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Pyridinium-based ionic liquids as anti-wear additives for calcium sulfonate greases

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Abstract

The present study showed the usage of ionic liquids as anti-wear additives for greases. New pyridinium-based ionic liquids bearing long alkyl chains were prepared and evaluated as wear-reducing additives in calcium sulfonate greases. The physical properties of the synthetic ionic liquids were identified. The obtained liquids were then added to greases at a concentration of 2 wt. %. The tribological performance of the greases was measured by using a standard benchtop test ASTM D2266. The results obtained allow us to conclude that the introduction of ionic liquids into polyalkylene glycol (PAG)-based calcium sulfonate grease has a positive effect on anti-wear properties since the wear decreases by several orders of magnitude. The interoperability of the synthetic ionic liquids with the calcium sulfonate greases and its potential influence upon solubility and tribological performance are tentatively proposed to be a result of the molecular structure.

1. Introduction

Greases are one of the most demanded lubricants, and they are used in a variety of tribological pairs. The range of greases includes several products, but a special place among them is occupied by calcium sulfonate-based greases. According to a survey by the USA National Lubricating Grease Institute (NLGI), the share of calcium sulfonate-based lubricants is about 5 % of the total volume of greases produced, and their number continues to grow [1-3].

Due to the specificity of their composition and structure, sulfonate greases have many noticeable physico-chemical and operational advantages: high water resistance, which allows this lubricant to ensure the operability of the tribo-unit for a long time even in contact with water; excellent extreme pressure properties due to the characteristics of the thickener composition; high thermal and thermo-oxidative stability; excellent protective and anti-corrosive properties [4].

Due to these properties, calcium sulfonate greases are actively used in the metallurgical and pulp industries, as well as highly loaded tribo-elements of mining and road construction equipment, tribological pairs of the glass and cement industries and even most high-temperature tribological pairs of food processing equipment, since in addition to all these advantages, these lubricants can be produced with food tolerance, which permits their use in cases of possible contact of food products with lubricants [4-6].

But despite the wide range of advantages, this product still has disadvantages. For example, when using low-viscosity oils as a dispersion medium, the anti-wear properties of this type of grease deteriorate, which can only be improved by the introduction of special additives [7].

Since 2001, ionic liquids have been of increased interest as anti-friction and anti-wear additives [8]. Ionic liquids are salts formed by a heteroorganic cation and an organic or inorganic anion, with melting points below 100 °C [9]. At the moment, a fairly large number of ionic liquids have been synthesised and studied, although an even larger number of compounds have not yet been obtained [10].

There are quite a lot of reports on the use of ionic liquids as lubricants in relevant articles and scientific and technical literature. Due to their structure, ionic liquids have the following positive properties: low saturated vapour pressure, high thermal and oxidative stability and low coefficient of friction. These properties make it possible to consider ionic liquids as a class of compounds that can be used as vacuum oils, oils for the space industry (the radiation resistance of ionic liquid should also be high enough), refrigeration, compressor oils and oils for bearings of electric motors [11-13].

From the point of view of ionic liquids usage as lubricants or lubricant additives, several compounds have previously been studied. The main ones were alkylammonium, phosphonium and imidazolium ionic liquids. However, pyridinium and pyrrolidinium ionic liquids are of particular interest to researchers, since there are known options for their production from cheap and easily accessible raw materials [14]. It is worth noting that these products have been little considered as anti-wear additives due to poor solubility in nonpolar and low-polar compounds [15].

Thus, Reeves et al. [16] present data on a high level of tribological properties at high temperatures of imidazolium-based ionic liquids using a pin-on-disc installation with an aluminium-steel tribo-pair at temperatures of 100 and 200 °C. It was found that tribological characteristics depend on the length of the chain and the chemical activity of the ionic liquid. In a study by Kreivaitis et al. [17], it is noted, using the example of fluorinated anions, that with an increase in the temperature of the medium, the chemical activity of ionic liquid increases, which directly affects the formation of the boundary film. It is worth mentioning phosphonium-phosphate ionic liquids separately since the anti-friction and anti-wear properties of these liquids can be compared with the properties of additives such as zinc dialkyldithiophosphates (ZDDP). Thus, the addition of 1 % ionic liquid to the base low-viscosity oil reduced the degree of wear by more than 60 % [14].

In this regard, an attempt was made to produce ionic liquids based on pyridinium. The purpose of the study was to test the possibility of using synthesised ionic liquids as anti-wear additives for greases, in particular sulfonate greases, since no work has been found on the study of ionic liquids in these products. To achieve an extremely high dropping point, calcium sulfonate grease was used, and polyalkylene glycol (PAG) oil was used as a dispersion medium. PAGs are unique products characterised by very high thermal and oxidative stability. They not only work effectively over a wide temperature range but are also notable for the fact that they practically do not form coke deposits [18]. It is worth noting that the choice of PAG as a dispersion medium is also due to the fact that ionic liquids are completely soluble in these oils.

2. Materials and methods

2.1 Preparation of ionic liquids

The main method of obtaining ionic liquids is metathesis reactions (ion exchange reactions). In the general case of an exchange reaction, they can be divided into two groups: an exchange reaction through acids, salts of metals of the first group or ammonium salts and an exchange reaction through silver salts. This method is the most commonly used for the synthesis of ionic liquids and is characterised by the simplicity of the hardware design and the fact that the procedure for the synthesis of various ionic liquids only slightly differs.

For the synthesis of ionic liquids, we used: N-cetylpyridinium chloride (purity 98 %) provided by "НПО Индикатор", Ufa, Russia, di(2-ethylhexyl) phosphate synthesised in the laboratory following procedure from patent SU389100A1 [19] and di(2-ethylhexyl)dithiophosphate synthesised in the laboratory. Both anions were subsequently introduced by a metathesis reaction with di(2-ethylhexyl)phosphoric acid, di(2-ethylhexyl) dithiophosphoric acid. The structures of two synthesised ionic liquids (IL 1 and IL 2) are shown in Figure 1.

2.2 Preparation of sulfonate greases

The process of preparing sulfonate greases is a rather long and complex process from the point of view of chemistry. According to the temperature conditions, the process of obtaining sulfonate grease is divided into five main stages.

In stage 1, the components are mixed and the reaction mixture is gradually heated. In stage 2, due to the mutual orientation of the thickener molecules and the dispersion medium, the structure of the product is formed. This process occurs when the mixture is kept at a certain

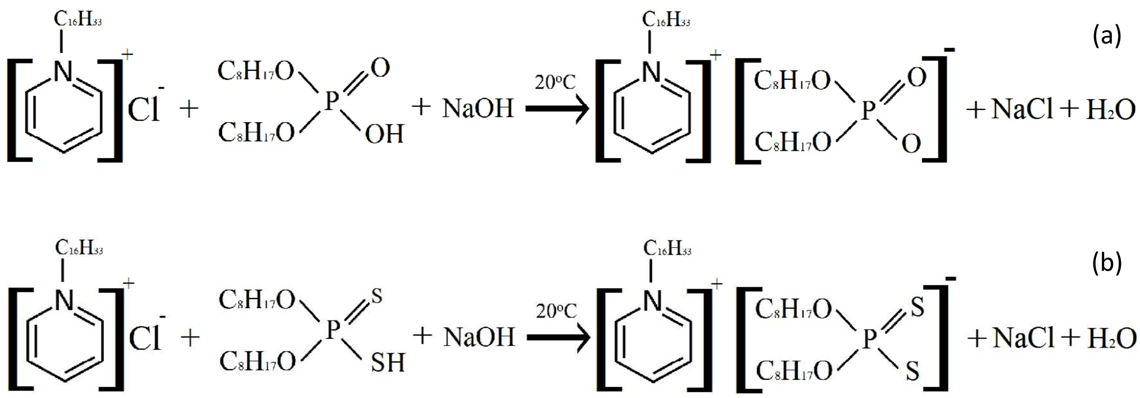

Figure 1. Structure of synthesised ionic liquids: (a) IL 1 and (b) IL 2

temperature for almost six hours. Further, at stage 3, the heating temperature of the reaction mixture begins to rise above a temperature of 120 °C. Finally, at stage 4, the reaction mixture is kept at an elevated temperature for complete evaporation of water, which plays the role of an auxiliary component for the formation of the required grease structure. The final stage is the cooling of the resulting grease sample, which is carried out in volume and without mixing. It is aged for at least 9 hours before unloading the resulting sample.

Two components: ADDITIVE CCK-400 (high alkaline calcium sulfonate, produced on synthetical alkylbenzene sulfonic acid) provided by AddiTECH (Novopolatsk, Belarus) and PAG 8.20 (copolymer ethylene oxide and propylene oxide in the molar ratio 1:3) provided by NORCHEM GC (Dzerzhinsk, Russia) were used as raw materials in the production of sulfonate grease.

It is worth noting that the choice of the dispersion medium in this work is due to the fact that polyalkylene glycols, depending on the structure, can be both water-soluble and oil-soluble. These products may differ in molecular weight, solubility in water and the ratio of ethylene oxide/propylene oxide [20]. Such a product should ensure the complete dissolution of the pyridinium ionic liquid in the grease and its effective operation as an anti-wear agent.

2.3 Tribological testing of greases

The study of the effect of ionic liquids on the wear-preventing properties of sulfonate greases was carried out using the ASTM D2266 standard test method for measuring the anti-wear properties of grease (four-ball method). During the test, three steel balls with a diameter of 12.7 mm are clamped together and covered with the test grease. A fourth steel top ball is pressed with a force of 392 N into the space formed by three clamped balls for three-point contact. The temperature of the grease sample is adjusted at 75 °C and the top ball rotates at 1200 rpm for 60 minutes. The diameter of the wear scar is the arithmetic mean of the six diameters of the wear scars measured at the lower balls after the test.

3. Results and discussion

As a result of the conducted syntheses, two types of ionic liquids were obtained, the main characteristics of which are shown in Table 1.

Table 1. The main characteristics of obtained ionic liquids

Property	Method	IL 1	IL 2
Colour	visual	yellow	orange
Kinematic viscosity at 40 °C, mm/s^2	ASTM D7042	85.2	215.6

The physical appearance of ionic liquids is shown in Figure 2.

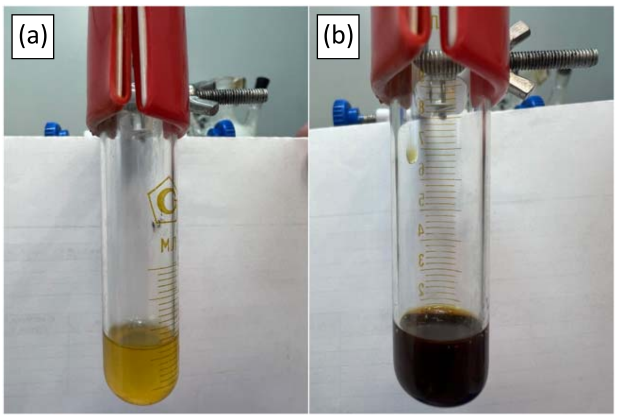

Figure 2. Physical appearance of synthesised ionic liquids: (a) IL 1 and (b) IL 2

The obtained ionic liquids were introduced into the grease sample in a total amount of 2 wt. % by homogenisation. In the first case only 2 wt. % of IL1 is added and in the second case only 2 wt. % of IL2 is added. Also, as part of the study, a mixture of synthesised ionic liquids (1 wt. % IL 1 and 1 wt. % IL 2) was introduced into the grease sample. The homogenisation process is carried out in two stages. In the first stage, a predetermined weight of ionic liquid is added to the grease. In the second stage, grease is homogenised in a special mixing device that rotates at a speed of 120 rpm.

For the resulting sulfonate grease, the main characteristics were determined before and after the introduction of synthesized ionic liquids into it, with only the best results of the ionic liquids addition presented (a mixture of ionic liquids). The results are shown in Table 2.

Table 2. Main properties of the produced sulfonate greases

Property	Standard	Value	
		grease	grease + IL 1 + IL 2
Worked penetra-tion, 0.1 mm	ASTM D217	289	297
Dropping point, °C	ASTM D2265	302	286
Cu corrosion (100 °C/24 h)	DIN 51 811	1a	1a
Four-ball weld point, N	ASTM D2596	7350	7350

As can be seen from Table 2, the sulfonate grease obtained using polyalkylene glycol oil (PAG 8.20) has a high level of physico-chemical and operational properties, however, the anti-wear properties do not meet the requirements for such products.

For the produced sulfonate grease samples, the diameter of the wear scar was determined according to ASTM D2266. The obtained results are shown in Table 3.

Table 3. Anti-wear properties of the produced sulfonate greases

Sample	Wear scar diameter, mm
Calcium sulfonate grease	0.70
Calcium sulfonate grease + IL 1	0.52
Calcium sulfonate grease + IL 2	0.56
Calcium sulfonate grease + IL 1 + IL 2	0.34

The effect of the introduced single ionic liquid into the sulfonate grease at a concentration of 2 wt. % significantly reduces the diameter of the wear scar. At the same time, the addition of 1 wt. % IL 1 and 1 wt. % IL 2 reduces the value of the wear scar diameter by half. This indicates a high level of influence of a mixture of ionic liquids on anti-wear properties. The exact mechanism of such a synergistic effect is not yet clear, but it is worth noting that similar results have already been noticed by Qu et al. [21] and Sun et al. [22].

In the work of Qu et al. [21], studies were conducted on ionic liquids containing dialkyl phosphate in the composition of the anion. These liquids exhibit a synergistic effect with zinc dialkyldithiophosphates (ZDDP). This phenomenon was explained by the formation in situ of a more active compound ZOTP, in which the dithiophosphate part of ZDDP was replaced by dialkyl phosphate. In the work of Sun et al. [22], a dianionic ion was synthesised, where one part was dialkyl phosphate, the second dialkyldithiophosphate, which also exhibits high anti-wear properties.

The authors of the article suggest that dialkyl phosphate anion and dialkyldithiophosphate anion exhibit a synergistic effect regardless of the presence of ZDDP (for the formation of ZOTP) in the oil composition.

4. Conclusion

Sulfonate greases deserve special attention because they are essentially a unique product that has conquered the market of greases in a short time. However, the final properties of this product directly depend on the raw materials used.

As the results of the study show, the use of polyalkylene glycol oil as a dispersion medium makes it possible to obtain a high-quality product with excellent extreme pressure properties. This is due to the presence of a large amount of sulphur in the thickener, which, during the decomposition of the lubricant at high temperature, forms a layer of iron sulphide on the surface of the steel, which prevents the adhesion of the two surfaces. However, the anti-wear properties of the resulting product are low.

The addition of ionic liquids to sulfonate greases has no fundamental effect on worked penetration, dropping point or Cu corrosion (100 °C/24 h). At the same time, ionic liquids, as promising anti-wear agents, have shown excellent results when added to sulfonate grease. Thus, it was possible to reduce the diameter of the wear scar from 0.70 mm to 0.52 and 0.56 mm, but the desired level has still not been reached.

The mixing of two ionic liquids with each other gave a synergistic effect, due to which the wear scar diameter decreased to 0.34 mm, which is an excellent result.

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