16th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2012, Dubai, UAE, 10-12 September 2012

ADVANTAGES OF BIODEGRADABLE FLUIDS APPLICATION AT METALWORKING OPERATIONS

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ABSTRACT
Lubrication fluids, including metalworking fluids, generally, contain base fluid and different types of additives according to application requirements. As the base fluid it is possible to use mineral oils, natural oils or synthetic fluid and also water separately or in combination. Besides of functional properties, the environmental and safety requirements have a strong influence on the fluid components selection. Based on that, the trend of new lubricants development leads to less harmful and to the environmental friendly products. Mineral base oils are widely used because of their advantages in stability in comparison to natural oils, or lower prices in comparison to synthetic fluids. Because of some disadvantages of mineral oil there is space for development new formulation free from mineral oil. Natural oils and fats, vegetable and animal, become important as petroleum oil replacement due to their excellent lubrication properties and good biodegradability. The synthetic biodegradable fluids include polyalphaolefins, that exhibit excellent low-temperature properties, synthetic esters have good antioxidant characteristics and polyalkylene glycols with good water miscibility. Biodegradable lubricants are desirable for equipment used in applications wherever the lubricants themselves might come into contact with the environment so at total-loss lubricant operations. Also that property is important at lubricant waste maintenance. This paper will show the examination results of biodegradable watermiscible metalworking fluids in laboratory and also in application.
Keywords: metalworking fluids, lubrication, metalworking operations, biodegradability

1. INTRODUCTION
Metalworking fluids are used for lubrication, cooling and clearing working zone at wide working operations on metals and also at other materials. Application of metalworking fluids decreases tribological effects that occur in working area, and increases process productivity [1]. There are two main families of metalworking fluids: neat oils and water miscible fluids.
Metalworking fluid manufacturers are faced with many new challenges. Various health, safety and environmental legislation related to transportation, usage and disposal of metalworking fluids are major challenges the fluid manufacturers have to address [2].
The especial family of metalworking fluids became biolubricants, product based on biodegradable components for total loss applications and with low toxicity to environment and workers [3].
Safety and environmental concerns and customers' demand for environmentally friendly products are forcing major changes in lubricants. Mineral oils are prime targets, particularly from the health aspect as they contain compounds like polycyclic aromatic hydrocarbons. The fumes and mists produced by the usage of these oils can cause breathing related sicknesses. Also those increase the risk of air pollution [4]. Disposal of the spent mineral type metalworking fluids and recyclability is another cause for concern.

Environmentally adapted lubricant is commonly used term for products that meet next properties: good biodegradability, low eco-toxicity, low pollution risk for water, air and soil, lower consumption, longer application life, recyclable, produce less waste, and also promote energy saving. From that wide group of products, also called biolubricants, vegetable oils and fats are especially interesting due to their availability and also physical and chemical properties. They can be used neat, improved by hydrogenation or used as base fluid for synthetic esters' production. Wasted oils and fats (cooking oils) can be also base fluids for synthesis [5]. Vegetable oils, especially rape seed oil, provide many excellent properties as are good lubrication, high viscosity index, high flash point, relatively good oxidative stability in comparison to other natural oils, and relatively acceptable volatility. They are free of aromatics, and have better skin compatibility so challenge less dermatological problems. Vegetable oils have several disadvantages that are poor oxidative and hydrolytic stabilities, low temperature fluidity limitation, partly worse smell and compatibility with sealing and paints [6]. Mixing with other fluids raises the level of performance in minimizing deposits, sludge and varnish as determined in lab testing while maintaining biodegradability and performance [7]. In Table 1 are presented some advantages and disadvantages of base fluids in comparison to mineral base oil.

Table 1. Comparison of base fluids properties

PROPERTIES	PLANT OIL natural	DIESTERS	UNSATURATED ESTERS	SATURATED ESTERS	COMPLEX ESTERS	GLYCOLE	Mineral base oil
Viscosity interval at 40 ^{0}C / mm^{2}s^{-1}	45 - 70	8 – 30	4 - 80	2 – 100	> 40	2 – 100 very wide	2 – 100 very wide
Viscosity index	very good	good	excellent	very good	excellent	excellent	good
Pour point	bad	excellent	low	very good	good	excellent	good
Oxidation stability	bad	good	good	excellent	very good	very good	good
Hydrolytic stability	bad	excellent	good	good	very good	good	excellent
Lubrication	very good	sufficient	excellent	good	very good	very good	poor
Biodegradability	excellent	sufficient	very good	very good	good	very good	poor
Renewable source	yes	no	yes	yes	yes	no	no

There are two most significant opportunities for bio lubricants, total-loss lubricants and high risk lubricants. Total-loss lubricants are used where lubricants ends up almost entirely in the environment, or on the material, by the equipment design and application. High-risk lubricants is application where is present a high probability of accidental exposure of lubricants to sensitive environment. In both of those applications there are also part possibilities for metalworking fluid.

2. BIODEGRADABLE CLASSIFICATION

Biodegradability is the biological transformation of a substance or a compound of substances by means of microorganisms, with or without the presence of oxygen. There are several guidelines for classification, testing and requirements published by the world and also EU agencies. Organization for Economic Cooperation and Development (OECD) is most recognized in the lubricant industry [8]. Generally exist following definitions:

- Primary biodegradability: is a change in the chemical structure of the substance tested, achieved through biological activity and resulting in the loss of the substance's specific property.
- Total biodegradability (aerobic): is the degree of achieved degradation when the microorganisms completely degrade the substance tested, resulting in the generation of carbon dioxide, water, mineral salts, and biomass. According to the criteria set, a substance is completely biodegradable if in a test lasting 28 days it achieves the degradation degree value of 70% DOC (dissolved organic carbon), or 60% CO_2, or 60% O_2.
- Ready biodegradability: is the degradation which, having achieved 10% of degradation, reaches the value of 70% DOC, or 60% CO_2, or 60% O_2 within the next 10 days (the so called "10-day window").
- Inherent biodegradability: is the one using a culture that has been previously adapted to the tested substance or compound in any of the recognized biodegradability tests.

Only the total biodegradability provides accurate information on whether a lubricant has been completely degraded into CO_2 and water. The choice of the method for biodegradability determination depends on the lubricant properties and composition. The OECD 301B Modified Sturm test is adequate for soluble and insoluble organic, non-volatile materials. This test measures carbon dioxide

evolved and therefore measures only complete oxidation. Test material is introduced into a flask containing mineral substrate and bacterial inoculum. Biodegradation is expressed as a percentage of the total amount of carbon dioxide evolved during the test, (corrected for the control), against the theoretical carbon dioxide that the test material could have produced.

3. EXPERIMENTAL PART

3.1. Objectives

The objective of this work is to develop new biodegradable metalworking fluid based on natural vegetable oil, and also biodegradable fluid based on polyalkylene glycol components. Requirements on that working fluids are, except of biodegradability and low toxicity for environment and workers, good fluid stability, good cooling of working zone, good lubrication and preventions of material sticking on worked area, good corrosion prevention, as well as all other common properties.

3.2. Test methods

For examination of additives and metalworking fluids we used standard ISO, DIN, ASTM, IP methods, Internal tests as well as other in house test. Stability of additives, metalworking concentrates and their fluids were tested at different temperatures on 4 till 70 ^{0}C, by Internal test 1 and 3. After 24 hours changes of original samples as separation, sedimentation, turbidity are examined visually. Foaming properties we examined on cylindrical shaking test IP 312. Method IP 312 assesses the foaming characteristic of test fluid mixed concentrate with synthetic water (200 ppm in terms of $CaCO_3$). Test solution, 100 mL, is shaken for 15 sec. in a graduated test cylinder of 250 mL. After shaking, cylinder is stand in vertical position and foam volume measured immediately and after 5 minutes. For examination of fluid lubrication properties, we used two mechanical dynamical machines. First is known as Four ball wear test machine, ASTM D 4172. Four metal balls are placed in test fluid, heated to 75 ^{0}C and then the top ball is rotated over three others at standard load for 60 min. After one-hour test running, scar area diameter of test balls are measured and showed as average value in mm. The second test is known as Reichert balance machine. Basic construction consists of static metal roll and rotated ring immersed in test fluid. By this method wear scar area on test roll is measured in mm^2. Higher lubrication capacity has fluid with lower wear surface area. pH Value we measured with electronic pH meters by ASTM D 1287 method. For estimation of corrosion prevention properties we used four methods. The most known corrosion method is Herbert test: DIN 51360/I. According to it chips, acts upon a cast iron plate in metalworking fluid through 24 h. Corrosion occurs on plate and estimated for intensity and corroded area: 0-no corrosion, 6–strong corrosion. Filter paper corrosion test DIN 51360/II consists of cast iron chips, splashed with fluid acting upon filter paper through 2 hours. Corrosion spots on filter paper are estimated from 0 to 6 based on corrosion intensity. Corrosion properties to yellow metals we examined on aluminium, brass, silumine and copper, with Internal test 11. Metal strips are immersed in fluid on 50 ^{0}C through 3 hours. After that period plates are examined on colour changes: if corrosion occurs, corrosion is positive and if not, corrosion is negative.

3.3. Test fluids

Industrial grade rape seed oil, mineral base oil (MO) and additives for composing test metalworking fluids used from the market based on theirs environmental characteristic. In Table 2 are presented final composition of test fluids, approximately.

Table 2. Composition of test formulations (aprox).

FORMULA	BIO EM C	BIO BPG	MO EM
Rape seed oil, %	<75	0	0
Mineral oil, %	0	0	<70
Surface active block, %	<25	<50	<25
Water, %	0	<25	0
Biodegradability	+	+	-

4. RESULTS AND DISCUSSION

In Table 3 are presented some physical chemical properties of final test metalworking fluids' concentrates and also working fluids emulsions or solutions. In process of examination we mixed numerous formulations till satisfying fluid quality. All fluids have good stabilities, foaming and anticorrosion properties to ferrous materials and also to yellow metals. Lubrication properties determined at Reichert balance test machine of fluids BIO EM C and BIO BPG are excellent and better in comparison to conventional metalworking emulsion MO EM. Four ball wear test machine (ASTM D 4172) measure wear scar diameter and the best result is achieved with BIO BPG fluid.

Table 3. Properties of test metalworking fluids

PROPERTIES / CONCENTRATE	BIO EM C	BIO BPG	MO EM
Appearance, Visually	clear, yellow	clear, yellow	clear, dark yellow
Stability, 4-70^{0}C /24h, 7days	stable	stable	stable
Viscosity, 40^{0}C, mm^2/s, ISO 3104	42	55	60
EMULSIONS/SOLUTION, 5% in tap water			
Appearance, Visually	white, milky	transparent	white, milky
Stability, 20^{0}C / 24h, 7days	stable	stable	stable
pH Value, ASTM D 1287	7.17	8.5	8.9
Corrosion, Herbert test, DIN 51360/I	S0R0	S0R0	S0R0
Corrosion, Filter test, DIN 51360/II	0	0	0
Corrosion to yellow Me	No	No	No
Foam volume, mL,/after 5 min, mL	30/0	20/0	30/0
Wear scar diameter, mm, ASTM D 4172	0.84	0.73	0.87
Wear scar area, mm^2, Reichert balance	17.9	18.7	31.7

Soluble oil BIO EM C is examined at two metalworking operations. Firstly it is used for cooling and lubrication at wood sawing process in environment where showed excellent properties. The second application is at welding process as anti-spatter fluid. After spraying of BIO EM C emulsion on process parts the result of examination its quality, corrosion inhibition and also air pollution measurements showed very good properties [9].

Solution of BIO BPG fluid is examined on plate deep drawing process where parts showed very good surface quality, less cleaning is needed, and no bad smell, sticking or corrosion.

5. CONCLUSION

Two formulations of biodegradable metalworking fluids are formulated: BIO EM C and BIO BPG. Bio fluids are less harmful to the environment and human health so they consist of biodegradable base fluids and selected surface active components. They do not contain aromatics, boron and other harmful compounds. Test formulations showed excellent properties in laboratory and also in application conditions. Biodegradability is investigated by certified institute. The result shows that fluids are total biodegradable.

6. REFERENCES

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