Serbian Tribology Society

SERBIATRIB '11

12th International Conference on Tribology

Faculty of Mechanical Engineering in Kragujevac

Kragujevac, Serbia, 11 – 13 May 2011

MULTIPURPOSE BIODEGRADABLE LUBRICATING GREASES

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Abstract: *Lubricants represent a large and diffuse pollution source both on soil and in water. Conventional lubricants, based on mineral oils contain toxic and non-biodegradable substances. Biodegradable lubricants represent the technical and ecological alternative for conventional lubrication. Lubricating greases are considered as colloidal dispersions of a thickener in a lubricating fluid. Their biodegradable properties and their lubricating ability depend both on the base oil and thickener.*
Soybean oil, rapeseed oil, sunflower oil, castor oil are the most used vegetable oils in biodegradable lubricants formulations. The lithium hidroxystearate thickener was selected to prepare the multipurpose ecological greases. For obtain good performances greases we used a technological method to form the thickener in the absence of base oil. The soap based greases with vegetable oils made by our proprietary technology are rapidly biodegradable (over 85% by equivalent CEC method.
To improve the EP and antiwear properties of the vegetable oils based greases sulfurizated vegetable oils was used. Ultrafine calcium carbonate has major improving on EP/AW properties, even it is not an usually additive for lubricants.

Keywords: *greases, biodegradability, additives, calcium carbonate, vegetable oils, thickener.*

1. INTRODUCTION

Lubricants facilitate the effective operation of mechanical equipment, reducing friction and wear, but in the same time they represent a large and diffuse pollution source both on soil and in water. Biodegradable lubricants represent the technical and ecological alternative for conventional lubrication. These lubricants are mostly required for equipment used in some resources industries such are forestry, mining, petroleum exploration and production or in cases when they might come in the contact with the environment.

Lubricating greases are considered as colloidal dispersions of a thickener in a lubricating fluid. Their biodegradable properties and their lubricating ability depend both on the base oil and thickener. Lithium greases are the most widely used, but Calcium, Aluminum, Polyurea, and organo-clay are also used.

Multipurpose biodegradable lubricating greases are high temperature, anti-wear extreme pressure (EP), greases with very high load carrying capacity and high dropping point engineered for machines and equipment subjected to extreme loads under wet or humid conditions at low and elevated temperatures.

2. BASE FLUIDS FOR BIODEGRADABLE LUBRICATING GREASES

Oil is considered to be readily biodegradable if minimum 70% of the hydrocarbons are removed after 21 days according with CEC L-33-A-94 test. Generally, the biodegradability of the vegetable oils and synthetics esters is over 90%, while that of the mineral oils is 20-40%. In table 1 we present the biodegradability of the most used lubricating oils.

Table 1 Biodegradability of the most used lubricants [6]

Lubricant	Biodegradability, %
Mineral Oils	15-35
White oils	25-45
Vegetable lubricants	70-100
Polyalphaolefins (PAO)	5-30
Polyether	0-25
Polyisobutylene (PIB)	0-25
Phthalate & Trimelitate Esters	5-80
Polyol Esters& Diesters	55-100

Soybean rapeseed-canola, sunflower, corn, peanut, olive, palm, castor oil are the most used vegetable oils in biodegradable lubricants formulations [1, 3, 5]. There are many applications for vegetal oils in the lubrication field, especially for fluid lubricants, such as hydraulic fluids, compressor oils, transformer coolant, two-stroke engine oils, metal working fluids and as the main component of lubricating greases. Due to their triglyceride molecular structures these vegetable oils have poor thermal, hydrolytic and oxidation stability. The presence of water even in small amounts can induce foaming and degradation problems. Also a great disadvantage of vegetable oils is their low cold-flow abilities. On the other hand the polar nature of these oils confers good lubricating capacity.

The stability of vegetable oils can be increased by the chemical modification of the oils in order to reduce the content of conjugated double bonds. There are many different ways to modify the multifunctional vegetable oils. Some reported changes that address the polyunsaturated problem include alkylation, acylation, hydroformylation, oligomerization, epoxidation, the hydrogenation of the conjugated double bonds by selective catalysts in specific conditions, the reaction of the oil with unsaturated esters, the reaction of unsaturated esters with aromatics, in the condition of Friedel-Crafts. Their sensitivity to hydrolysis and oxidation of the vegetal oils can be reduced by different methods like hydrogenation of the conjugated bonds, which also reduces the iodine number of the oil. The structure of the fatty acids of the vegetal oil determines the lubricating properties. An excess composition of certain saturated fatty acids leads to poor cold flowing characteristics of the lubricant. On the contrary, certain polyunsaturated fatty acids impart unfavorable oxidation and chemical stability at high temperatures. The level of oleic acid also influences the oxidative stability. A higher content in oleic acid also determines a lower change in viscosity - Table 3.

Table 2. Iodine value of vegetal oils.

Oil Types	Iodine Value, g/100g I_2
Rapeseed	94…106
Soybean	103…109
Castor	82…90
Sunflower	127…136
Olive	80…85

Table 3. Oleic acid content, viscosities and changes in viscosities of different vegetal oils.

Oil	Oleic acid, %	Kinematic Viscosity, cSt		Δ Visc. @40°C* cSt
		40°C	100°C	
Rapeseed	32	51	10	21
Soybean	27	28.5	7.5	43
Castor	3	293	20	78
Linseed	20	30	7	46
Palm	40	32	6.5	13

* (1000 hrs, 3 l/h, 93°C)

Genetic modifications can also increase their thermal and oxidative stability [1, 7].

Synthetic biodegradable lubricants include diesters and polyalkylene glycols which are rapidly biodegradable. The synthetic esters in lubricants improve the following properties: thermal stability, hydrolytic stability, solvency, lubricity, and biodegradability [4].

To obtain good performances synthetics esters, selected branched alcohols and pure oleic acids are used. The branched alcohols improve the flow properties at low temperatures and in the same time the hydrolytic degradation is inhibited [1]. The synthetic esters in lubricants improve the following properties: thermal stability, hydrolytic stability, solvency, lubricity, biodegradability. These types of fluids exhibit longer service life then vegetal oils [4]. The selection of the acids and alcohols allows combining biodegradability with the very good performance properties. Diesters and phthalates are the most used synthetic esters in lubricating greases formulation. In Table 4 some of their properties are presented.

Table 4. Properties of some synthetic esters.

Properties	Diesters	Phthalates
Viscosity at 40°C, cSt	6…46	29…94
Viscosity at 100°C, cSt	2…8	4…9
Viscosity Index	90…170	40…90
Pour Point, °C	-70 to -40	-50 to -30
Flash point, °C	200…260	200…270
Thermal stability	good	very good
Biodegradability, %	75…100	46…88

Another class of synthetic oils is Polyalkylene Glycols- PAGs. PAGs can be either polyethylene or polypropylene oxide-based. Their water solubility can be differed according to the type. Polyethylene glycols are highly water soluble, present poor miscibility with mineral oils and are very polar structure. Their water solubility helps to provide biodegradability, but also provide some disadvantage as lubricants, due to their frequently free water contamination tends.

3. EXPERIMENTAL

3.1 Manufacturing process and equipment

The process of manufacture the biodegradable lubricating greases must take into account the particularities of components and do 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, castor oil, other vegetable oils) are much time reactive than the fatty acids used to manufacture soap based greases [7]. For obtain good performances greases we used a technological method to form the thickener in the absence of base oil.

The usual equipment is satisfactory for the manufacture of biodegradable greases, but this must be properly cleaned to prevent contamination with conventional greases and their components.

3.2 Test Methods

The experimental greases were characterized using the following test methods:

Table 5. Test Methods

Characteristics	Test Methods
Dropping point	ASTM D 2265
Penetration, 25°C, 1/10mm	ASTM D 217
Mechanical stability, 10000 strokes	ASTM D 217
Oil Separation, 30 hours, 100°C, %	ASTM D 972
Evaporation loss, 30 hours, 100°C, %	ASTM D 972
Colloidal stability, % oil separated	STAS 3793
Biodegradability, %, 21 days	CEC L-33-A-94
Bomb oxidation test	ASTM D 942

3.3 Greases formulated with vegetal oils

The lithium hidroxystearate thickener was selected to prepare the soap based greases with vegetal oil. We present bellow the characteristics of biodegradable greases made with soybean oil - Table 6, and mixture of soybean oil and rapeseed oil (grease 6 in Table 7) and also mixtures of soybean and castor oil (greases 4, 5 in Table 7). The greases made with vegetal oils by authors' technology are rapidly biodegradable (over 85% by CEC L-33-A-94 test). They present high dropping points (over 185°C) and good physico-mechanical characteristics. However, it must be mentioned that a high content of thickener for the same class of consistency is required as comparing to conventional greases.

3.4 Greases formulated with synthetic esters

The rapidly biodegradable greases containing diesters (di-octyl adipate – DOA and di-octyl-sebacate – DOS) and organo-clay [1, 3] were made by a new technology which consists in adding the polar solvent dispersant in two steps. This method confers to the final product higher mechanical and storage stability values than those of the similar greases obtained by classical technologies. The characteristics of the greases containing di-octyl sebacate (7, 8, and 9) and di-octyl adipate (10, 11, and 12) as base fluid are shown in Table 8 and 9. The characteristics of the greases R1 and R2 made by classical technology from di-octyl sebacate and di-octyl adipate are comparatively presented.

Table 6. The characteristics of soybean greases.

Characteristics	Grease		
	A 1	B 2	C 3
Dropping point	190	196	197
Penetration, 25°C, after 60 strokes, 1/10mm	294	275	250
Roll stability, % change	2.1	0	0
Oil Separation, 30 h, 100°C, %	2.4	1.9	1.7
Evaporation loss, 30 hours, 100°C, %	0.3	0.24	0.2
Biodegradability, %, 21 days	87	86	85

Table 7. The characteristics of greases made with vegetal oils mixtures.

Characteristics	Grease		
	D 4	E 5	F 6
Dropping point, °C	193	188	185
Penetration, 25°C, after 60 strokes, 1/10mm	241	279	306
Roll stability, % penetration changes after 10000 strokes	1.7	0.8	9
Oil Separation, 30 h, 100°C, %	0	0.84	1.2
Evaporation loss, 30 h 100°C, %	0.58	0.10	0.61
Biodegradability, %, 21 days	85	87	87
Type of base oil, %	Soybean, Castor	Soybean, Castor	Soybean, Rapeseed

Table 8. The characteristics of DOS greases.

Characteristics	**Greases**			
	G **7**	**H** **8**	**I** **9**	**R1**
Dropping point, °C	>260	>260	>260	>260
Penetration, @ 25°C, 60 strokes, 1/10mm,	278	265	246	262
Mechanical stability, penetration change after 10000 strokes	5.2	4.8	4.6	12.6
Colloidal stability, % oil	2.8	2.3	1.6	9.6
Biodegradability, %, 21 days	86	86	86	-

Table 9. The characteristics of DOA greases.

Characteristics	Greases			
	J 10	K 11	L 12	R2
Dropping point	>260	>260	>260	>260
Penetration, @ 25°C, 60 strokes, 1/10mm,	265	270	324	282
Mechanical stability, penetration change after 10000 strokes	3.9	4.3	4.8	13.2
Colloidal stability, % oil	3.2	4.4	4.6	10.6
Biodegradability, %, 21 days	80	80	80	-

The biodegradability of greases prepared with synthetic oils (DOS and DOA) and bentone tested by the CEC method is 86% and 80%, respectively. Their dropping point, over 260°C are specific for this type of lubricants. The values of mechanical stability measured by penetration change, after 10000 strokes are higher than those of the greases made by adding the polar solvent in a single step. Using this new technology the authors obtained high stability storage products (shown by the values of colloidal stability in accordance to Romanian test method).

3.5 Some additivation aspects in multipurpose biodegradable lubricating greases

Additivation is the solution to improve the properties of the biodegradable greases. The polarity of the vegetal oils and synthetic esters can generate competitive reactions on metallic surfaces [9]. To obtain similar properties as mineral oil based greases a higher proportion of additives is necessary. On the other hand it must be taken into account the biodegradability of the additives, too [1, 8]. In a finished lubricant, additives normally constitute a sufficiently low fraction that their function can be the primary consideration, rather than their environmental behavior.

An additive consisting of sulphurizated soybean oil – Table 11, was used to improve the EP and antiwear properties of biodegradable grease made with the same base oil – Table 11.

Table 10. The characteristics of the sulphurizated soybean oil, used as EP/AW additives.

Characteristics	Values	Method
Density @ 20 °C	1.05	ASTM D1298
Suphur content, %,	20	ASTM 4294
Saponification Number, mg KOH/g,	118	ASTM D1962
Biodegradablity, %, 21 days	78	CEC

Table 11. The effect of sulphurized soybean oil on the biodegradable greases containing vegetal oils.

Characteristics	Greases	
	M 13	N 14
Dropping point°C	196	192
Penetration, @ 25°C, 1/10mm, after 60 strokes	282	297
Roll stability, % change	0	2.4
Oil Separation, 30 hours, 100°C, %	1.9	2.4
Evaporation loss, 30 hours, 100°C, %	0.24	0.36
Biodegradability, %, 21 days	85	85
Four ball test: -Wear scar diameter, mm, -at 40 daN / 60 min -at 150 daN / 1 min -Welding load, daN	 0.86 - 150	 0.62 1.12 280

The sample 13 is non-adittivated grease while the grease grade 14 contains 3.5% sulphurizated soybean oil. The sulphurizated soybean oil improves the antiwear and EP properties of the vegetal base greases – Table 11. The oxidation stability of biodegradable greases made with vegetal oil can be improve using α-tocoferol acetate (pressure drops only 0.22 psi after 100 hours-Table 12). The additive α- tocoferol acetate (vitamine E) used as antioxidant is a pharmaceutical grade product, 30% active substance in sunflower oil.

Table 12. The antioxidant effect of the α-tocoferol acetate in biodegradable lithium greases.

Characteristics	Greases	
	O 15	P 16
Dropping point	196	190
Penetration, 25°C, 1/10mm -unworked -after 60 strokes	 275 282	 280 304
Bomb oxidation test, Δp, psi	0.35 after 25h	0.22 after 100h

3.6 Behaviour of calcium carbonate in Polyurea greases

Due to their suitable properties, the polyurea greases made with high purity white oils, or poly alpha-olefins as base stocks are frequently used in food processing. More over, polyurea greases formulated with suitable oils present very high biodegradability. 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. Polyurea greases have outstanding resistance to oxidation. The oxidation resistance of these products is attributed to the absence of metals. Generally, soap base thickener can helps the promotion of oxidation of the greases. By comparison, a polyurea-base thickener system offers temperature range limits similar to the soap-thickened grease, but additionally it has antioxidant and antiwear properties confer by thickener itself. Polyurea thickeners might become wide used, but they are difficult to manufacture, requiring the handling of several toxic materials. Some polyurea lubricating grease was formulated using preformed thickener (16%) which has no toxicity.

Precipitated calcium carbonate, even it isn't a biodegradable material can be considered a suitable additive, which improve the extreme pressure and anti wear properties of ecological greases. Its non toxicity confer this material, very good attribute to be use in food grade bio-lubricants formulation. Precipitated calcium carbonate used in ours formulation consisted in a mixture of all three polymorphs of calcium carbonate, obtained using two nonionogene additives: polyoxyethylen sorbitan monolaureate, (Tween 20) and polyoxyethylen sorbitan trioleate (Tween 85). In the $CaCO_3$ precipitation process these additives behave as block copolymers with only one hydrophilic group (polyglycolic group). Usually the presence of an electric charged functional group (R^+ or R^-) induces polymorph selectivity. Their absence in Tween 20 (85) structural formulate explains the mixture of polymorphs. They may influence only the particles size distribution. Optic microscopy analysis of the solid phase and SEM micrographs show needle-like aragonite, plates and dendrite-like vaterite, rhombohedral-like calcite.

Table 13. Characteristics of calcium carbonate used in lubricants formulations

Characteristics	Values
Specific surface area, m^2/cm^3	0.73
Average diameter, μm	20.535
Nature of the solid phase	aragonite, vaterite and calcite

Tabele 14. The influence of calcium carbonate as additives in polyurea greases

Characteristics	Calcium carbonate,%			
	0	2,5	3	3,5
Penetration, @ 25°C, 1/10mm, after 60 strokes	269	267	265	262
Dropping point, °C	>230	>230	>230	>230
Four ball test: - Welding load, daN -Wear scar diameter, at 150 daN / 1 min, mm	 140 -	 150 3,2	 170 1,8	 220 0,7
Colloidal stability, % oil separated	4,26	4,05	4,01	3,8
Mechanical stability: penetration after 10 000 strokes, % change	5,6	4,8	5,02	4,3
Corrosion test (OL, 3 hours at 100°C)	pass	pass	pass	pass
Water resistance, 5 hours at 90°C	Stab.	Stab.	Stab.	Stab.

Table 15. The caracteristics of polyurea greases aditivated with diferent morphologycal types of calcium carbonate, versus molibdenum disulphide

Characteristics	Solide additive			
	a	v	c	MoS_2
Penetration, 25°C, 1/10mm, 60 strokes	270	269	275	290
Dropping point, °C	198	196	199	192
Four ball test: -Welding load, daN -Wear scar diameter, at 150 daN / 1 min, mm	 >300 1,2	 290 1	 290 1,2 5	 290 0,85

a: aragonite; v: vaterite; c: calcite

4. CONCLUSION

The greases made with vegetal oils by authors' technology are rapidly biodegradable (over 85% by CEC L-33-A-94 test). They present high dropping points (over 185°C) and good physico-mechanical characteristics. A higher content of thickener for the same class of consistency is required as comparing to conventional greases.

The rapidly biodegradable greases containing diesters (DOA, DOS) and organo-clay were made by a new technology which consists in adding the polar solvent dispersant in two steps.

To improve the EP and antiwear properties of the vegetable greases sulfurizated vegetable oils was used.

The oxidation stability of vegetable greases was improved using α-tocoferol acetate;

Ultrafine calcium carbonate has major improving on EP/AW properties of polyurea based grease, even it is not an usually additive for lubricants.

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