

# Preparation of Silver-Copper Core-Shell Nanoparticles as Anti-Wear Oil Additive

A.R. Kytsya<sup>1,\*</sup>, L.I. Bazylyak<sup>1</sup>, Yu.M. Hrynda<sup>1</sup>, V.A. Vynar<sup>2</sup>, S.A. Korniy<sup>2</sup>

 <sup>1</sup> Physical Chemistry of Combustible Minerals Department, Institute of Physical Organic Chemistry and Coal Chemistry named after L. M. Lytvynenko, NAS of Ukraine, 3a Naukova Str., 79053 Lviv, Ukraine
 <sup>2</sup> Physico–Mechanical Institute named after G. V. Karpenko, NAS of Ukraine, 5 Naukova Str., 79060 Lviv, Ukraine

(Received 06 Juny 2013; revised manuscript received 15 August 2013; published online 01 September 2013)

Silver-copper core-shell nanoparticles containing of 1 % per mass of the silver have been synthesized in accordance with the two-stage scheme. With the use of the scanning electron microscopy it was determined that the obtained nanoparticles represent by themselves the nanospheres by diameter of 50 - 100 nm. The composition of obtained powders has been studied with the use of the XRD method. It was determined that the obtained nanoparticles don't contain the copper and silver oxides. In accordance with the «ball-on-plate» method the tribological behavior of the friction pair «steel-steel» was studied in the medium of I–20A oil. It was determined, that the addition of 500 ppm of synthesized nanoparticles decreases the friction coefficient in twice, and the friction track width on 25 %.

Keywords: Copper Nanoparticles, Core-shell, Anti-wear Additive.

PACS numbers: 81.05.Bx, 81.07.Wx

### 1. INTRODUCTION

Decrease of the negative effects from the friction under the mechanisms exploitation is one among the priority tasks of the modern machine-building field. Decrease of the friction coefficient and also of the wearability is achieved both at the expense of the special coatings application for the surfaces of the conjugate pairs [1], and due to the using of the special additives to the oil media [2]. Recently, the nanoparticles (NPs) of copper and silver [3-4] are widely investigated as the antifrictional additives, which not only form the metal-plating layer on a surface of the contacting details and, in such a way, decrease the friction coefficient, but also represent by themselves the initiator and the material for the selective transfer phenomenon. Nanopowders based on the alloys of copper and silver applying in special remedial compositions [5] call a special attention. However, in spite of the availability of such antifrictional additives they hadn't a much wide application in technology of the oil materials production. Their main lacks are as follow: i) high cost of the NPs of copper and silver and *ii*) high catalytic activity of the NPs that can lead to the acceleration of the oxidized destruction of oil materials. That is why the aim of our work was to develop of simple and cheap technique of the silver-copper core-shell nanoparticles (Ag@Cu NPs) obtaining and also to study an influence of the low concentrations of Ag@Cu NPs on the tribological behavior of the friction pair «steel-steel».

### 2. EXPERIMENTAL

### 2.1 Materials for Ag@Cu NPs synthesis

Crystalline AgNO<sub>3</sub>, CuSO<sub>4</sub>×5H<sub>2</sub>O and NaOH were materials for produsing of Ag@Cu NPs. N<sub>2</sub>H<sub>4</sub>×H<sub>2</sub>O was used as a reductant. The trisodium citrate (TSC)As was used as a complexing agent. Purity of the all reactants was > 99,0 %.

### 2.2 Methods

The size, form and structure of silver NPs and Ag@Cu NPs were characterized by UV/Vis spectroskopy (Shimadzu Uvmini–1240), SEM (EVO–40XVP, Carl Zeiss) and XRD-analysis (DRON–3.0).

Tribological testings were carried out accordingly to the scheme «ball-on-plate» with the use of the installation having the inversely-transitional movement of the indentor [6]. It was investigated the tribological behaviour of «steel–steel» pair in the medium of I-20A oil.

### 3. DISCUSSION

# 3.1 Synthesis and characterization of Ag@Cu NPs

Ag@Cu NPs were obtained in two-stage procedure by reduction of copper ions with hydrazine on the surface of spherical silver nanoparticles (Ag–NPs). On the first stage a sol Ag–NPs was obtained via reaction of the silver nitrate reduction with hydrazine in the presence of TSC and NaOH. Results of the XRD-analysis and UV/Vis spectroscopy (Fig. 1) showed that the diameter of Ag–NPs consists of 15±3 nm.

Concentration of Ag–NPs in the sol was  $1,5 \times 10^{15}$  l<sup>-3</sup>. Next, the solution of CuSO<sub>4</sub> was added to the obtained sol of Ag–NPs. Concentration of the Cu<sup>2+</sup> ions was calculated in such a way that the diameter of Ag@Cu NPs was 100 nm. After that, the solution of NaOH and N<sub>2</sub>H<sub>4</sub> in stoichiometric to the CuSO<sub>4</sub> quantity was added to the reactive medium. Nanoparticles were separated by centrifugation at 10000 rpm. For the hydrophobization of the surface of Ag@Cu NPs, the sediment was treated by the solution of the oleic acid in methanol.

<sup>\*</sup> andriy\_kytsya@yahoo.com



Fig.  $1-\rm X\text{-}ray$  diffraction pattern of Ag–NPs (a) and UV/Vis spectra of their aqueous sol (b).

Obtained Ag@Cu NPs were analyzed with the use of the scanning electronic microscopy (Fig. 2) and XRDanalysis (Fig. 3).



Fig. 2 - SEM image of Ag@Cu NPs.

As we can see from the presented SEM image, the obtained Ag@Cu NPs represent by themselves the nanospheres by 50 - 100 nm diameter.



Fig. 3 - X-ray diffraction pattern of Ag@Cu NPs

Results of the XRD-analysis show, that the content of silver in obtained Ag@Cu NPs consists of near 1 % per mass. At the same time, the peaks corresponding to the copper oxide are absent on the X-ray diffraction pattern.

# 3.2 Studies of the antifrictional properties of Ag@Cu NPs

In order to study the antifrictional properties of the obtained Ag@Cu NPs, the tribological behavior of pair «steel-steel» in the medium of I-20A oil it was investigated. The investigations were carried out in accordance with the scheme «ball-on-plate» (Fig. 4), the loading on the indentor (rider) was 200 MPa, the concentration of Ag@Cu NPs was 500 ppm.



Fig. 4–«Ball on plate» investigation scheme for the measurement of the friction coefficient: 1 – sample; 2 – moving plate; 3 – contact area; 4 – rider; 5 – lever with strain sensor; P – load.

It was determined that an addition of the Ag@Cu NPs to the oil medium decreases the friction coefficient from 0,15 till 0,07 (Fig. 5), and the friction track width – from 200 till 150  $\mu$ m.



Fig. 5 – Dependence of the average values of friction coefficient on time for the «steel–steel» friction pair

#### 4. CONCLUSIONS

A simple and cheap method of obtaining of the Ag@Cu NPs with the hydrophobic surface has been proposed. It was shown their efficiency as the anticorrosive additive to the oil media at their low content.

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## AKNOWLEDGEMENTS

This work was performed via the framework of the

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Task Complex Program TCPSI «RESURS» (grant # P 8.2–2013/K).

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