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Tribological properties of protic ionic liquid and functionalized copper oxide nanoparticles as additives to base oil

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1. Introduction

Room-temperature ionic liquids (ILs) are molten salts, which consist of bulky organic cations with organic or inorganic counter anions and are liquid at room temperature [1]. Recently, ionic liquids have attracted significant attention due to some unique properties, such as nonflammability, negligible volatility, low melting point and high thermal stability [2]. The application of ILs as lubricants has shown remarkable protection against wear and significantly reduced friction of materials. Recent studies have shown good potential for using ILs as base lubricants or lubricant additives. Several studies have been focused on imidazolium [3,4] based ILs and a limited number have investigated ammonium- [5] and phosphonium-based [6] ILs. Unfortunately, the complicated synthesis process, limited solubility in oils and relatively high price are limiting IL application as lubricants. Therefore, protic ionic liquids (PIL) with comparatively cheap and easy stoichiometric combination of a Bronsted acid with a Bronsted base have gained much attention [7]. To date a few reports on protic ILs as lubricants or lubricant additives are available in the scientific literature [8]. Due to the high polarity of ILs, like imidazolium based ILs, and low polarity of oils, ILs commonly show very poor miscibility with them, therefore it is important to synthesize ILs with long alkyl chains.

Copper nanoparticles have a wide variety of uses, one of which is the use as an additive in lubricant oils, because they have perfect tribology performances especially in reducing friction and enhancing wear-resisting properties [9, 10, 11]. Nanoparticles are said to enhance lubrication because they decrease the surface roughness [9], melt on contact faces and create a protective layer [10] or act as ball-bearings [11]. Although there are studies that outline the positive effect of copper nanoparticles on lubrication, little information is found on synthesizing particles that would be suitable for this specific use. The lubricating power could be assured by a perfectly stable dispersion of nanoparticles, where surface functionalization is necessary. Therefore, a simple and easy-to-modify thermal decomposition method was developed to prepare nanoparticles used in this study. To assure that the particles stay non-agglomerated, they were covered with a mixture of thiol molecules.

The main purpose of this study was to elaborate a novel oil additives, protic IL and copper oxide nanoparticles. In this article, oil-soluble protic IL and oil dispersible copper oxide nanoparticles were synthesized, characterized, and their tribological behaviours as additives in base oil PAO were studied. To our knowledge, this work is the first report on the synthesis, characterization and tribological behaviour of an oil-soluble protic IL and copper oxide nanoparticles as oil additives.

2. Experimental

1.1. Materials and reagents

The chemicals used in the experiments were 1-octanethiol (≥98.5%), 1-octadecanethiol (≥98%), benzyl alcohol (≥99.0%), methanol (≥99.8%), octadecylamine (≥90%), toluene (≥99.3%), copper(II) acetate monohydrate (≥98%), octylamine (99%), nonanoic acid (96%) all purchased from Sigma-Aldrich and 3-mercaptopropionic acid (99%) from Alfa Aesar.

1.2. Synthesis of ionic liquid

Protic IL was synthesized according to the Fig. 1. Octylamine (0.03 mol) was slightly warmed and an equimolar amount of nonanoic acid (0.03 mol) was carefully added. The mixture was stirred at 80°C for 24 h under an inert atmosphere. The obtained ionic liquid was vacuumed at room temperature for 12 h. Ionic liquid was added to base oil and stirred for 2 h at 50°C.

1.3. Synthesis of functionalized copper/copper oxide nanoparticles

A mixture of the copper salt precursor (55.734 mmol/l), 1-octadecanethiol (0.683 mmol/l), 1-octanethiol (5.224 mmol/l), octadecylamine (0.683 mmol/l), 3-mercaptopropionic acid (0.64 mmol/l) in benzyl alcohol was prepared in a round-bottomed flask. The flask was submerged into an oil bath with 230°C and the mixture was kept at that temperature under reflux magnetic stirring for 60 minutes, during which, the originally blue solution turned brown.

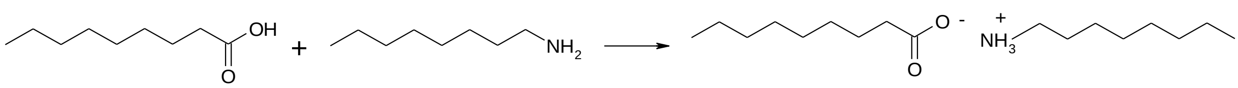


Fig. 1 Synthesis of protic IL

Next, the fresh solution containing nanoparticles was cooled to room temperature. The nanoparticles were separated and washed with methanol by repeated centrifugal precipitation at 5000 G for half an hour. Washed nanoparticles were dispersed in toluene for storage. The dispersion of nanoparticles was added to base oil and stirred for 2 h, after that toluene was evaporated.

1.4. Characterization

The IR (infrared) spectra were measured on a Bruker Vertex 70 FT-IR instrument. Thermogravimetric analysis (TGA) was performed on a Thermal analyzer Set-Sys Ev 1750 at heating rate 10°C/min up to 600°C in Ar flow 60 ml/min. Size of the nanoparticles was determined by SEM (Helios NanoLab 600) and their chemical composition studied by x-ray diffraction (Rigaku SmartLab 2000), x-ray fluorescence (Rigaku ZSX 400). Friction and wear were measured with a Four-Ball tribometer, according to ASTM standard D 4172 – 94 [12]. AISI E52100 balls with diameter 12.7 mm were used. Temperature was regulated with tolerance of ±2^{o}C at 75^{o}C and the load was 15 kg for 60 minutes. The rotational speed for the top ball was 1200 rpm. Wear scars were analysed by a Helios NanoLab 600 Oxford Instruments X-Max. For all the samples the average of three similar results were used. The worn surfaces were analysed by an Olympus BX 51 optical microscope.

2. Results and discussion

Infrared spectroscopy was performed to identify the structure of protic IL as shown in Fig. 2. The absorption maxima in region 2700-2250 cm^{-1} and 1536 cm^{-1} were assigned to NH_3^+ of primary amine salt [13]. Due to the fact, that there was no absorption bands in amine region (3350-3310 cm^{-1}) of octylamine, the formation of ionic liquid is confirmed. In Fig. 3 there is shown an IR spectrum of nonanoic acid. The strong absorption band at 1706 cm^{-1} and large absorption band at 3300-3000 cm^{-1} were assigned to C = 0 band and to OH band of carboxylic acid, correspondingly. The formation of carboxylate [14] is confirmed by the presence of two bands at 1626 cm^{-1} and at 1401 cm^{-1}, while no carboxylic acid absorption bands were not observed in ionic liquid spectra in Fig. 2.

The TGA thermogram in Fig. 4 shows the mass loss with increasing temperature for the synthesized protic IL. It was found that protic IL possessed good thermal stability, the first decomposition was observed at above 200°C.

X-ray fluorescence analysis was carried out to find the extent of thiolation of copper oxide during the synthesis. Monothiols were used for creation an organic layer on copper oxide nanoparticles to prevent agglomeration and therefore the ratio of copper to sulfur in a sample would give the necessary information. A sample film on a silicon substrate was analyzed for all chemical elements and a molar ratio of 40.5:1 of copper to sulfur was calculated from the data. Comparison to the molar ratio of 13.0:1 of copper to sulfur in the mixture of starting compounds of the synthesis showed, that roughly 1/3 of the initial organic ligands were attached to nanoparticles. Therefore, the particles were well-covered with an organic layer.

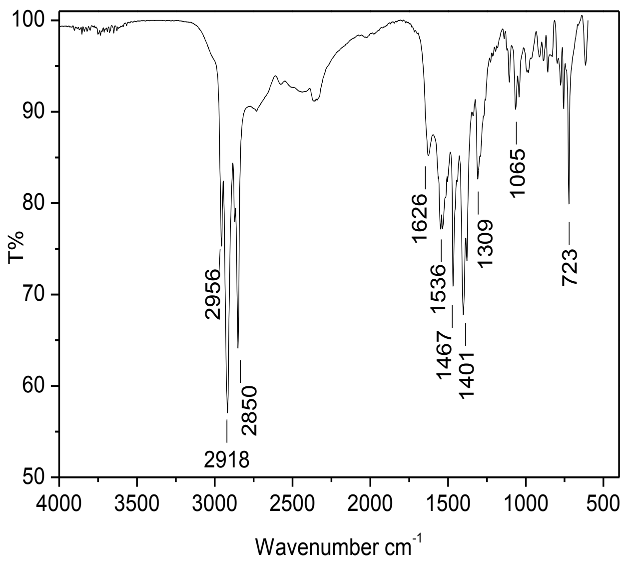


Fig. 2 IR spectra of synthesized protic IL

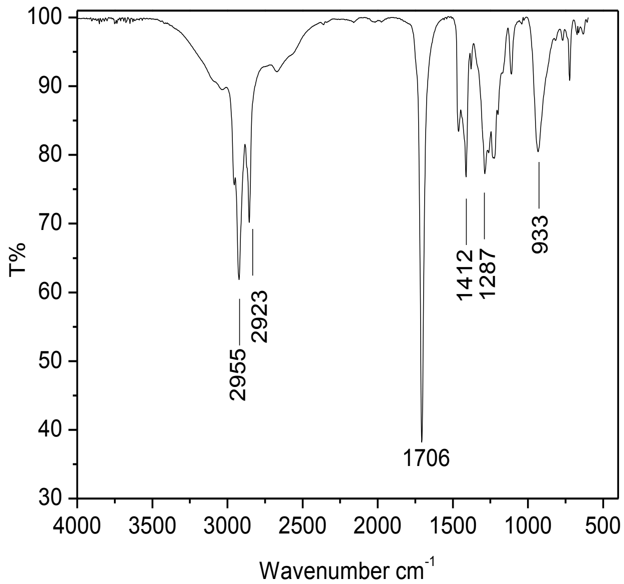


Fig. 3 IR spectra of nonanoic acid

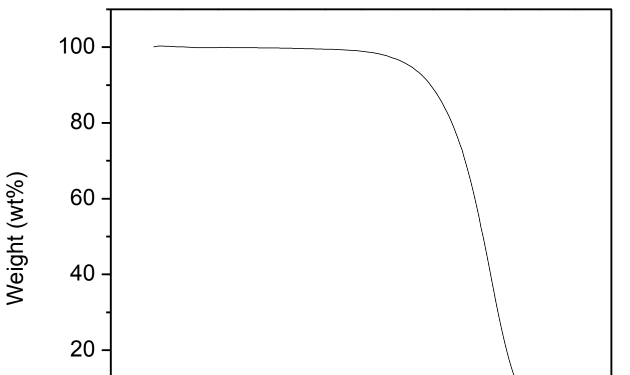


Fig. 4 TGA curve of protic IL

X-ray diffraction analysis was conducted to establish the oxidation state and chemical composition of copper in nanoparticles. Fig. 5 shows the spectrum of the as-prepared copper oxide nanoparticles. The XRD spectrum contains five peaks that are clearly distinguishable and widened. All of the diffraction peaks can be indexed to 110, 111, 200, 220 and 311 peaks of Cu_2O [15]. XRD results showed that the synthesized particles contained Cu_2O and no diffraction peaks related with Cu or CuO_2 were seen.

SEM measurements were carried out to determine the size and morphology of copper oxide nanoparticles (Fig. 6). The results showed, that nanoparticles were spherical and non-agglomerated with diameters in the range of 30-90 nm. This showed that the particles were suitable for tribological testing, because agglomerated particles may not disperse in oil and may act as abrasive on surface contact [16].

Both, protic IL and copper oxide nanoparticles were found to be fully miscible with lubricating oil, such as Neste PAO base oil, regardless of their concentration. By visual inspection, the oil-IL-copper oxide nanoparticle mixtures appeared clear yellow liquids without any aggregation or phase separation, and no changes were observed even after one month since preparation. The good solubility of protic IL in oil, compared to imidazolium based ILs, can be attributed to long alkyl chains.

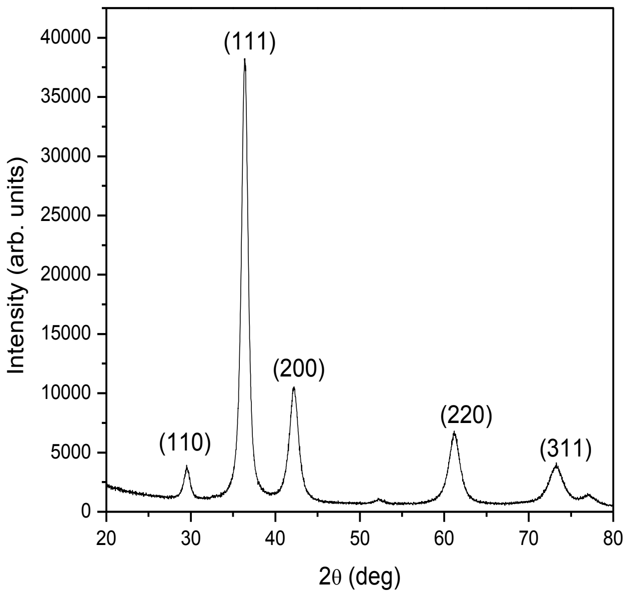


Fig. 5 XRD spectrum of copper oxide nanoparticles

The lubricating performance of protic IL and copper oxide nanoparticles as additives in base oil was evaluated. Wear scar diameters and coefficient of frictions (COF) of base oil with different additives are shown in Fig. 7 and optical microscopy pictures of wear scars are shown in Fig. 8. Copper oxide nanoparticles additive showed good antiwear behaviour, as the wear scar diameter of steel ball was reduced up to 12% with respect to that of pure base oil. A wear reduction of 47% was achieved by adding 1% or 3% of protic IL to base oil. The combination of protic IL and copper oxide nanoparticles decreased wear about 35%, with respect to base oil. It is very interesting to note, that unlike similar systems comprising of nanoparticles/IL combination [17], protic IL alone as an additive to base oil decreases wear more than its combination with and copper oxide nanoparticles. The wear reducing mechanism of IL is related to the physical adsorption of the IL to the wear surface [18]. The protic IL has carboxyl group, which is known to have an affinity towards steel surfaces and acts as an anchor for adsorption of IL to the surface [18]. When lubricant contains both IL and nanoparticles, there might occur competition between IL and nanoparticles over the adsorption centers on the wear surface and since IL has a stronger physical adsorption, it covers most of the surface and interferes the nanoparticle wear reduction mechanism. The wear reduction mechanism of nanoparticles depends on their concentration if the concentration is too high they tend to aggregate and form large clusters, which act as abrasive bodies [19]. However, a comprehensive wear reduction mechanism of protic IL/copper oxide nanoparticle co-additives to base oil relative to their concentration remains to be explained in further studies.

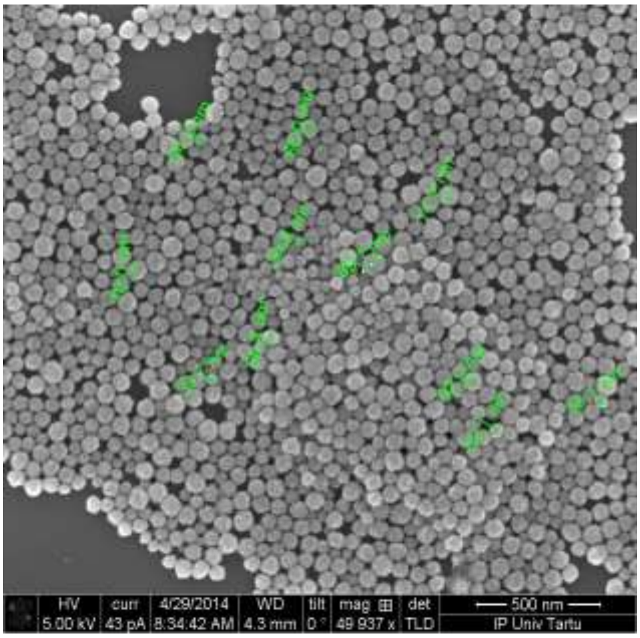


Fig. 6 The SEM image of copper oxide nanoparticles

The coefficients of friction of base oil and base oil with different additives are shown in Fig. 7. The results show that the friction coefficients were reduced by adding copper oxide nanoparticles or protic IL to base oil, which is in good agreement with wear scar data. In literature it has been shown that nano-copper forms a protective layer on steel surface, by diffusing and permeating during rubbing [10]. The physical adsorption and tribochemistry reaction can take place when the steel balls are rubbing, so the contact temperature is raised and the copper oxide surface metal is softened or melted.

In case of both additives, protic IL and copper oxide nanoparticles, the coefficients of friction were increased, while wear scars were decreased. Since protic IL has long alkyl chains they may orient crosswise to metal surface, while acting as barrier and therefore a stronger force is required to move the steel balls; i.e. simultaneously forming a protective layer on surface and minimizing wear.

In order to get better understanding of the protic IL and copper oxide nanoparticle wear reduction mecha-

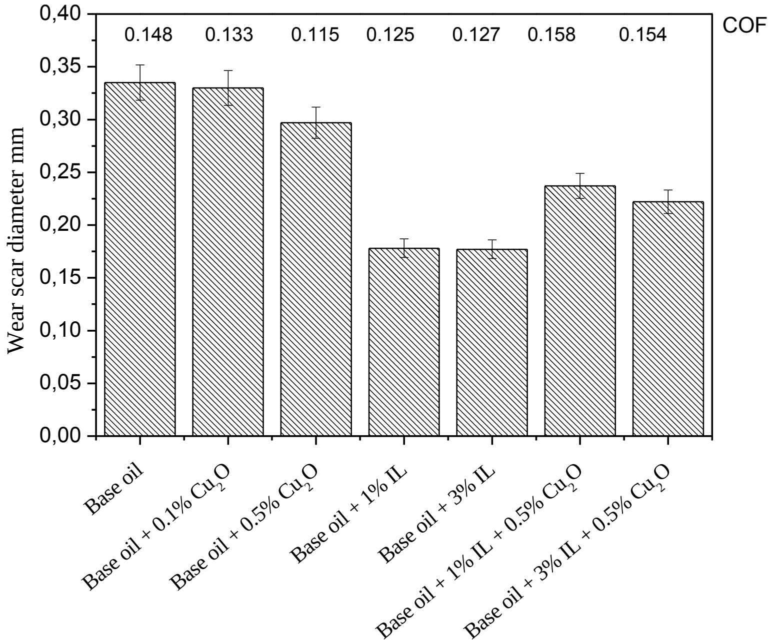
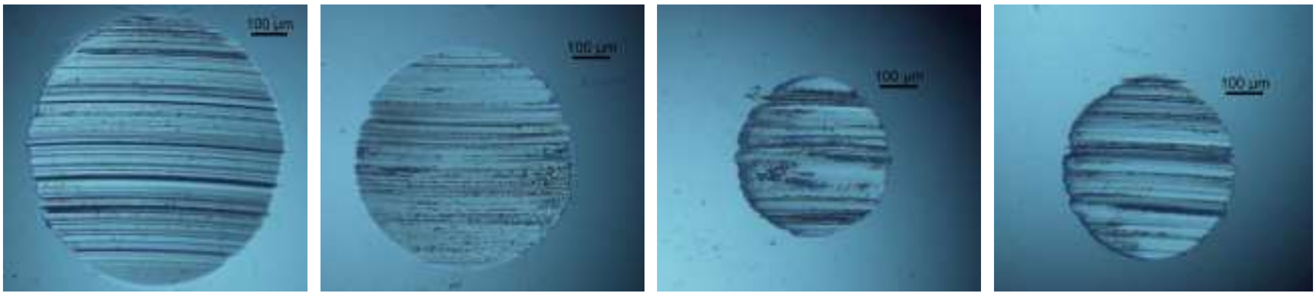


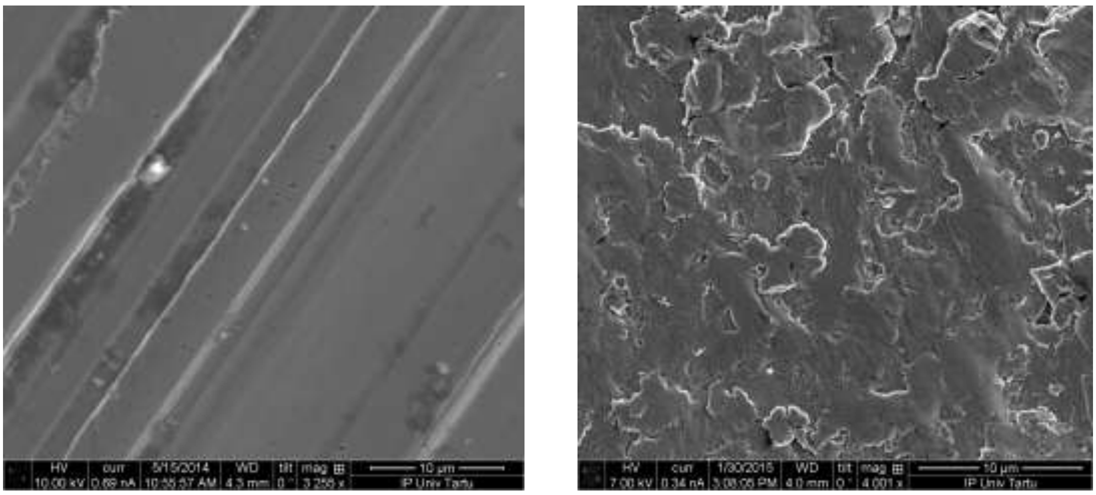
Fig. 7 Wears scar diameters and coefficient of frictions of base oil with different additives



a b c d

Fig. 8 Optical microscopy pictures of wear scars of a) base oil, b) base oil + 0.5% Cu_2O, c) base oil + 3% IL, d) base oil + 3% IL + 0.5% Cu_2O

nism, EDX (Energy-dispersive x-ray spectroscopy) from wear scars was performed. For the sample subjected to wear test with both copper oxide nanoparticles and protic IL, a flake-like surface was seen, but it was not observed for the sample that was treated with base oil without any additives, as seen in Fig. 9. In surface analysis in Fig. 10, both copper and nitrogen were detected, with copper originating from nanoparticles and nitrogen from the protic IL. These results indicate the formation of the tribofilm, consisting of protic IL and copper oxide nanoparticles.



a b

Fig. 9 SEM images from wear scars obtained in a) base oil and b) base oil + 1% IL + 0.5% Cu_2O mixture

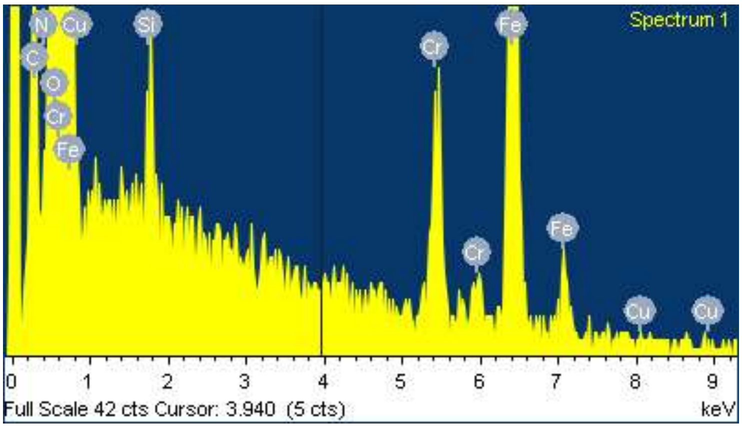


Fig. 10 EDX analysis results of base oil + 1% IL + 0.5% Cu_2O mixture

3. Conclusions

A new composite consisting of protic IL and copper oxide nanoparticles was developed and used as a lubricant additive for the first time. Both nanoparticles and protic IL were fully soluble and stable in oil. Lubricant additive tribological performance was measured with a four-ball tribometer according to the standard. It was found that, base oil with protic IL and copper oxide nanoparticles can reduce wear up to 35%, while protic IL alone may decrease wear up to 47%. The good lubricating performance of protic IL can be attributed to the formation of the adsorbed ordered layers. Long alkyl chains of protic IL increase their surface separation ability. The presence of a dispersed nanophase would improve the oil load carrying ability, providing a more effective surface separation and minimizing wear.

Acknowledgments

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TRIBOLOGICAL PROPERTIES OF PROTIC IONIC LIQUID AND FUNCTIONALIZED COPPER OXIDE NANOPARTICLES AS ADDITIVES TO BASE OIL

S u m m a r y

The aim of the present study was to investigate a novel composite as lubricant additive for metal wear parts, composing of protic ionic liquid and functionalized copper oxide nanoparticle composite. A simple and an easy-to-modify synthesis method for the preparation of thiol covered copper oxide nanoparticles was developed. A long process of optimization of reaction parameters was carried out that resulted in preparing non-agglomerated oil dispersible copper oxide nanoparticles with an estimated average diameter of 60 nanometers based on SEM measurements. Novel protic ionic liquid, which dissolves in oil was synthesized. Lubricant tribological experiments with the standardized four-ball-method were conducted with 15 kg. The addition of 3% ionic liquid and 0.5% copper oxide nanoparticles to base oil reduced the wear up to 35% compared to base oil without any additives, while 1% of protic IL reduced wear up to 47%. In addition, the novel type lubricant additive has many advantages and can also widen the range of applications, e.g. wider temperature range and preserved functionality at harsh conditions where oil-based lubricants fail.

Keywords: ionic liquids, tribology, nanoparticles, copper oxide nanoparticles.

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