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# Lanthanum dithiocarbamates as potential extreme pressure lubrication additives

Rashmi B Rastogi<sup>\*</sup>, Jiya L Maurya, Vinay Jaiswal and Dhanesh Tiwary

# Abstract

**Background:** The extreme pressure lubrication (EPL) properties of bipyridyl adducts of different lanthanum dithiocarbamates of the type LaL<sub>3</sub>·bipy (where LH = dimethyl dithiocarbamate (Me<sub>2</sub>DTCH), piperidine dithiocarbamate (PipDTCH), morpholine dithiocarbamate (MorphDTCH), and diphenyl dithiocarbamate (Ph<sub>2</sub>DTCH); bipy = 2,2'-bipyridyl) have been evaluated with a four-ball lubricant tester using steel balls of 12.7-mm diameter and molybdenum disulfide as a reference additive. Various tribological parameters, *viz.* mean wear scar diameter, friction coefficient, mean specific pressure, initial seizure load, 2.5-s seizure delay load, weld load, flash temperature parameter, mean Hertz load, pressure wear index, etc., have been determined. The surface topography of wear scar has been studied by atomic force microscopy and scanning electron microscopy. Energy-dispersive X-ray analysis has been performed to give the composition of the wear scar surface.

**Results:** Experimental results indicate that admixtures containing bipyridyl adducts of lanthanum dithiocarbamates in paraffin oil exhibit better EPL properties than paraffin oil alone or with a reference additive (MoS<sub>2</sub>).

**Conclusions:** In view of very high efficiency, the synthesized compounds can be recommended for their application as EPL additives.

Keywords: Lanthanum dithiocarbamates, Extreme pressure lubrication additives, SEM, EDX, AFM

# Background

Among organic sulfur compounds, dithiocarbamates are well known as antiwear agents or multifunctional additives to lubricants [1-8]. Investigations on tribological applications of dithiocarbamates of antimony, boron, bismuth, cerium, copper, lead, molybdenum, and zinc have been carried out [9,10]. The use of oil-soluble molybdenum dithiocarbamates as lubricant additives for reducing friction and wear, increasing load-carrying capacity, and promoting fuel economy and as antioxidants has been related to their structures and chemical properties [6]. Synergistic effect on frictional characteristics due to a combination of molybdenum dithiocarbamates and zinc dialkyl dithiophosphates has been studied in detail by many workers [11-17]. Junbin has investigated the antiwear synergism of borates and cadmium diamyl dithiocarbamate [16]. Boron-based dithiocarbamates have been recently found as good antiwear, friction modifier, thermally stable, miscible in oils, and environment-friendly additives compared

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Department of Applied Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India to commercial additives, such as zinc dialkyl dithiophosphates [8]. A few reports are also available on tribological properties of lanthanide dialkyl dithiocarbamates [17] and their phenanthroline adducts [5,18,19]. Recently, we have reported the synergistic activity of substituted thiosemicabazones and their zinc(II) complexes with organoborate [20,21]. We have also studied Schiff bases of salicylaldehyde with 1,2-phenylenediamine, 1,4-phenylenediamine, and 4,4'-diaminodiphenylenemethane as zero SAPs and ash-free antiwear additives and their synergistic interactions with borate ester [22]. The present work was undertaken with a view to synthesize bipyridyl adducts of lanthanum dithiocarbamates and evaluate their activity as extreme pressure (EP) additives with a four-ball tester in paraffin oil using steel balls of 12.7-mm diameter and molybdenum disulfide as a reference additive.

# Methods

# Materials



Analytical-grade reagents were used in the present investigation. Alloy steel-bearing balls of 12.7-mm diameter were used for testing. The composition of the balls was 0.53%

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## Surface study

A ZEISS SUPRA 40 scanning electron microscope (SEM; Oberkochen, Germany) coupled with energydispersive X-ray (EDX) was used to investigate the surface morphology and composition of the entire tribofilm on the rubbed surface of steel balls. A contact-mode atomic force microscope (model no. BT 02218, Nanosurf Easyscan 2 Basic AFM, Liestal, Switzerland) was used to investigate the surface roughness of worn surfaces with a Si<sub>3</sub>N<sub>4</sub> cantilever (CONTR type, Nanosensors, Neuchatel, Switzerland) having a spring constant of approximately 0.1 N/m and tip radii better than 10 nm.

## AFM roughness parameters

The AFM roughness parameters are as follows:

1 Line roughness

(a) Roughness average,  $R_a = \frac{1}{N} \sum_{l=0}^{N-1} |z(x_l)|$ (b) Root mean square,  $R_q = \sqrt{\frac{1}{N}} \sum_{l=0}^{N-1} z(x_l))^2$ (c) Peak valley height,  $R_y = A_p - A_v$ (d) Peak height,  $R_p$  = Highest value (e) Valley depth,  $R_v$  = Lowest value (f) Mean value,  $R_m = \frac{1}{N} \sum_{l=0}^{N-1} z(x_l)$ 

2 Area roughness

(a) Roughness average,  

$$S_{a} = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} |z(x_{k}, y_{l})|$$
(b) Root mean square,  

$$S_{q} = \sqrt{\frac{1}{MN}} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} (z(x_{k}, y_{l}))^{2}$$
(c) Peak valley height,  $S_{y} = S_{p} - S_{v}$ 
(d) Peak height,  $S_{p}$  = Highest value

Table 1 Physicochemical properties of neutral liquid paraffin oil

Physicochemical properties	Value
Specific gravity at 25°C	0.82
Kinematic viscosity at 40°C	30 cSt (3 $\times$ 10 <sup>4</sup> Pa·s)
Kinematic viscosity at 100°C	5.5 cSt (5.5 $\times$ 10 <sup>4</sup> Pa·s)
Viscosity index [23]	122
Cloud point	-2°C
Pour point	-8°C
Flash point	180°C
Fire point	200°C

(e) Valley depth,  $S_v = \text{Lowest value}$ (f) Mean value,  $S_m = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} z(x_k, y_l)$ 

# **Results and discussion**

The observed tribological data for different additives along with the reference additive are recorded in Table 2.

Figure 1 illustrates variation of the mean wear scar diameter as a function of applied load. In general, the nature of the graph is the same for all the additives. Initially, the wear scar diameter increases very slowly with increase in load. The slow increase in mean wear scar diameter is ascribed to the formation of a thin film of lubricant and additive adsorbed on the sliding surface. The first discontinuity in the graph appears at initial seizure load (ISL) when desorption of the additive just starts. The region of the wear-load curve up to ISL is known as the antiwear region, and beyond that, it is termed as the extreme pressure region. After ISL, there is a steep rise in wear scar diameter up to the 2.5-s seizure delay load (2.5 s SDL), the second discontinuity where desorption is completed resulting into very large wear scar. The desorption process might have been accelerated by an increase in temperature due to an increase in applied load. At 2.5 s SDL, the additive decomposes and the decomposition products interact with the surface, resulting into in situ formation of a combined layer of lanthanum/iron oxide/sulfide, etc., salts and alloys. These metal compounds and alloys possess very low shear strength; therefore, the increase in wear scar is very sluggish up to the weld load.

It is apparent that in the absence of additives, ISL is observed at a very low load, 549 N. In the presence of the reference additive, it is 617 N, while in the presence of new additives, its value rises between 784 and 1,235 N. Similarly, the value for 2.5 s SDL in the absence of an additive, 617 N, rises to 706 N in the presence of the reference additive and lies in the range of 882 to 1,392 N in the presence of the synthesized additives. This shows that all the compounds behave as efficient extreme pressure lubrication additives. However, the maximum values of ISL and 2.5 s SDL are observed in the case of lanthanum complex of dimethyl dithiocarbamate and piperidine dithiocarbamate, respectively, making them the best additives. The weld load could not be observed in any case because all the tested compounds weld beyond 4,900 N and testing could be done up to 4,900 N only by the four-ball tester.

The effect of applied load on the friction coefficient in paraffin oil with or without additive is depicted in Figure 2. Initially, the friction coefficient is low up to ISL. At ISL, it starts increasing, reaches maximum at 2.5 s SDL, and then recovers it partially. Thus, the curves for all additives are characterized by a peak representing the region ISL-2.5 s SDL approaching the weld load. The variation in friction

Serial number	Lubricants	ISL (N)	Observation at ISL		2.5 s SDL	Observation at JBWL			WL (N)	FTP (max)	Load wear	PWI (N/mm <sup>2</sup> )		
			<b>d</b> *	μ*	P <sub>m</sub> (N/ mm <sup>2</sup> )	(N)	Wear load (N)	d*	μ*	P <sub>m</sub> (N/mm <sup>2</sup> )			index	
1	Plain paraffin oil (without additive)	549	0.65	0.162	56	617	1,098	2.93	0.398	66	1,235	132.54	142	30.00
2	Paraffin oil + [La(MorphDTC) <sub>3</sub> bipy]	784	0.69	0.052	1,333	882	4,900	2.50	0.167	408	>4,900	255.00	583	28.71
3	Paraffin oil + [La(PipDTC) <sub>3</sub> bipy]	784	0.44	0.022	2,136	1,372	4,900	2.34	0.116	465	>4,900	210.00	663	56.84
4	Paraffin oil + [La(Ph <sub>2</sub> DTC) <sub>3</sub> bipy]	980	0.58	0.020	1,525	1,098	4,900	2.44	0.087	427	>4,900	215.00	613	42.63
5	$Paraffinoil + [La(Me_2DTC)_3bipy]$	1,098	0.68	0.080	1,231	1,235	4,900	2.42	0.087	435	>4,900	257.40	711	54.88
6	Paraffin oil + reference additive $(MoS_2)$	617	0.86	0.036	434	706	1,960	2.81	0.106	144	2,195	160.00	294	47.63

Table 2 Tribological parameters for paraffin oil in the presence and absence of different additives at different loads

 $d^*$  = mean wear scar diameter,  $\mu^*$  = friction coefficient,  $P_m$  = mean specific pressure at contact points.

coefficient with increase in applied load can be explained similarly as above. Thus, the adsorption of the additive on the ball surface resists the increase in friction up to ISL, desorption followed by decomposition causes abrupt increase in its value, and formation of a tribofilm made up of triboactive metal compounds and alloys again resists further increase in its value.

Figure 3 exhibits the correlation between  $P_{\rm m}$  and the applied load in paraffin oil in the absence and presence of additives. The nature of the curves is approximately similar. The  $P_{\rm m}$  at contact point decreases steeply up to 2.5 s SDL and then increases slightly to attain almost a constant value. Figure 3 shows that in plain paraffin oil,  $P_{\rm m}$  decreases from 56 to 6 N/mm<sup>2</sup> and then increases to 66 N/mm<sup>2</sup>, whereas with the MorphDTC derivative of lanthanum,  $P_{\rm m}$  decreases from 1,333 to 18 N/mm<sup>2</sup> and then rises again to 408 N/mm<sup>2</sup>. Similarly, with the PipDTC derivative, these values are 2,136, 43, and 465 N/mm<sup>2</sup>, respectively; for the Ph<sub>2</sub>DTC derivative, 1,525, 16, and 427 N/mm<sup>2</sup>, respectively; for the Me<sub>2</sub>DTC

derivative, 1,231, 28, and 435 N/mm<sup>2</sup>, respectively; while for the reference additive, 706, 63, and 144 N/mm<sup>2</sup>, respectively. The values of  $P_{\rm m}$  for paraffin oil alone and different additives indicate that all of the synthesized additives appear to be promising extreme pressure additives, but the best behavior is exhibited by dimethyl and piperidine dithiocarbamate complexes.

# Surface studies

AFM and SEM have been used to study the surface topography of the wear scar on the steel balls formed after extreme pressure testing in paraffin oil in the presence of bipyridyl adduct of lanthanum(III) piperidine dithiocarbamate. The roughness parameters obtained through processing of the AFM images by the instrument software are collected in Table 3. Figure 4a,b displays two- and threedimensional (deflection) images of the wear scar, respectively, at ISL. Figure 4c,d shows the images at 2.5 s SDL, while Figure 4e,f exhibits the images just before weld load (JBWL). It is evident from the data and the figures that at



ISL (784 N), the roughness of the surface is low ( $S_a$  32.608 nm), and it increases to 89.225 nm at 2.5 s SDL (1,372 N) and 96.763 nm at JBWL (4,900 N). Thus, with increase of 10% applied load (from ISL to 2.5 s SDL), the roughness has increased by 173%, but with further increase of load of about 3,528 N (257%, from 2.5 s SDL to JBWL), roughness has increased by about 8% only. This correlation of magnitude of applied load and the observed roughness can be satisfactorily explained by taking into account the decomposition of the additive at 2.5 s SDL, resulting into formation of a tribologically active chemical film of lanthanum and iron compounds which does not allow the roughness to increase to that extent.

The SEM micrographs in the presence of lanthanum complex of piperidine dithiocarbamate are presented in  $\times 100$  and  $\times 500$  magnifications at JBWL in Figure 5. It is

evident from the SEM micrographs at JBWL that smoothening of the surface occurred due to decomposition of the additive, leading to formation of low-shearing metal compounds in the tribofilm.

The EDX spectrum of the wear scar in the presence of the above additive at JBWL is shown in Figure 6. The EDX analysis shows the presence of nitrogen, sulfur, and lanthanum on the worn surface (Table 4). The EDX spectrum in conjunction with a very slow increase in the wear scar diameter and friction coefficient after 2.5 s SDL provides an evidence in favor of the reported mechanism that decomposition products of the additive interact with the metal surface to form a chemical film of lanthanum and iron compounds, namely sulfides/alloy, etc., that satisfactorily bears the load until the weld load is reached.





Roughness parameter	[La(PipDTC)₃bipy]						
	ISL (784 N)	2.5 s SDL (1,372 N)	JBWL (4,900 N)				
Area roughness (area = $2.496 \text{ nm}^2$ )							
S <sub>a</sub>	32.608 nm	89.225 nm	96.763 nm				
Sq	43.218 nm	138.3 nm	127.35 nm				
Sy	265.56 nm	3.3386 µm	962.95 nm				
Sp	166.38 nm	1,418.5 nm	601.27 nm				
Sy	–99.175 nm	-1,920.1 nm	-361.68 nm				
S <sub>m</sub>	131.81 pm	139.06 pm	125.3 pm				
Line roughness							
R <sub>a</sub>	32.945 nm	49.13 nm	43.024 nm				
R <sub>q</sub>	40.945 nm	57.624 nm	51.863 nm				
Ry	176.31 nm	188.53 nm	255.74 nm				
Rp	119.78 nm	82.671 nm	65.23 nm				
R <sub>v</sub>	-56.536 nm	–105.86 nm	–190.51 nm				
R <sub>m</sub>	129.56 pm	138.94 pm	123.6 pm				

Table 3 Surface roughness parameters obtained from the digital processing software for [La(PipDTC)<sub>3</sub>bipy] at different loads

# **Experimental**

# Synthesis of additives

Bipyridyl adducts of lanthanum dithiocarbamates of general formula  $LaL_3$ ·bipy (where LH = dimethyl dithiocarbamate (Me<sub>2</sub>DTCH), piperidine dithiocarbamate (PipDTCH), morpholine dithiocarbamate (MorphDTCH), and diphenyl dithiocarbamate (Ph<sub>2</sub>DTCH)) were prepared by mixing alcoholic solutions of lanthanum chloride, sodium salts of dithiocarbamates, and bipyridyl [18,24]. Structures and acronyms of the dithiocarbamates used in the present investigation are given in Figure 7.

The sodium salts of dithiocarbamates were prepared according to the following reaction by the reported method [25]:

$$R_2NH + CS_2 \xrightarrow[4^\circ C]{\text{Ethanol}}_{4^\circ C} R_2CS_2Na.$$

The equation for the synthesis of the bipyridyl adduct of lanthanum(III) piperidine dithiocarbamate is given below:

$$LaC1_3.7H_2O + bipy + 3 PipDTC \xrightarrow{\text{Ethanaol}} [La(PipDTC)_3(bipy)]$$

The adduct was prepared by mixing solutions of 0.03 mol (5.5 g) piperidine dithiocarbamate in 30 ml of ethanol and 0.01 mol (3.71 g) lanthanum chloride in 15 ml of ethanol. To this mixture, 0.1 mol of 2,2'-bipyridyl was added slowly. The mixture was stirred and left to stand for several hours; the complex precipitate was filtered, washed several times with ethanol, and dried *in vacuo*. A single spot observed in TLC of the adducts in a solvent mixture containing 60% dimethyl sulfoxide (DMSO),

20% ethyl alcohol, and 20% water indicates that the complexes formed are new entities and not a mixture of reactants and or products.

# Characterization of additives

The structure of bipyridyl adducts of lanthanum dithiocarbamates was elucidated on the basis of elemental analysis, molar conductance, and infrared (IR) data. On the basis of the analytical data presented in Table 5, the general formula LaL<sub>3</sub>·2,2'-bipy (where LH = dimethyl dithiocarbamate (Me<sub>2</sub>DTC<sup>-</sup>), piperidine dithiocarbamate (PipDTC<sup>-</sup>), morpholine dithiocarbamate (MorphDTC<sup>-</sup>), and diphenyldithiocarbamate (Ph<sub>2</sub>DTC<sup>-</sup>); bipy = 2,2'-bipyridyl) is proposed for the synthesized complexes. The complexes are insoluble in common organic solvents but soluble in coordinating solvents like DMF, DMSO, etc. Molar conductance values of the complexes are indicative of their nonionic behavior. Magnetic susceptibility measurements show the diamagnetic nature of the complexes.

# **IR** spectra

The characteristic absorption frequencies of the lanthanum complexes are presented in Table 6. IR spectra of dithiocarbamates exhibit strong bands at about 1,450 and 980 cm<sup>-1</sup> due to vC-N and C-S stretching vibrations, respectively. These bands undergo a positive shift of 25 to 40 and 5 to 25 cm<sup>-1</sup>, respectively, in the corresponding lanthanum complexes. Thus, IR data indicate bidentate behavior of dithiocarbamate moiety [26-29]. The bands at 1,598, 1,562, and 769 cm<sup>-1</sup> are characteristic bands of coordinated 2,2'-bipy. The weak intensity



(784 N), (**c**, **d**) 2.5 s SDL (1,372 N), (**e**, **f**) JBWL (4,900 N).

bands at  $380 \pm 10$  and  $305 \pm 10$  cm<sup>-1</sup> in the far IR region are due to vLa-N and vLa-S vibrations [30].

On the basis of analytical, IR, and electronic spectral data, the structure in Figure 8 is proposed for bipyridyl adducts of lanthanum(III) dithiocarbamates.

# Test procedure for EPL additives

The tests were performed at 1,475 rpm (equivalent to a sliding speed of 567 mm/s) using different loads for a 1-min time duration [31,32]. Three types of springs were used according to the range of load: a weak spring for a

load of up to 784 N, a medium spring for loads from 784 to 3,920 N, and a stiff spring for loads from 3,920 to 7,840 N. The synthesized additives/MoS<sub>2</sub> (reference additive, 0.5% w/v) were mixed with paraffin oil, and the mixture was heated up to 60°C with continuous stirring to make a uniform suspension. The Seta-Shell Four-Ball EP Testing Machine (Stanhope Seta, London, UK) was used to perform the tests. The extreme pressure testing experiments were performed in triplicate, and the mean values of the experimental data were used to determine tribological parameters employing standard procedures

Figure 5 SEM micrographs of the worn steel surface lubricated with  $[La(PipDTC)_3bipy] 0.5\% w/v$  concentration at JBWL.

# Iubricated with [La(PipDTC)3bipy] (0.5% w/v) at JBWLElementAtomic per

Table 4 EDX analysis data of the worn steel surface

Element	Atomic percent
NK	04.70
SK	03.79
LaL	00.56
CrK	00.38
FeK	90.57

 $\mathsf{Matrix} = \mathsf{ZAF}.$ 

prescribed by the manufacturer [33]. For the purpose of illustration, a wear-load curve ABCD is shown diagrammatically in Figure 9.

# Measured parameters

# Hertz line

The Hertz line is obtained by plotting the load against the calculated value of Hertz diameter  $(d_h)$ . The Hertz line indicates the diameter of the contact area  $(d_h)$  produced by the elastic load.

Diameter of contact area  $(d_h)$ 

$$= 8.77 \times 10^{-2} \sqrt[3]{P}(mm),$$

where *P* is the applied load.

# Initial seizure load

The initial seizure load (ISL) is the load at which the wear-load line deviates from the Hertz line. It shows the commencement of plastic deformation of the balls.







# Weld load

The weld load (WL) is the load at which lubricants fail completely and so much heat is generated that the fusion of metal between the rubbing surfaces occurs. It is detected by apparent fusion of the rubbing surfaces of steel balls. It is reported by point D in Figure 9.

# Second seizure delay load of 2.5 s

The load for which the seizure delay is 2.5 s provides a reliable method for testing the protection against seizure afforded by the lubricant used in gears. This load corresponds with the second discontinuity at point C in the wear-load curve (Figure 9).

#### Mean Hertz load

The mean Hertz load (MHL) is a single number reported as a load in Newton which is used to express the overall wear-load plot that covers loads from well below seizure to welding. It may be expressed as

$$MHL = \frac{\sum_{i=l}^{n} \frac{P_i \cdot d_{hi}}{d_i}}{n}$$

1

where *P* is the applied load,  $d_h$  is the Hertz diameter, *n* is the total number of occurrences, and *d* is the mean wear scar diameter.

# Mean specific pressure

The mean specific pressure  $(P_m)$  over the area of contact may be expressed as

$$P_m = 52P/d^2 \times 100 (N/mm^2),$$

where  $P_{\rm m}$  is the mean specific pressure at contact points (N/mm<sup>2</sup>), *P* is the applied load (N), and *d* is the mean wear scar diameter (mm).

Table 5 Analytical data and general behavior of the lanthanum(III) dithiocarbamate bipyridyl complexes

Complex	Color	C% found (calculated)	H% found (calculated)	N% found (calculated)	La% found (calculated)
[La(Me <sub>2</sub> DTC) <sub>3</sub> (bipy)]	White	35.00 (34.81)	3.98 (3.97)	10.60 (10.68)	20.50 (21.22)
[La(PipDTC) <sub>3</sub> (bipy)]	White	43.15 (43.35)	4.95 (4.90)	9.00 (9.03)	17.86 (17.94)
[La(MorphDTC) <sub>3</sub> (bipy)]	White	38.00 (38.41)	4.10 (4.09)	8.85 (8.96)	17.50 (17.79)
[La(Ph <sub>2</sub> DTC) <sub>3</sub> (bipy)]	White	57.22 (57.25)	3.72 (3.70)	6.82 (6.81)	13.52 (13.53)

Table 6 IR adsorption bands (cm<sup>-1</sup>) of the lanthanum(III) dithiocarbamate bipyridyl complexes

Complex	v (C-N)	v (C-S)	v (Віру)
[La(Me <sub>2</sub> DTC) <sub>3</sub> (bipy)]	1,479	1,005	1,600, 1,565, 769
[La(PipDTC) <sub>3</sub> (bipy)]	1,475	995	1,598, 1,562, 770
[La(MorphDTC) <sub>3</sub> (bipy)]	1,487	985	1,602, 1,561, 772
[La(Ph <sub>2</sub> DTC) <sub>3</sub> (bipy)]	1,490	990	1,597, 1,562, 768

# Flash temperature parameter

The flash temperature parameter (FTP) is a number used to express the critical temperature above which a lubricant will fail under given conditions. For conditions existing in the four-ball machine, the following relationship is used:

$$FTP = \frac{P}{d^{1.4}}(\max),$$

where *P* is the applied load, *d* is the mean wear scar diameter (mm), and FTP is the maximum value of the ratio  $P/d^{1.4}$  (max) obtained for various runs.

#### Pressure wear index

Pressure wear index (PWI) represents antiwear and antiseizure properties of oil. PWI is represented as

$$PWI = P_2 - P_1/d_2^2 - d_1^2,$$

where  $P_1$  and  $d_1$  are the load and mean wear scar diameter, respectively, corresponding to ISL and  $P_2$  and  $d_2$  are the load and mean wear scar diameter, respectively, corresponding to the second discontinuity observed from the load versus wear scar plot.





*Friction coefficient* Friction coefficient ( $\mu$ ) is represented as

$$\mu = \frac{0.22F.L}{P},$$

where F is the friction force exerted on the indicator spring (N), L is the length of the torque lever arm (mm), and P is the applied load (N).

# Conclusions

On the basis of the data discussed above, it is apparent that the weld load for all the synthesized additives is observed to lie beyond 4,900 N and all of them behave as highly effective extreme pressure lubrication additives. Though there is not much difference, the best efficiency is shown by piperidine and dimethyl derivatives.

#### **Competing interests**

The authors declare that they have no competing interests.

#### Authors' contributions

RBR conceived and designed the study. JLM carried out most of the experiments. VJ carried out some of the experiments particularly using AFM. Both of them drafted the manuscript. DT helped in the surface studies. All authors read and approved the final manuscript.

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