#### **SUPPORTING INFORMATION**

# Tribological studies of Stearic acid-modified CaCu<sub>2.9</sub>Zn<sub>0.1</sub>Ti<sub>4</sub>O<sub>12</sub>

# nanoparticles as effective zero SAPS antiwear lubricant additives in paraffin

oil

Vinay Jaiswal<sup>†</sup>, Rashmi B. Rastogi<sup>†</sup>\*, Rajesh Kumar<sup>‡</sup>, Laxman Singh<sup>¥</sup>

and K.D. Mandal<sup> $\dagger$ </sup>

<sup>†</sup>Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi-

221005, India

<sup>‡</sup>Department of Mechanical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi-221005, India

<sup>\*</sup>Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, India

Corresponding Author: Rashmi Bala Rastogi

**E-mail:** rashmi.apc@iitbhu.ac.in

**Fax:** +91 542 2368428

#### **S1. Experimental details**

The wear scar diameter of each of the three horizontal balls was measured in two mutually perpendicular directions, one in the sliding direction  $(d_s)$  and the other perpendicular  $(d_p)$  to it using an optical microscope. Geometric mean of the two perpendicular diameters on the same ball was taken as given by the equation 1.

For each experiment arithmetic mean of the above diameter of each ball  $(d_1,d_2 \text{ and } d_3)$  was taken as given by equation 2. The three stationary balls were not disturbed while taking the readings and the wear scar diameter was taken by tilting eye piece of the microscope at an angle of 70.5<sup>0</sup> making it perpendicular to the surface of the scar. All of the antiwear and load bearing tests were performed in triplicate and their mean values are cited in **Tables S1 and S2**.

#### **S1.1 Tribological Parameters**

#### S1.1.1 Mean wear scar diameter (MWD)

$$d_1 = \sqrt{(d_s d_p)}$$

$$d = \frac{d_1 + d_2 + d_3}{3}$$
2

#### S1.1.2 Mean wear volume (MWV)

Wear volume, 
$$V = \frac{\prod d_0^4}{64 r} \{ (\frac{d}{d_0})^4 - (\frac{d}{d_0}) \}$$
 3

Hertzian diameter, 
$$d_0 = 2(\frac{3 \operatorname{Pr}}{4E})^{\frac{1}{3}}$$

Where, 
$$\frac{1}{r} = \frac{1}{r_1} + \frac{1}{r_2}$$
  
 $\frac{1}{E^*} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}$ 

Where,  $E^*$  = Resultant modulus of elasticity

v = Poissons ratio r = Radius of steel ball

$$E_1 = E_2 = 206 \text{ GPa}$$

$$v_1 = v_2 = 0.3$$

P = Actual load in Newton on each of the three horizontal balls that is 0.408 times of applied load.

#### S1.1.3 Friction coefficient (μ)

The coefficient of friction for different antiwear additives is calculated from the pattern observed on the friction paper with the help of equation 4.

$$\mu = \frac{0.222F}{r} \cdot \frac{L}{P}$$
 4

L/P = 0.628r = 0.367 mm

$$F = \frac{springcons \tan t}{6} \times Y$$

Where, F = Friction force in kgf exerted on the indicator spring.

L = Length in mm of the torque-lever arm.

r = Distance of contact surface of balls from the axis of rotation (0.367 mm).

Y = Displacement after 2.5 s from the baseline.

Value of spring constant upto 80 kgf is 0.226 kgf/cm.

#### S1.1.4 Wear rate

Overall, running-in and steady-state wear rate have been calculated on the basis of observed mean wear volume data at different time intervals.

#### **S1.2 AFM Roughness Parameters**

#### **S1.2.1 Line Roughness:**

Roughness Average, 
$$R_a = \frac{1}{N} \sum_{l=0}^{N-1} |z(x_l)|$$

Root Mean Square, 
$$R_q = \sqrt{\frac{1}{N}} \sum_{l=0}^{N-1} z(x_l))^2$$

Peak-Valley Height, 
$$R_y = A_p - A_v$$

- Peak-Height,  $R_p =$  Highest value
- Valley Depth,  $R_v =$  Lowest value
- Mean Value,  $R_m = \frac{1}{N} \sum_{l=0}^{N-1} z(x_l)$

#### S1.2.2 Area Roughness:

Roughness Average, 
$$S_a = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} |z(x_k, y_l)|$$

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A This journal is The Royal Society of Chemistry 2013

Root Mean Square, 
$$S_q = \sqrt{\frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} (z(x_k, y_l))^2}$$

Peak-Valley Height,  $S_y = S_p - S_v$ 

- Peak-Height,  $S_p =$  Highest value
- Valley Depth,  $S_v =$  Lowest value

Mean Value, 
$$S_m = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} z(x_k, y_l)$$

## Table S1. Tribological Parameters for paraffin oil in the presence and absence of different SCCZTO nanoparticles (1%w/v) for 90

minute test duration at 392 N applied load.

S.N.	Lubricants		Time (Minutes)													
		15		30		45		60		75		90				
		MWD ±(SD) (mm)	MWV 10 <sup>-4</sup> mm <sup>3</sup>													
1	Paraffin oil	0.6220 (0.0011)	20.56	0.6745 (0.0012)	29.18	0.8231 (0.0014)	67.53	0.8370 (0.0012)	72.43	0.8923 (0.0014)	94.29	0.9510 (0.0013)	121.50			
2	SCCZTO-6h	0.4237 (0.0013)	03.22	0.5146 (0.0021)	08.69	0.5360 (0.0012)	10.53	0.5471 (0.0014)	11.57	0.5802 (0.0013)	15.11	0.5917 (0.0011)	16.89			
3	SCCZTO-8h	0.4816 (0.0013)	06.31	0.5484 (0.0016)	11.69	0.6055 (0.0013)	18.25	0.6380 (0.0015)	22.95	0.6380 (0.0012)	22.95	0.6610 (0.0016)	26.76			
4	SCCZTO-12h	0.5579 (0.0013)	12.65	0.7027 (0.0016)	34.77	0.7813 (0.0014)	54.37	0.8040 (0.0011)	61.25	0.8598 (0.0013)	80.89	0.9380 (0.0014)	115.77			
5	ZDDP	0.4170 (0.0012)	02.94	0.5560 (0.0011)	12.47	0.6259 (0.0014)	21.12	0.6580 (0.0015)	26.25	0.6920 (0.0013)	32.51	0.8151 (0.0012)	64.85			

MWD= Mean wear scar diameter,  $\mu$ = Friction coefficient, MWV= Mean wear volume.

### Table S2. Tribological Parameters for paraffin oil in the presence and absence of different SCCZTO nanoparticles (1%w/v) at

different loads for 30 minute test duration.

	Lubricants	Applied load														
S.N.		294N			392N			490N			588N			686N		
		MWD ±(SD) (mm)	μ± (SD)	MWV 10 <sup>-4</sup> mm <sup>3</sup>	MWD ±(SD) (mm)	μ± (SD)	MWV 10 <sup>-4</sup> mm <sup>3</sup>	MWD ±(SD) (mm)	μ± (SD)	MWV 10 <sup>-4</sup> mm <sup>3</sup>	MWD ±(SD) (mm)	μ± (SD)	MWV 10 <sup>-4</sup> mm <sup>3</sup>	MWD ±(SD) (mm)	μ± (SD)	MWV 10 <sup>-4</sup> mm <sup>3</sup>
1.	Paraffin oil	0.6550 (0.012)	0.027 (0.002)	25.73	0.6990 (0.013)	0.032 (0.003)	33.99	0.7440 (0.016)	0.036 (0.005)	42.27	Fails	-	-	-	-	-
2.	Stearic acid	0.5990 (0.013)	0.020 (0.003)	17.41	0.6354 (0.013)	0.024 (0.003)	22.55	0.6990 (0.016)	0.027 (0.004)	33.99	Fails	-	-	-	-	-
3.	SCCZTO-6h	0.4990 (0.014)	0.011 (0.002)	07.51	0.5468 (0.012)	0.016 (0.002)	11.54	0.5560 (0.013)	0.018 (0.001)	12.46	0.6220 (0.013)	0.021 (0.002)	20.55	0.6670 (0.012)	0.027 (0.001)	27.82
4.	SCCZTO-8h	0.5220 (0.012)	0.016 (0.001)	09.30	0.5683 (0.013)	0.020 (0.002)	13.76	0.5960 (0.012)	0.022 (0.001)	17.02	0.6300 (0.016)	0.023 (0.003)	23.91	0.6990 (0.011)	0.032 (0.003)	33.99
5.	SCCZTO-12h	0.5880 (0.013)	0.018 (0.002)	16.03	0.6350 (0.017)	0.020 (0.001)	22.49	0.6560 (0.015)	0.025 (0.002)	25.90	0.7027 (0.014)	0.027 (0.002)	34.77	0.7256 (0.013)	0.036 (0.003)	39.83
6.	ZDDP	0.5110 (0.014)	0.018 (0.001)	08.41	0.5560 (0.014)	0.022 (0.001)	12.46	0.6220 (0.012)	0.024 (0.002)	20.55	0.6440 (0.014)	0.025 (0.003)	23.91	Fails	-	-

MWD= Mean wear scar diameter,  $\mu$ = Friction coefficient, MWV= Mean wear volume.



**Figure S1.** Determination of running-in wear rate by varying mean wear volume with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and SCCZTOs nanoparticles at 392N applied load



**Figure S2.** Determination of steady-state wear rate by varying mean wear volume with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate and SCCZTOs nanoparticles at 392N applied load

# Figure S3.a



## Figure S3.b



# Figure S3.c



## Figure S3.d







**Figure S3.** 3D-AFM images of the worn steel surface with and without SCCZTOs nanoparticles (1% w/v) in paraffin oil for 90 min test duration at 392N applied load: (a) Paraffin oil, (b) Zinc dibutyldithiophosphate, (c) SCCZTO-6h, (d) SCCZTO-8h and (e) SCCZTO-12h

Figure S4.a



Figure S4.b



**Figure S4.** EDX analysis data of the worn steel surface lubricated with paraffin oil in presence additives (1% w/v) for 30 min test duration at 588N applied load: (a) ZDDP and (b) SCCZTO-6h