

ASSESSMENT OF AUTOMOTIVE LUBRICANT OIL EVOLUTION THROUGH TECHNOLOGY PROSPECTING*

Renata Cristina Teixeira¹ Eduardo Dominguez Trindade²

Abstract

The lubricant oil is a complex mixture of different basestocks and additives. Engine oils evolved from the use of pure mineral basestocks back in the early years of automotive industry to the advent of synthetic, fully formulated, low ash lubricants. This evolution was driven by a number of factors, such as new engine designs, extended durability needs, increased fuel economy needs, environmental concerns, feedstock prices and availability and legal issues. This paper uses technology prospecting on literature and patents databases to allow an investigation on the historical evolution of engine oils. Main basestocks (mineral, hydrotreated, polyalphaolefins, esters) and additives (antioxidants, antiwear, friction modifiers, detergents and dispersants) are characterized according to their research effort. Technology prospecting data is crosschecked against the evolution of engine oil classes, allowing an analysis of how the main drivers push the development of lubricant oil quality. A research effort was identified in late 1990's until mid-2000's and related to the adoption of chemical limits for lubricants. Different patterns for the articles and patents publication account for the high value technological knowledge has in this industry. Technology prospecting is seen as a useful methodology for the understanding and forecast of lubricant technology movements.

Keywords: Lubricant; Base oil; Lubricant additive; Technology prospecting.

¹ Librarian, Master of Science in Technology, Research and Development Centre, Petrobras S.A., Rio de Janeiro, RJ, Brazil.

² Chemical Engineer, Master of Science in Mechanical Engineering, Research and Development Centre, Petrobras S.A., Rio de Janeiro, RJ, Brazil.

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



1 INTRODUCTION

1.1 Foreword and objectives

Lubricant oils like those used in automobile engines are liquid, complex mixtures of base oils and additives. As for the present state of the art of lubricant formulation, this means that an engine oil may well be composed of different base oils (mineral, synthetic or both at once) and about a dozen additives. Each component is aimed at achieving specific targets, like to guarantee optimal viscosity at given temperatures, deposits control, oil stability, low friction and controlled levels of wear, rust and corrosion. A component balance by no means easy is necessary to allow the optimal performance of the lubricant. The technology of automotive lubricant formulation has evolved through the years following developments on combustion engines, petroleum refining environmental requirements and marketing trends. The objectives of this paper are to summarize key aspects of this evolution, to present a method for evaluation of technological development and to discuss some general trends in lubricant technology.

1.2 Historical background

The first successful internal combustion engine automobiles are regarded to be invented in the late XIX century after the work of several German engineers. Particularly, Karl Benz, who had his first engine patent granted in 1879 and his first automobile patent in 1886 [1], is usually recognised as father of the modern automobile. Benz's first efforts were in a petrol-fuelled two-stroke engine, soon switching to four-stroke engines.

The world-famous Ford Model T, whose production started in 1908, is regarded as the first affordable automobile, marketed to the middle-class. It was also the first car mass-produced in assembly lines. The more than 15 million Model T produced and its influence in the popular culture made of this vehicle one of the biggest successes ever of the automotive industry, arguably the biggest success. [2]

By the first decades of the XX century, automobile engines used straight mineral oil as lubricant. Cars did not have air filter or oil filter and, as a result of this, worked with a degree of contamination which is unthinkable nowadays. Table 1 compares typical engine oil metals content from a 1931 Ford Model A (the car which succeed Model T after the end of its regular production in 1927) driven in 2013 with some recommended limits for present cars.

Table 1. Engine oil draining interval and metals content of a 1931 Ford Model A and a present	car

	1931 Ford Model A driven in 2013 with an SL oil	2013 automobile limits (*)
Draining interval (km)	400	10000
Iron (mg/kg)	940	100
Cooper (mg/kg)	38	50
Lead (mg/kg)	48	50
Aluminium (mg/kg)	49	25
Silicon (mg/kg)	66	25
Boron (mg/kg)	45	25

(*) Typical values. Actual figures depend on several factors, like the exact car model, driving behaviour, fuel and oil composition.

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



Given the lack of oil filter and the poor stability of the straight base oil, the lubricant changing interval was remarkably lower than what is presently practiced. Until the 1930's, Ford manuals recommended changing the engine oil each 500 mi (about 800 km). Also, there wasn't multiviscous oil at that time: the car manufacturer recommended the use of a lighter oil during colder months. In the case of Ford Model A, that meant an SAE 40 oil for use during summer and an SAE 20 oil for use during winter [3].

The straight mineral oil for use in automotive petrol-fuelled engines was known in the United States as SA according to API service classification. It had no performance requirements and remained the oil of chose until 1930, when antioxidants started to be added to the oil, making the API SB category. By that time, air filter and oil filter were also introduced as original factory equipment. Initially engine oil was filtered in a by-pass system which treated about 10% of the total flow. The first full-flow oil filter was introduced in 1943.

API SC was released in 1964 and incorporated much of the additives technology developed up to that year. Oils designed for this service provided some control of deposits, wear, rust and corrosion [4]. API SC oils also reflected the introduction, in 1934, of base oil solvent-refining for removal of aromatic compounds, what led to higher viscosity indexes. Multigrade oils were introduced in 1950, after the ability of some polymers further improve the viscosity index was discovered. [5] Also by that time, the first hydrotreated base oils were being produced, as well as the first polyalphaolefinic base oils. Both were first developed for use in steam turbines, but found some application in some high demanding engines.

API SD came into use in 1968 and offered more protection against wear, rust, corrosion and the occurrence of deposits than that given by API SC oils.

Further protection was achieved by API SE, released in 1972. The 1970s saw the growing of synthetic oils – based namely on polyol esters and polyalphaolefins – for use in racing and other special applications, driven by the increased quality demand and by the rising costs of petroleum-derived products.

API SE was followed by SF in 1980, SG in 1989 and SH in 1994. The traditional synthetic base oils faced the competition of hydrotreated and hydrocracked base oils. Hydrocracked base oils offered the same quality level of polyalphaolefins at a lower price, and thus gained market share. [6]

API SJ was introduced in 1997 and API SL came to light in 2001.

API SM was introduced in November 2004, aiming at providing improved oxidation resistance, improved deposit protection, better wear protection, and better low-temperature performance over the life of the oil. API SM also included chemical limits for lighter grades and a non-mandatory Energy Conserving qualification.

API SN, introduced in October 2010, provided improved fuel economy, turbocharger protection, emission control system compatibility, and protection of engines operating on ethanol-containing fuels. [7-8]

The evolution of lubricant oil classification for petrol engines as discussed here illustrates the historical and technological evolution of the engine oil industry. Similar movements could be tracked according to European classification, regulated by the Association des Constructeurs Européens d'Automobiles (ACEA) or even according to diesel engine oil classifications. These, albeit retaining their specificities, have all developed in the same direction over the years – increasing oil stability, wear protection and low-temperature performance.

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



2 METHODS

The technology prospecting was the method used in this paper to investigate the historical evolution of the automotive oils. This methodology is widely used by companies to monitoring developments in fields of strategic interest. The lubricant research and development efforts were fathomed by the appraisement of its literature and patents published, since these documents have the ability to narrate all the life technologies circles. [9] So, in this paper, the state of the art and the prior art were undiscovered by analysing 6748 papers from EnCompassLIT[™] bibliographic database (Engineering Village) and 6647 patent documents from Derwent[®] patent database (Thomson Reuters).

These databases were chosen for the survey due to the breadth of its collection and the ease of access and retrieval data. The search strategies used in the databases were the combination of the keywords that characterized the mineral and synthetic basestocks and the additives as listed in table 2.

All the searches were limited to retrieve publication date up to the end of 2013 and the fields used were "all text fields – DWPI" for patents and "title, keywords and abstract" for literature.

Table 2. S	Search	strategies	used	in	patent	and	literature	databases	and	number	of	retrieved
documents								_				

	# Patents	# Papers					
1) BASE OILS							
1.1) MINERAL (GROUP II/III)							
("base oil" or "base stock" or basestock) AND (mineral or "solvent refined" or paraffinic)	2520	1115					
1.2) GROUP III		-					
("base oil" or "base stock" or basestock) AND (hydrocracked or "group III")	360	337					
1.3) PAOs (GROUP IV)							
("base oil" or "base stock" or basestock) AND (polyalphaolefin or PAO)	197	332					
1.4) ESTERS (GROUP V)							
("base oil" or "base stock" or basestock) AND (engine) AND (ester or polyolester or	695	261					
polyester or diester or "group V")	035	201					
2) ADDITIVES							
2.1) ANTIOXIDANT							
(lubricant or lubricating) AND (engine or automotive) AND (antioxidant or "oxidation	1220	923					
inhibitor")	1220	525					
2.2) ANTIWEAR							
(lubricant or lubricating) AND (engine or automotive) AND (antiwear or "zinc	876	1408					
dialkyldithiophosphate" or "zinc dithiophosphate" or ZDDP or ZnDTP)	0/0	1400					
2.3) FRICTION MODIFIER							
(lubricant or lubricating) AND (engine or automotive) AND ("friction modifier" or							
"molybdenum dialkyldithiocarbamate" or "molybdenum dithiocarbamate" or	483	572					
"molybdenum dithiophosphate" or MoDTC or MoDTP)							
2.4) DETERGENT							
(lubricant or lubricating) AND (engine or automotive) AND (detergent or "base reserve")	978	1006					
2.5) DISPERSANT							
(lubricant or lubricating) AND (engine or automotive) AND (dispersant or	1318	794					
polyisobutylene)	1010	7.54					

3 RESULTS AND DISCUSSION

3.1 Retrieved Data

Figure 1 shows the evolution of technical papers mentioning lubricant base oils by year. Figure 2 shows the evolution of patents on the same subject.

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



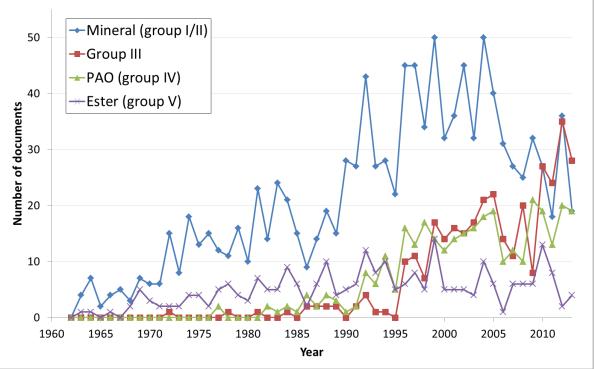


Figure 1. Technical articles published on base oils by year

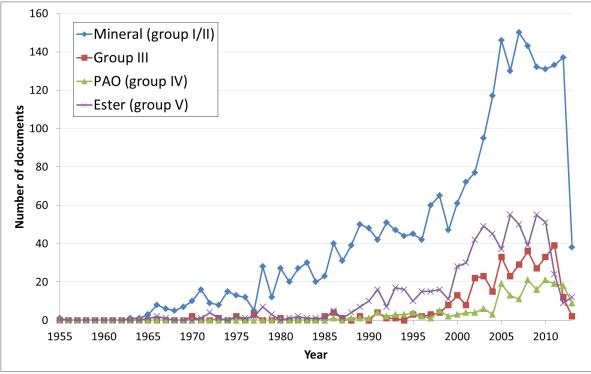


Figure 2. Patents published on base oils by year

The evolution of technical papers and patents mentioning the studied additive families by year can be seen in Figures 3 and 4, respectively.

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



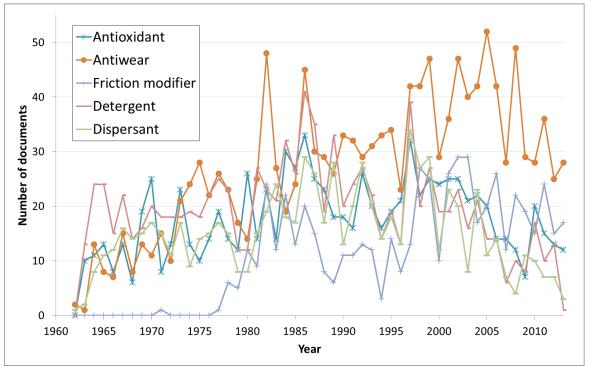


Figure 3. Technical articles published on lubricant additives by year

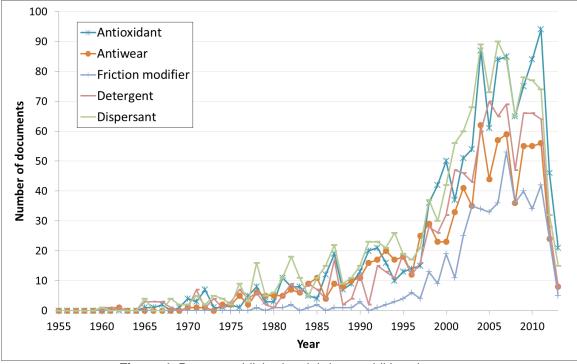


Figure 4. Patents published on lubricant additives by year

The patents publication distribution on the studied subjects according to the country of priority is shown in figure 5 for base oils documents and in figure 6 for additives documents. As has been noticed over the years by patent researchers, in the great majority, companies tend to adopt the strategy of prioritizing its domestic market, chosen its country of origin for priority patent [9].

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



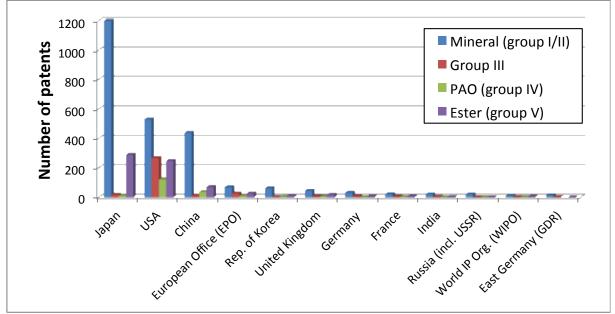


Figure 5. Patents published on base oils by country

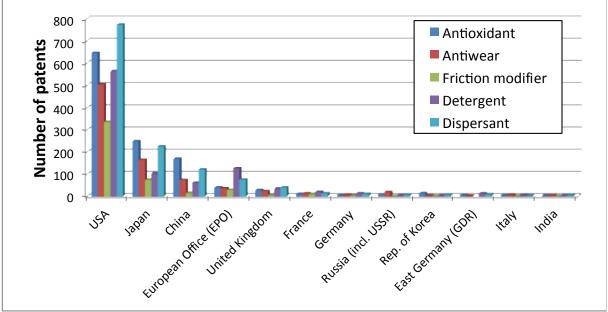


Figure 6. Patents published on lubricant additives by country

3.2 Overall Comments

The evolution profile of the publication of articles is different from the evolution profile of the publication of patents. This can be seen as a consequent of the different focus given to each kind of document. It is also an evidence of the interest industry has on the technology application and on the protection of the knowledge on the subject. In fact, lubricant formulation is regarded as a confidentiality sensitive information that can provide significant competitive advantage.

It can be seen in figure 5 that Japan is the country with the biggest number of patents on mineral oils. The detailed analysis of this documents shows that this fact is due to a large number of patents on engine oil formulation plus some patents on lubricants for electrical devices. USA has the second biggest share of patents on base oils and

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



these patents are well distributed between the different base oil groups. China patents publishing has grown significantly in early years and is today the third country in number of documents on base oils.

USA dominates the patents publication on lubricant additives, as it can be seen on figure 6. Japan is the second biggest publisher and China the third one, followed by European countries.

3.3 Base Oils

As expected, mineral base oils account for the majority of the number of patents recovered in the database. This is due to a number of reasons like: they were the first ones to be developed, they are readily available worldwide and were, until recently, the most used base oil group. [10] This market dominant presence is thus reflected in the patent data, as many patents account for real formulations employing that kind of base oils. Nevertheless, figures 1 and 2 show a period of stabilization and even some decline in the number of issued documents in the latest years. This is in line with the decrease of interest in mineral basestocks for use in engine oils, as specifications got more stringent and hydrogenated or synthetic basestocks became more popular. By 2005, at the same time that API SM category was issued, the number of patents mentioning mineral oils ceased to increase. The easing up of the number of technical articles appeared some years before. This can be explained by the fact that, as the purest group III and group IV oils became more readily available, they became the base oils of choice for researchers. Also, this can be view as an anticipation of the twilight of group I base oils.

The case study of the development of esters as lubricant component is an interesting one. Both figures 1 and 2 show that esters appeared before group III and group IV base oils. But, while the yearly number of articles remained almost steady, the number of patents increased since 1988 and yet more significantly since 2000. It seems that, once esters were available, there was an increased incorporation of them in newly developed formulations subject to patenting. Research on ester base oils technology did not perform in the same way, as the number of articles did not have the same rate of growth.

3.3 Additives

Except by the friction modifiers, all the other considered additives had already some development reflected in the number of published articles at the beginning of the data base (figure 3).

Detergents and dispersants had a quite steady articles production until the mid-1980's and then faced a decline in the research effort. A quite similar profile is seen for the antioxidants-related articles. The year of 1997 is marked by a returning interest in most of the additives studied classes. That was related to the pushing for modifications in lubricant chemistry aiming at better compatibility with exhaust catalytic treatment systems. In 2004, API SM was released and imposed chemical limits (sulphated ash, phosphorous and sulphur) for some lubricants, having a direct impact on the additives industry. A boom in the number of deposited patents dealing with lubricant additives was recorded by the same time, probably reflecting the effort seen some years before in the articles publication profile.

Antiwear additives also show a gradual rising in the number of articles up to the mid-1990's and a new level of publication after 1997, making evident the push for newer,

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



low-ash additives. The research effort on antiwear additives, as measured by the number of articles, did not fall significantly in the latest years. In fact, wear remains a main concern related to lubricant performance and the durability requirements are expected to get even higher in the forthcoming years. [11]

Compared to these additives, a consistent publication of articles dealing with friction modifiers only appeared later on. This article profile had a step rise in 1998, in line with the already discussed new generation of additives, which lead to low-ash, organic friction modifiers. It is also related to the push for fuel economy oils, which requires lower friction.

The patents yearly profile (figure 4) did not show the same movements apparent in the articles profile (figure 3). Actually, as historically each kind of additive is incorporated into formulations more and more complex, the number of patents dealing with each kind of additive is ever increasing. Nevertheless, friction modifiers are a more specific class of additives and are not as widely employed as the other classes, as it can be seen by their lower number of patents.

3.4 Time-Shift Analysis

The evolution pattern of technical publication along the time is a useful tool for investigating the development of a given technology. A rapid growth in the publication rate may indicate a growing interest in the technology, while a subsequent steady rate may indicate its maturity. More than this, the kind of technical publication issued is also of interest, as technical articles and patents can be regarded to follow different trends during the technological evolution. While articles are expected to be published at any stage of the development, including at a quite early stage, patents are expected when the technology achieves such a maturity degree in which its commercial exploration is readily foreseen by the publisher. Confidentiality issues can also interfere in the publication decision Given all this, the comparison of articles and patents publication behaviour can give a hint on how close is the commercial use of the technology.

Figure 7 shows the correlation coefficient between the number of base oils articles and patents published yearly considering different time-shifts. Figure 8 does the same for documents on lubricant additives. A high correlation between the number of articles and the patents published a given number of years later indicates that this number of years is a measure of the time lapse until an average piece of technology evolves from an early, more academic stage, to a stage in which commercial advantage due to this technology is expected.

According to figure 7, it can be said that, for group I to IV base oils, there is a delay of about 5 to 10 years before a research effort apparent in the number of articles reach a maturity degree such as to be subject of patenting. Ester base oils (figure 7) and additives (figure 8) follow a different pattern: the correlation coefficient is everincreasing with the time-shift raise. This can be interpreted as these technologies having an incremental evolution behaviour: each class of component do not fall apart of the formulation, but is replaced by more recent developments with the same purpose. In other words, the trend is that each kind of the studied additives (antioxidant, detergent, dispersant and so on), once discovered, is used in all ongoing formulations, but with the incorporation of new developments (e.g. low-ash additives instead of organometallic compounds).

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



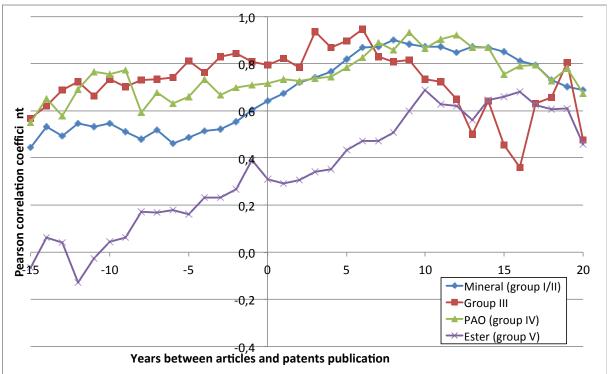


Figure 7. Time-shift analysis for base oils documents

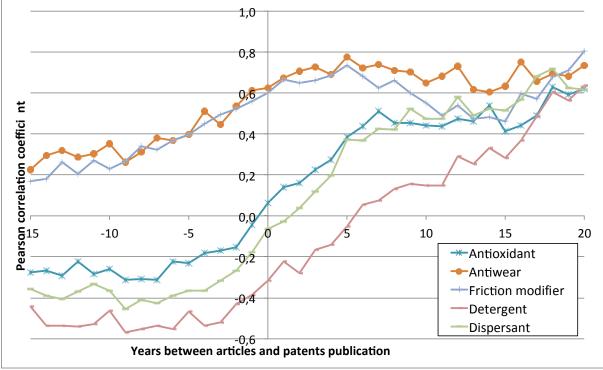


Figure 8. Time-shift analysis for additives documents

4 CONCLUSION

There is a difference between articles and patents evolution patterns and this can be interpreted as a consequence of the degree of interest in the use of technology in commercial applications. Lubricant formulation is a highly confidentiality-sensitive subject.

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.



The studied lubricant additives, as well as ester base oils, follow an incremental evolution behaviour. Base oils of the groups I to IV, on the other hand, have a different trend in which the more basic research (translated in articles publication) evolves to technology protection (patents) in a timeframe of about 5 to 10 years. Industry movements like the introduction of chemical limits for lubricant oils in the mid-2000's is reflected in the patents publication by the same time and could be anticipated by the rise in articles publication dealing with additives development. Technology prospecting is a useful methodology for the study of lubricant technology to different areas of the lubricant technology, like specific additives or base oils, may give hints about the future trends of the industry.

REFERENCES

- 1 Benz & Co. in Manheim. Fahrzeug mit gasmotorenbetrieb, DE Patent 37435, January 29th, 1886.
- 2 Laird RA, Sherratt TN. The economics of evolution: Henry Ford and the Model T. Oikos. 2010; 119(1): 3-9.
- 3 Ford Motor Company. Model A Instruction Book. Detroit: Ford Motor Company; 1931.
- 4 Lubrizol. Ready reference for lubricant and fuel performance. Wickliffe: The Lubrizol Corporation; 2002.
- 5 Dowson D. History of Tribology. 2nd ed. London: Professional Engineering Publishing; 1998.
- 6 Rizvi SQA. A comprehensive review of lubricant chemistry, technology, selection and design. West Conshohocken: ASTM International, 2009.
- 7 American Petroleum Institute. Which oil is right for you? [Internet page]. American Petroleum Institute [cited 2014 July 31]. Available at: http://www.api.org/certificationprograms/engine-oil-diesel-exhaust-fluid/~/media/Files/Certification/Engine-Oil-Diesel/Publications/MOM_GUIDE_ENGLISH_2013.pdf
- 8 American Petroleum Institute. API 1509: Engine oil licensing and certification system. 17th ed. Washington: American Petroleum Institute, 2012.
- 9 Teixeira RC. Análise das tecnologias de hidrorrefino através da utilização de técnicas de prospecção tecnológica e análise de redes sociais [master degree dissertation]. Rio de Janeiro: Centro Federal de Educação Tecnológica Celso Suckow da Fonseca; 2014.
- 10 Lindemann L, Gosalia A. New challenges in the global lubricants industry: how the market changes in view of raw material availability, lubricants supply and competitive landscape. In: International Colloquium Tribology, 19. Proceedings... January 21-23, 2014, Ostfildern, Germany. Ostfildern: Technische Akademie Esslingen, 2014.
- 11 Spikes H. The history and mechanisms of ZDDP. Tribol Lett. 2004; 17(3): 469-489.

^{*} Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.