

# Preparation and Performance of Novel Lubricating Oil Additives Derived from 2-Mercaptobenzothiazole

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**ABSTRACT:** Three 2-dialkylaminomethylthiobenzthiazoles were prepared, and their thermal stability, corrosion-inhibiting and lubricating characteristics as additives in lubricating oil were evaluated. The novel additives possess higher load-carrying capacity and better lubricating property.

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**KEY WORDS:** Lubricating oil additive, lubricating property, 2-mercaptobenzothiazole.

Zinc dialkyldithiophosphates (ZDDP) are widely used in lubricating oil, especially engine oil, both as antiwear agents and oxidation inhibitor (1,2). However, increasing concern over exhaust catalyst poisoning from the phosphorus element in ZDDP has promoted research to provide effective replacement additives. The preparation of novel additives derived from 2-mercaptobenzothiazole are described herein, and their thermal stability, corrosion-inhibiting and lubricating properties are evaluated.

## EXPERIMENTAL PROCEDURES

2-(Di-*n*-octylaminomethyl)thiobenzothiazole(III), prepared with a solution of di-*n*-octylamine (0.1 mol) in 50 mL ethanol, was added dropwise with stirring into a solution of 2-mercaptobenzothiazole (0.1 mol) and paraformaldehyde (0.1 mol) in 100 mL ethanol. The mixture was refluxed for 4 h. On removal of solvent, crystallization gave 2-(di-*n*-octylaminomethyl)-thiobenzothiazole (III) in 72% yield. Elemental analysis (%) was as follows: C: 68.81, H: 9.31, N: 6.76 (found); C: 68.57, H: 9.52 and N: 6.67 (required). <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) ( $\delta$  ppm): 7.4 (*m*, 4H, Phenyl), 5.2 (*s*, 2H, SCH<sub>2</sub>), 1.2 [*m*, 28H, 2(CH<sub>2</sub>)<sub>7</sub>], 0.9 (*m*, 6H, 2CH<sub>3</sub>). Other derivatives were prepared in a similar way.

The lubricating properties of the novel additives were evaluated by a four-ball machine under the following conditions: load: 294 N, testing time: 15 min, rotating rate: 1480 rpm and room temperature. The load-carrying capacity and corrosion-inhibiting properties of additives were carried out by American Society of Testing and Materials (ASTM) meth-

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ods (3,4). Thermal stability was evaluated by a Perkin-Elmer model 7 thermal analyzer system.

## RESULTS AND DISCUSSION

The authors previously reported that organic benzotriazole derivatives, such as *S*-(1H-benzotriazole-yl)-methyl *N,N*-dialkyldithiocarbamates, *S*-(1H-benzotriazole-yl)-methyl alkyl xanthates, are novel effective multifunctional lubricating oil additives (5,6). In this paper, we extended our research to benzothiazole derivatives. The Mannich salts of 2-mercaptobenzothiazole, 2-(dialkylaminomethyl)thiobenzothiazoles, were prepared from the reaction of dialkylamine and 2-mercaptobenzothiazole in the presence of paraformaldehyde as shown in Equation 1.



I (R = butyl), II (R = ibutyl) and III (R = octyl)

Bt = 2-benzothiazolyl [1]

The lubricating properties of these new compounds were evaluated at the concentration of 0.5% in base stock; the results are summarized in Table 1. For comparison, the performance of ZDDP, a commercial additive, is also included. An effective additive should have as high a Pb value and as small a wear scar diameter (WSD) as possible. We found that the novel additives are effective at reducing the wear and increasing the load-carrying capacity of base stock. The performance

**TABLE 1**  
Summary of Characteristics of 2-(Dialkylaminomethyl)-Thiobenzothiazole

Additives	Pb value <sup>a</sup> (N)	WSD <sup>b</sup> (mm)	Corrosion test	Thermal decomposition temperature (°C)
I	—	0.52	1a	—
II	—	0.54	2a	—
III	706	0.48	1a	181
ZDDP <sup>c</sup>	764	0.38	1a	—
Base stock	392	0.58	—	—

<sup>a</sup>Maximum no-scuffing load (N).

<sup>b</sup>Wear scar diameter (mm).

<sup>c</sup>Zinc dialkyldithiophosphates.

is similar to ZDDP. Furthermore, the novel additives have good thermal stability and excellent corrosion-inhibiting properties. Based on the above observations, it can be concluded that the benzothiazole derivatives are novel potential additives for use in lubricating oil.

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