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Biodegradable lubricating greases for special work conditions

Key words

Greases, environment, lubricating fluids, vegetable oils, synthetic esters.

Summary

Lubricants facilitate the effective operation of mechanical equipment, reducing friction and wear, but at the same time, they represent a large and diffuse pollution source both in soil and in water. Eliminating or reducing the formation of pollutants and waste pollution prevention makes an important contribution to environmental protection. Biodegradable lubricants represent the technical and environmental 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 on the main components: base oil, thickener, and the additives. The aim of our work is to find the most suitable formulations of ecological lubricating greases having good performances, in order to use them as multifunctional lubricants.

1. Introduction

The most effective means of protecting the environment is pollution prevention. Eliminating or reducing the formation of pollutants and waste pollution prevention makes an important contribution to environmental protection.

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Lubricants facilitate the effective operation of mechanical equipment, reducing friction and wear, but at the same time, they represent a large and diffuse pollution source both in soil and in water. Conventional lubricants, based on mineral oils, contain toxic and non-biodegradable substances. Biodegradable lubricants represent the technical and environmental 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. The problem is to find the most suitable composition to make lubricating greases with good performances, so to use them as multifunctional lubricants. In the case of environmentally friendly products, the main components of the greases must be rapidly biodegradable materials and must present minimum risk to health human and the environmental.

The most rapidly biodegradable oils as lubricating grease components are vegetable oils, synthetic esters [1, 3] and glycols. 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. The additives (antioxidants, antiwear-EP, corrosion inhibitors, and polymers) for ecological greases should also be environmentally acceptable.

2. Base fluids for biodegradable lubricating greases

The most used biodegradable fluids for lubricating greases synthesis are vegetable oils and synthetic esters. Oil is considered to be readily biodegradable, if a minimum of 70% of the hydrocarbons is removed after 21 days, according to CEC test. Generally, the biodegradability of the vegetable oils and synthetics esters is over 90%, while that of the mineral oils is 20-40%, as it is show in Table 1. Due to their polar nature, which confer great affinity for metal surfaces, vegetable oils, and synthetic esters have good lubricity properties.

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

2.1. Vegetable oils

Soybean oil, rapeseed oil, sunflower oil, and castor oil are the most used vegetable oils in biodegradable lubricant formulations and have the advantage of being almost completely biodegradable. There are many applications for vegetable oils in the lubrication field, especially for fluid lubricants such as hydraulic fluids, compressor oils, transformer coolant, two-stroke engine oils, and metal working fluids. The chemical stability of vegetable oils is low, because of their polyunsaturated acids content. The resistance to ageing of vegetable oils is directly related to the level of the iodine value. Table 2 gives the iodine value of some vegetable oils [2, 3].

Table 2. Iodine value of vegetable oils

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

The sensitivity to hydrolysis and to oxidation can be reduced by different methods like the hydrogenating of the conjugated bonds, which also reduces the iodine number of the oil. The structure of the fatty acids of a vegetable 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 unfavourable oxidation and chemical stability at high temperatures. The level of oleic acid also influences the oxidative stability. A higher content of oleic acid also determines a smaller change in viscosity (Table 3).

Table 3. Oleic acid content, viscosity and changes in viscosity of various vegetable oils

Oil	**Oleic acid, %**	**Kinematic Viscosity, cSt**		**Δ Viscosity 40°C, cSt** (1000 hrs, 3 l/h, 93°C)
		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

The stability can be increased by the chemical modification of the oils in order to reduce the content of conjugated double bonds. There are several possibilities to do this:

– The hydrogenation of the conjugated double bonds by selective catalysts in specific conditions;
– The reaction of the oil with unsaturated esters (Figure 1);
– The reaction of unsaturated esters with aromatics, in the condition of Friedel-Crafts.

Opportunities in the vegetable-based lubricant field were opened by the use of oils obtained from genetically modified seeds. Oil obtained from a genetically modified sunflower, with a very high content of oleic acid has very good rheological properties and chemical stability. Another genetically modified oil is "Canola Oil" obtained from the rapeseed plant. Canola is used as a lubricant, fuel, soap, and synthetic rubber base.

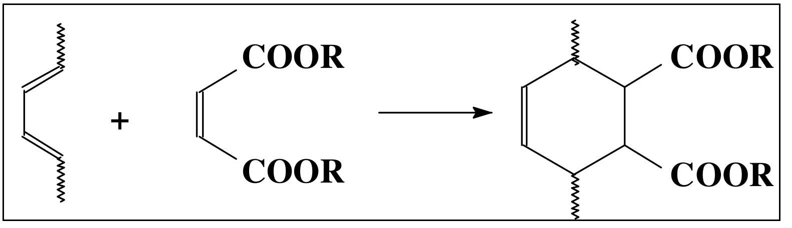

Fig. 1. Reaction scheme of the unsaturated fatty acids with an unsaturated ester

2.2. Synthetic esters

To obtain good performance synthetic esters, selected branched alcohols and pure oleic acids are used. The branched alcohols improve the flow properties at low temperatures and at the same time the hydrolytic degradation is inhibited [3]. The synthetic esters in lubricants improve the following properties: thermal stability, hydrolytic stability, solvency, lubricity, and biodegradability. These types of fluids exhibit a longer service life then vegetable oils (3). 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

3. Experimental

3.1. Manufacturing process and equipment

Rheological and tribological properties are related to the characteristics of the base oil, the nature and concentration of thickener, and the type of the structure of three dimensional structure of the soap fibres [5].

The process of manufacturing 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 more time reactive than the fatty acids used to manufacture soap based greases [4]. For obtaining good performance greases, we used a technologically method form of 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 characterised 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-93
Bomb oxidation test	ASTM D 942

3.3. Greases formulated with vegetable oils

The lithium hidroxystearate thickener was selected to prepare the soap-based greases with vegetable oil. In Table 6, we present the characteristics of biodegradable greases made with soybean oil (grease A, B and C), and a mixture of soybean oil and rapeseed oil (grease F) and also mixtures of soybean and castor oil (greases D, E).

The greases made with vegetable oils by our proprietary technology are rapidly biodegradable (over 85% by CEC method). Except grease made with soybean and rapeseed oils (F), they present high dropping points (over 185°C) and good physical-mechanical characteristics. However, it must be mentioned that a high content of thickener for the same class of consistency is required compared with conventional greases.

Table 6. The characteristics of vegetable base oil greases

Characteristics	**Grease**					
	A	**B**	**C**	**D**	**E**	**F**
Dropping point	190	196	197	193	188	175
Penetration, 25°C, 60 strokes, 1/10 mm	294	275	250	241	279	310
Roll stability, % change	2.1	0	0	1.7	0.8	11
Oil separation, 30 h, 100°C, %	2.4	1.9	1.7	0	0.84	1.2
Evaporation loss, 30 hours, 100°C, %	0.3	0.24	0.2	0.58	0.10	0.78
Biodegradability, 21 days, %	87	86	85	85	87	87
Type of base oil	Soybean	Soybean	Soybean	Soybean, Castor	Soybean, Castor	Soybean, Rapeseed

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 (12) were made by a new technology, which consist in adding of 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 (G,H, I) and di-octyl adipate (J,K,L), as a base fluid, are shown in Table 7. The characteristics of the greases R1 and R2 made by classical technology from di-octyl sebacate and di-octyl adipate are comparatively presented.

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 points, 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 the new technology, we obtained high stability storage products (shown by the values of colloidal stability in accordance with the Romanian test method).

Table 7. The characteristics of DOS and DOA greases

Characteristics	Grease							
	G	**H**	**I**	**R1**	**J**	**K**	**L**	**R2**
Dropping point, °C	>260	>260	>260	>260	>260	>260	>260	>260
Penetration, at 25°C, 60 strokes, 1/10mm	278	265	246	262	265	270	324	282
Mechanical stability, penetration change after 10000 strokes, %	5.2	4.8	4.6	12.6	3.9	4.3	4.8	13.2
Colloidal stability, % oil	2.8	2.3	1.6	9.6	3.2	4.4	4.6	10.6
Biodegradability, 21% days	85	86	86	-	80	80	80	-
Type of base oil	DOS				DOA			

3.5. Behaviour of some additives on biodegradable lubricating greases

Using additives provides the solution to improving the properties of the biodegradable greases. The polarity of the vegetable oils and synthetic esters can generated competitive reactions on metal surfaces [3]. To obtain similar properties as mineral oil based greases, a higher proportion of additives is necessary. On the other hand, one must take into account the biodegradability of the additives. An additive consisting of sulphurizated soybean oil (20%S) was used to improve the extreme pressure (EP) and antiwear properties (AW) of a biodegradable grease made with the same base oil (Table 8).

Table 8. The effect of sulphurizated soybean oil on the vegetable greases

Characteristics	Greases	
	M	**N**
Dropping point°C	196	192
Penetration, at 25°C, after 60 strokes, 1/10mm	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, 40 daN, 60 min, mm – Wear scar diameter 150 daN, 1 min, mm – Welding load, daN	 0.86 1.68 150	 0.62 1.12 280

The grease M represents greases without additives, while grease N contains 3.5% sulphurizated soybean oil. Sulphurizated soybean oil improves the antiwear and EP properties of the vegetable base greases and also reduces the wear scar diameter (Table 8).

The oxidation stability of biodegradable greases made with vegetable oil grease can be improved using α-tocoferol acetate (pressures drop only 0.22 psi after 100 hours) grease P (Table 9). The additive α- tocoferol acetate (vitamine E) used as antioxidant is a pharmaceutical grade product, 30% active substance in sunflower oil.

Table 9. The antioxidant effect of the α-tocoferol acetate in biodegradable lithium greases

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

4. Conclusions

1. The biodegradable greases made with the above vegetable oils by our proprietary technology exhibit over 85% biodegradability by CEC method and good physical-mechanical characteristics.
2. We obtain biodegradable diesters greases with high stability storage capacity and over 80% biodegradability according to the same CEC method.
3. To improve the EP and antiwear properties of the vegetable grease sulfurizated vegetable oil was used. The oxidation stability of vegetable greases was improved using α-tocoferol acetate.

References

[1] Grives, P. R., *The Manufacture of Biodegradable Nontoxic Lubricating Greases*, NLGI Spokesman, vol. 63, No. 11, Feb. 2000;
[2] Barriga, J., Aranzabe, A., Galda, P., *Sunflower Based Grease For Heavy Duty Applications,* Mecanica Experimental, vol. 13, pag 129-133, 2006;
[3] Florea, O., Luca, M., Florescu, D., *The Influence of Lubricating Fluid on the Preoperties of Biodegradble Greases,* J. Synthetic Lubrication 19-4. Jan. 2003;
[4] Florea, O., Luca, M., Popa ,D., *Biodegradable lubricating greases for earth moving equipments,* Journal of the balkani tribological association, vol. 13, no. 1, 2007, PAG 96-102;
[5] Delgado, M. A., *Relationship among microstructure rheology and processing of a lithium lubricating grease*, Chem. Eng. Res.Des.83, 1085-1092, 2005.

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