COMPOSITIONS OF HYDRAULIC FLUIDS BASED ON RAPESEED OIL AND ITS DERIVATIVES

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Abstract. The awareness on the harmful impact of lubricants and industrial fluids entering the environment due to leakage or spillage has increased considerably during the last years. Hydraulic fluids can be classified as "high risk loss" lubricants - they are used in large volumes in equipment that is susceptible to spills. Hydraulic fluids currently used in Latvia in wood harvesting and other environmentally sensitive areas still are mainly based on mineral oils which are not biodegradable and are dangerous to the environment. Completely different is the situation in other EU countries, e.g., in Sweden, where the Swedish standard SS 155434 is a legal requirement: lubricants not fulfilling these criteria for biodegradable hydraulic fluids are not permitted on the Swedish market. There is an obvious need for elaboration of compositions of hydraulic fluids based on renewable natural resources in order to initiate and to promote production of such products in Latvia. Vegetable oil-based lubricants have excellent lubricity and biodegradability, but two major problems exist with vegetable oils as functional fluids: low resistance to thermal oxidation and poor performance at low temperatures. We developed compositions of hydraulic fluids using as base stocks rapeseed oil and esters of its fatty acids with polyols - neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) – as well as 2-ethylhexyl esters of estolides of rapeseed oil. Besides that mixture of rapeseed oil with pentaerythritol esters of fatty acids (7:3) also was made. We used *tert*-butylhydroquinone (TBHQ) as oxidation inhibitor, *Lubrizol* 7671A as pour point depressant and polymethylsiloxane as antifoam agent in our formulations. The following technical parameters of our compositions were tested: kinematic viscosity at 40 ˚C and 100 ˚C, viscosity index, oxidative stability, cold-flow properties, acid value, foaming, air release, flash point. The elaborated formulations corresponded to the main requirements set for biodegradable hydraulic fluids.

Key words: hydraulic fluid, rapeseed oil, estolide, esters of polyols, biodegradable.

Introduction

Hydraulic fluids are used in earthmoving equipment and tractors, in agricultural and forestry applications. Hydraulic fluids based on vegetable oils are completely biodegradable and have low ecotoxicity. Vegetable oils display excellent tribological properties – ester functions stick well to metal surfaces, lower friction coefficients than mineral-oil-based fluids, lower evaporation (up to 20 % less than in case of mineral-oil-based fluids), higher flashpoints and viscosity index, low water pollution [1]. The disadvantages of vegetable oils are low resistance to both oxidation and high temperature treatment, poor fluidity at low temperatures. Different additives usually are applied to improve these properties, e.g., oxidation inhibitors and pour point (PP) depressants.

The properties of vegetable oils that are important for hydraulic fluids can be improved by replacement of glycerol in triglycerides with other polyol such as TMP, NPG or PE. These esters display extraordinary thermal stability, biodegradability, high viscosity and good shear stability [1]. Besides that, synthetic esters have superior low temperature properties, e.g., pour points of TMP esters are –45 up to –20 ˚C, while PP of vegetable oils ranges between –20 and –10 ˚C [2].

Base fluids of hydraulic oils can be prepared by mixing of vegetable oils with esters of polyols; such mixtures have improved properties in comparison with vegetable oils [3].

Another group of derivatives of vegetable oils are estolides and their esters, e.g., 2-ethylhexyl esters of estolides. These compounds have low melting points (e.g., –34 ˚C), high viscosity index (169-200), good oxidative stability; esters of estolides demonstrate even better properties than estolides themselves [2].

The esters of both polyols and estolides of fatty acids of vegetable oils are perspective base stocks for lubricants and functional fluids, which do not need expensive additives and are biodegradable at the same time.

Presently, the biodegradable functional fluids are widely introduced in the world market, especially in Europe, where environmental protection standards are severe. Unfortunately, the hydraulic fluids based on vegetable oils cannot compete with mineral oils in price.

Due to high price of biodegradable lubricants and lack of environmental policy, the hydraulic fluids used in Latvia still are based on mineral oil and pollute soil and groundwater. There is an obvious need to initiate and to promote production and use of environmentally more friendly hydraulic oils in our country. Therefore, we elaborated biodegradable compositions of hydraulic fluids based on local renewable raw materials.

Materials and methods

We used cold-pressed rapeseed oil purchased from *"Iecavnieks" Ltd.*, rapeseed oil methyl esters (RME) and byproducts of biodiesel synthesis (mixtures of free fatty acids, mono- and diglycerides) produced by *"Mežrozīte" Ltd.* Antioxidant TBHQ, polyols (TMP, NPG, PE), 2-ethyl-1-hexanol, isooctane, antifoaming agent polymethylsiloxane were purchased from ACROS ORGANICS and used without further purification. Acetic acid, chloroform, potassium iodide, diethyl ether, ethanol were supplied by PENTA. Pour point depressant for vegetable oils *Lubrizol* 7671A and hydraulic oil *Hydraway Bio SE* 32-68 were purchased from commercial suppliers.

Two types of base fluids were synthesized by us:

- TMP, NPG and PE esters of fatty acids of rapeseed oil were synthesized according to the known procedures [4, 5] by transesterification of RME with corresponding polyols in the presence of catalyst (sodium hydroxide or calcium metoxide).
- Estolides of rapeseed oil and their 2-ethylhexyl esters were synthesized analogously as it is described in patent [6]. Mixtures of fatty acids, mono- and diglycerides (obtained as by-products in RME production) were utilized as a source of fatty acids; mono- and diglycerides beforehand were saponified and converted to free fatty acids.

We characterized our base fluids and elaborated compositions by the main parameters detected according ISO 15380 "Lubricants, industrial oils and related products (class L) – Family H (Hydraulic systems) - Specifications for categories HETG, HEPG, HEES and HEPR": kinematic viscosity at 40 ˚C and 100 ˚C (LVS EN 3104), viscosity index (LVS EN 2909), flash point (LVS EN 22719), acid number (LVS EN 14104), peroxide value (ISO 3960). Low temperature properties were characterized by fluidity of oil after 7 days storage at –20 ^{o}C [7]; foaming at 24 ˚C, 93 ˚C, 24 ˚C (ISO 6247) and air release at 50 ˚C (ISO 9120) also were measured.

Elastomer compatibility was determined after 168 h storage of elastomer in a corresponding oil sample at 60±1 ˚C temperature (testing conditions set by ISO 6072:2002).

Elastomer change in Shore-A-hardness was determined with a digital hardness measuring device according to the standard ISO 48:2007.

Elastomer change in tensile strength was determined with *Zwick Roell* materials testing device with tensile rate 200 mm/min according to the standard ISO 37:2005; instead of dumbbell-shaped samples we used OR type profile with ϕ 9.99 mm produced by company *Klinger ramikro*.

Elastomer change in volume and change in elongation were determined in air and water on SARTORIUS 5 decimal places balance with hydrostatic weighting according to the standard ISO 1817:1999.

We used for elastomer testing OR type profile made of acrylonitrile-butadiene rubber (NBR) by *Klinger ramikro* – this elastomer is applied in machinery produced by company *Valmet technik forest* and it can be explored at the temperature range from –40 ˚C to 120 ˚C.

Oxidation stability was characterized by measuring kinematic viscosity at 40 ˚C and acid value after 96 h storage of oil at 121 ˚C in the presence of copper plate [8].

Results and discussion

Rapeseed oil and its derivatives – TMP, NPG and PE esters of fatty acids of rapeseed oil and 2-ethylhexyl esters of rapeseed oil estolides - were prepared as base fluids of hydraulic oils. Quality parameters of base fluids were determined according to the requirements of ISO 15380 (Table 1).

Table 1

Quality parameters of base fluids of hydraulic oils

Parameter	Units	Esters of fatty acids of rapeseed oil NPG	TMP	PE	2-Ethylhexyl esters of rapeseed oil estolides	Limit
Density at 15 ˚C	kg m^{-3}	886	900	909	901	-
Colour	-	light yellow	light yellow	light yellow	black	-
Flash point	˚C	92	95	168	184	≥165
Kinematic viscosity at 40 ˚C	$mm^2 s^{-1}$	15.16	33.78	52.81	29.11	*
at 100 ˚C	$mm^2 s^{-1}$	4.10	7.09	9.91	5.83	
Viscosity index	-	186.56	179.86	176.77	146.47	-
Low temperature (-20 ˚C) fluidity after 7 days	S	do not flow	<15	<15	<15	≤15
Acid number, max	mg KOH g^{-1}	0.39	0.39	0.32	2.87	-
Water content	mg kg^{-1}	190	150	210		≤1000
Peroxide value	meq O_2 kg^{-1}	6.68	6.31	2.91	0.00	-
Oxidation stability after 96 h storage at 121 °C						
Viscosity at 40 ˚C	$mm^2 s^{-1}$	21.19	44.48	82.71	31.14	-
Increase of viscosity at 40 ˚C	%	39.72	31.67	56.59	7.00	≤20
Viscosity index	-	174.07	208.39	186.67	152.81	-
Alteration in acid value	mg KOH g^{-1}	+0.24	+0.19	+0.27	+4.00	≤2
Copper corrosion	%	0.027	0.015	0.004	0.089	≤0.05
Alteration in peroxide value	meq O_2 kg^{-1}	+0.21	–0.94	+3.89	+0.92	-

*				
Viscosity grade:	22	32	46	68
Viscosity at 40 ˚C, $mm^2 s^{-1}$:	19.8-24.2	28.8-35.2	41.4-50.6	61.2-74.8
Viscosity at 100 ˚C, $mm^2 s^{-1}$:	≤4	5.0	6.1	7.8

In order to ensure quick hydrosystem start and satisfactory work at the broad temperature interval, viscosity of the hydraulic fluids should be medium. At the same time viscosity should be sufficient to provide regularity of action and to prevent wear of rubbing components and loss in glands (especially at high pressure). Therefore, high viscosity index is necessary.

Apparently, kinematic viscosity and viscosity index of the most of synthesized esters (except NPG esters) correspond to the requirements set for hydraulic base fluids. Accordingly viscosity grading TMP esters as well as 2-ethylhexyl esters of estolides correspond to grade 32, but PE esters fit in the interval between 46 and 68. Unfortunately, NPG and TMP esters had inadmissibly low flash points.

Base fluids of hydraulic oils should be chemically and thermally stable; they might not change the composition or precipitate by time and heating within the working temperature range. These properties were examined by oxidation test – samples of base fluids were stored 96 h at temperature 121 ˚C in the presence of copper plate; alteration of viscosity at 40 ˚C and acid value, as well as corrosion of copper plate were determined. It was found out that all samples of base fluids could not pass oxidation stability test – NPG, TMP and PE esters of fatty acids failed due to increase of viscosity, but 2-ethylhexyl esters of estolides of rapeseed oil had too high increase of acid value and showed strong copper corrosion.

Low temperature properties of elaborated base fluids were determined after storage (7 days) of samples at -20 ˚C temperature. Almost all samples (except NPG esters of fatty acids) successfully passed this fluidity test.

As all synthesized esters failed oxidation stability test (see Table 1), we elaborated various compositions of hydraulic oils based on the above mentioned esters or rapeseed oil, as well as the mixture of rapeseed oil with PE esters (7:3). In order to improve essential properties of these compositions we added antioxidant TBHQ, PP depressant *Lubrizol* 7671A and antifoaming agent – polymethylsiloxane. The main quality parameters of our compositions were determined and compared with commercially available hydraulic oil *Hydraway BIO SE 32-68* (Tables 2 and 3).

Hydraulic fluids should be inert to the material of glands. The compatibility of acrylonitrile-butadiene rubber with base fluids and compositions was tested; measurements were taken after 168 h storage of NBR in oils at 60 ˚C (Table 2). Obviously, PE esters are not compatible with NBR.

Table 2

Elastomer compatibility of NBR with synthesized base fluids and compositions of hydraulic oils

Characteristics	Unit	Limit	Base fluids of hydraulic oil		Compositions of hydraulic oils	
			2-Ethylhexyl esters of rapeseed oil estolides	PE esters of rapeseed oil	Rapeseed oil + additives*	*Hydraway Bio SE 32-80*
Change in Shore-A-hardness, max	grade	≤10	–1.4	–13.4	–0.1	+0.5
Change in volume	%	–3…+10	–2.35	+11.61	+4.29	–4.14
Change in elongation, max	%	≤30	–2.19	+1.18	–9.62	–6.64
Change in tensile strength, max	%	≤30	–4.93	+7.00	+0.81	+15.10

* Additives – 0.25 % TBHQ, 0.05 % polymethylsiloxane, 1 % *Lubrizol* 7671A

Table 3

Quality parameters of compositions of hydraulic oils

Parameter	Units	Compositions of hydraulic oils*							Limit
		N#1	N#2	N#3	N#4	N#5	N#6	*Hydraway Bio SE* 32-68	
Density at 15 ^oC	kg m^{-3}	920	917	887	901	910	902	915	-
Colour		light yellow	light yellow	light yellow	light yellow	light yellow	black	light yellow	-
Flash point	˚C	232	170	152	183	186	184	211	≥165
Kinematic viscosity at 40 ˚C	mm^2 s^{-1}	52.47	32.22	16.54	42.47	64.15	42.76	37.43	See
at 100 ˚C	mm^2 s^{-1}	11.71	7.77	4.59	8.84	12.49	8.74	7.37	Table 1
Viscosity index		225.65	227.17	216.67	192.94	197.74	187.73	168.44	-
Low temperature (–20 ˚C) fluidity after 7 days	S	<15	<15	<15	<15	<15	<15	<15	≤15
Acid number	mg KOH g^{-1}	1.92	3.93	0.46	0.48	0.42	3.09	0.81	-
Water content	mg kg^{-1}	900	800	80	175	50	380	530	≤1000
Air release, 50^{o}C	Min	5.0	4.72	nd	nd	1.41	2.02	0.92	≤7

Table 3 (continuation)

Oxidation stability after 96 h storage at 121 ˚C									
Increase of viscosity at 40°C	%	9.9	8.5	1.5	10.8	7.2	11.7	9.3	≤20
Alteration in acid value	mg KOH g^{-1}	–0.99	–1.3	+0.27	+0.04	+0.26	+3.71	–0.14	≤2
Copper corrosion	%	0.04	0.035	0.003	0.001	0.015	0.083	0.05	≤0.05

* N#1 – rapeseed oil + additives

N#2 – rapeseed oil:PE esters of rapeseed oil (7:3) + additives

N#3 – NPG esters of rapeseed oil + additives

N#4 – TMP esters of rapeseed oil + additives

N#5 – PE esters of rapeseed oil + additives

N#6 – 2-ethylhexyl esters of estolides of rapeseed oil + additives

Additives – 0.25 % TBHQ, 0.05 % polymethylsiloxane, 1 % *Lubrizol* 7671A

nd – not detected

Determination of the main quality parameters of elaborated compositions showed that hydraulic oils N#1, N#2, N#4 and N#5 in general corresponded to the requirements of the standard ISO 15380.

Conclusions

1. Neat NPG, TMP, PE esters of fatty acids, as well as 2-ethylhexyl esters of estolides of rapeseed oil are not stable enough against oxidation on prolonged heating.
2. The sufficient improvement of the most unreliable properties of base fluids and compositions of hydraulic oils - oxidative stability and low temperature behavior – can be reached with the following combination of additives: antioxidant (0.25 % TBHQ), PP depressant (1 % Lubrizol 7671A) and antifoaming agent (0.05 % polymethylsiloxane).
3. Several biodegradable compositions of hydraulic oils based on rapeseed oil, TMP and PE esters of fatty acids of rapeseed oil, as well as mixture of rapeseed oil with PE esters (7:3) and containing the above mentioned minimum of additives have been elaborated; these fluids fulfill the main requirements of ISO 15380.

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