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DEVELOPMENT OF LUBRICATING OILS AND THEIR INFLUENCE ON THE SEALS

Abstract

Lubricants industry is going through significant changes due to various influences. On the one hand are the requirements of engines manufacturers, cars and boats regarding improved quality of lubricants, and on the other hand stringent government regulations that concern the industry. The occurring changes reflect inevitably on producers in complementary industries, whereat the seal production is one of the most exposed. The changes in the composition and properties of lubricants, especially lubricating oils, affect their behavior, primarily compatibility in contact with seals. Detailed research shows that the observed interactions are complex and that trends and behavior model can not be unequivocally predicted. The rubbers on the same base, such as NBR, due to the composition differences exhibit significantly different behavior in the oils of the same group, i. e. is the same rubber in various oils shows swelling or shrinkage. This paper classifies the most important types of rubber used for seals and their behavior in contact with products of mineral base, aliphatic, aromatic and chlorinated hydrocarbons, as well as other used for the brake fluids of glycole base, silicone and PAO oils. Seven types of elastomers regarding their compatibility with group I, III, GTL and PAO base oils are compared. For selected examples the influence of esters and additives on the swelling behavior of seals is shown. It was found that the addition of ester causes improvement while addition of swelling additives has a significant influence and the ultimate effect on the swelling / shrinking in group III base oils matches approximately the group I oils.

Keywords: lubricant oil, rubber, seals, elastomer compatibility index, swelling behavior

Introduction

Lubricants industry is exposed to various influences to which it must adjusted along with a whole range of interdependent industries. The automobile industry is among the most apparent example, as well as the industry of various devices such as pumps, etc. It is important to point out the economic effect that is omnipresent.

When talking about lubricants industry and the challenges it faces, there are primarily: increased demand in the market due to the growing Asian market, especially Chinese, the closure of the old refinery facilities, diverting of production flows within the refinery to more cost-effective fuels, bad technical condition in many old refineries in Europe and the associated frequent unplanned shutdowns. Lubricants market has been weakened significantly by narrowing the supply source of base oils on an unprecedented scale as a result of significantly increased crude oil prices over the past ten years.

Actually, the situation regarding the availability of base oils has improved, but the prices remained high. In addition to the issues of the base oils access, industry of lubricants is faced with another change on the market: up to now on the market dominant conventional base oils (solvent type raffinate) will be increasingly replaced with new group II, II⁺, III base oils and specially a fully synthetic oil produced by GTL Fischer-Tropsch synthesis. GTL oils are classified into III⁺ group.

Analysis of the brands and trends of lubricating oils

According to studies conducted regularly by Kline & Co., the overall need for paraffinic oils in 2004 was approximately 30.5 million tonnes, with a forecast increase of 21 % by 2020 (approx. 37 million tonnes) [1]. Most of it concerning the conventional group I base oils, and about 23 % of the groups II and III, which are planned to increase up to 50 %. However, this increase was achieved much earlier; namely Kline & Co. reported that the total world demand was 37.4 million tonnes in 2010. It was an increase of 6.9 % compared to 2009 [2]. World consumption of lubricants in 2012 was 38.7 million tons and was unchanged compared to the year 2011. Growing demand for base oils of groups II and III continues, although the planned change has not yet happened. The assessment that the future development of the market will be towards the supply with base oils of superior performance regarding current technical requirements, are still valid. The group I base oils prevailed with over half of the total sum in the 2012, and the group II / II⁺ base oils amounted slightly more than a quarter, while the remaining amount consisted of the group III / III⁺ base oils and naphthenic base oils. Occasionally on the market appears the excess supply of groups II and III base oils [3].

In Table 1, the classification of lubricating oils of American Petroleum Institute (API), which was introduced 1995 is given. It was accepted also by ATIEL, a professional Association of European Lubricant Manufacturers (equivalent to the American API) in its guideline Code of Practice, which was adopted in the lubricants industry worldwide as the best guidance for the development and production of motor oils in accordance with European ACEA sequences [4].

Groups I-III include base oils based on mineral and hydrocracked oil. For the classification purpose the sulfur content, the proportion of saturated chemical bonds and viscosity index are important. In group I are the conventional mineral oils (solvent raffinate, solvent neutral).

Hydrocracked oils with the viscosity index $IV < 120$ have been included in group II, and severely hydrocracked oils with viscosity index $IV \geq 120$ in group III. Over the last 10 years, group I base oils are replaced by group II base oils in many lubricants for vehicles. Many of these changes are caused by the new stringent requirements to reduce emissions and improve fuel economy.

Table 1: Classification of lubricating oils according API and ATIEL*

	Mass percent sulphur (%)	Mass percent saturates (%)	IV
Group I	> 0.03	< 90	80-119
Group II	≤ 0.03	≥ 90	80-119
Group III	≤ 0.03	≥ 90	≥ 120
Group IV	PAO (polyalphaolefins)		
Group V	Esters		
Group VI	PIO (poly(internal olefins))*		

Group II base oils are also commonly used in some formulations of industrial lubricants. Due to the large supply, the market price of group II base oils has decreased and become more competitive relative to the price of group I base oils. Moreover, the logistical advantages when using only one type of base oil cause the group II base oils to become crucial for lubricants manufacturers. Group III base oils have become an important component in the formulation of lubricants for vehicles. They are one of the key types of base oils necessary in lubricant formulations to meet the requirements of the latest specifications of the European Original Equipment Manufacturer (OEM). However, ATIEL guidelines for permissible replacement of base oils for the formulation within the group III differ from the API, because the additional qualification tests are required if the share of the replaced base oil is greater than 10 %. On the other hand, in Appendix E API guidelines the additional testing is not required if the proportion of the replaced oil is less than 30 % and if the viscometric properties are favourable [2]. Most base oil manufacturers declare groups IV-VI as a fully synthetic base oils, while other base oils (e. g. ester and poly(internal olefins)), introduced in 2003 as a group V or VI (ATIEL Classification for Europe only) are less used in lubricant formulations, mainly for some specific application. It is known that the conventional base oils obtained by crude oil refining consist mainly of three groups of hydrocarbons: paraffins, naphthenes and aromatics. Comparison of specific, important working characteristics of representatives of groups I, II, III, GTL and PAO is given in Table 2. The benefits of group III, GTL and PAO base oils compared to the conventional group I can clearly be seen: higher IV, lower pour point, much lower viscosity at low temperatures, lower volatility. In addition, the base oils with a high content of paraffins stand out distinctly because of higher oxidation stability, so that with the addition of antioxidant much longer service life and durability can be achieved.

Table 2: Comparison of properties of lubricating oils (Groups I-IV)

	Group I	Group II	Group III	GTL	Group IV (PAO)
Kin. visc. (100 °C), mm ² /s	4.0	4.1	4.2	4.1	3.8
IV	98	102	123	> 135	124
NOACK, mas. % (D-5800)	-18	-14	-15	< -21	-70
CCS (-35 °C), cP	28	26	15	< 12	13,5
Sulphur content, ppm	5200	4500	2900	1400	1450
Aromatics content, mas. %	> 1000	< 40	< 5	< 2	< 2

Polymer materials for seals

Changes in the production and quality of certain lubricants open a whole range of issues and indicate problems that arise during application such as their behavior in contact with elastomeric seals. The basic polymeric part of an elastomere is rubber: natural or produced synthetically. The most important representatives of more than 30 types of synthetic rubber currently used are listed in Table 3 [4]. Elastomers commonly contain 50 to 60 % of the basic polymer. Bulk of an elastomer contains various fillers, curing agents and other chemical additives that affect the intrinsic physical properties of the polymer and improve them to meet the specific requirements for a particular application. Elastomers used for the seals manufacture, especially those for the O-rings production, ensure reliable operation and no leaks if the basic requirements are fulfilled. Crosslinking of polymer chains occurs in the vulcanization process (Figure 1). Rubber changes from plastic to elastic material by this proces. After the vulcanization, including the subsequent heating if necessary, the elastomer achieves physical properties required for the seal material.

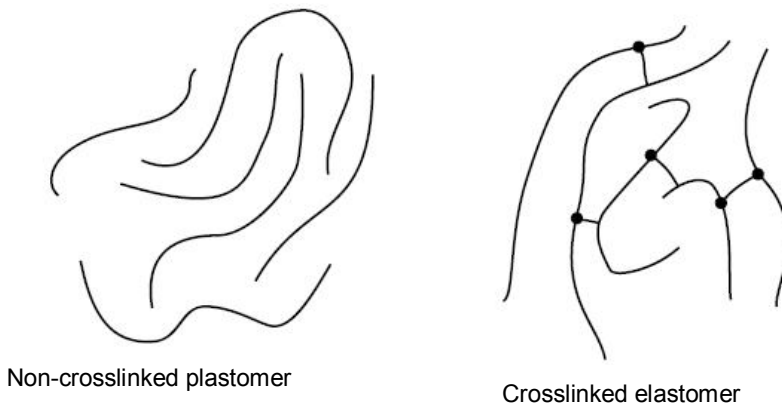


Figure 1: Schematic representation of the polymer chains before and after crosslinking

Table 3: Most important types of synthetic rubber, classification and labels

Chemical name	Symbol	
	DIN/ISO 1629	ASTM D1418
M-Group		
Polyacrylate Rubber	ACM	ACM
Ethylene Acrylate	/	AEM
Chlorosulfonated Polyethylene Rubber	CSM ^{*)}	CSM ^{*)}
Ethylene Propylene Diene Rubber	EPDM	EPDM
Ethylene Propylene Rubber	EPDM	EPM
Fluorocarbon Rubber	FPM	FKM
Tetrafluoroethylene Propylene Copolymer	FEPM	FEPM
Perfluorinated Elastomer	/	FFPM
O-Group		
Epichlorohydrin Rubber	CO	CO
Epichlorohydrin Copolymer Rubber	ECO	ECO
R-Group		
Butadiene Rubber	BR	BR
Chloroprene Rubber	CR	CR
Chlorobutyl Rubber	CIIR	CIIR
Isoprene Rubber	IR	IR
Isobutene Isoprene Rubber	IIR ^{**))}	IIR ^{**))}
Nitrile Butadiene Rubber	NBR	NBR
Styrene Butadiene Rubber	SBR ^{***))}	SBR ^{***))}
Hydrogenated Nitrile	/	HNBR
Carboxylated Nitrile	XNBR	XNBR
Q-Group		
Fluorosilicone Rubber	FMQ ^{****))}	FVMQ ^{****))}
Methyl Silicone Rubber	MQ	MQ
Methyl Phenyl Silicone Rubber	PMQ	PMQ
Methyl Phenyl Vinyl Silicone Rubber	PMVQ	PVMQ
Methyl Vinyl Silicone Rubber	VMQ	VMQ
U-Group		
Polyester Urethane	AU	AU
Polyether Urethane	EU	EU

* / ** / *** / **** PE-CSM instead CSM, PIBI instead IIR, PBS instead SBR, MVFQ instead FMQ / FVMQ [5]

Selection of polymers

When selecting a polymer material for the seal the main criteria are operating temperature of the device where the seals will be inbuilt and behavior of the seal in contact with the working fluid (compatibility). When making a particular type of seal often a compromise must be made between material of high quality and the declared sealing capability and cheaper commercial products, which generally contain small amount of the basic polymer and high content of cheap fillers. When exposed to high operating temperatures the subsequent cross-linking between polymer chains can take place, resulting in reduced elasticity of seals. Increased strength of polymer material prevents reshaping of the ring seal to the original form after the deformation. Due to exposure to pressure at a given time there is a change of shape of seals. In the case of additional high operating temperatures, there is a loss of elasticity which causes leakage from the system. Operating temperatures higher than the maximum provided always result in a shorter lifespan. All elastomers are prone to physical and chemical changes when exposed to the working medium. The proportion of change depends on the chemical characteristics of the media as well as on temperature because aggressive media becomes even more dangerous with increasing temperature. Physical changes are the result of two mechanisms that occur simultaneously:

- a) elastomer swells in a surrounding medium
- b) plasticizers and other additives dissolve and are extracted or leached out by the media.

As a result the volume changes, a swelling or shrinkage of elastic seals occurs. The degree of change depends on the medium, the molecular structure of rubber, temperature, the seal geometry (thickness of the workpiece) and strength (compressive or tensile). If exposed to the deformation and fluid rubber seal in the bearing swells much less (50 %), for several reasons, including smaller contact area. The limit of permissible volume change varies with the application. In the case of static seals a volume change from 25 % to 30 % can be tolerated. Swelling causes some deterioration of the mechanical properties. In dynamic applications, swelling causes increased friction. Therefore, a maximum swell of 10 % should generally not be exceeded. Shrinkage should also be avoided because it increases the risk of leakage. Sometimes the removal of plasticizer is compensated by absorption of the contact medium or by swelling of the seal. However also in this situation, the leaking may occur due to shrinkage when an elastomer dries out and the absorbed fluids evaporate. Chemical reactions between fluids and elastomers can cause structural changes in the way that crosslinking or degradation take place. The minimum chemical change of the elastomer can lead to significant changes in physical properties, such as brittleness. The suitability of a particular elastomer for specific purposes can be established only if the properties of the working fluid and elastomer at typical operating conditions are known. Table 4 provides the most commonly used elastomers and their behavior, chemical resistance, compatibility and incompatibility, in the most frequently used fluids (fuels, lubricants, brake fluids etc.).

Elastomer seals in contact with lubricating oils

Some features of standard test methods, which include the procedures for assessment and comparison of certain rubber and elastomers to withstand contact with various fluids, without going into details of a complex area will be highlighted here. They can be performed on test bodies: 1) prepared by cutting out a standardized piece of vulcanized rubber (Method D3182), 2) prepared by cutting the fabric covered with a layer of vulcanized rubber (Method D751) or 3) made out of the final commercial product (Method D3183) [6].

Table 4: Commonly used elastomers and their behavior with most common fluids [4,7]

	Chemical resistance	Not compatible	(Limited) Compatible
NBR, Nitrile Butadiene Rubber	aliphatic hydrocarbons	aromatic and chlorinated hydrocarbons, fuels of high aromatic content, brake fluid with glycol base	
XNBR, Carboxylated Nitrile	aliphatic hydrocarbons	aromatic and chlorinated hydrocarbons, fuels of high aromatic content, brake fluid with glycol base	
AEM, Ethylene Acrylate	(moderate) resistance to mineral oils	fuels, brake fluid	
EPM, EPDM, Ethylene Propylene Diene Rubber	brake fluid with glycol base, silicone oil and grease	mineral oil products (oils, greases and fuels)	
IIR, PIBI, Isobutene Isoprene Rubber	brake fluid with glycol base, silicone oil and grease	mineral oil products (oils, greases and fuels)	
BR, Butadiene Rubber	not suitable as a sealing compound		
CIIR, Chlorobutyl Rubber	not suitable as a sealing compound		
CR, Chloroprene Rubber	paraffin base mineral oil (ASTM oil No. 1), silicone oil and grease	aromatic and chlorinated hydrocarbons	naphthalene based mineral oil (oils IRM 902 and IRM 903), brake fluid with glycol base, low molecular aliphatic hydrocarbons

CSM, PE-CSM Chlorosulfonated Polyethylene Rubber	silicone oil and grease	aromatic and chlorinated hydrocarbons	low molecular aliphatic hydrocarbons (propane, butane, fuel), mineral oil products (oils and greases), limited swelling in paraffin base mineral oil (ASTM oil No. 1), high swelling in naphthene and aromatic base oils (IRM 902 and IRM 903 oils)
CO, ECO, Epichlorohydrin Rubber	mineral oil products (oils and greases), aliphatic hydrocarbons, silicone oil and grease	aromatic and chlorinated hydrocarbons, brake fluid with glycol base	
FKM, Fluorocarbon Rubber	mineral oil products (oils and greases) (low swelling in ASTM oil No. 1, and IRM 902 and IRM 903 oils.), silicone oil and grease, aromatski, aliphatic, aromatic and chlorinated hydro- carbons, fuels and fuels with methanol content, vegetable oil and grease	brake fluid with glycol base	
FVMQ, MVFQ Fluorosilicone Rubber	aromatic mineral oils, low molecular weight aromatic hydrocarbons, fuels		
HNBR, Hydrogenated Nitrile	aliphatic hydrocarbon, vegetable and animal fats and oils	chlorinated hydrocarbons	
FFKM, Perfluoroelastomer	aliphatic, aromatic and chlorinated hydrocarbons	fluorinated refrigerants	

ACM, Polyacrylate Rubber	mineral base oils	aromatic and chlorinated hydrocarbons, brake fluid with glycol base	
AU, EU, Polyester Urethane, Polyether Urethane	aliphatic hydrocarbons (propane, butane, fuel), mineral oil and grease, silicone oil and grease		
Q, MQ, VMQ, PVMQ, Silicone Rubber	engine and transmission oil, vegetable and animal fats and oils, brake fluid (non-petroleum base)	aromatic mineral oil, aromatics, fuels	
SBR, PBS, Styrene Butadiene Rubber		mineral oils, greases and fuels	brake fluid (non-petroleum base), silicone oil and grease
AFLAS® (FEPM), Tetrafluoroethylene Propylene Rubber		aromatics	motor oils

Some kind of reform was conducted in 2005 among the oils used for rubbery properties testing, when new terminology and types of test oil were introduced. Instead of oil labels No. 1, No. 2, No. 3 and No. 5, according to ASTM standards, new labels: IRM 902 (formerly No. 2), IRM 903 (formerly No. 3) and IRM 905 (formerly No. 5) are introduced [8]. It should be emphasized that the replacing oils are similar but not completely equivalent to those previously used. In general, oils having similar aniline point display similar effect on rubber: the lower the aniline point, the more severe is the swelling action. ASTM reference oils cover a range of aniline points found in lubricating oils [4]. Thus, ASTM Oil No. 1, having a high aniline point (124 °C), causes a slight swelling or shrinkage. IRM 902 oil has a high aniline point of 93 °C and causes moderate swelling. IRM 903 oil has a low aniline point (70 °C) and causes large or very large swelling of seals. As stated previously, the changes in the physical properties due to the contact with the working fluid and mineral oil are the result of the two different processes:

A. Diffusion of the oil into the rubber causes its swelling, the proportions of which differs from one elastomer to another

B. Chemicals of the elastomer can be dissolved or extracted, which causes shrinkage of the workpiece.

The processes can be concurrent and the resulting volume change may not be noticeable. The effect depends not only on the type and characteristics of elastomers but also on the sealed fluid itself.

The base elastomer contains between 15 and 50 % acrylonitrile (ACN). The higher the ACN content the better compatibility with oil. Analogously, a higher content of aliphatic components, such as in paraffinic oil, causes lesser swelling (also with small ACN content). Opositely, aromatic based oils cause swelling, whereat in some elastomers an equilibrium has not been established, e. g. with NBR. A high ACN content is necessary to prevent swelling, which occurs in the naphthenebased oils.

Any other commercial oil with the same or similar aniline point as the corresponding ASTM test oil will have similar effects on the sealing material. However, it has been found that the aniline point method is not always reliable. Some commercial oils with the same aniline point can cause significantly different swelling because they contain different types and amounts of additives. A quick and effective method for predicting the compatibility of commercial rubber with mineral base oils involves the application of a representative reference compound, denoted as NBR 1. The action of mineral oils against this standard rubber can be evaluated by the elastomer compatibility index (ECI). ECI values for various oils are in the range 2.2 -24.0 (T. 5).

Table 5: Elastomer compatibility index (ECI) for various oils [4]

Type of Oil	ECI
IRM 901 (ASTM oil No. 1)	2.2-3.2
IRM 902 (ASTM oil No. 2)	9.4-10.4
IRM 903 (ASTM oil No. 3)	23.0-24.0

The straight-line graph (Figure 2) for a specific compound X is called the Swelling Behavior (SB). To determine the volume change of compound X in a mineral oil having an ECI of 10 for volume, follow the 10 % vertical ECI line until it intersects the slanted line. Follow the horizontal line from that point to the vertical axis. Compound "X" will have a volume swell of approximately 2% in that oil. By using the ECI, the volume change of the test material in a mineral oil can be predicted, which saves laboratory time. The ECI values for oils were determined previously in the laboratory (Table 5). Also, ECI values can be plotted on a compound specific graph. Based on the graphic dependence ECI - volume change (%) the expected volume change can be read directly from the vertical axis for known ECI, which helps to rate the elastomer compatibility with given oil. The procedure developed by Parker technologists has been standardized under International Standard ISO 6072.

To determine the ECI for the specific oil according to the ISO 6072 standard, it is necessary to follow the procedure: a change in weight of the test elastomers, e.g. NBR 1 is determined after the sample was immersed in the specific oil for 168 hours at 100 °C. Afterwards, the ECI can be easily read from the graph in Figure 3 plotting the weight change.

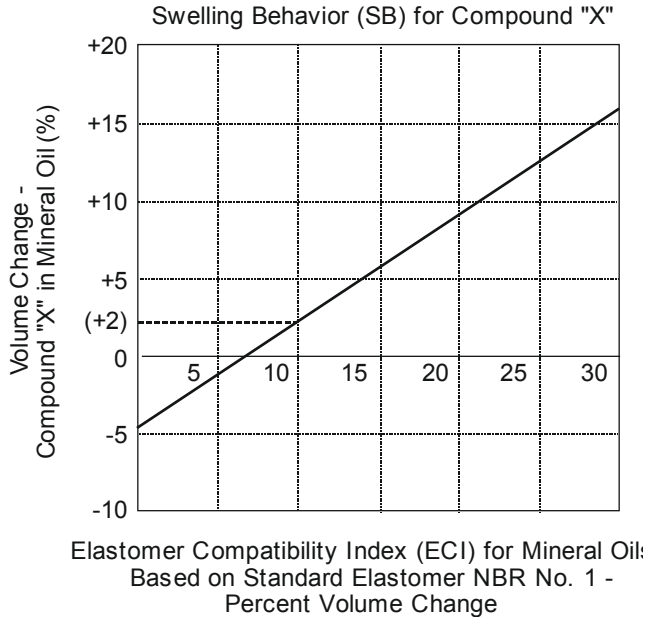


Figure 2: Swelling Behavior (SB) for compound X [4]

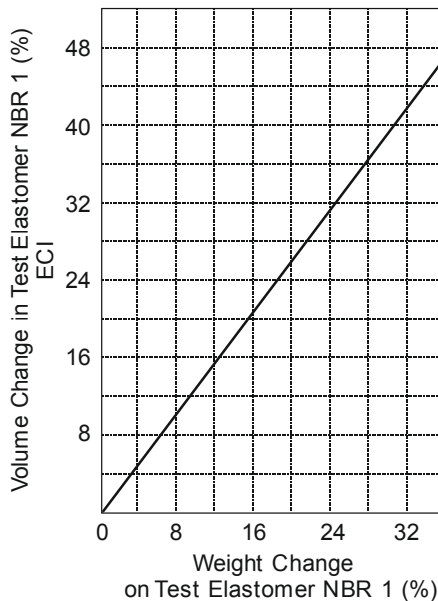


Figure 3: Weight change on test elastomer NBR 1 (%)

In Tables 6 and 7 are given the possible applications of the most abundant individual elastomers and polymer materials for work with PAO oils [9].

Table 6: Materials for seals that are (not) recommended for usage with PAO oils

Recommended	Not recommended
Fluorocarbon (FKM, FFKM, Viton®)	Natural Rubber
Fluorosilicone (FVMQ, MVFQ, FSI)	Polyisoprene (IR, synthetic rubber)
Polytetrafluoroethylene (PTFE, Teflon®)	Isobutene Isoprene Rubber (PIBI, IIR)
Acrylonitrile-Butadiene (H-NBE, L-NBR, Buna N®)	Ethylene Propylene Rubber (EPM)
Epichlorhydrin (CO, ECO)	Ethylene Propylene Diene Rubber (EPDM, Nordel®)
Polysulfide (T, PPS, selected versions)	Styrene Butadiene Rubber (PBS, SBR, Buna S®)
Polyurethane (AU, EU, selected versions)	Silicone Rubber (MQ, VMQ, PMQ, SI)
Polyester (selected versions)	Propylene Oxide (PO)
Polyacrylate (ACM)	Butadiene Rubber (BR)
Ethylene-Acrylate (Vamac®)	
Low temperature service only	
Polychloroprene (CR, Neoprene®)	
Chlorosulfonated polyethylene (PE-CSM, CSM, Hypalon®)	
Chlorinated Ethylene copolymer (CM, Alcryn®)	

Table 7: Plastics that are (not) recommended for usage with PAO oils

Recommended	Not recommended
Fluorocarbon	Polystyrene
Polyamide (Nylon®)	Polyvinyl Chloride (PVC, CPVC, Tygon®)
Polyacetal (Delrin®, Celcon®)	Acrylonitrile Butadiene Styrene (ABS)
P Polytetrafluoroethylene (PTFE, Teflon®)	Polycarbonate (Lexan®)
Polyethylene HD	Polyethylene LD
Polyurethane (selected versions)	Polypropylene
Phenolic (selected versions)	Polybutylenr
	Polymethacrylate (Acrylic, Lucite, Plexiglass®)
	Polyalkylene Terephthalate (PET, PBT)
	Polysulfone (PSO, PES)

Comparison of compatibility of elastomer with group I and III, GTL and PAO base oils

As an example how difficult it is to define generally interactions of certain elastomer and oil the study performed by J. Braun can be used [10]. The example of a typical hydraulic oil formulation containing Zn was used to investigate the tolerability of the NBR based elastomers with group I and III, GTL and PAO base oils. All oil samples: four representatives of the group III (from Europe, Korea and Canada) as well as two samples from the GTL pilot plant, PAO and group I conventional oil, in contact with the elastomer 72NBR 902 cause the shrinkage, with the similar volume changes (4.4 to 5.5 %), except in the group I base oil where it was 1.4 %. On the other hand, all kinds of oils in contact with the SRE NBR 1 elastomer, the reference in most specifications, cause its swelling, except PAO that causes a slight shrinkage (0.5 %). Swelling in group III base oils was 0.4 % - 1.1 %, in the GTL base oils 0.1 % and 0.9 %, while the most intense swelling of 5.2 % was observed in the group I base oils. In addition to these two types of elastomers, five different samples were tested in order to predict compatibility with group I, III and PAO base oils. All samples showed various shrinkage (0.7 % - 9.4 %) in the PAO and group III base oils. They behave differently in contact with the group I base oil; two samples (80 NBR 873 and N 3571-71) showed shrinkage while three samples (N 3578-75, N 3580-80 and 82 NBR 1329199) showed swelling. It is interesting that some special materials, considered as well swelling, in contact with unconventional oils show shrinkage. However, the established differences regarding the volume change of elastomers show that the manufacturers have formulations suitable for the new base oils among the existing elastomers, i.e. the development of appropriate new elastomer compounds is promising.

The influence of esters and swelling additives on the seals

Apart from elastomers manufacturers the lubricants manufacturers can eliminate or compensate the impact of non-conventional base oils on the seals shrinking. Ester base oils cause swelling and additive manufacturers offer special additives for the seals swelling. A combination of five different saturated esters (5 %) and swelling additives (1 %) in SRE NBR were tested with the group III base oils, which show significantly inferior swelling in comparison to the group I base oils. Only with the swelling additive the volume changes similar to that in the conventional group I base oil (5 – 6 % increase) is achieved. The storage time extension from 7 to 42 days (1000 h) did not lead to the significant differences in the volume change. However, the elastomer 72 NBR 902 behaves oppositely to the SRE NBR 1, the negative volume change i. e. shrinkage occurs in the group I base oil, which is even stronger in the group III base oil.

In the formulations of ester base lubricating oils (two kinds) and the swelling additives the compensating effect is present, which is more pronounced with the swelling additive.

By increasing the concentration of esters, with the strongest capability of swelling, up to 10 % in SRE NBR 1 and 72 NBR 902 (and keeping the concentration of swelling additives at 1 %), a volume change like in conventional oils takes place. However, in this way the cost of oil increases by approximately 15-25 %, which is a significant expenditure for the hydraulic oil customers. Especially considering that this is one of the cheapest saturated esters on the market. Other, more expensive esters can cause even higher prices.

In order to study the long-term effect of the ester and swelling additives on properties of the elastomers, in particular elastic properties (tensile and breaking strength), different NBR materials were examined after 42 days (1000 hours) at 100 °C in contact with the modified formulations of group III base oils. Thereby, the test materials SRE 1 NBR, 72 NBR 902, 80 NBR 878, N 3580-80 and 82 NBR 132919 showed no deterioration of the elastic properties as compared to formulations based on the conventional or group III base oils without swelling additive. However, a significant reduction in tensile strength is evident, which in tested elastomers amounted between 40 % and 76 %, regardless of the base oil (Table 8) [10].

Table 8: Average changes of breaking strength for various NBR based elastomers

Material	Breaking Strength Change, %
SRE NBR 1	- 40
72 NBR 902	- 58
80 NBR 878	- 74
N 3580-80	- 76
82 NBR 132919	- 54

The limited thermal stability of NBR material

Numerous tests of thermal stability of elastomers showed significant reduction in tensile strength of the NBR material. The old specification for lubricants commonly gave only the volume change and hardness after storage for 7 days at 100 °C. Nowadays, in the revised standards relating to lubricants (e.g. DIN 51517-3 [11]) and the manufacturer's specifications (e.g. Flender specifications for gears [12]), related to the elastic properties, the limits of tensile and breaking strength are set. The test period is increased to 42 d (1000 h). Thereby, the value of the maximum allowed change, according to producers, is often below the experimental values. Since the manufacturers scarcely present the results of their own investigation, the given recommendations have been accepted.

Results of the experiment of storing (1000 h / 100 °C) elastomer in the air (without lubricant), presented in 2005, showed deterioration of tensile strength of approx. 60 %, an order of magnitude that one encounters in the gear oils with additives [13]. In order to rule out the bad values to be result of the decrease of the base oils resistance against oxygen during the storage and air contact, the examined elastomers are stored not only in the standard test hydraulic oils, but also in group I base oil of the same viscosity (ISO VG 46). The results showed that there was no significant difference after the storage in the pure base oil or oil with additive. The decrease of tensile strength in both cases is almost identical. In the sample 72 NBR 902 values after the storage in air and in pure PAO are determined, as well. Regarding the accuracy of the method, the changes in the material can be considered as equal.

It can be concluded that the worse characteristics of most elastomers based on NBR after storage 42 days at 100 °C can be associated with their well-known poor thermal stability and are not necessarily the result of the addition of lubricant additives. Naturally, the NBR formulations with a high content of additives and sulfur compounds are more susceptible to decay. In most cases this is mainly a result of the thermal instability of the NBR. It should be borne in mind by setting the lubricant specification limits.

Conclusion

All stated underlines the importance of development of materials in today's industry. It is a constant race against time and competition, which can only be obtained by quality. Investment in the development of new materials and technologies is an imperative in order to make a step forward to the new environmentally friendly products with improved properties. These examples show the necessity of knowing the structure and properties of materials, the behavior during the application and pathways of modification of individual properties. Also, increased attention is paid to the method of material testing and improvement of test methods. Therefore, in addition to the knowledge and experience the continuous improvement and surway of the field are necessary in order to react timely and adequately.

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