Development history, current situation and prospect of international vegetable oil-based hydraulic oil

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Abstract—Vegetable oil-based hydraulic oil is one of the biodegradable lubricants. With the strengthening of environmental awareness, especially in the context of the increasingly serious pollution of the marine environment by mineral oil used in ships, people are increasingly aware that the pollution of mineral oil-based hydraulic oil to the environment is very serious, and many solutions have been proposed. The use of biodegradable plant-based hydraulic oil instead of traditional mineral oil-based hydraulic oil can fundamentally solve the pollution of marine hydraulic oil to the marine environment. The development of vegetable oil-based hydraulic oil in the world is systematically summarized, including its material composition, physical and chemical properties. By analysing its practical prospect and future development direction, it is concluded that vegetable oil-based hydraulic oil is the most environmentally friendly hydraulic oil in the future shipbuilding, industrial manufacturing and other industries, and it is the development trend of " green shipping " in China in the future.

1. Introduction

Lubricating oil mainly includes hydraulic oil, gear oil, etc. Hydraulic oil is a kind of lubricating oil. Hydraulic oil is widely used in ships, automobiles, machinery and equipment manufacturing and other industries. In some open systems or circulatory systems, due to normal use loss, leakage, sputtering and other factors, hydraulic oil will inevitably be released into the surrounding environment, and will accumulate and enrich in the natural environment for a long time, thus causing pollution to the natural environment and forming various environmental protection problems[1].

According to the statistics of Clarksons Research, there are about 473 marine pollution accidents around the world in the five years from 2016 to 2020, with an average of more than 80 such accidents every year. It is further concluded that in the past five years, marine pollution accidents accounted for about 1.5 % of the total number of marine accidents[2]. As early as the 20th century, the Bodensee Lake, on the border between the Swiss Confederation and Germany, had a very strong hydrocarbon sediment layer at the bottom of the lake, which attracted the attention of the authorities. The authorities had ordered restrictions on the use of mineral-based insulating lubricants for all externally mounted motor ships and external generators of more than seven amperes[3].

The base oil is undoubtedly the decisive factor for the positive or negative effects of hydraulic oil on the ecology. Therefore, the base oil of biodegradable and environmentally friendly hydraulic oil is the research hotspot and future development trend under the theme of "green navigation".

2. Basic concept of vegetable oil based hydraulic oil

2.1. Definition

Vegetable oil-based hydraulic oil is a kind of environmentally friendly lubricating oil and a degradable green hydraulic oil. Similar to the general mineral oil hydraulic oil, the composition of vegetable oil-based hydraulic oil is also the base oil and additive. However, the specific composition of the two is different from that of the general mineral oil hydraulic oil. Vegetable oil-based hydraulic oil refers to the hydraulic oil with vegetable oil or modified vegetable oil as its base oil. At the same time, in order to ensure that its biodegradability is not destroyed, the specific components of additives are not the same.

2.2. Composition

2.2.1. Base oil

The concentration of base oil in modern hydraulic oil is generally 80 % to 90 % (Fig.1), which plays a decisive role in the properties of hydraulic oil. Such as high biodegradability, low volatility, high solubility of hydraulic oil additives, etc. In addition, the base oil is a key factor that can determine the important properties of

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hydraulic oil, such as oxidation resistance, temperature stability, and hydrolysis stability. In foreign countries, there are two types of base oils commonly used in biodegradable hydraulic systems : HETG vegetable oil type) and HEES (synthetic ester type)[45].

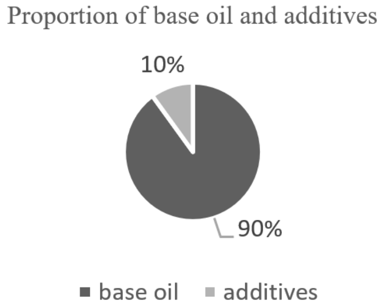

Fig.1 A schematic diagram of the proportion of base oil and additives

The vegetable base oil (HETG) has very good lubrication performance, and because it has no biochemical risk to the natural environment, it can easily achieve biochemical decomposition. The base oil of vegetable oil type hydraulic oil, such as rapeseed oil, sunflower oil, wheat oil and soybean oil. In terms of physical properties, after more than 90 °C, vegetable base oil is easily oxidized at such a temperature, so the service life is greatly reduced; the pour point of vegetable base oil is also above-20 °C, which is also very different from mineral base oil (table 1)[46].

Table 1 Comparison table of properties of vegetable base oil, synthetic ester base oil and mineral base oil[4]

	mineral oil	Vegetable base oil	Synthetic ester base oil
Biodegradability (ASTM D 5864, %)	10-40	40-80	30-80
viscosity index	90-100	100-250	120-220
pour point°C	-54—15	-20—10	-60—20
Compatibility with mineral oil	—	good	good
oxidation stability	good	bad-good	bad-good
useful life	2 years	0.5-1 years	1-3 years
relative cost	1	2-3	4-6

2.2.2. Additives

The additives of traditional hydraulic oil are generally set according to mineral oil. However, due to the different biological, physical and chemical characteristics of vegetable oil-based hydraulic oil and traditional mineral hydraulic oil, in order to ensure the degradability, additives with low toxicity, low pollution and biodegradable are needed. However, traditional mineral oil additives have a great influence on the bioactive bacteria or proteases in the process of base oil degradation, which in turn affects the biochemical degradation of base oil. The problem of developing additives to ensure biodegradability is the key issue to realize the practical use of vegetable oil-based hydraulic oil. The ' Blue Angel ' organization in Germany has made the following provisions regarding the addition of biodegradable lubricants[47]:

(1). No carcinogens, no genetic mutagenesis, distortion substances;
(2). No chlorine and nitrite;
(3). Containing metal (except calcium);
(4). The maximum can use more than 7 % of the potential biodegradable chemical additives;
(5). Can also add not more than two percent of non-biodegradable chemical additives, but must be low toxicity;
(6). It has no effect on biodegradable additives.

3. Standard of vegetable oil-based hydraulic oil

Biochemical degradation characteristics are the most important technical indicators of vegetable oil-based hydraulic oil. It refers to the process in which chemical substances are degraded into a single chemical substance, such as carbon dioxide and water, through biological action in an active organism. Therefore, total organic carbon (TOC) and dissolved organic carbon (DOC) can be used to evaluate the degradation performance[4]. Theoretically, the biodegradability of vegetable oil-based hydraulic oil can be evaluated by referring to the biodegradability standard of lubricating oil. At present, there are two main internationally recognized test indicators. One is the L-33-93 verification method proposed by the European Union National Standard, namely the Coordinating European Council (CEC)[8]. The second standard is the 301B / ASTM D5864 specification proposed by the Organization for Economic Co-operation and Development (OECD). These two standards constitute the basis of the biodegradability evaluation standard of lubricating oil, and most of the subsequent inspection standards are the improvement and perfection of these two standards.

3.1. The development process of European testing standards

The initial evaluation method of biochemical degradation of lubricating oil was CECL-33-T-82, which was established according to the European Community in 1982, and the CECL-33-A-93 test method was formally adopted in 1993[3]. If it is tested according to the requirements of CECL-33-93, more than 80 % of the lubricating oil will be decomposed. If tested according to the requirements of OECD301B, the degradable part of the lubricating oil should also reach more than 60 %[910].

British environmental organization ECP (EnvIronmentaL ChoIce Program) in 1988 in accordance with the OECD301A-F and CECL-33-A-93 standard detection of oil products, it must be biodegradable ; the concentration of additives should not be greater than 5 %, and the amount of non-biodegradable adjuvants should not be greater than 3%[911].

The international environmental agency called ' White Swan ' was established in 1989, covering four countries in northern Europe, namely Iceland, Norway, Finland and Sweden. In 1997, the agency developed the versjpon 4.2 specification, which regulates the technical conditions for biodegradability[912].

In 1994, the German Institute of Machinery and Product Production issued the biochemical degradation hydraulic oil specification VIMA24568, which was abolished when the ISO15380 specification was issued. The Environmental Protection Agency, known as ' Blue Angels ', was established in Germany in 1977, and in 1996 it issued a new standard for RAIUZ79 rapid biochemical degradation hydraulic oil products[912].

Sweden has issued a national standard SS155434ed4 for biochemically degradable hydraulic systems. The national standard stipulates that oil products must use both the non-water-soluble component biodegradability detection method OECD301B and the water-soluble component biodegradability detection method OECD301F.Later, the national standard was modified according to the national standard RO15380 (Sweden)[913].

3.2. American testing standards

According to the OECD301 test standard of the United States, the definition of biodegradable lubricating oil is: after mixing the test sample with the test solution, after 28 days of decomposition process, more than 70 % of the lubricant sample is required to be degraded, and the residue must be harmless substances such as water, metal oxides, and microorganisms[911].

At present, Renewable Lubricants Inc.is a leading company in the plant-based biodegradable hydraulic oil industry, and its standards can be regarded as the most advanced inspection standards in the United States. The company uses ASTM D-5864-00 standard test method, OECD-301B improved Sturm method, and CEC L-33-T-82 test method to evaluate the degradability of lubricating oil. The ASTM Committee of the United States adopted the OECD 301-B standard, which modifies the Sturm process within the ASTM D-5864-00 standard test method to determine the ability of lubricants to be aerobically and aquatically biodegradable (originally published in 1995)[14].

Among them, the standard classification of ASTM D-6046-02 hydraulic oil on environmental impact is (quoted from ASTM D 5864)[14]:

Biodegradable-It is achieved when a material can be completely decomposed using bacteria and only produce carbon dioxide (and methane can be biodegraded anaerobically), water, inorganic compounds, and new microbial cell components (biomass or secretions or both).

Ultimate biodegradation test-a test of the degree to which carbon in a substance is converted into CO2 or methane, or a test to measure the consumption of O2 by directly or indirectly measuring the produced CO2 or methane, or for aerobic biodegradability.

Environmental persistence classification criteria (also used by the US military) :

Pw1 $\geqslant$ 60 % at 28 days = final (ASTM) / readily biodegradable (OECD)

Pw2 $\geqslant$ 60 % at 84 days (12 weeks).

Pw3 $\geqslant$ 40 % at 84 days (12 weeks).

Pw4 < 40 % at 84 days (12 weeks)

The common hydrocarbons and typical biodegradability values in the CEC L-33-T-82 biodegradability test (Table 2)[1415]:

Table 2 CEC L-33-T-82 Biodegradability test results

Types of sample oil	Degradability value
mineral oil	15%~35%
white mineral oil	25%~45%
natural vegetable oil	70%~100%
PAO	5%~30%
polyether	0~25%
PIB	0~25%
phthalic acid ester	5%~80%

Polyol ester & diester	55%~100%

In short, there are many evaluation criteria for vegetable oil-based hydraulic oil, and there is no completely unified standard in the world. However, with the development of vegetable oil-based hydraulic oil technology, this problem is expected to be solved.

4. Application of vegetable oil-based hydraulic oil

4.1. Application as lubricant, cutting fluid and hydraulic oil

Although most of the reported work on vegetable oil-based hydraulic oils is laboratory-level testing, more actual performance data will be available as commercial bio-based lubricants begin to enter the market. Vegetable oil-based lubricants are mainly used in applications where equipment inevitably leaks or systems are designed to operate by losing lubricants, such as: two-stroke engine oils, chain saw oils, agricultural, mining and forestry equipment, open gear lubricants, greases and fuels[16][17].

In addition, vegetable oils are widely used as metalworking fluids in the machining industry. Talib et al. prepared a vegetable oil-based metal cutting fluid named MJO5A and used it to carry out successful cutting experiments. The results show that MJO5A can reduce cutting force, cutting temperature, chip thickness, chip contact length and specific energy, thus obtaining excellent machining performance[18]. If the mixed additive of sunflower oil and rapeseed oil is used to cut aluminum 7075T6, compared with industrial mineral base oil, the cutting force is increased by 38 %, and the wear of tool tip and flank surface is reduced[19]. Ojolo et al. used ground nut oil, coconut oil, shea butter and palm kernel oil as metalworking fluids for turning low carbon steel. Plant-based metalworking fluids significantly improve product quality by reducing cutting force[20].

Mamuda et al. studied the applicability of plant-based lubricants in wire drawing. Vegetable oil-based lubricating oil was prepared by using neem seed and jatropha seed oil as lubricants and antimony dialkyl-dithiocarbamate (ADTC) as additive. They used tungsten carbide molds and formulated lubricants to conduct tensile tests on low-carbon steel and medium-carbon steel bars with diameters of 6mm and 8mm respectively on a tensile test bench at 20 °C ~ 750 °C. When drawing medium carbon steel, the reduction rate can reach 45 %, and there is no wire fracture. The results show that the oil is a good non-toxic, biodegradable, renewable high temperature drawing alternative lubricant[21].

Another practical application of vegetable oil-based hydraulic oil was found in the elevator of the Statue of Liberty in New York Harbor. The elevator now runs on a biodegradable hydraulic oil made from soybean oil. This soybean oil-based hydraulic fluid was developed by the National Agricultural Utilization Research Center led by Sevim Erhan and Atanu Adhvaryu at the request of the National Park Service[22].

4.2. Application prospect in shipbuilding industry

Although plant-based hydraulic oil has good performance and absolute environmental protection characteristics, it has not been widely used in industrial fields such as ships due to cost and technical reasons, but its application prospects are still very broad. Taking Ruianbo Lube Oil Company as an example, its research and development of biodegradable food-grade vegetable-based hydraulic oil and food-grade vegetable oil-based lubricants, using vegetable oil as base oil, can be applied to ships, beverage filling, food processing, baking industry, pharmaceutical industry, water treatment and kitchen appliances and other industries[23].

In the field of marine oil, Ryanbo Company produces biodegradable hydraulic oil, transmission oil of transmission parts such as gears, and other renewable mechanical lubricants. The fleets of research ships and small ships of the United States National Aeronautics and Space Administration (NOAA) are using biodiesel and biodegradable vegetable oil-based hydraulic oil to replace traditional diesel and petroleum-based hydraulic oil production. Not only that, but a NOAA-affiliated research group called the Great Lakes Environmental Research Laboratory (GLERL) has in the early years involved about 40 ships in the U.S. Green Ship Initiative, which uses biodegradable vegetable oil-based lubricants, such as crankcase oils, gearboxes, and hydraulic control systems, to help prevent damage to the marine environment from additional or other accidental spills[24].

4.3. Difficulties to be overcome in the application of the ship industry

Although vegetable oil-based hydraulic oil has a variety of good properties as described above and has a good prospect of replacing mineral oil in the application of marine lubricating oil, the wide application of vegetable oil as hydraulic oil base oil faces considerable challenges. On the one hand, the performance limitation of vegetable oil-based hydraulic oil stems from the inherent characteristics of vegetable base oil, rather than the composition of additives. Vegetable oil will increase wear under high temperature and sliding conditions; oxidation stability, thermal stability, low temperature (cold flow) performance and hydrolysis stability are still inferior to mineral oil. With the increase of temperature, the viscosity of vegetable oil increases, and it is easy to be oxidized after contact with air. In addition, the increase in total acid number (TAN) caused by hydrolysis of vegetable oils and additives is considered to be the cause of excessive corrosion and failure[25]; as a kind of food, vegetable oil has high production cost. On the other hand, its lubricity, wear resistance, carrying capacity, corrosion resistance (rust), acidity, hydrophobicity and other performance parameters mainly depend on the additives or the impurities and pollutants.

To solve these problems, the focus is not necessarily on the vegetable oil-based hydraulic oil itself. The equipment of the ship's hydraulic system can also be technically innovated to make it more suitable for the use of vegetable oil-based hydraulic oil, better play its advantages, and try to avoid the shortcomings caused by its shortcomings. At present, there are still many areas in urgent need of improvement in the ship hydraulic system. For example, to reduce the abrasive wear of the hydraulic system, friction and wear will increase the temperature of the plant-based hydraulic oil, thereby accelerating its oxidation and reducing its service life. The sediment generated after oxidation will cause the blockage of the ship hydraulic system. In addition, due to the ship hydraulic system works in a humid, high salt, highly corrosive marine environment, the equipment is easy to be corroded, aging, coupled with the inevitable wear and tear, may occur hydraulic system leakage fault. Leakage will cause the safety and stability of the system to decrease, reduce operating efficiency, increase the loss of hydraulic equipment, and lead to the waste of vegetable oil-based hydraulic oil, thereby increasing the cost of use[26]. In short, improving the equipment of ship hydraulic system is also one of the important prerequisites for the wide application of vegetable oil-based hydraulic oil ship industry.

5. Conclusion

From the perspective of protecting the marine environment, this paper introduces the definition and composition of plant-based biodegradable hydraulic oil, which is composed of vegetable base oil and specific additives that do not destroy biodegradability. The standards and development history of plant-based biodegradable hydraulic oil were expounded. The inspection standards still need to be further standardized in the process of future development and practical application. It shows that vegetable oil-based hydraulic oil has a good application prospect in various industries including shipbuilding industry, and points out that the wide application of vegetable oil as hydraulic oil faces many challenges, including improving the equipment of ship hydraulic system, which still needs continuous technical improvement. In general, although the development of vegetable oil-based hydraulic oil is difficult, its absolute environmental protection characteristics can fundamentally solve the problem of marine pollution, which is in line with the development trend of ' green shipping ' and determines that it will inevitably become the development direction of China 's future shipbuilding and other industries.

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