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Biobased – Biodegradable –

Environmentally aware lubricants

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Historical Summary

The interest in biobased lubricants and particularly greases are on the rise. Interestingly, the original introduction of environment friendly lubricants began in Europe during the early 1980s. US researchers and lubricants experts followed Europe's lead and the 1990s saw a huge developmental activity in the United States. Companies like The Lubrizol Corporation invested significant amount of resources to develop additive packages for vegetable oil based hydraulic oils and focused on high oleic and ultra-high oleic sunflower oils as base oils. In the early 1990s, the giant US agricultural equipment manufacturer Deere and Company introduced a Universal Tractor Transmission Hydraulic Fluid called Bio-Hy-Gard which had the research cooperation of The Lubrizol Corporation's additive technology. It was specifically designed to accommodate prevailing mandates in the Black Forest areas in Germany. Caterpillar too later introduced, a hydraulic fluid called Bio-Hydo.

Figure 1: *OEM produced biobased hydraulic fluids in the United States Early 1990s, ELM[3] brands*

Introduction

In 1991, this author founded a biobased research center at the University of Northern Iowa with support from the Iowa Soybean Promotion Board (ISPB) and the US Department of Agriculture among many other funding agencies. In 1997 a soybean oil-based version of Bio-Hy-Gard was introduced as a soybean oil-based universal tractor transmission hydraulic fluid with funding support from ISPB. This product has been under the ELM brand (Figure 1). Europe's interest peaked again during the current century after research and developmental activities in the US had blossomed into a growing business. Most importantly, the US government initiated purchase preference programs for federal purchasing agents in order to create usage history and a model for the private industry to emulate. The United State's Department of Agriculture in cooperation with the United Soybean Board created the terms Biobased and Bio-preferred and has an extensive program that lists available biobased products and their manufacturers. **www.biopereffered.com** and **www.usb.org**. Figure 2 illustrates a number of retail packaged biobased products that are sold nationwide in large big box stores. These products are sold based on performance and price without overtly emphasizing the environmental adders that are only visible upon inspection of the packaging.

Figure 2: *Biobased Retail Products Sold in Major US Big Box Stores*[4]

While in Europe the emphasis has been primarily on biodegradability, in the US the focus is on renewability and petroleum substitution to the extent possible. As a result, since PAOs are considered biodegradable, in Europe they are preferred over non-biodegradable lubricants. But, PAOs are not biobased since they are not derived from renewable materials and in the US, they are not considered bio-preferred. Biobased lubricants in most cases are also biodegradable; whereas not all biodegradable lubricants are biobased.

Biobased Base Oils

There appears to be a general misunderstanding among the end users about the base oils used in environmentally aware products. The expectations give the impression that all biobased products are supposed to be vegetable oil based and/or that all lubricants can be made from vegetable oils.

Vegetable oils offer many inherently advantageous properties when used as lubricants, but they also have inherent limitations when compared with mineral or synthetic oils. As a result, there are vegetable oil derivatives such as simple and complex esters, estolides, and an array of other chemically modified oils that offer base oils for different end use applications. A thorough understanding of the properties of the base oil along with an appreciation of the performance requirements of the end use are essential in preparing a superior biobased product. Table 1 shows a list of vegetable oils with their select properties. For example, castor oil shows a superior oxidation stability and low temperature performance. The Oil Stability Index (OSI) is an American Oil Chemists' Society (AOCS) official method Cd 12b-92 re-approved 2017. For castor oil the OSI is 105.13 hours which is the highest stability of all oils listed in this table. But, castor oil also has the lowest viscosity index of all vegetable oils at 85. So, if used as hydraulic fluid, for instance, it would present good oxidation stability and cold temperature performance, but it would also thin down excessively at high operating temperatures. This makes it unsuitable as hydraulic fluid if used by itself.

Vegetable oils are often chemically modified, mixed together, or extracted from genetically enhanced seed oils with higher built-in stability. So, a combination of vegetable oils could enhance the properties of the mixture of one or more vegetable oil. An understanding of the properties of each vegetable oil alone or as a mixture when considered as base oil for lubricants is important when formulating biobased lubricants.

Base oil developers have often sought out oils that could be used across the application spectrum. As a result, there are several biobased derived or chemically modified base oils available with the intention of addressing the shortcomings of natural oils. Examples of these oils include a line of biobased derived esters from Zschimmer & Schwarz that offer cold temperature performance down to -70C with high levels of oxidation stability, and hydrolytic stability. Under the brand Lexolube, these esters come in viscosities ranging from 4 cSt ro 220 or higher.

Croda offers a line of complex esters, under the brand Priolube, that present performance and stability for use as hydraulic oil and other liquid lubricants. Ranging in viscosities from these esters offer highly stable base oils for various lubricants. The biggest barrier in using these biobased derived, chemically modified oils are that they are 3x-5x more expensive than the vegetable oils used to synthesise them.

Applications

As biobased lubricant and grease technologies mature, their ultimate success will depend on matching the performance and price of conventional mineral oil products. High quality and high-performance products that are expensive find success in niche markets. But, to reach the mainstream lubricant markets or to capture a significant portion of select lubricant fields, the end use application must closely match the performance and price of conventional lubricants.

Table 1: Properties of selected vegetable oils

Source: Environmental Lubricants Manufacturing, Inc.

Oil	Oil Stability Index (OSI) (hours)	Total Acid Number TAN	Flash Point (PM)	Flash Point (COC)	Fire Point (COC)	Pour Point (°C)	Cloud Point (°C)	Viscosity @ 40	Viscosity @ 100	Viscosity Index	4 Ball Wear	Pin & Vee Block load (lbs)	Iodine Value*
Apricot Kernel	23.42	0.2844	284.5	324	348	-16	-10.8	36.49	8.202	210	0.615	1732	
Avocado	18.53	0.185	217.5	320	348	-3	-0.2	39.26	8.432	199	0.609	1975	85.656
Babassu	57.8	N/A	261.5	308	327	N/A	N/A	28.65	6.133	170	0.586	1706	
Castor	105.13	0.252	282.7	300	320	-28	N/A	249.5	19.02	85	0.633	1674	93.030
Coconut	75.38	N/A	275.3	306	324	N/A	N/A	27.8	5.947	167	0.504	1738	-6.394
Corn	3.73	0.198	180	324	346	-15	-10.2	32.58	7.72	220	0.628	1997	
Cottonseed	4.35	0.13	262	330	350	-6	-3.7	34.23	7.911	215	0.588	1812	
Flaxseed	1.17	0.8399	268	322	348	-12	-7.4	27.35	7.112	243	0.639	1622	173.712
Grapeseed	2.83	0.229	248	324	346	-12	-6.9	33.28	7.858	220	0.623	1736	
Hempseed	0.10	1.6488	248	328	356	-15.8	-28	26.71	6.972	242	0.608	1556	
Jojoba - Refined	42.15	0.13	282.7	304	330	9	9	25.1	6.519	234	0.630	1673	75.152
Jojoba - Golden	38.3	0.752	268.7	304	330	10.7	8	24.82	6.452	233	0.606	1558	
Lard	6.02	N/A				N/A	N/A	N/A	8.543	N/A	0.525	1676	
Macadamia	6.87	0.126	276	328	344	-5	-1.9	39.24	8.441	200	0.594	1797	
Oleic acid	0.10					3	5.9	19.05	4.778	186	0.605	1341	
Olive	5.08	0.132	264	316	342	-6	-5.4	37.56	8.242	203	0.616	1683	74.710
Palm Kernel		N/A	272	322	329	N/A	N/A	31.96	6.606	169	0.461	1622	
Palm	21.52	N/A	287	320	347	N/A	N/A	41.77	8.56	189	0.517	1726	
Poppyseed	17.86	0.151	256	326	356	-18	-15.5	30.52	7.46	226	0.601	1908	
Ricebran	20.82	0.194	248	342	360	-9	-3.9	36.49	8.177	208	0.581	1549	
Ricinoleic Acid	117.1	NA	253	NA	NA	-19	-5.5	NA	NA	NA	0.519	1277	NA
Safflower	17.98	0.1268	244	322	350	-22	0.4	37.9	8.325	206	0.634	1660	84.459
Sesame	5.8	0.136	266	334	342	-9	-5.7	34.1	7.923	216	0.49	1842	
Soybean	17.67	0.1602	292	328	346	-9	-5.1	31.08	7.552	226	0.601	1835	126.839
High Oleic Soybean	35.95	0.2346	248			-12	-9.9	39.12	8.492	203	0.608	1768	
Sunflower	10.23	0.132	272	326	356	-15	-9.9	38.58	8.453	205	0.621	1864	
Walnut	16.48	0.1269	186.7	322	346	-19	-14.5	29.91	7.441	232	0.584	1887	

Table 1: *Properties of selected vegetable oils*

Synthetic Ester	Chemistry	Viscosity @40 ℃(cSt)	Viscosity @100C(cSt)	Viscosity Index	Flash pt. (℃)	Pour pt. (℃)
Lexolube CG-3000	Polyol	3000	290	230	320	-20

Table 2: *Lexolube CG-3000: an example of a biobased complex ester*

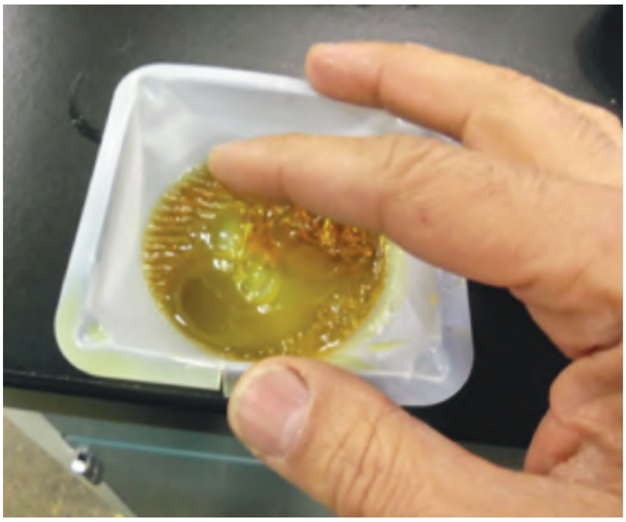

Figure 3: *Vegetable oil exposed to heat and air forming a layer of polymer Source: Environmental Lubricants Manufacturing, Inc.*

Vegetable oils that are not oxidatively stable such as linseed oil or even used frying oils that are partially oxidised could be used as base oils for water emulsifiable dust control, concrete form and asphalt release agents (figure 3). In those applications the oil when exposed to air and light polymerise and form a protective coating and contain dust. More stable oils could be used for wire rope grease, drill rod grease and rail curve greases. Oils with highest levels of oxidation stability such as genetically enhanced high oleic varieties can be used along with potent anti-oxidants for formulating gear oils and chassis and bearing greases.

As an example, none of the vegetable oils in their natural state could be recommended for formulating aviation hydraulic fluids where they are exposed to extreme cold temperatures. Similarly, for northern cold climates hydraulic oils made from biobased derived

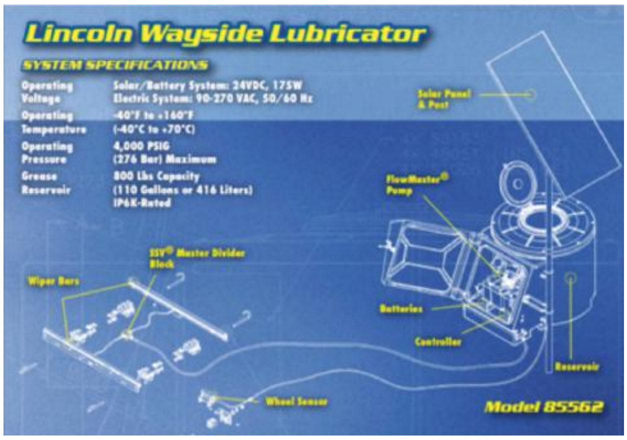

Figure 4: *Schematic illustration of a Wayside Lubricator*

synthetic esters would be preferred over vegetable oils in their natural form. But, vegetable oils could offer high performance and economical alternatives in many applications when selected carefully.

Grease made with vegetable oils offer economy and environmental friendliness if prepared properly. Especially in applications where the product is in direct contact with the environment as in railroad curve grease. Figure 4 shows a schematic illustration of a wayside rail lubricator. A battery-operated pump delivers the grease through hoses to the grease delivery bars attached to the insides of the tracks. As the flanges of the wheels come in touch with the grease, they carry and rub the grease to the inside of the tracks as they roll through the curves (Figures 5). Continuous lubrication over time results in large quantities of grease come in direct contact with the environment.

Other examples include, drill rod grease, truck and chassis greases, and food processing greases.

The requirement of the Vessel General Permit (VGP) by the US Environmental Protection Agency has resulted in increased demands for biobased wire rope grease. Figure 6 shows a greasy applicator that allows application of grease to wire ropes rapidly as the rope travels through the clamshell design applicator. This design comes with two chambers one filled with a biobased liquid penetrant and the other with biobased grease. Wire brushes help to push the greases through the strands.

A new manufacturing process that utilises microwaves for reaction heating has reduced exposure time to a fraction of conventional heating. Also, since there are no hot spots in microwave processing, as in the walls of conventional reactors, the biobased grease prepared with microwaves offers superior stability. Due to advances in seed oil technologies resulting in higher stability vegetable oils, advances in additives and anti-oxidant technologies, and now the microwave processing, today there are many biobased greases that meet industry standards but are priced the same as mineral oil-based greases.

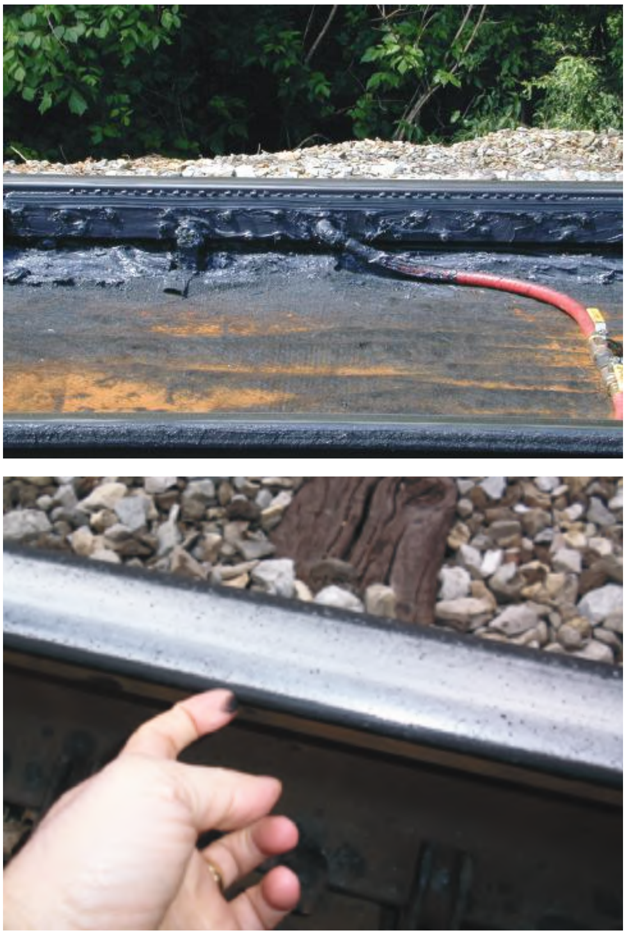

Figure 5: *(Left): 48" grease dispensing bar attached to the inside of track to deliver grease to the wheel flange of rail car; (Right): Shows the presence of rail curve grease on the track wheel point of interface*

In the United States, the biobased rail curve greases used by large Class I freight railroads are priced below their mineral oil-based counterparts. Just 15 years ago, the biobased versions were twice as expensive as the mineral oil version of rail curve greases.

But, even for the so called lost-in-use or used-once applications, biobased grease making is fraught with pitfalls. This is because grease making often requires high temperature reactions exceeding 200°C. Furthermore, the hot walls of the reaction vessels are often at much higher temperatures of near 300°C or more. Vegetable oils in general should not be exposed to temperatures of 150°C or higher.

Figure 6: *A dual chamber clam shell type wire rope lubricator Courtesy of Lubitec UK*

Exposure to such temperatures initiate the process of polymerization within the oil followed by propagation of polymers. If not terminated by some deliberate action, the propagation continues to full polymerization. Therefore, it is important to reduce exposure to high temperatures and complete the reaction process quickly. Additionally, upon completion of the reaction process anti-oxidants and other additives are needed to help terminate the propagation of polymers. If prepared improperly the biobased grease could continue the polymerizate albeit slowly during storage.

Summary

Biobased lubricants are made with renewable oils and are biodegradable; whereas biodegradable lubricants could be derived from mineral oils that are not biobased. Examples of biobased lubricants are canola oil-based rail curve and wire rope greases that are biobased and biodegradable. An example of biodegradable lubricant would be a PAO-based grease that would pass the biodegradability standards of OECD 301 series tests but is not biobased.

In manufacturing biobased lubricants it is important to match the end use requirements with the base oil. Expensive base oils that are often chemically modified versions of vegetable oils are suitable for application where high levels of oxidation stability and sub-zero temperature performances are required. The more economical vegetable oils could be selected based on their fatty acid profiles for different end uses especially the lost-in-use type applications.

Grease manufacturing with vegetable oils require stable oils matching the end use requirements, suitable anti-oxidants, short exposure to high reaction temperatures, terminators to disrupt ensuing propagation of polymers that are initiated due to exposure to high temperatures, and economical pricing.

Today's biobased base oils fall on a spectrum ranging from the least oxidatively stable and inexpensive oils to high stability vegetable oils that are reasonably priced and to the extreme biobased derived synthetic simple and complex esters that offer stability and cold temperature flowability at 3x-4x higher price than vegetable oils. The end use performance and price dictate which base oil to be used. Ultimately, many of the lost-in-use applications where the lubricants are directly released into the environment will be using biobased products.

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