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Tribological properties of lubricant additives of Fe, Cu and Co nanoparticles

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Tribological investigations were performed on mineral oil containing Fe, Cu and Co nanoparticles and their combinations. The tribological tests showed that each set of nanoparticles significantly reduced the friction coefficient and wear (up to 1.5 times) of friction pairs. The use of Cu nanoparticles provides the most effective reduction of friction and wear in each combination of nanoparticles. Surface analysis shows that the constituent elements of nanoparticles precipitated on the contact surface during the use of the oils with nano-additives. Different structures formed on the friction surface are observed in the contact zone and over the remainder of the ball surface. The SEM micrographs and EDX chemical analysis confirm the formation of a tribo-layer composed of the elements from the nanoparticles.

1. Introduction

Recent research papers have reported that the addition of nanoparticles to lubricant is effective for the reduction of wear and friction in mechanical systems. Because of the remarkable tribological properties of nanoparticles, nanotechnology is regarded as the most revolutionary technology of the 21st century [1].

Numerous nanoparticles have recently been investigated for use as oil additives. Nano-powders of some metals and their compounds exert an especially effective influence on the characteristics of lubricants. The use of nanoparticles that include Cu, CuO, Fe, Ni, TiO_2 and other metallic nanoparticle additives in lubricating oils provides good friction reduction and anti-wear behavior [2–10]. Among these additives, Cu nanoparticles have received significant attention because they deposit on the friction surface, improve the tribological properties of the base oil and display good anti-friction and wear reduction characteristics [2–9]. When CuO was added to API-SF oil (engine oil SAE 30) and base oil for friction testing, the friction coefficients were reduced by 18.4% and 5.8%, respectively, in comparison to the oils without nanoparticles [2]. The measurements of the friction coefficient and the surface temperature during the tribological tests showed that the oils with added copper nanoparticles had lower friction coefficients than the raw oil. According to AFM and EDS analyses, oils with nano-additives fill the scars and grooves on the friction surface when the nanoparticles precipitate between the friction surfaces [3].

The tribological efficiency of metallic nanoparticles is mostly explained by the formation of anti-wear film on friction surfaces [2–4,8,9]. The formation of copper film from oil containing Cu particles is explained by two possible mechanisms: first is based on the chemical and electrochemical effects (at the onset of the rubbing, Cu nanoparticles deposit on the worn surface, which is "fresh", having removed surface oxide layer in sliding through electrostatic adhesion caused by sliding of the friction surfaces) and the second is based on fundamentals of mechanical metallurgy (the Cu nanoparticles partly melt due to their low melting point, the local overheating and high flash temperature on friction surface in spite of the oil cooling) [4,8].

In addition to reducing the friction coefficient, liquid lubricants with solid additives increase the load carrying capacity of the lubricating fluid [3,11]. The friction-reduction and anti-wear behavior is dependent on the characteristics of the nanoparticles. Investigations of DDP-modified copper nanoparticles show that small size nanoparticles improve the tribological characteristics more efficiently [3]. Concentration of nanoparticles in oil plays significant role in tribological efficiency of such additives [7]. This shows that the formation of the tribological film takes place at certain conditions which are related to the state of nanoparticles in the lubricating fluid. Furthermore, diverse effects such as decreased friction and changes in the lubrication regime have also been reported [1].

The mechanisms by which oils with nano-additives reduce friction and wear are the colloidal effect, rolling effect, small-size effect, protective film effect and third body effect [2–4,8,9].

Chinas-Castillo and Spikes investigated the action mechanism colloidal solid nanoparticles in lubricating oils. Their study showed that colloid nanoparticles in thin film contacts penetrate

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elastohydrodynamic (EHD) contacts, mainly by the mechanism of mechanical entrapment. They also found that colloids formed a boundary film in rolling contacts at slow speeds that was at least one or two times the particle size [11]. Choi et al. investigated the tribological efficiency of copper nanoparticles at different lubrication regimes. It was evident that the Cu nanoparticles were more effective in mixed lubrication than in full-film lubrication [9]. It means that the possible interaction of friction surfaces is important in the formation of copper film and its tribological efficiency. The friction reduction mechanism works when the Cu nanoparticles fill the scars and grooves of the friction surface and the physical film forms above the nanoparticles. It makes the friction surface flat and smooth resulting in a decrease of frictional force [9].

The purpose of this work is to determine the tribological effect of different mixtures of metallic nanoparticles and their compounds added to mineral oil for the lubrication of steel–steel friction pairs.

2. Experimental

2.1. Preparation of testing materials

The nanoparticles added to the tested oils were produced by the method, in which converse emulsions of water in lubricant solution (CEWLS) were used. The nanoparticles were created by the filling of minimal contents of water solutions of the reagents, according to the calculated concentration for the planned synthesis. A "water-in-oil" micro emulsion is formed when water is dispersed in a hydrocarbon-based continuous phase, which is normally located towards the oil apex of a water/oil/surfactant triangular phase diagram. In this region, thermodynamically driven surfactant self-assembly generates aggregates known as reverse or inverted micelles [12]. Spherical reverse micelles, which minimize the surface energy, are the most common form.

The CEWLS method provides a stable dispersion of nanoparticles in SAE 10 mineral oil, which was used as the base oil. The viscosity of the oil at a temperature of 100 °C was 14.1 mm^2/s, and at a temperature of 40 °C it was 98.3 mm^2/s. The same oil was used for the control version of the tests (in which it is called SAE 10). Table 1 presents the groups of oil-additives prepared for the tests.

To prepare the oils with nano-additives using the CEWLS method, 100 ml of SAE 10 mineral oil emulsion was prepared with 0.2 ml H_2O that contained dissolved sulfates of certain metals, such as $FeSO_4$, $CuSO_4$, or $CoSO_4$ and 0.5 g cetyltrimethylammonium bromide (CTAB). This mixture was added to 10 ml hydrazine emulsion, and the entire volume was mixed intensively for 5 min.

The following chemical reactions took place during the CEWLS synthesis:

$$2Fe^{2+} + N_2H_4 + 4OH^- \rightarrow 2Fe + N_2 + 4H_2O$$

$$4Cu^{2+} + 2N_2H_4 \leftrightarrow 4Cu^0\downarrow + 2N_2 + 8H^+$$

$$Co(II) + \tfrac{1}{2}\, N_2H_4 + 2OH^- \rightarrow Co + \tfrac{1}{2}\, N_2 + H_2O$$

Capek [13] used a similar procedure of microemulsion preparation, which is presented in Fig. 1. However, his method does not include the mechanism of formation of mixtures and the core/shell structure of the nanoparticles.

Fig. 2(a) and (b) presents the difference between the synthesis of the nanoparticle mixtures (Fe+Cu, Fe+Co and Co+Cu) and the core nanoparticles (Fe) with shells of another metal (Cu).

The CEWLS synthesis process includes the reduction of any chemical residues in the oil. The added hydrazine (2–5% of oil content) reacted during the synthesis and disappeared. The salt anion-containing residues of the water emulsion were eliminated by drying with natrium sulfate.

Table 1
Marking and content of nano-oils.

Title of nano-oil	Nanoparticles	Content of metal (g/100 ml oil)
SAE 10+Fe	Fe	0.5
SAE 10+Cu	Cu	0.5
SAE 10+Co	Co	0.5
SAE 10+Fe+Cu	Mixture of Fe and Cu	0.25/0.25
SAE 10+Fe+Co	Mixture of Fe and Co	0.25/0.25
SAE 10+Co+Cu	Mixture of Co and Cu	0.25/0.25
SAE 10+FeCu	Fe coated by Cu shell	0.25/0.25
SAE 10+FeCo	Fe coated by Co shell	0.25/0.25

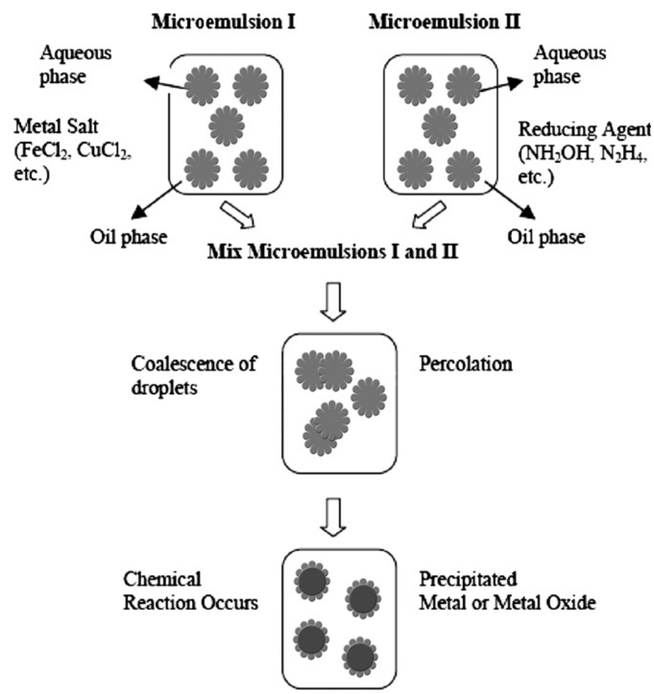

Fig. 1. Diagram of nano-mixture preparation [13].

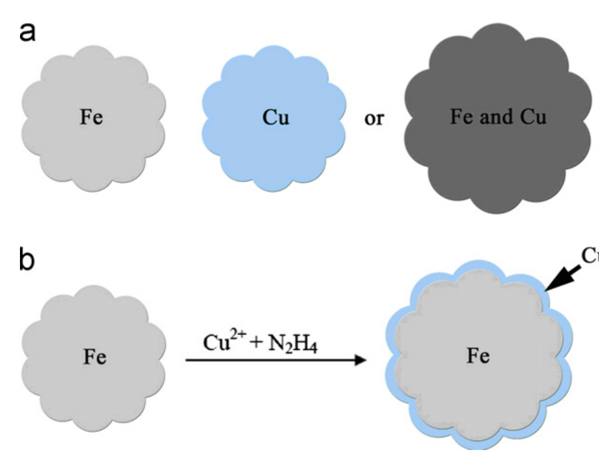

Fig. 2. Illustration of nanoparticle synthesis: (a) mixture of nanoparticles (Fe+Cu) and (b) nanoparticles with Fe core and Cu shell (FeCu).