SERBIATRIB '19

16th International Conference on Tribology

Serbian Tribology Society

Faculty of Engineering
University of Kragujevac

Kragujevac, Serbia, 15 – 17 May 2019

EXCELLENT LUBRICATING PROPERTIES OF IONIC LIQUID – MYTH OR TRUTH

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Abstract: *Due to numerous good physical-chemical properties, Ionic Liquids should be ideal candidates for a new lubricant, suitable for use under harsh conditions, where conventional oils and greases fail****Error! Reference source not found.****. This is especially true for hydraulic fluid and gearbox oil. In the paper, the lubricating properties of selected Ionic Liquids have been tested and confirmed by using some of the classical tribological tests: e.g. the four-ball welding point test and wear test. Another approach to check the quality of lubrication is to do it with the Stribeck's curve, representing the friction coefficient, depending on the Stribeck's parameters, including viscosity, relative surface velocity, and loading. In most cases, the results achieved with Ionic Liquids have been considerably better than those achieved with classical mineral-based hydraulic oil.*

Keywords: *ionic liquids, lubricants, tribological tests, four-ball test, Stribeck's curve, results*

1. INTRODUCTION

Today, out of all the hydraulic fluids, mineral oils of different properties are used in 90 % of cases, whilst the remainder are fire-resistant and faster bio-degradable hydraulic fluids. As a minor share, the universal fluid lubricants are used for gearing, engine and hydraulic parts. Furthermore, in specific cases, e.g. in the foodstuff industry, those fluids compatible with foodstuffs are used, while elsewhere, sea water, as well as electro-rheological fluids are preferred. However, none of the fluids is so universal that it could meet the different requirements within their individual areas of use.

Engineers still exert substantial effort, time and resources into finding a lubricant that would be near the ideal fluid. It would have to be non-flammable, non-poisonous, and corrosion resistant, would have excellent lubricating properties, temperature-independent physical-chemical properties, be resistant, and guarantee a long service life for the components where it is used.

One of the principal duties of lubricant producers is searching for alternatives to existing lubricants, and accompanying the discoveries within related spheres. In that way, new market niches are opened, thus raising the market competitiveness. In the future, this might be essential for survival on the market, as, in the developed world, lubricant consumption is being reduced, and the number of lubricant producers diminishing, whilst the conditions on the lubricant market are being tightened up. Therefore, in spite of the great number of different conventional lubricants, an approximation to the ideal liquid is still being searched for.

2. IONIC LIQUIDS AS LUBRICANTS

Today, it is difficult to say which lubricant will have an important role in the future, in the pending “post-oil period”. That depends on the results of present and future research and tests on the development directions of fluid technology, fluctuations in the prices of raw materials on the world markets etc. However, in all probability, in the near future, a universal liquid of superior quality and near ideal will not be discovered to supersede all others.

Ionic Liquids (ILs) are one of the more promising candidates, because of their good properties with which they have already excelled within many spheres of industry.

The simplified definition of Ionic Liquids says that ILs are liquid or molten salts. The term IL was introduced in order to cover the systems of temperatures below 100 °C. One of the reasons for that was to avoid the words “molten salt” in terms such as the “molten salt ambient temperature”; another reason was to create the impression of coldness, and a possible third reason was the intention for patenting [1]. The IL “consists fully of ions (molten sodium chloride, while NaCl in water is only the water solution of ions). ‘It was formerly called molten salt, implying the idea of work at high temperatures with highly viscous and corrosive media” [2], [3].

Ionic Liquids with a melting point at ambient temperature consist of extensive and asymmetrical organic cations, such as 1-alkyl-3-methylimidazolium, 1-alkyl pyridine, 1-methyl-1-alkyl pyrrolydine or ammonium salts. The anions used range from simple halides, reducing the high temperatures of the melting point, to inorganic anions such as tetrafluoroborates and hexafluorophosphates, and to extensive organic anions such as bis(trifluorosulphony)amides, triflates or tosylates [4]. An example of a basic cation and anion structures is shown in Fig. 1.

The cations (usually organic) and anions (usually inorganic) present in IL are so formulated that the resulting salts hardly crystallize. Therefore. the IL is liquid within a wide temperature range [4]. An important feature of ILs is the possibility of adapting these physical-chemical properties through changing the natures of the anions and cations. The number of possible combinations is extremely high, that is why the best Ionic Liquid is supposed to be adapted for any case of use.

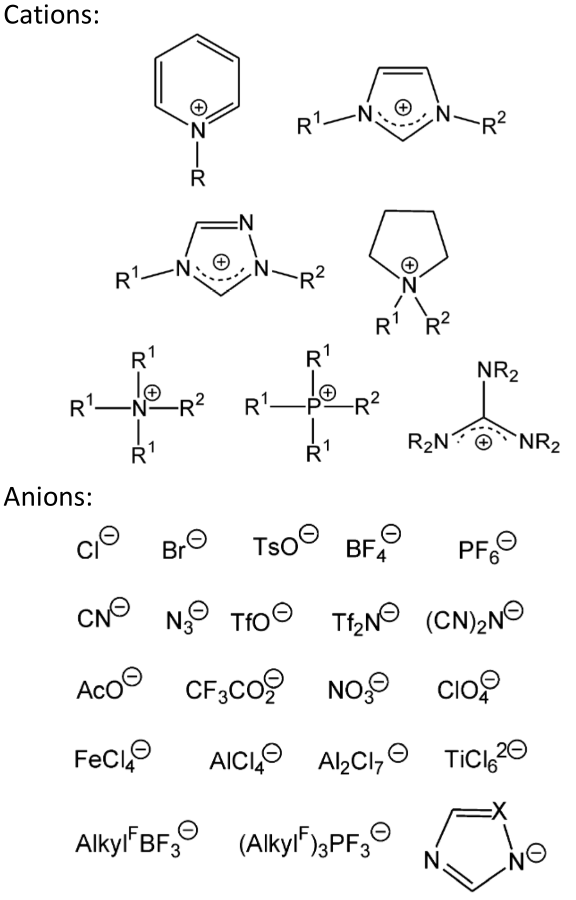

Figure 1. Basic structures of Ionic Liquids [4]

2.1 Impact of anions on lubrication

It must be emphasised that the anion and cation properties of Ionic Liquid cannot be differentiated between. However, such a division would be useful from the point of view of categorising those tribological properties affected dominantly by anions and cations.

In general, anions can be grouped into halogenated and non-halogenated. Most halogenated anions, particularly the fluorinated ones, are inappropriate as lubricants. Otherwise, the halogenated anions have good lubricating properties, because of their iron-halide layer formation, such as FeFx on the steel material's surface [5], [6].

However, in the presence of water during anion hydrolyses, aggressive hydrogen halide is formed, for example HF. The results are very high friction and wear, because of the corrosion and degradation of the steel material. This has been detected on the popular anions such as $NTf2^-$, $BF4^-$ or $PF6^-$. As far as $NTf2^-$ is concerned, a greater obstacle to its use as a lubricant is its high price and high toxicity [5], [6], [7], [8]. Here, a special place is occupied by the $PF6^-$ anion. It has been proved that it may have exceptional properties in comparison with other halogenated anions. It works as an anti-wear agent and corrosion inhibitor because of the phosphorus within its molecular structure. On the surface a phosphate film is formed, preventing the formation of Fe-halide and improving resistance to wear [7].

The adding of corrosion inhibitors, for example tricresyl phosphate, into the pure IL may allow good lubricating properties of those Ionic Liquids with halogenated anions, and the formation of a protective surface phosphate film [9]. However, the $PF6^-$ anion inclines towards hydrolysis, and decomposes within a short time when in contact with water.

In view of the negative effects of most halogenated anions in ILs (toxicity, non-resistance to water, corrosion, high wear), the use of IL with non-halogenated anions is highly recommendable. So far, the methyl sulphate anion ($MeSO4^-$) has already been used as an additive for the lubricant based on glycerol. The best results have been gained by the lowest tested concentration (0,625 weight per cent). In that case, the friction was reduced by 30 to 50 %, whereas the wear was 2,5 to 4,6 times smaller than with pure glycerol, depending on the cation used in the Ionic Liquid [10], [11].

This IL type seems to be suitable as an additive in poly-alcohol matrices, as it is already active in concentrations lower than 1 weight %. However, the methylsulphate anion is hydrolytically unstable, and causes corrosion over a longer time period according to the experiences of an IL-supplier. It has already been proved that, when using anions with phosphorus, the dimethylimidazolium dimethylphosphate is a worse lubricant than ILs with halogenated anions [9].

Various ILs with phosphorus groups in anions and/or cations are also already being used. In comparison with standard anti-wear additives, identical or better results with respect to friction and wear have been obtained with 1 % addition of IL. The best results were obtained when phosphorus was present in the anion and in the cation. Comparable results were gained by Zhang and colleagues, who did not find corrosion with the use of dialkylphosphate IL, and found intensive corrosion with the use of $BF4^-$ or $PF6^-$ as anions [12], [13]. Somers [14] used trihexyl(tetradekyl) phosphonium cations with various disubstituted phosphates, and also conventional (halogenated) anions as counter-ions for tests with steel balls.

In comparison with the engine oil SAE 15W-50 as a reference lubricant, better results were gained with respect to friction and wear with the use of the diphenylphosphate (DPP) anion. The IL with dibutylphosphate as the anion showed worse results, but better than the reference oil [14], [15]. It can be assumed that the aromatic phosphate anions in tribology are better than the aliphatic anions. It was also shown that the properties of IL as a lubricant do not only depend on the anion. A great impact is also exerted by the used load. At low loading the DPP had better properties than NTf2. That changed when higher loadings were used [16].

2.2 Impact of cations on lubrication

Also the cations within ILs for lubrication have so far been different. One of the more common IL-classes is IL based on imidazole cations. Qu [17] found out that the friction of those ILs was higher than that of the compared conventional oils. Fox and Priest [9] found that if lengths of imidazolium cation chains were used there was no friction and wear lowering or increasing trend. Only the “normal” 1, 3-dialkyl imidazolium cations have not been used as lubricants so far. Zhu [18] synthesised the imidazolium ILs, where, on one side of the ring they added the ester functionality. On the other side, there was the standard aliphatic chain.

For their ILs they used the halogenated anions. They used PFPE (perfluoropolyether) and BMIM-BF4 as references. The results of their new ILs were better than with PFPE, but worse than with BMIM-BF4. After the test, identical difficulties were noticed, as met with the majority of ILs with halogenated anions (e.g. corrosion).

Li [20] used another function, namely a hydroxyl group, on the cation. In the end, they obtained almost equal results as Zhu and colleagues. They obtained slightly higher friction coefficient and better anti-wear properties than with non-functionalised ILs. Li also tested other functionalised imidazole tetra fluoroborates $BF4^-$. They introduced the vinyl group on one side of the imidazolium ring, but they did not manage to produce an ionic liquid with better lubricating properties. Using the standard imidazolium tetra fluoroborates they could only perform tribological tests under 120-160 kg loading, whilst, with the new functionalised ILs, they could only carry out the tests with less than 50 kg loading. In some cases, the imidazolium cation functionalising could be a concept for ILs usable as a lubricant.

In regard to ILs based on ammonium cations, Qu [21] reached lower friction and wear, if compared with the usual oils. That was not only for pure liquids, but also in those cases when they were used as additives to the usual oil (10 weight %). Those $NTf2^-$ likely to cause the mentioned corrosion problems were used as anions in those liquids.

The ILs with phosphorus cations, if compared with ammonium cation Ionic Liquids, have proved to be of superior quality. Some researchers tested the holin (2-hydroxyethyl-trimethyl-ammonium)-based ILs and compared the two results with the standard engine oil SAE 5W-30.

The compared ILs had the same friction coefficient. However, the friction coefficient had already increased after a short time to the level as found during the dry sliding test without oil. Therefore, the ILs of such types are inappropriate as lubricants.

Jiang [8] introduced a new category of ILs, appropriate as lubricants, i.e. ILs with crown-shaped cations. They synthesised a few ILs with cations gained from crown-shaped ethers with (2-ethylhexyl) phosphate as the anion. The new ILs had better friction and anti-wear properties than ordinary lubricants, such as X1-P and PFPE. They may also be used at high temperatures.

Some authors have also researched ILs with phosphorus in the cations and anions. Somers has already been mentioned [14]. Yu [19] also synthesised some phosphonium alkylphosphates, and tested them as additives for ordinary lubricating oils. Comparison between the results of those compounds with pure base oil witnessed important friction and wear reduction. The ILs were thermally more stable than the standard lubricants, and were not corrosive for alloys.

3. USED TEST METHODS

Generally, the analyses were conducted by standard testing methods that are normally used for laboratory analysis of conventional hydraulic fluids. Lubricating properties can be determined and verified in different ways. As primary tests for the determination of lubricating ability they used the four ball welding point test and the wear test.

Another approach was to check the quality of lubrication based on Stribeck’s curve, representing the friction coefficient depending on the Stribeck’s parameter. Analyses were carried out in comparison with classical mineral based hydraulic oil HLP type and VG46 viscosity grade.

3.1 Welding-load and wear-diameter

Welding-load (or welding-point) and wear-diameter determination according to standardised procedure (e.g. IP 239-85), with the use of the four-ball apparatus (Hansa Press), is one of the common methods for testing the lubricating ability of a lubricant.

This method is based on load application to four standardised steel balls of 12,7 mm diameter. The top rotating ball slips onto the lower three fixed balls at constant loading, and at constant rotating velocity of 1440 min^{-1} (Figure 2). The welding-load measurement and the wear test of lubricating oils, can be performed on the same apparatus.

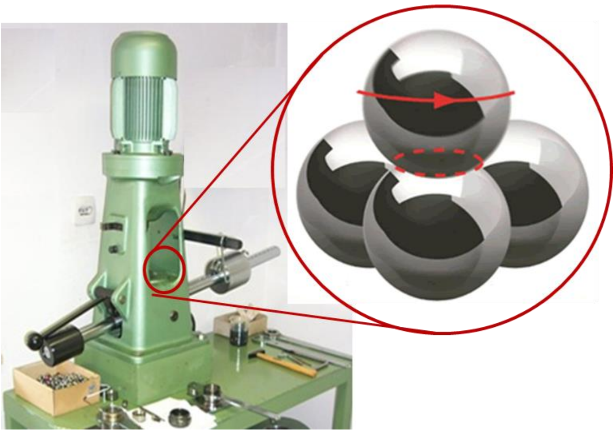

Figure 2. Principle of welding-load and wear-diameter measurement

The welding-load is measured at specific loading and/or to ball pressure for 10 seconds. The top ball rotates and presses with the test loading against the lower three immovable balls dipped into the tested liquid.

The measurement result is given in kg, and comprises two numbers (e.g. 140/160). The first number indicates the maximum loading at which ball welding did not occur during the test (10 s). The second number indicates the minimum loading at which complete steel ball welding and/or automatic deactivation of the device occurred during the test.

The wear test lasts much longer, namely for 60 min ±1 min at constant temperature and loading, depending on the tested hydraulic liquid. The ball wear depends on the loading, velocity, duration of the test, and the properties of the lubricant tested. As all parameters except the lubricating properties are constant, the result and/or the ball wear depends only on the lubricating properties of the liquid tested.

After completion of the test, the wear test result is obtained by measuring the wear of the lower three steel balls under a microscope, where the diameters of the wear cavities are measured on the three immovable balls. The wear extent is defined as the average diameter of ball wear under known conditions.

3.2 Stribeck's curve

The next approach to presenting the quality of lubrication is to do it with the so-called Stribeck's curve, representing the friction coefficient depending on the Stribeck's parameters, including viscosity, relative surface velocity, and loading.

Basically, the qualities of lubrications improve when moving on the horizontal axis of the Stribeck's curve to the right. The combination of low velocity, low viscosity and high loading will cause the boundary lubrication, characterised by a small quantity of lubricant in the space between the two surfaces and a great surface of direct contact. On the Stribeck's curve it can be seen that this is expressed by very high friction. In tribological systems, the boundary lubrication occurs at the start-ups and stoppages. In this range, the lubricant acts mainly chemically and has a very great influence. With the increase of velocity and viscosity or reduction of loading, both surfaces are gradually separated and the lubricating film is formed, which, though thin and imperfect, already improves the lubrication quality expressed by abrupt reduction of the friction coefficient. This range is called mixed lubrication. The surface separation continues with the increase of velocity and viscosity and decrease of loading, until a perfect lubricating film without direct surface contacts is created; as a result, the friction is minimised, and this implies passage into the hydrodynamic lubrication range, practically without wear. The lubricant within this range acts mainly physically.

The measurements of Stribeck's curve for the mineral hydraulic oil and Ionic Liquids were carried out using an MTM device for measuring friction and lubricating film thickness with ball-disc configurations. The appearance of the device is shown in Figure 3.

The ball, of 19,05 mm diameter with roughness Ra<0,02 µm and hardness 800 HV-

929 HV under loading, sits on a disc of 46 mm diameter with roughness Ra <0.01 µm and hardness 720 HV-780 HV. Both are made from identical material, DIN 100Cr6. The disc is dipped completely into the tested liquid, the quantity of which amounts to about 35 ml. The ball and disc are driven independently of each other, so that the test can be performed with different slide-to-roll ratios. The friction force between the ball and disc is measured by a force transducer.

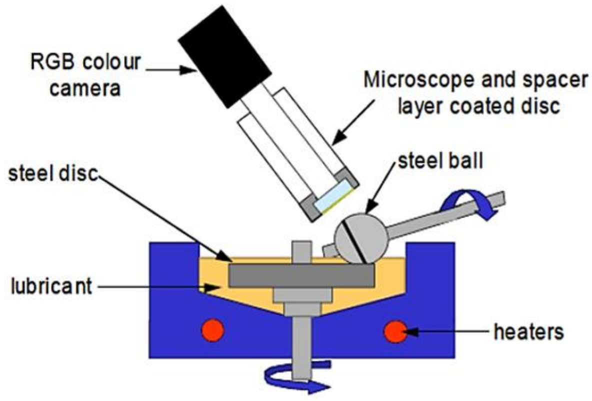

Figure 3. MTM device: pin on disc

During the Stribeck test the velocity was changed with constant slide-to-roll ratio. In 20 logarithmic decrements the velocity was reduced from 2 m/s to 0.01 m/s with a slide-to-roll ratio of 50 %. In that way, different lubrication modes were reached. The pressing force amounted to 35 N, giving the Hertzian contact pressure of 1 GPa with the given ball and disc geometry. The slide-to-roll ratio is defined by equation (1). For a specific ratio, the device during the measurement once rotates the disc faster, and the next time it rotates the ball faster.

$$SRR = \frac{U_{\text{slide}}}{U_{\text{av}}} = \frac{|U_{\text{ball}} - U_{\text{plate}}|}{(U_{\text{ball}} - U_{\text{plate}})/2} \cdot 100 \ . \qquad (1)$$

where represent U_{slide} – sliding velocity of ball and disc, U_{av} – average sliding velocity of ball and disc, U_{ball} – ball velocity and U_{plate} – plate velocity.

Since, in devices, we do not only deal with rotational and rolling movements of sliding contacts, such as in bearings, camshafts or gears, we also tested the resistance to friction with the test, where the translational sliding movement is at the forefront. These movements of contact surfaces, in addition to the aforementioned rolling movements, occur in hydraulic energy conversion components, e.g. in all types of hydraulic pumps and hydromotors, and in almost all hydraulic valves, such as directional, pressure and flow valves, either by switching or continuous operation. In the latter case, these are hydraulic control valves, and the friction conditions are extremely important.

4. RESULTS

The pre-selection of tested ILs was carried out on the basis of a prior corrosion test in a humid chamber, compatibility with materials used predominantly within hydraulic components [22], and the selection of appropriate viscosity and density.

The comparison between the welding-loads and wear-diameters for different samples of ILs compared with mineral hydraulic oil (Hydrolubric) ISO VG46, are shown in Figure 4. The lubricating properties of some ILs samples are considerably better than those of the mineral oil.

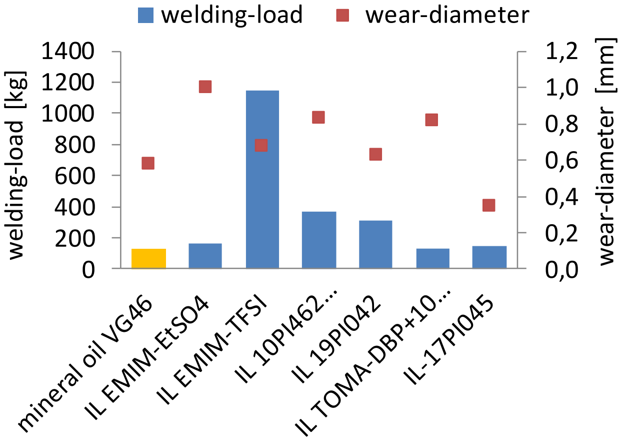

Figure 4. Welding-load and wear diameter of tested ILs vs. mineral oil

Some samples have an exceptionally high welding load, for example EMIM-TFSI had as much as 1150 kg, which pointed out exceptional properties at extreme pressures but, interestingly, the wear diameter was even greater than that of the mineral oil, implying that the anti-wear properties were worse. As in the case of hydraulic oils, the anti-wear properties are more important, so that liquid would be potentially more suitable for use in gearings, maybe even as metalworking fluid during metal machining. In regard to other liquids with high welding loads, the limitation was, in particular, bad corrosive protection in the presence of moisture, or in proper viscosity for use in hydraulic systems.

The measured Stribeck's curves for oil and two ILs at the ambient temperature T_o and 60 °C are shown in Figure 5.

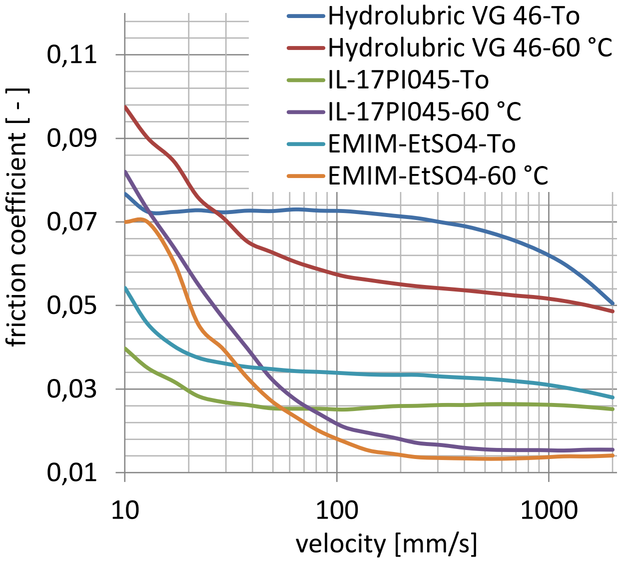

Figure 5. Stribeck's curves of two tested ILs vs. Hydraulic mineral oil

It can be seen that the friction coefficient of the mineral oil within the entire range is considerably higher than that of both Ionic Liquids. The two ILs have a very similar friction coefficient within the entire range, the IL-17PI045 having a slightly lower friction coefficient at room temperature, and the EMIM-EtSO4 at 60 °C. All three liquids showed much greater difference between the lowest and highest measured values at 60 °C than at room temperature. Furthermore, at higher temperature, the friction coefficient was higher in the range of boundary and mixed lubrication, and lower in the range of elastohydrodynamic lubrication. That is probably caused by a smaller lubricating film thickness at higher temperatures, resulting in more direct contacts of the ball and disc surfaces within the range of the boundary and mixed lubrication.

5. CONCLUSION

The performed lubrication tests based on standard test methods have proved that certain types of ILs have comparable, and in some cases much better, lubricating properties than conventional mineral oils.

That can be explained by the fact that ILs have unique bipolar structures, thus allowing them easy adsorption to the sliding surfaces of contacted mechanical parts. Consequently, an effective boundary film is formed, thus reducing friction and wear. That applies particularly, to lower contact pressures and large surface areas.

By measuring the welding-load and the wear-diameter on a four-ball apparatus, it was discovered that the tested ILs had better lubricating properties than the mineral hydraulic oil. This fact is also confirmed by the research results of other authors, who have used different types of ILs. But, it should be noted that these are more or less laboratory tests. The results of lubrication tests on real components, e.g. endurance pump-tests, carried out with the real, specified hydraulic pumps used under real, constant or changing operating conditions, can lead to different conclusions. Therefore, it is not always necessary, that the results of the durability pump-tests, correspond directly to the results of the laboratory tests.

For use within a hydraulic system additional pump tests regarding lubricating abilities need to be carried out to have complete information regarding the lubricating properties.

Apart from lubricating properties, it is necessary to check the applicative suitability of other physico-chemical properties of the ILs used as lubricants, e.g. suitable viscosity, viscosity index, density, thermal conductivity, compatibility with component materials, electrical conductivity and corrosion impact.

Before using ILs as a new type of lubricant, we need to obtain all the necessary information on important fluid properties. To this end, it is necessary to carry out a very extensive and relatively expensive selection process.

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