 965 cm^{-1} in the IR spectrum; such a peak is typical of P-O-C bonds in the lubricating additives (ZDDP) in GL-3 oils.

In the literature a mechanism of the surface asperity softening due to a significant tribochemical modification is often attributed to fatigue life improvement achieved for lubricating additives. In this way surface asperities may be flattened, which reduces contact stress and in turn improves the fatigue life (Wang et al., 1996). So, worsening fatigue lives observed for the oxidised GL-3 oil (Fig. 27 a) may be attributed to the decrease in the concentration of sulfur in the worn surface (Fig. 28 a).

Another reason for reduction in the fatigue life for the oxidised GL-3 oil is related to the very high content of oxygen in the wear track surface layer (Fig. 28 a). Presumably, this comes from iron oxides. The role of such compounds seems rather deleterious as they can contribute to creation on the lubricated surface numerous corrosive micropits, being potential nuclei of fatigue cracks.

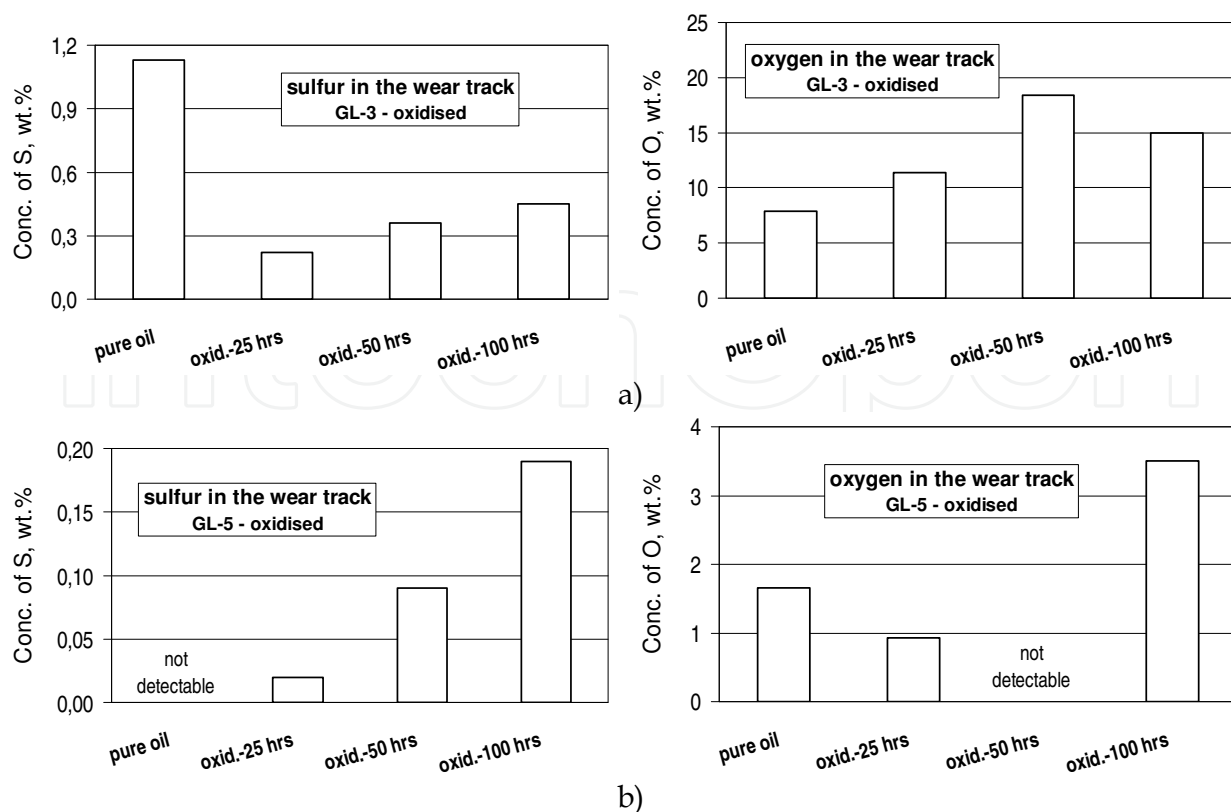


Fig. 28. Average concentration of sulfur and oxygen in the surface layer of the wear track for the oxidised gear oils: a) GL-3 oil, b) GL-5 oil

In case of the oxidised GL-5 oil, in the surface layer of the wear track a steady rise in the sulfur concentration takes place, although it is rather small (Fig. 28 b). A beneficial role of sulfur compounds has been mentioned earlier, so it may be a reason for fatigue life improvement observed for the oxidised GL-5 oil (Fig. 27 b).

The rise in fatigue lives given by the oxidised GL-5 oil can also relate to a decrease in the lubricating additives in the oil due to precipitation of their oxidised products. The symptoms of additives decrease in the oxidised GL-5 oil are: threefold drop in TAN for the longest oxidation time (Fig. 18 b) as well as nearly threefold drop in the area under the peak at 965 cm^{-1} in the IR spectrum (Fig. 20). The beneficial action of EP additives decrease is explained below. EP type lubricating additives used in GL-5 gear oils are known for their high corrosion aggressiveness. It leads to creation on the lubricated surface numerous depressions and micropits due to corrosive wear, being potential nuclei for bigger “macropits”. In this way the chance of failure increases, hence the fatigue life lubricated by EP additives tends to be reduced (Torrance et al., 1996). So, unlike in case of the oxidised GL-3 oil, the EP additives decrease in GL-5 oil due to oxidation exerts a beneficial influence on the surface fatigue life. Like in case of the water contaminated oils, an adverse role of hydrogen embrittlement should not be neglected in case of oxidised gear oils.

7. Summary and conclusions

7.1 Scuffing tests

The contamination of the automotive gear oils of API GL-3 and GL-5 performance levels with the test dust practically does not affect their extreme pressure properties.

The contamination of the gear oils by water has a deleterious effect on their extreme pressure properties, however GL-3 oil is much more vulnerable to water contamination.

Oxidation exerts in general a positive effect on the both oils, however GL-3 oil shows a significant decrease in its extreme pressure properties after oxidation for the longest time.

SEM and EDS surface analyses show that there is a relationship between the extreme pressure properties of the aged gear oils and elemental concentration (sulfur and phosphorus) of the tribochemically modified surface of the wear scars.

So, from the point of view of the resistance to scuffing the most dangerous contaminant in automotive gear oils is water. However, ageing of such oils may even have a positive effect, like in case of the oxidised GL-5 oil.

7.2 Pitting tests

The ageing of the automotive gear oils generally exerts an adverse effect on the surface fatigue life (resistance to pitting). The only exception is for the oxidised API GL-5 oil - the fatigue life significantly improves for the longest periods of oil oxidation.

SEM, EDS and AFM analyses of the worn surface made it possible to identify factors having a deleterious (or beneficial) effect on the surface fatigue life due to action of the aged oils. So, dust in the oil produces numerous surface defects acting like stress raisers and accelerating initiation of surface fatigue cracks in this way. Water causes a drop in the oil viscosity, followed by a decrease in the EHL film thickness, leading to more frequent action of surface asperities, hence shorter fatigue life. For the oxidised GL-3 oil the fatigue life reduction results from a drop in the sulfur concentration in the worn surface; sulfur compounds formed by oil-surface interactions play a positive role in fatigue life improvement. A beneficial effect of oxidation of GL-5 oil on the fatigue life is related to a decreasing content of highly corrosive EP type lubricating additives due to precipitation of their oxidised products.

Although not investigated here, an adverse role of hydrogen embrittlement and iron oxides produced on the worn surface may also be at stake in case of oils contaminated with water and oxidised.

So, from the point of view of the resistance to rolling contact fatigue the most dangerous contaminants in automotive gear oils are dust and water.

7.3 Conclusions

Like in case of scuffing, also from the point of view of the resistance to pitting the GL-5 oil is generally more resistant to deterioration due to ageing than GL-3 oil.

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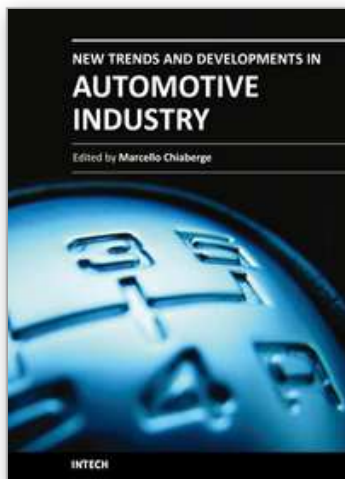
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This book is divided in five main parts (production technology, system production, machinery, design and materials) and tries to show emerging solutions in automotive industry fields related to OEMs and no-OEMs sectors in order to show the vitality of this leading industry for worldwide economies and related important impacts on other industrial sectors and their environmental sub-products.

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