

Research Progress Trend of Water-Soluble Lubricating Additives

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Abstract: In the field of industrial lubrication, water-soluble lubricant additives determine the performance of water-based lubrication system. In recent years, some new water-based lubricant additives with special structure and composition show excellent performance and broad application prospects. Research and development of high-performance water-soluble lubricant additives is the key to improve the comprehensive performance of water-based lubricants and broaden their application range. The research status and characteristics of water-soluble lubricant additives at home and abroad were analyzed, and the research and application of water-soluble lubricant additives such as carboxylic acid and its salts, water-soluble organic metal lubricant additives, water-soluble lubricant additives containing active elements such as sulfur and phosphorus, boron-containing water-soluble lubricant additives and nano-water-soluble lubricant additives at home and abroad were introduced in detail. At the same time, combined with the complexity of compatibility of water-soluble lubricant additives and the limitations of remaining in the stage of experimental synthesis and theoretical exploration, the multi-functional development trend of water-soluble lubricant additives integrating lubrication, rust prevention and biodegradation was analyzed and predicted. The problems existing in the current research are analyzed, and the development trend is prospected. It is suggested that the research on water-soluble lubricating additives should be strengthened to further improve the performance of these additives.

Keywords: Water Solubility, Lubrication Additives, Research Status, Development Trend

1. Introduction

With the shortage of energy and the enhancement of environmental protection awareness, water-based fluids have been rapidly developed due to their excellent economic, cooling, safety, low cost, pollution-free and easy cleaning properties. They have been gradually applied to metal processing fields such as cutting, grinding, rolling, stamping, drawing, tapping, and the field of refractory hydraulics in underground coal mines [1, 2] to replace oil-based fluids. Water-based lubricant additive is an important part of water-based fluid. With the rapid development of mechanical processing industry and water-based fluid, the application scope of water-based lubricant additive is also expanding. Water based lubricant additives are mainly divided into oil soluble and water soluble. At present, the lubricating additives used in water-based liquid are mainly oil-soluble, and most of them are compounded. However, the composition of water-based liquid is complex, the stability is poor, and it is easy to precipitate. The

biodegradability of mineral oil-based lubricant additives is poor, which not only pollutes the environment, but also aggravates the energy consumption. These limitations largely limit the development of oil-soluble lubricating additives, and thus turn to water-soluble lubricating additives [3]. Water-soluble lubricant additives have excellent stability, cooling, low pollution, flame retardancy, good safety and biodegradability. Based on the purpose of low-carbon environmental protection and energy conservation, all countries in the world have increased the development of water-based lubricants, especially in the research of water-based hydraulic fluids and metal cutting fluids, which is one of the hotspots in lubricant research in recent years. Liu Zhong, Mei Huanmou of Chemistry Department of Hunan University and Li Maosheng of Guangzhou Machine Tool Research Institute have synthesized many water-soluble lubricant additives, and have done a lot of work in using molecular design theory to synthesize additives. Based on this, the research and application of water-soluble lubricant additives at home and abroad are described, and the

development trend of water-soluble lubricant additives is prospected.

2. Classification and Application of Water-Soluble Lubricating Additives

2.1. Water Soluble Lubricant Additives of Carboxylic Acids and Their Salts

Water soluble fatty acids and their salts (esters) have outstanding characteristics as lubricating additives. Firstly, the synthesis process of these compounds is mature, which provides conditions for industrial production. Secondly, fatty acids (salts, esters) with different chain lengths have different lubrication selectivity, and some fatty acids (salts, esters) also have certain antirust and cleaning effects. Therefore, fatty acids and their salts (esters) are water-soluble lubricating additives that have many industrial applications [4].

Long-chain fatty acids have always been the preferred material for oil-soluble lubricating additives due to their unique lubricating and anti-rust properties. With the research of water-soluble lubricating additives, some scholars have made a lot of research on the lubricating properties of water-soluble fatty acids and their salts (esters) as lubricating additives in recent years, and have made many achievements. At present, there are many water-soluble additives used in industrial practice. The research on fatty acids and their salts (esters) in China mostly focuses on the modification of the friction properties of traditional water-soluble fatty acids (salts, esters). Such as Mei Huanmou synthesized 2-methylic acid [5] with better lubricity than oleic acid and lower foaming ability than oleic acid; Zhou et al [6]. studied a variety of malonic acid derivatives, found that they have excellent extreme pressure anti-wear properties, such as 1% mass fraction of BT-S-CH (CH_2COOH) COOH solution PB value (maximum no bite load, representing the oil film strength) is 755 N, also has good rust resistance; there are many reports on N-acyl amino acids as lubricating additives in foreign literature. For example, adamantane carboxylic acid chain alkanolamine ester is a multifunctional water-soluble lubricating additive that integrates lubrication, sterilization, anti-foaming and anti-rust. Some ester additives have been synthesized by using trihydroxymethane and different fatty acids in foreign countries, so that they have a variety of properties such as lubrication, rust prevention, anti-corrosion and anti-foaming [7].

2.2. Water-Soluble Organic Metal Lubricant Additives

As early as in the 1960s, Ranny et al. synthesized zinc dioctadecane diepoxy vinyl sulfate, which had good effects in lubricating oil and water-based lubricants [8]. Mei Huanmou et al [9]. modified by polyethylene glycol and diethanolamine oleic acid to obtain a new type of organic molybdenum water-soluble lubricant additive, which has excellent lubricity and extreme pressure wear resistance. Guanwenchao [10] used alcohols containing $(\text{CH}_2\text{CH}_2)_n$, $-\text{COOH}$, $-\text{OH}$ and other hydrophilic groups to react with P_2O_5 to form phosphate, and

then neutralized with 'Mo-Zn' complex to obtain a water-soluble dialkyl zinc molybdenum phosphate compound, which has excellent anti-wear lubrication effect and good corrosion inhibition effect on Cu and Fe.

2.3. Water-Soluble Lubricating Additives Containing Active Elements Such as Sulfur and Phosphorus

Sulfur and phosphorus as active elements show excellent extreme pressure and wear resistance in oil-soluble and water-soluble lubricant additives. Sulfur-containing phosphorus additives react with metal surface to form sulfur-containing phosphorus chemical film under high load and show excellent extreme pressure and wear resistance. For example, the PB value of the sulfur-containing quaternary ammonium salt derivative synthesized by Guan et al [11]. reached 745 N in water. After further introduction of zinc element into the compound, sulfur and zinc had synergistic effect, and the PB value increased to 1969 N.

The analysis results of Guan et al [12]. on the lubricating film of water-soluble alkyl zinc thiophosphate further verified the anti-wear theory of inorganic ferrous phosphate film formed by dialkylphosphite proposed by Forbes in 1974, indicating that the friction reduction effect was very significant after the introduction of P and S into water-soluble lubricating additives. Some studies have shown that the introduction of polyoxyethylene chain into water-soluble additives containing P or S and P will lead to hydrolysis in water medium. After hydrolysis, the wear resistance is significantly reduced, and the stability in weak alkaline solution is poor [13].

Therefore, the key to determine whether water-soluble lubricating additives containing sulfur and phosphorus can be widely used in water-based lubricating additives is to solve their hydrolysis stability. At the same time, the use of sulfur-containing phosphorus compounds is limited due to their large odor and corrosion to the skin. In addition, although phosphorus compounds have excellent extreme pressure and wear resistance, phosphorus compounds are easy to cause eutrophication or red tide of rivers, lakes and other water quality, which has been prohibited by relevant laws and regulations, so phosphorus lubricating additives are gradually restricted.

2.4. Boron-Containing Water-Soluble Lubricant Additives

The boron-containing special surfactants have not been industrialized at home and abroad, and the research is also in the initial stage. Internationally, Japan was active in the 1970s – 1980s, but most of them were anionic and non-ionic fatty acids of diglyceride borate. In China, the research work of Jiangnan University was carried out earlier, and a small number of laboratory products were used for flame retardant textile products. In recent years, other research units have also carried out research in this area, mainly nitrogen-boron surfactant [14]. Boron-containing water-soluble lubricant additives mainly include inorganic borates and organic borates. Organic borates have attracted extensive attention and

in-depth research at home and abroad due to their excellent properties such as extreme pressure wear resistance, rust resistance, sterilization and corrosion resistance, non-toxic, harmless and easy synthesis. In recent years, some research results of organic borates as water-soluble lubricant additives have been reported. Such as Watanabe et al [15]. reaction of boric acid and alkanolamine, the boric acid grease has good rust resistance and microbial resistance, and has a certain anti-wear effect. Zhang Xiuling and other polymethacrylate boron-containing lubricant additives were synthesized by emulsion polymerization. The PB value of 5% aqueous solution reached 902 N, and the rust resistance and foam resistance were excellent [16]. Li Bindong and Lv Chunxu synthesized boric acid diethanolamine with diethanolamine and boric acid as raw materials, and then synthesized dodecylamide boric acid diethanolamine and N-dodecyl boric acid diethanolamine with methyl dodecyl sulfate and bromododecane, which had high surface activity and lubrication and rust resistance [17].

Wang et al. synthesized a new type of polymerizable boric acid ester, and synthesized the copolymer P (BES-AM) by free radical copolymerization with acrylamide. The emulsification performance of P (BES-AM) was better than that of Span-80, and it had good rust resistance. At the same time, it had obvious synergistic effect with sodium dodecyl benzene sulfonate [18]. In summary, as a multifunctional water-soluble lubricant additive, organic borates not only have excellent extreme pressure and wear resistance, good rust resistance and sterilization and corrosion resistance, but also are nontoxic, harmless and easy to synthesize. Therefore, more and more research and application have been carried out, and boron-containing organic compounds will have great development potential. However, how to solve the hydrolysis problem of borate esters and the research on their combination with other surfactants is the key to the industrial application of water-soluble borate esters.

2.5. Nano-Water-Soluble Lubricating Additive

The special structure of nanomaterials makes them have physical and chemical properties that traditional materials do not have. Using nanomaterials as lubricating additives can play a special role in reducing friction, anti-wear and extreme pressure. In the past, the research on nano-lubrication additives mostly focused on oil-soluble lubricant additives, and in recent years it has been reported as water-soluble lubricant additives. Oleic acid modified TiO_2 nanoparticles were synthesized by Gao Yongjian et al [19]. When the mass fraction of oleic acid modified TiO_2 nanoparticles was 0.1% ~ 1.0%, the water carrying capacity was increased by 6 ~ 12 times and the sintering load was increased by 51% ~ 100%. A series of nano-water-soluble additives were synthesized by fullerene (C_{60}), and their tribological properties were investigated. The results show that fullerene nanoparticles can play an elastic 'ball' lubrication role under friction conditions, thus effectively isolating the friction surface, improving the bearing capacity of water-based liquid and reducing wear [20-22].

It should be noted that nanoparticles also have the defects of

poor dispersion and stability. If this problem can be effectively solved, the application prospect of nano water soluble lubricant additives will be very broad.

3. Development Trend of Water-Soluble Lubricating Additives

Due to the particularity of water medium, water-soluble lubricant additives have the disadvantages of poor lubrication and rust resistance compared with oil-soluble lubricant additives, which limits the development of water-soluble lubricants to some extent. In addition, at present, the research on water-soluble lubricating additives in China and abroad mostly focuses on simple rust prevention or lubrication, and the complexity of the compatibility of additives is also encountered in practical applications. At the same time, the research on water-soluble lubricating additives mostly stays in the stage of laboratory synthesis and theoretical exploration, and there is no industrial report.

Therefore, the key to broadening the application range of water-soluble lubricating additives and improving their performance is to develop high-performance water-soluble lubricating additives. Environmental protection and multifunction are the development trend of water-soluble lubricant additives in the future. The development of multifunctional lubricating additives with lubrication, rust prevention and biodegradability can not only reduce the polarity of water molecules and the interaction with additives, but also simplify the compatibility selectivity of additives, reduce costs and shorten the development cycle. At the same time, it can improve the universality of water-based lubricant, so that it can be used in more products (such as water-based hydraulic fluid and cutting fluid) and more friction conditions. From a technical point of view, multi-functional water-soluble lubricating additives are a major progress for the water-based additive industry. The oil solubility is modified to water solubility or the molecular design method uses the functional groups with different characteristics to be assembled in the same molecule [23], and different characteristics are 'adjusted' between molecules, so as to effectively avoid the complex problems in the physical blending and compounding used in the past, reduce external interference and the compatibility process of additives, so that the composite additives can be used for multiple purposes, eliminate interference, and promote the development of water-based lubricants to standardization, serialization, generalization and productization.

4. Conclusion

It can be seen from the current research that the research on water-soluble lubricating additives has made some progress. In order to further improve the performance of these additives, improve their lubrication mechanism and realize their application value, it is still necessary to explore the following aspects:

Finding more efficient methods to further improve the

dispersion and stability of nanomaterials in water, and developing large-scale preparation technology of nanomaterials are necessary means to promote the transformation of nano-water-based lubricant additives from basic research to practical application.

With the advantages of strong molecular design and controllable molecular weight of polymer, the molecular structure was optimized, and the active elements were appropriately introduced to make it a multifunctional water-based additive with viscosity enhancement, anti-wear and friction reduction, anti-rust and anti-corrosion.

The structure of ionic liquid was further improved to solve the problems of its hard degradation and corrosion. The influence of mixed compatibility of different anions and cations in water on lubrication was explored. The production process was optimized to reduce costs and promote its transformation to application.

At present, the research on water-soluble lubricating additives in China is at the initial stage. However, due to the excellent characteristics and good application prospect of water-based lubricants, with the enhancement of environmental awareness and the development of science and technology, especially the introduction of some new methods and technologies such as molecular design and nanotechnology, the development of water-based lubricants will be accelerated and its application prospect will be more broad.

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