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ECOLOGICAL LUBRICATING GREASES

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Abstract

Lubricating greases are considered as colloidal dispersions of a thickener in a lubricating fluid. The biodegradable properties as well as the lubricating ability of the ecological lubricating greases depend on both the base oil and thickener.

The vegetable oils are widely used in many formulations of biodegradable lubricants. They have the advantage of being almost completely biodegradable. As thickeners the lithium, and aluminium soaps, inorganic thickeners, such as bentone, or silica are considered to be not harmful to the environment. The additives for biodegradable greases should also be biodegradable.

Biodegradable lubricating greases made from soybean oil are less toxic to the environment and human health than the petroleum based products, and in the same time they are good tribological properties.

The paper presents data regarding the characteristics of some biodegradable greases formulated with soybean oil. These non-toxic and biodegradable greases made with aluminium complex soap, lithium soap and bentone, obtained by our proprietary technologies exhibit over 85% biodegradability by CEC method and good phisico-mechanical characteristics. The improvement of the load carrying properties of the vegetal-oils based greases and the antioxidant effect of some suitable additives such are sulfurizated soybean oil, talcum powder and α-tocoferol acetate was also studied.

Keywords: *Grease, environment, lubricating fluids, vegetable oils.*

1. INTRODUCTION

Lubricants facilitate the effective operation of mechanical equipment, reducing friction and wear, and other effects including heat transfer or corrosion protection.

Between 5 000-10 000 different lubricant formulations are necessary to fulfil more than 90% of all lubricant applications [1].

In 2004, European lubricant consumption was [1]:

47% - automotive industry

32% – industrial lubricants, including hydraulic oils, which account for approximately 15% of, total lubricant consumption

11.3% - process oils

9,4% - marine and aviation.

In the same time the lubricants represent a large and diffuse pollution source both on soil and in water.

Around half of these lubricants are being spilled somewhere in the environment, deliberately or accidentally. Those assert to stimulate the use of biodegradable, non-toxic lubricants.

Conventional lubricants, based on mineral oils contain toxic and non-biodegradable substances. Biodegradable lubricants represent the technical and environmental alternative for conventional lubrication. It is assessing that over 90% of all lubricants could be replaced by biolubricants [1].

2. ENVIRONMENTAL FRIENDLY GREASES COMPOSITION

Lubricating greases are considered as colloidal dispersions of a thickener in a lubricating fluid. In the case of environmentally friendly products the main components of the greases must be rapidly biodegradable materials.

Oil is considered to be readily biodegradable if minimum 70% of the hydrocarbons are removed after 21 days according with CEC test. The most rapidly biodegradable oils as lubricating greases components are vegetable oils, synthetic esters [3, 5] and glycols, as it is shown in table 1.

As thickeners the lithium, lithium-calcium and aluminium soaps, inorganic thickeners, such as bentone, or silica are considered to be not harmful to the environment [5, 7].

The additives (antioxidants, antiwear-EP, corrosion inhibitors, polymers) for biodegradable greases should also be biodegradable. Addition of some solids ingredients such are graphite, zinc oxide or talcum will improve the anti-wear and extreme-pressure characteristics and in the same time they are allow of environment

Generally it can declare that the additives determine the toxicity of (bio) lubricants, while the base fluids determine the biodegradability.

Table 1: Biodegradability of base fluids for greases

Base Fluid	**Biodegradability,%,** CEC Test
Mineral oil	20-40
Vegetable oil	90-98
Synthetic esters	65-100

Synthetic oils offer improved performance over vegetable oils, but at very high price.

Soybean oil, rapeseed oil, sunflower oil, castor oil are the most used vegetable oils in biodegradable lubricants formulations. They have the advantage of being almost completely biodegradable. Chemical stability of vegetable oils is low, because of their polyunsaturated acids content. The stability can be increased by the chemical modification of the oils in order to reduce the content of conjugated double bonds.

Soybean oil competes for a share of the emerging biodegradable lubricants market with other vegetable oils (particularly rapeseed oil) and with synthetic lubricants.

Soybean oil is cheaper than rapeseed oil and could have an advantage if the base oil can be modified to improve their thermal, hydrolytic and oxidative stability.

Soybean based lubricants protect metal better than petroleum lubricants, are a renewable resource and also biodegradable – a big plus for the environment and a major advantage over other similar products.

3. EXPERIMENTAL

The manufacture of biodegradable lubricating greases must take into account the particularities of components and it does not affect the functionality, toxicity and biodegradability of the final product. An important factor is that many biodegradable fluids are readily saponifiable and in some cases (such as soybean oil, or other vegetable oils) are much time reactive than the fatty acids used to manufacture soap based greases [7]. The usual equipment is satisfactory for the manufacture of biodegradable greases, but this should be properly cleaned to prevent contamination with conventional greases and their components.

There are several desired characteristics for biodegradable greases such as: consistency, stability and biodegradability. Many tests can be performed on greases to measure these properties. The experimental greases produced were characterized using the test methods listed in table 2. We had in view the termo-chemical stability and water stability of our biodegradable lubricating greases using the laboratory specific tests: The tendency of automotive wheel bearing grease to separate oil and/or grease was evaluated by **ASTM 1263** test method. The test is performed at elevated temperature in a modified automotive spindle-hub assembly rotated at 660rpm. Any leakage of oil or grease during the test period is collected and weighed. The **FTIR spectra** of the fresh grease and those of the greases collected from the bearing and spindle- hub after test period was compared. A thermo Nicolet Avator 320 spectrometer, equipped with a denaturated triglycine sulphate (DTGS) detector, KBr beamsplitter and Globar Source was utilised for recording IR spectrums of the grease samples. The horizontal crystal surface (ZnSe with 45 degree angle of incidence) of the AVATOR Multi- Bounces is used for obtaining high quality infrared spectra without any sample preparation. To study the stability of grease in presence of water **ASTM 1294** was selected.

Table 2: Test methods

Characteristics	Test Methods ASTM D
Dropping point	2265
Penetration, 25°C, 1/10mm	217
Mechanical stability, 10000 strokes	217
Oil Separation, 30 h, 100°C, %	972
Evaporation loss, 30 h, 100°C, %	972
Colloidal stability, % oil separated	3793
Biodegradability, %, 21 days	CEC Test
Bomb oxidation test	942
Leakage tendencies of wheel bearing grease	1263
Water resistance	1264

3.1 Soybean lithium grease

Lithium hidroxystearate thickener was selected to prepare the soap based greases with soy oil and the thickener was produced in the absence of the base oil.

The experimental greases produced were characterized using the test methods listed in table 2. The characteristics of the biodegradable greases made with soybean oil and lithium C-12 hidroxistearate are shown in table 3

Table 3: Characteristics of lithium soybean greases

Characteristics	r.A	Gr.B	Gr.C
Dropping point,°C	96	193	187
Penetration, 25°C, 1/10mm : - after 60 strokes , - after 360 strokes	78 82	277 276	280 277
Roll stability, % change	.1	0	0
Oil Separation, 30 h, 100°C, %	.4	1.9	1.7
Evaporation loss, 30 hours, 100°C, %	.3	0.24	0.2
Leakage tendencies of wheel bearing grease, 660rpm, 80 °C, 6 hours	.68	1.66	1.61
Water washout, at 80 °C, %			
Biodegradability, %, 21 days	85	> 85	> 85

3.2 Biodegradable Food-Grade Greases

Due to their suitable properties, the aluminum complex greases are frequently used in food processing. These type of greases provide high protection for the equipment in the food processing industries (which requirement lubrication under hot and wet conditions) such as conveyor in bakery ovens, in canneries, dairies, beverage and fish processing plants [7, 10, 12].

Table 4 Characteristics of aluminium complex soybean greases

Characteristics	r.D	r.	r. F
Thickener, %	6	8	0
Dropping point, °C	68	01	27
Penetration, 10^{-1} mm 60 strokes 360 strokes	31 31	71 71	30 34
Colloidal stability, % separated oil	.6	.2	
Biodegradability, %, 21 days	2	0	6

To obtain ecological grease, simultaneously non-toxic and biodegradable, we propose an aluminium complex grease formulated with soybean oil. The samples were prepared with 16-20% of thickener also obtained in situu. In table 4 we present the characteristics of the biodegradable non-toxic greases, special formulated for food industry,

3.3 Environmental acceptable lubricating grease

Concerning modified clay greases they present moderate biodegradability, as attribute of based oil. However, the thickener, such is an inert material, makes these kind of greases acceptable by environment

As additive we used another non-toxic and environmentally acceptable ingredient, graphite.

Table 5 Characteristics of bentone soybean greases

Characteristics	Grease. G
Thickener, %	12
Additive, graphite, %	5
Penetration, 25°C, after 60 strokes 1/10mm	325
Dropping point,°C	260
Four ball test: -Wear scar diameter, mm - 40 daN, 60 min - 150 daN, 1 min - welding load, daN	 0,64 mm 1,1 mm 250 daN
Biodegradability, %, 21 days	72

3.4 Behaviour of some additives on biodegradable lubricating greases

Additivation is the solution to improve the properties of the biodegradable greases. The polarity of the vegetable oils and synthetic esters can generated competitive reactions on metal surfaces [8, 9, 11]. To obtain similar properties as mineral oil based greases a higher proportion of additives is necessary. On the other hand must be taken into account the biodegradability of the additives too [8], An additive consisting of sulphurised soybean oil (table 6) was used to improve the EP and antiwear properties of a biodegradable grease made with the same base oil (table 7). The oxidation stability of biodegradable greases made with vegetable oil can be improve using α-tocoferol acetate (table 8).

Table 6: Characteristics of sulphurised soybean oil

Characteri stics	V alue	Met hod
Density at 20°C	1, 05	AST M D 1298
Saponificat ion number, mg KOH/g		AST M D 1962
Sulph content, %	2 0	AST M D 4294
Biodegrada bility,%, 21 days	7 8	CEC L- 33-A-94

Table 7: Effect of sulphurised soybean oil

Characteristics	Grease	
	H	I
Dropping point°C	1 96	1 92
Penetration, @ 25°C, 1/10mm, after 60 strokes	2 82	2 97
Roll stability, % change	0	2 ,4
Oil Separation, 30 h, 100°C, %	1 .9	2 ,4
Evap. loss, 30 h. 100°C, %	0 .24	0 .36
Biodegradability, %, 21 days	8 5	8 5
Four ball test: -Wear scar diameter, mm - 40 daN, 60 min - 150 daN, 1 min - **w**elding load, daN	0 .86 - 1 50	0 .62 1 .12 2 80

Table 8: Effect of α-tocoferol acetate

Characterist ics	Greases	
	J	K
Dropping point, °C	1 96	190
Penetration, 25°C, / 60 strokes, 1/10mm	2 82	304
Bomb oxidation test, Δp, psi,	0. 35/25h	0.2 2/100h

4. RESULTS AND DISCUTIONS

The grease made with soybean oil and lithium C-12 hidroxystearate by our technology are rapid biodegradable (over 85%, by CEC method). They present dropping points over 185°C, specific for this type of lubricants and good phisico-mechanical characteristics. The weight loss after water washout test shows good resistance in presence of water, or wet atmosphere. The evaluation of the leakage tendencies of wheel bearing greases tested under mentioned conditions show low values of the materials collected. That is in according with the FTIR spectra. The spectres were recorded in the range 4000-650 cm^{-1}, at 4 cm^{-1} resolution, with 64 scans and automatic gain. IR spectrum of the three grease samples (fresh grease, collected grease on the wheel bearing and collected grease on the spindle hub-figures 1, 2, 3) shows:

The presence of the functional group carbonyl in the compounds type ester (1744 band is caused by the esters in soybean oil). The presence of the functional group COO^- (carboxylate) and of the associate hydroxyl groups (1579, 1560 and 3400 cm^{-1} bands are caused of the presence lithium hidroxystearate). The presence of the Si inorganic derivate (1010 cm^{-1} is caused of the presence of talcum). IR spectrum of the grease collected on the spindle hub is similar with the spectrum of fresh grease (similarity matches 99,8)-the match value will be sealed from 0 to 100, where 100 is a perfect match). These assignments what in this zone the essential changes in the composition of the grease not takes place. IR spectrum of the grease collected on the wheel bearing the changes presents against the IR spectrum of the fresh grease (similarity match is 89,9). In the used grease sample the content of the carbonylic groups type ester decrease. The changes in the simetry of 1744cm^{-1} band present in meaning of the appearance of the carbonyl group type acid. Also the content of the carboxylate and hydroxyl groups increases. There are important conclusions can be made from this study: a small part from the base oil grease's lost and the oxidation processes of the grease take place. This is in according with similar spectra of the greases tested in service, on tractor's wheel bearings, after 500 hours.

As concerns the aluminium complex greases made with soybean oil have acceptable characteristics, biodegradability over 75% (table 4) and in the same time they fulfil the requirements for food-grade lubricants.

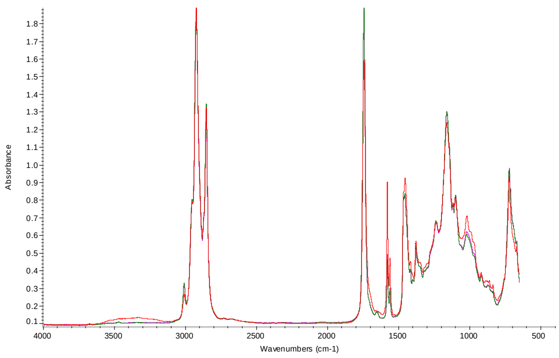

Fig.1

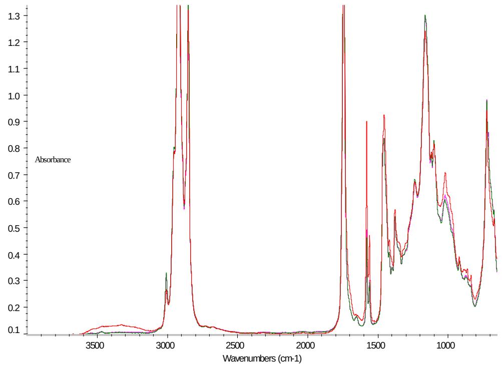

Fig. 2

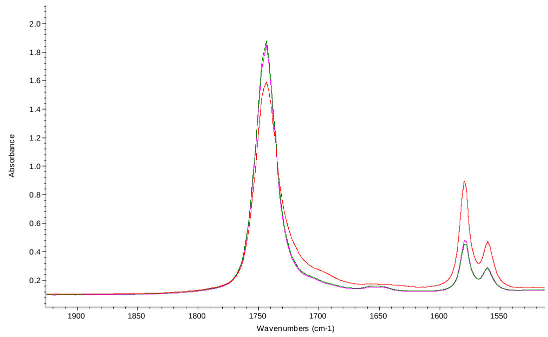

Fig.3

Bentone greases present moderate biodegradability, as attribute of based oil. The thickener and the additive are inert materials, so that these kind of greases are recognise as acceptable by environment, even their biodegradability is not very high. Their physico-chemical and tribologycal characteristics and the non-toxicity of the components, compensate their moderate biodegradability.

5. CONCLUSIONS

1. The most rapidly biodegradable oils as lubricating greases components are vegetable oils, synthetic esters, glycols and other synthetic fluids. Like other vegetable oils, soybean based oil confer upon lubricants protect metal better than petroleum lubricants, is a renewable resource and also biodegradable and present the major advantage of the price over other similar products.

2. Using soybean oils we prepared three ecological type of greases:

- **Biodegradable lubricating grease** formulated with lithium hidroxistearate and soybean oils. The product are rapid biodegradable (over 85%, by CEC method). It presents dropping points over 185°C, specific for this type of lubricants and good phisico-mechanical characteristics. The weight loss after water washout test shows good resistance in presence of water, or wet atmosphere. To improve the EP and antiwear properties of the vegetable greases a sulfurizated soybean oil was used. The oxidation stability of vegetable greases was improved too, using α-tocoferol acetate. That means that our greases made with soybean oils and C-12 hidroxystearate guarantees a good lubrication of the rolling parts of the earth moving equipment
- **Food-grade and simultaneously biodegradable grease,** which is an aluminium complex grease. This kind of grease is made from non-toxic raw materials accept by USDA, as H1 type.
- **Environment acceptable lubricating grease** obtained from modified clay, soybean oil and graphite. Even their biodegradability is not very high (about 70%), due to their composition (raw materials tolerate by environment) these kind of greases are recognize as acceptable by environment.

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