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ANALYSIS OF THE INFLUENCE OF THE CHARACTERISTICS OF WORKING FLUIDS IN HYDRAULIC SYSTEMS ON FUNCTIONAL PERFORMANCE

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Abstract: *By following the expression of the binding force of the molecules (resistance of fluid to flow) under controlled pressure and temperature conditions and the influence of the characteristics on the efficiency of the components of the hydraulic mechanism, one can evaluate the compatibility and optimize the potential of the lubricating fluid (subjected to physical-chemical stress) and its impact (toxicity and loading) on the environment after the cycle of use. Phenomena inside the lubricant layer have a great influence on lubrication, as a result of the association of molecules under the action of existing polar substances, but also through intra-molecular friction. The phenomena occurring at the friction surface, at the micro level of the peaks in contact, where the temperature and pressure are significantly increased, can be studied and diminished to reduce energy losses, by creating a protective layer, thus providing better resistance and elasticity of the molecular contact surface. Starting from the aspect of element interactions and the study of chemical transformations between friction surfaces and reaction media, the action of (tribological and rheological) phenomena on the durability of mechanical systems can be analysed and developed. This action can be carried out through mathematical modeling and parameter calculation methods, which define the phenomena that take place at the collision, for the extension and improvement of the experiments at the prototype level. The cumulative influence of the phenomena inside the lubricant layer with those occurring at the lubricant-metal interface is determined by the surface properties of the lubricant but also by the attraction forces from the surface of the metals with which the lubricant is in contact.*

Keywords: *Tribology, durability, lubricant, viscosity, hydraulic systems*

1. Introduction

The development of applications involving friction, wear and lubrication processes at the level of interactions of surfaces in relative motion requires interdisciplinary connections of mechanics, mathematics, physics and chemistry, materials science, biology and engineering sciences. This type of movement between two surfaces highlights specific basic tribological phenomena (lubrication, friction and wear). The methods used for the synthesis of lubricant composite materials aim to ensure certain performance characteristics of the resulting product. Thus, the lubricating oil is recommended for one or more essential properties of a given application: thermal properties, very good chemical resistance, ordered texture on a micro or nanometric scale.
The main aspects of molecular interactions are aimed at:
- geometry, kinematics and dynamics of interactions;
- friction phenomena in the absence and/or presence of the lubricant;
- wear phenomena at the level of interactions between fluid layers;
- lubrication phenomena in limit, mixed, hydrodynamic (HD), elastohydrodynamic (EHD) regime, etc.

The quality of a hydraulic fluid is strongly influenced by the characteristics provided by the finished product. In order to meet the quality criteria of hydraulic oils, lubricating oil compositions have been developed which, among other things, ensure:
- energy transmission and saving;
- provides superior protection against fluid losses (through leaky seals, contaminants, pump wear and irregular operation);

- lubrication, friction protection (between metal components, anti-wear);
- anti-corrosion protection of lubricating circuits;
- increasing both thermal and oxidation stability;
- neutralization of acid products and maintenance of oil characteristics even under conditions of exposure to moisture and extreme temperatures;
- demulsifying properties (for rapid water separation) and good filterability, with high anti-wear and EP characteristics;
- decreasing tendency foaming agents (containing antifoam agents to control the release of entrained air);
- compatibility with non-ferrous metals;
- increasing machine reliability/operating time between lubricant changes;
- maintaining and extending machine lifespan;
- preventing rust and corrosion, etc.

The lubrication and flow characteristics of the oils are represented by:

- unctuousness, a property that depends on the polarity and the length of the molecules in the lubricant,
- fluid viscosity, a property that is strongly influenced by the molecular orientation in the fluid layers and the temperature of the flow. This property can affect power losses in hydraulic systems, hydraulic-mechanical losses (friction losses in pipes) and volumetric losses (leakage losses). These two properties have an influence on the wear of the hydraulic system, namely: the operation of the system in a wide range of temperatures, lower oil consumption, better sealing between the piston, segments and cylinder.

Accidental oil leaks and spills from various hydraulic devices are a medium and long-term environmental polluter. These residual oils have a content of toxic, dangerous particles (metallic and hydrocarbons) with a high migration potential (in soil and groundwater) and complex volatile, hydrophobic, biodegradable, etc. mixtures, which produce damage with a major impact on the soil, with effect on the ecosystem such as:

- the disappearance of some species;
- danger to health and food safety (weaker harvests);
- threatens the well-being of ecosystems and the environment;
- climate change (release of CO_2);
- desertification (arid regions);
- population dislocations (emigration), but also economic (local, zonal, regional) impact.

The pollution aspects as much they are known, they are as much debated, this topic being of real interest also for the Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services (IPBES), which dealt with this topic in a Report on soil degradation. Soil pollution is a global threat, extremely serious especially in regions such as Europe, Asia and North Africa, according to the Food and Agriculture Organization of the United Nations (FAO) [1]. Phenomena such as erosion, loss of organic carbon, high salt content, compaction, acidification and chemical pollution are the main causes of current soil degradation. FAO shows that both intense and moderate degradation already affects a third of the planet's soil, and recovery is slow, practically 1000 years would be needed to create a layer of 1 centimeter of arable soil. Therefore, choosing the lubricant for fixed or mobile equipment with hydraulic systems is an extremely important issue, which requires knowledge of the existing working conditions and environment, the required physical-chemical properties, the degree of loading, the special requirements and the compositional content of these hydraulic oils.

2. Analysis methods and hydraulic oils characterization mechanisms

The main characteristics of these oils can be grouped as follows:

- to ensure superior lubrication qualities (viscosity, viscosity index, unctuousness);
- to determine the field of use (viscosity variation with temperature and pressure, volatility);
- to determine the stability under conditions of use (resistant to oxidation, to the formation of deposits);

- for purity and anticorrosiveness (content of mechanical impurities, water, anticorrosive properties),
- various, for oils depending on their field of use.

Therefore, it is very important that the hydraulic oil has the best and long-lasting stability with temperature variation. The specialized literature confirms that the addition of additives with combined effects leads to an increase in the viscosity index [2, 3]. Additives are chemical substances, organic compounds, based on metals or polymers, in a proportion of 25-15%, whose chemical composition must be compatible with the sealing system and which confer the anti-wear, anti-corrosion and maintaining functions of lubricant viscosity.

From the point of view of the type and nature of the additives introduced into the base oil, they can be:

✓viscosity modifiers
✓anticorrosive and antirust
✓defoamers
✓pour point depressants

These additives are used to prevent the formation of crystal networks or to inhibit the growth and solvation of nascent paraffin crystals by adsorption.

✓dispersants (detergents)

Due to the super basic nature of these additives, low operating temperatures, solid impurities are kept in suspension and thus corrosion can be combated.

The action of these additives can be explained by three types of mechanisms:

- adsorption, mechanism by which agglutination is prevented;
- solubilisation, a mechanism leading to the formation of water-in-oil micelles that encapsulate oil-insoluble particles;
- chemical neutralization, a mechanism that can stop the phenomenon of polycondensation.

✓antioxidants (inhibitors of radicals and hydroperoxides)

This type of additives can interfere with the propagation mechanism at different stages of the process through free radicals. These are the most used additives, being practically added in the formulation of all lubricating oils.

✓extreme pressure and anti-wear

These adhesives have as their first role the formation of a protective pellicle layer as a result of the orientation and adsorption of the polar functional groups on the polymer chain. During lubrication, physical or chemical adsorption phenomena occur and the orientation of surfactant molecules from the lubricant at the metal surface takes place. The molecules orientation in the first layer is much more stable than that of the other layers, so the disorder gradually increases in the volume of the lubricant.

The following transformations can occur in the lubricating mechanism system:

- plastic deformations in the metal, without it being destroyed, as a result of the adsorption mechanism at the level of the first layer;
- increasing the contact surface with the formation of compounds with lower mechanical resistance (surfactants with groups of sulfur, chlorine, phosphorus, etc.) as a result of some chemical reactions taking place;
- arching of the chain of oriented molecules as a function of speed, which is stronger the longer its length and stability, but above a certain speed, breakage of hydrocarbon molecules or pairs of molecules in the oriented boundary layer may occur, as a result of the fact that in the hydrocarbon planes the bond energy is lower than in the surfactant planes.

The tendency to break increases with increasing chain length, therefore with the thickness of the lubricant film.

One can expect different phenomena developed by contaminants, especially secondary products resulting from thermal decomposition or oxidation reactions. Numerous compounds (alcohols, aldehydes, ketones, lactones, esters, acids, condensation products - resins) with characteristic effects were identified in the used oils. Thus, acid radicals attack metals, oil-soluble salts favour the formation of emulsions, oxygen compounds lead to colloidal deposits, so through oxidization the volume of molecules increases and blocks the filter and hydraulic valve, water generates emulsions,

causes foaming (aeration increases the compressibility of oils, the cavitation effect appears) and accelerates oil oxidation, suspended solid particles contribute to premature wear of hydraulic oil, the presence of sulfur in oils leads to the appearance of corrosive compounds during use, the increase in hydrogen content leads to a decrease in relative density, oil vaporization leads to the formation of insoluble condensation products, condensation products settle, increase viscosity, form corrosive acidic substances and impede transmission.
To combat phenomena induced by various contaminants, manufacturers resort to specific additives with various effects for the protection of hydraulic drive systems. The best known of these specific additives are:

- Ashless dispersant type additives

From this category, the most commonly used additives contain polyisobutene, where the polar part is an amine and the linking group is maleic anhydride or the phenolic nucleus.

- Additive with depressant effect

From this category, the most frequently used additives are based on polyalkyl acrylates and polyalkyl methacrylates, substances with functional groups that occupy an important place in the production of additives of this type.

- Ameliorating type additives

This type of additives contains copolymers of fumaric esters with vinyl acetate, copolymers of alpha olefins, styrene-butadiene or styrene-isoprene copolymer and polyalkyl-styrenes, as well as naphthalene and phenol derivatives, the best known being a polyalkyl-naphthalene and ditetra alkyl-phenol phthalate or polymers of these copolymeric derivatives. However, too high a content of ameliorate additives is not recommended for closed systems because they reduce the rate of water-oil separation.
Other types of specific additives are also:

- Viscosity index modifiers

These additives have in their composition organic polymers, soluble in oil, such as polyisobutylenes, polymethacrylates, copolymers of methacrylates with alkyl radicals of different lengths, ethylene propylene copolymers, hydrogenated block copolymers of isoprene and styrene as well as polyacrylates, from the range of acrylic copolymers with alkyl radicals of different lengths. Polymer additives are made up of macromolecules with different degree of polymerization; they can be characterized by chromatographic analysis, the most used being the gel permeation method. At high temperatures or at friction between lubricated parts, at high pressures and speeds, macromolecules break. For this reason, shear strength becomes an important characteristic of polymers.

- Antioxidant additives

Like the ameliorate additives, these additives contain phenol derivatives but also aromatic amines such as: di-tert-butyl-paracresol, also known as Topanol, with an antioxidant effect up to 180^{o}C, octyl-diphenyl-amine, alkyl phenyl-beta - naphthylamine. Among the most widely used peroxide removers there is the zinc alkyl dithiophosphate compound that acts as an anti-wear additive, but there are also compounds with sulfur, with selenium, or their combinations, for example compounds with sulfur and nitrogen, with sulfur and phosphorus, etc.

- Additives for extreme pressure and anti-wear

This type of additives forms a film protective, a coating layer that contains several types of polar organic compounds such as: alcohols, esters, amines, fatty acids, sulfur compounds as disulfides, sulfurized olefins, esters of sulfurized unsaturated fatty acids of the dialkyl polysulfide type, dithiophosphate of zinc, and above all, additives with sulfur and phosphorus or sulfur, phosphorus and nitrogen which give appropriate anti-deposition qualities to hydraulic oils.
Filterability is an important characteristic for the good operation of hydraulic equipment. Mixed oils contain constituents of different origins, each type of oil has specific properties in certain amounts and provides a certain contribution, resulting in a beneficial and balanced oil for the hydraulic system. Their composition contains an ideal percentage of polyunsaturated fatty acids such as linoleic and linolenic acids, monounsaturated fatty acids and other constituents. Vegetable oils contain a mixture of technological plants, seeds (sunflower, soybean, corn germ, rapeseed, cotton, sesame) or fruits (walnuts, hazelnuts, coconuts), according to special technologies, the unsaturated fatty acids being

in the form of cis-cis (of the same side of the unsaturated bond). However, a large intake of polyunsaturated fatty acids has negative effects, the most common of which is the peroxidation effect, which favours the accumulation of toluidine and aniline. It is known that the basic effect of aniline is a precursor for obtaining polyurethanes and that it leads to the formation of mineral accumulations (stones), and in extreme cases, through certain peroxidising compounds, it can favour the aging of hydraulic oil.
Hydraulic fluids, depending on their composition and properties, as one can see in the diagram in Figure 1, have an important role in industry.

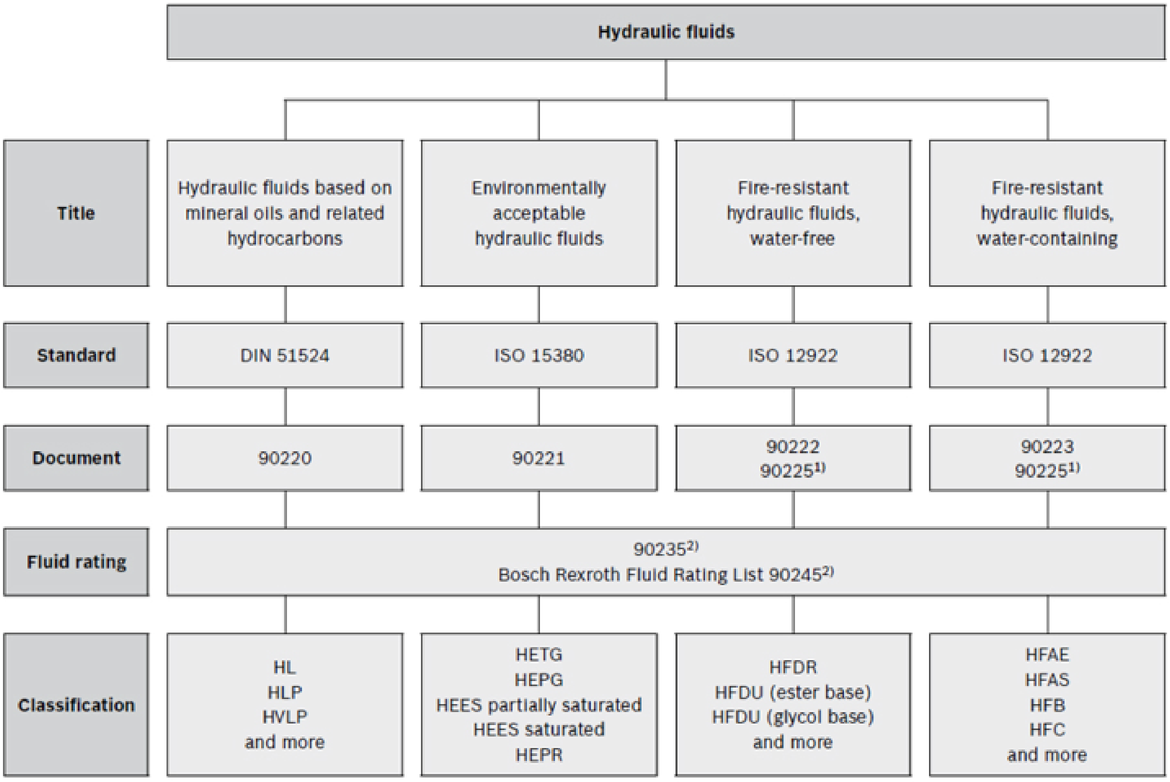

Fig. 1. Classification and properties of hydraulic fluids [4]

Therefore, their demand and the type of use led to their diversification and improvement in the context of the sustainable concept for increasing efficiency.
The German norm DIN 51524 notes them with HL, HLP, HVLP. HL, HLP, HVLP.
- HL: contains active ingredients to reduce aging and protect against corrosion;
- HLP: other active ingredients are added compared to HL to reduce wear, additives that improve particle transport and water dispersibility; it has the largest field of applicability in practice.

As such, the major manufacturers of such products have also developed environmentally friendly hydraulic fluids, so-called biofluids, which must meet the technical requirements of DIN ISO 15380 as environmentally acceptable hydraulic fluids and the classification of fluids used in hydraulic applications defined in ISO 6743-4 [5, 6]. These ecologically acceptable biofluids with a minimum base fluid content for each product group of at least 70% (m/m) are grouped into several categories, namely:
- vegetable oils HETG (Hydraulic Oil Environmental TriGlyceride) whose composition is based on triglycerides, is technically limited by lower resistance to oxidation and temperature stability, as a result of their "double bonds".
- Synthetic Esters - HEES (Hydraulic Oil Environmental Ester Synthetic). Group HEES further splits into 2 sub-categories with different levels of performance properties:

a) Unsaturated (or partially saturated) synthetic esters are products based on vegetable resources or their mixtures. Their technical applicability in high demanding applications individually depends on composition of the mixture;
b) Saturated synthetic esters currently provide the most sophisticated, environmentally acceptable solution for hydraulic systems. Technical advantages of saturated synthetic esters are performance benefits, extreme stability, wide temperature range, compatibility, high levels of biodegradation and renewable resources.
- HEPR (Hydraulic Oil Environmental PAO (polyalphaolefins) and Related products) (and other synthetic hydrocarbons). HEPRs are produced in very low viscosities, limiting their primary applicability. Viscosity modifiers are required to improve their usability in common hydraulic applications. However, their environmental acceptance is often compromised (similar to HEPG).
- HEPG (Hydraulic Oil Environmental PolyGlycol) - in their composition, the majority of compounds are of the polyglycol type. Performance-wise HEPGs are highly sophisticated products. However, their severely limiting factors are incompatibility with sealing materials, hoses, and virtually any other type of hydraulic oil. HEPGs are also questioned for poor biodegradation and not meeting criteria for renewable resources, e.g., unable to obtain Ecolabels. HEPG oils are used only on a small scale.
Environmental compatibility means minimal toxicity, easy biodegradability and no bioaccumulation.
Biodegradable hydraulic oils have favourable rheological properties compared to mineral oils, they have a reduced tendency to degrade, they are coatings materials, carbonation products or resins with good adhesion capacity, which leads to the increase in the efficiency of hydraulic oils, they do not undergo changes in viscosity for large temperature ranges during operation, etc.

Table 1: Classification of Biodegradable Hydraulic Fluids and typical characteristics [7]

Classification of Biodegradable Hydraulic Fluids and typical characteristics

Classification ISO	Composition	Base Fluid	Typical Temperature Range (ISO)	Characteristic Features
HETG	Triglyceride	Vegetable	-20 to +70°C	+ Excellent biodegradation - Lower oxidation resistance
HEES	Synthetic Ester 1) unsaturated 2) saturated	Synthetic	-30 to +90°C	+ Stable, High-performing + Excellent biodegradation
HEPR	Poly alpha olefin (PAO)	Synthetic	-35 to +80°C	+ Good stability - Only available in low viscosities
HEPG	Poly alkyl glycol (PAG)	Glycol	-30 to +90°C	+ Stable, often water-soluble - Incompatible

The most important characteristic features of these biofluids are:
✓ great lubrication performances
✓ outstanding thermal oxidation stability
✓ wide operating temperature range, very low pour point
✓ very long oil-change interval
✓ neutral to seal materials and elastomers
✓ readily biodegradable; non-toxic, with non-foaming additives, CO_2 emissions reduction
✓ EU Ecolabel Certificate of Environmental Excellence.

These types of oils are high performance hydraulic fluids, some have a mixed composition with partial content of saturated and unsaturated synthetic products, some without zinc, easily biodegradable. A special additive package provides excellent extreme pressure properties, thermal oxidation resistance, anti-wear control and non-foaming.
Another characteristic of these hydraulic oils with an important value is the iodine number. This number is a value for the amount of unsaturated organic esters in grease and oil. The value is determined by adding iodine to the grease or oil until the ability of the grease or oil to chemically bind is stopped; essentially, the iodine number is how many grams of iodine were added per 100 grams of substance tested.

A higher iodine number defines the level of unsaturated esters in the liquid, which could combine with other substances to produce a chemical bond. In unfavourable circumstances such as contaminated oil, high temperature or extended drain intervals, high levels of unsaturated organic esters, as found in plant-based industrial oils (e.g., rapeseed), they will react and bind with other substances, e.g., oxygen, and can cause gumming and residues.

Table 2: Typical data for three readily biodegradable fluids in comparison with mineral oil [8]

Typical Available Data	**Standard Mineral Oil**	**HETG (Rapeseed Type Oil)**	**Unsaturated HEES**	**Saturated HEES**
	ISO VG 32			
Density @ 15°C (g/ml)	0.880	0.922	0.929	0.918
Flash point (°C)	204	255	198	240
Pour point (°C)	-29	-33	-36	-58
Viscosity @ 40°C (mm^2/s)	32.0	34.0	35.0	31.8
Viscosity @ 100°C (mm^2/s)	5.4	8.0	8.1	5.8
TAN (mg KOH/g)	0.96	0.40	0.60	0.70
Viscosity index	103-140	210-250	175-215	140 -150
Iodine value	-	80-120	40-80	<10
Optimum temp range (°C)	<80	<60	<80	>80

The types of fluid available are many and varied; it is therefore essential to evaluate the criteria of a particular environmentally sound hydraulic fluid (ESHF) before use. Table 3 highlights the various properties of the typical fluids available.

Table 3: Properties of typical fluids [8]

Typical Available Data	**HETG**	**HEES (Unsaturated)**	**HEES (Saturated)**	**HEPR**	**HEPG**
Flowability at low temp.	-	+/-	++	+	++
Oxidation stability	-,#	+/-	++	+/-	++
Evaporation loss	+	+	++	-	++
Water separation	-	+/-	++	+	Water soluble ##
Anti-rust protection	++	++	++	++	-
Miscibility with mineral oils	Yes* after clarification	Yes* after clarification	Yes* after clarification	Yes* after clarification	No
Compatibility with seals	+	+	+	+	+
Hydrolytic stability	-	+/-	+/-	+	++
Price	+	+/-	+/-	+/-	+
Storage times	-	+	++	+/-	+

++ = Very Good
\+ = Good
+/- = Average
\- = Poor
= Can cause sticking
= Water content increases corrosion, cavitation
* = Mixtures should be avoided, they are not advantageous

Oxidation, or ageing, of a fluid is caused when a fluid reacts with oxygen.

The result is extreme thickening and gumming of the fluid, producing varnish deposits which can lead to catastrophic system failures. Chemically speaking, vegetable-based and unsaturated ester-based fluids have many open bonds that react with oxygen when exposed to thermal load causing the fluid to age more rapidly. Saturated esters, on the other hand, have significantly fewer open bonds so they do not oxidise rapidly and will last much longer when subjected to high temperatures. Most fluids will have adequate anti-corrosion properties although the chemical structure may differ across the number of functional groups and degree of unsaturation of the polymer chain. The compatibility of the hydraulic fluid with the materials of the cylinder/equipment sealing components is mainly influenced by the chemistry of the respective fluid, parameters such as viscosity or product formulations differ between lubricant manufacturers. It is therefore essential to know detailed seal compatibility data from the supplier for the fluid to be used. Table 4 shows an example in this sense.

Table 4: Detailed data on sealing compatibility according to different viscosity classes of hydraulic oils [8]

Characteristics of Test	**Units**	**Requirements**				**Test Method or Standard**
Viscosity Grade		**22**	**32**	**46**	**68**	**ISO 3448**
Elastomer compatibility after 1,000 h at given test temperature						ISO 6072
NBR I	°C	60	80	80	80	
HNBR	°C	60	80	80	80	
FPM AC 6	°C	60	80	80	80	
AU	°C	60	80	80	80	
Change in Shore-A-hardness, max.	grade	±10	±10	±10	±10	
Change in volume, max.	%	-3 to +10	-3 to +10	-3 to +10	-3 to +10	
Change in elongation, max.	%	30	30	30	30	
Change in tensile strength, max.	%	30	30	30	30	

Consideration should be given to the relationship between the viscosity, temperature and pressure of a fluid. Viscosity index (VI) is an arbitrary measure for the change of viscosity with temperature. Knowledge of the chemistry involved is important in order to ensure the correct choice of fluid. Most fluids will thicken as the pressure exerted on them is increased. Table 4 gives an indication of typical changes of viscosity with pressure. More detailed information can be obtained from the supplier of the product used. The temperature of the oil varies in a wide temperature range (from -40^{o}C to 120^{o}C), so for bio-hydraulic oil the viscosity index is in the range of 150-220, and for mineral oil the viscosity index is around 100. Oil concentrations in test solutions are inherently unstable and sensitive to experimental methods affecting the amount, bioavailability and estimated toxicity of dissolved hydrocarbons. ATIEL (Technical Association of the European Lubricants Industry), together with ATC (Additive Technical Committee) and ACEA (European Automobile Manufacturers' Association), define the limits of the tests and monitor compliance with the declared qualities. One of the most important problems is to establish the chemical nature, structure and composition of the additives and the quantitative ratio in which these additives must be introduced into the oil, so that the resulting lubricating oil composition has specific physical-chemical characteristics.
Mainly these characteristics are: preservation of the viscosity index in operation, dispersing capacity against solid impurities, reduced wear of the device parts by friction, antioxidant properties, prevention of the formation of liquid residues, etc. These aspects must be followed and maintained within the appropriate parameters to ensure the fulfilment of quality norms in the operation of the hydraulic device.

3. The influence of chemical composition on the toxicity of hydraulic oils

The composition of the lubricating oil consists mainly of components such as:
- carboxylic acid derivative, preferably ethylene polyamine, and a substituted succinic acylating agent consisting of a polyalkylene group, preferably polyisobutylene, of medium molecular weight;
- succinic groups with a polydispersity index, preferably in the range of 2...4 [9];
- alkali metal salt of a carboxylic or sulfonic acid, preferably sodium or potassium alkyl benzene sulfonates, with increased basicity;
- dithiophosphate dihydrocarbons, preferably of zinc, calcium, magnesium, or copper, dihydro-dithiophosphoric acid being prepared by the reaction of phosphorus pentasulphide with a mixture of isopropyl or isooctyl alcohol with primary alcohols, containing at least 20% molecules of isopropyl alcohol or sec- butyl, preferably with a mixture of isopropyl and isooctyl alcohol;
- carboxylic acid ester derivative, which is a product of the reaction between a substituted succinic derivative and a polyol, with a polyamine compound, preferably ethylene polyamines, the components being introduced into the oil as such or in the form of a concentrate;
- polymerized hydrocarbons such as polypropylenes, polybutenes, copolymers of propylene and isobutylene;
- alkylbenzene derivatives, such as dodecylbenzene, tetradecylbenzene, dinonylbenzene, di(2-ethylhexyl)-benzene but also products of chemical synthesis;
- polymerized hydrocarbons such as polypropylenes, polybutenes, propylene and isobutylene copolymers;
- their halogenated derivatives, poly(l-hexene), poly(l-octene), poly(l-decene), as well as their mixtures;
- alkylbenzene derivatives, such as dodecylbenzene, tetradecylbenzene, dinonylbenzene, di(2-ethylhexyl)-benzene, etc.;
- polyphenyl compounds, such as diphenyl, terphenyl, alkylated polyphenyl compounds, etc.;
- alkylated diphenyl ethers and alkylated diphenyl sulfides and other synthetic compounds with similar structures and properties, in the form of their derivatives and homologues;
- polymers and copolymers of oxyalkylenes, in which the terminal hydroxyl groups have been etherified or esterified, with alcohols, phenols and respective acids such as polyoxyethylenes or polyoxypropylenes, dimethyl ether of polypropylene glycol, diphenyl ether of polyethylene glycol, diethyl ether of polypropylene glycol;
- esters with monocarboxylic acids with polyols or polyol ethers, such as trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.
- esters with monocarboxylic acids or esters of polycarboxylic acids etherified or esterified at the terminal groups such as esters with acetic acid, mixtures of esters with fatty acids, or the diester tetraethylene glycol with an oxoacid with a large number of carbon atoms;
- esters of some dicarboxylic acids (phthalic acid, succinic acid, alkyl succinic acids, maleic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenylmalonic acids, etc.) with different alcohols (such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.), such as dioctyl phthalate, dodecyl phthalate, linoleic acid dimer 2-ethylhexyl ester (tetraethylene glycol and 2-ethylhexanoic acid);
- some organic silicon compounds, examples: polyalkylsiloxanes, polyarylsiloxanes, polyalkoxysiloxanes, polyaryloxysiloxanes or organic silicates, such as tetraethylsilicate, tetraisopropylsilicate, tetra(2-ethylhexyl) silicate, tetra(4-methylhexyl) silicate, hexyl (4-methyl-2-pentoxy)disiloxane, polymethylsiloxanes, poly(methylphenyl)siloxanes, etc.;
- some liquid phosphoric acid esters, such as tricresyl phosphate, trioctyl phosphate, or decanephosphonic acid diethyl ester, as well as polymeric tetrahydrofurans can also be used as synthetic oils.

The olefinic monomers from which the polyalkylenes are derived from copolymers having double terminal bonds. They can rarely form polymers due to spherical hindrance [9]. Aliphatic polyalkylenes, those without aromatic or cycloaliphatic substituents, are preferred.

Polyalkylenes with relatively low molecular weights are preferred; they can be obtained starting from the corresponding polymers with high molecular weights by known destruction processes, such as thermal, mechanical, oxidative destruction. Known polymerization and copolymerization techniques include, among others, ways to adjust the molecular parameters by controlling the polymerization temperature, adjusting the concentration and nature of the initiator or catalyst, or introducing chain transfer agents [10]. Obtaining substituted succinic acylating agents is carried out by processes, which usually consist in the direct reaction of one or more polyalkylenes with a maleic or fumaric reactant (maleic acid, fumaric acid, maleic anhydride, fumaric anhydride, as well as mixtures of two or more of these reactants). Acylation reagents are in fact only an intermediate in the process of obtaining carboxylic acid derivatives and consist in the reaction of one or more such substituted succinic acylation reagents (agents) with one or more amino compounds. Amines (alkylene polyamines and polyalkylene polyamines) with primary amino groups (-NH_2 type) and polyamines (two -NH- groups) such as aliphatic, cycloaliphatic, aromatic or heterocyclic amines are preferred. Compositions derived from polyamines have characteristic dispersing properties, superior qualities in terms of the viscosity index of the lubricating oil composition. The compositions of carboxylic acid derivatives resulting from the reaction with amino compounds are complex mixtures containing acylation products of amines, namely amine salts, amides, imines and imides. The ratio between the acylation reactant and the amine one highlights the fact that with the increase in the functionality of polyamines, there is the possibility of using larger amounts of amine, obtaining an additive product with appropriate properties [11]. These compounds can be carboxylic acids, from which alkali metal salts can be derived, usable as an additive agent with the role of dispersant in the compositions of different types of hydraulic oils. As a rule, these compounds are aliphatic, cycloaliphatic or aromatic, without alkylenic unsaturation, mono or polybasic, or naphthenic acids, cyclohexanoic acids, cyclopentanoic acids, alkyl or alkenyl substituted aromatic carboxylic acids [12-14]. Dispersing agents, based on acylated nitrogen, soluble in oil, are characterized by the presence in their structure of a polar group substituted with hydrocarbons selected from the acyl type class, acylimidoyl and acyloxy radicals in which the hydrocarbon substituent contains a large number of carbon atoms aliphatic. In the case of acylated nitrogen compounds with two or more polar groups in one molecule, the hydrocarbon substituent must contain at least half the number of aliphatic carbon atoms per polar functional group. Radicals must be substantially saturated, with saturated carbon-carbon covalent bonds. An excessive percentage of unsaturated bonds makes the molecule susceptible to oxidation, degradation and polymerization resulting in hydrocarbon-based decomposition products that can influence the degree of flammability of hydraulic oils, according to the scheme in Figure 2.

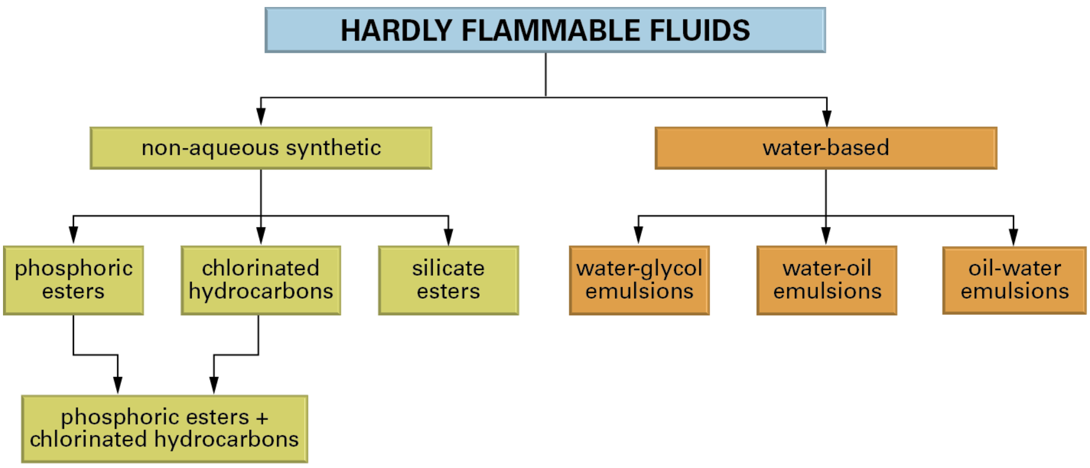

Fig. 2. Scheme of hardly flammable fluids [15]

Reports of toxicity testing methods for different types of hydraulic oil have shown the influence of this characteristic on the composition and stability of oil solutions.

Toxicity tests are essential components of ecological risk and impact assessments of hydraulic oil on the contaminated / affected area (leaks, spills, mishandling, etc.) [16 - 18]. Measured toxicity varies with test methods [19]. The benchmarks are based on the hydrocarbon concentrations measured in the test solutions [20, 21].

4. Conclusions

By measuring toxicity under standard conditions, one can gain insight into the relative hazard of each type of oil. The Organization for Economic Co-operation and Development (OECD, Report 2018) has provided practical strategies to test "difficult substances and mixtures" and to systematically mitigate the effect of test conditions on the stability and toxicity of test solutions before conducting definitive tests.
Standard oil toxicity tests performed in parallel with tests under site-specific conditions can provide an understanding of how test methods and conditions affect measured oil toxicity. The toxicity analyses carried out help to characterize the rapid and varied changes in the concentrations and composition of the oil during the tests, which determines the most accurate estimate of toxicity. Repeating the test under site-specific conditions enables a systematic evaluation of the influence of each condition on the measured toxicity. Improved approaches are needed to generate reliable benchmarks and to understand how site-specific experimental conditions affect oil toxicity. Improved protocols are needed to support reliable and repeatable toxicity estimates and comparisons between oils and test conditions; toxicity is determined by the concentration and composition of dissolved hydrocarbons, which in turn depend on the composition of the test oils and the methods of preparation of the oil solutions [18]. Thus, new combined toxicity testing methods will reduce uncertainty in measured toxicity, calculated reference values and estimated ecological risks.

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References

[1] United States Environmental Protection Agency (EPA). "When are You Required to Report an Oil Spill and Hazardous Substance Release?" July 24, 2023. Accessed October 2, 2023. https://www.epa.gov/emergency-response/when-are-you-required-report-oil-spill-and-hazardous-substance-release.
[2] Deuster, S., and K. Schmitz. "Experimental investigation of the influence of fluid viscosity on the efficiency of a crawler excavator." Paper presented at the 17th Scandinavian International Conference on Fluid Power, SICFP'21, Linköping, Sweden, June 1-2, 2021.
[3] Hawe Hydraulik. "Pressure fluids - notes for selection", D 5488/1, February 2007. Accessed October 3, 2023. https://www.hidracomp.com.br/wp-content/uploads/2013/01/Informacoes-sobre-Selecao-de-Fluido.pdf.
[4] Bosch Rexroth Pty Ltd. "Hydraulic fluids." Accessed October 2, 2023. https://www.boschrexroth.com/en/au/products/engineering/hydraulic-fluids/.
[5] German Institute for Standardization / Deutsche Institut für Normung. "DIN ISO 15380:2020. Lubricants, Industrial Oils And Related Products (Class L) - Family H (Hydraulic Systems) - Specifications For Hydraulic Fluids In Categories HETG, HEPG, HEES And HEPR (ISO 15380:2016)." *ANSI webstore*. Accessed October 2, 2023. https://webstore.ansi.org/Standards/ DIN/DINISO153802020.
[6] Forest Stewardship Council (FSC). Deutscher FSC-Standard. Version 3-0, 2018. Accessed October 2, 2023. https://www.fsc-deutschland.de/preview.fsc_x0002_waldstandard-3-0.a-1208.pdf.
[7] Biona Jersín s.r.o. "Technical Topic: Biodegradable Hydraulic Fluids." Accessed October 2, 2023. https://www.biona-oils.com/news/technical-topic-biodegradable-hydraulic-fluids.

[8] International Marine Contractors Association (IMCA). *Understanding Biodegradable Lubricants: An Introduction to 'Green' Oil in Hydraulic Systems Offshore*. IMCA R 019, October 2014.
[9] Ripple, David Eugene, and William Bricker Chamberlin III. "Lubricating oil composition"/ "Compozitie de ulei lubrifiant". RO Patent no. 108801B1. August 30, 1994. Accessed October 3, 2023. https://patents.google.com/patent/RO108801B1/ro.
[10] Le Suer, William M., and George R. Norman. "Lubricating composition containing an acylated nitrogen compound." US Patent no. 3272746A. September 13, 1966. Accessed October 3, 2023. https://patents.google.com/patent/US3272746A/en.
[11] Bera, G., T. Parkerton, A. Redman, N.R. Turner, D.A. Renegar, J.L. Sericano, and A.H. Knap. "Passive dosing yields dissolved aqueous exposures of crude oil comparable to the CROSERF (Chemical Response to Oil Spills: Ecological Effects Research Forum) water accommodated fraction method." *Environmental Toxicology and Chemistry* 37, no. 11: (November 2018): 2810–2819.
[12] Theissen, H. "The German Market Introduction Program for Biobased Lubricants." *Tribology Online* 5, no. 5 (2010): 225-229.
[13] Sivriu, A.M., C.I. Koncsag, G. Jinescu, and A.M. Mareș. "Thermal cracking of waste vegetable oil – A preliminary research." *UPB Scientific Bulletin, series B: Chemistry and Material Sciences* 79, no. 3 (2017): 67-74.
[14] Lenzi, F., G. Campana, A. Lopatriello, M. Mele, and A. Zanotti. "About the Use of mineral and vegetable Oils to improve the Sustainability of Steel Quenching." *Procedia Manufacturing* 33 (2019): 701-708.
[15] Bonanomi, Anna. "Hydraulic Fluids: Risks of fire and toxicity." *Power Transmission World*, July 17, 2018. Accessed October 2, 2023. https://www.powertransmissionworld.com/hydraulic-fluids-risks-of-fire-and-toxicity/.
[16] Hodson, Peter V., Julie Adams, and R. Stephen Brown. "Oil toxicity test methods must be improved." *Environmental Toxicology and Chemistry* 38, no. 2 (February 2019): 302-311.
[17] Aurand, D., and G. Coelho (eds.). "Cooperative aquatic toxicity testing of dispersed oil and the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF)." Technical Report. Ecosystem Management & Associates, Inc., Lusby, MD, USA, 2005.
[18] Redman, A.D., and T.F. Parkerton. "Guidance for improving comparability and relevance of oil toxicity tests." *Marine Pollution Bulletin* 98, no. 1-2 (September 2015): 156–170.
[19] Kobasko, N.I., E. Carvalho de Souza, L.C.F. Canale, and G.E. Totten. "Vegetable Oil Quenchants: Calculation and Comparison of the Cooling Properties of a Series of Vegetable Oils." *Strojniški vestnik - Journal of Mechanical Engineering* 56, no. 2 (2010): 131-142.
[20] Bejarano, A.C., J.R. Clark, and G.M. Coelho. "Issues and challenges with oil toxicity data and implications for their use in decision making: A quantitative review." *Environmental Toxicology and Chemistry* 33, no. 4 (April 2014): 732–742.
[21] Redman, A.D., J.D. Butler, D.J. Letinski, and T.F. Parkerton. "Investigating the role of dissolved and droplet oil on aquatic toxicity using dispersed and passive dosing systems." *Environmental Toxicology and Chemistry* 36, no. 4 (April 2017): 1020–1028.