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Borate Esters Used as Lubricant Additives

Abstract

Borate esters possess friction-reducing, antiwear, and anti-oxidant characteristics when blended in lubricating oils. However, borate esters are susceptible to hydrolysis. The formation of a stable five-member ring structure in the ester molecules, involving coordination of nitrogen with boron, contributes substantially to the resistance to hydrolysis of borate esters. The susceptibility of borates to hydrolysis can be reduced by introducing N,N-dialkylaminoethyl groups with alkyl radicals containing more than three carbon atoms. X-ray photoelectron spectroscopy and X-ray diffraction reveal that the borate ester can be adsorbed on the rubbing surface, and some of the adsorbed borate film degrades and forms boron nitride. Four-ball wear tests indicate that the combination of oil-soluble copper, tin, and cadmium compounds with organoborates gives better antiwear properties than the components separately. An antiwear synergistic mechanism is postulated in which borates with electron-deficient boron p orbitals catalyse the tribo-reduction of the metal compounds on the rubbing surfaces, producing elemental metals.

Keywords

borate esters, antiwear properties, lubricant additives, synergistic effects, hydrolytic stabilisation

INTRODUCTION

In recent years, much effort has been focused on the research and development of new types of friction-reducing and antiwear additives for lubricating oils. One such group of additives is borate esters.^{1,2} It is commonly accepted that these boron-containing compounds not only have excellent antiwear and antifriction characteristics, but also have good oxidation stability and compatibility with seals. Furthermore, they are non-volatile, relatively nontoxic, and have a pleasant odour. However, a serious drawback which has restricted the use of borate esters in lubricants is their susceptibility to hydrolysis, resulting in the liberation of oil-insoluble and abrasive boric acid.

Kreuz *et al.*³ studied the extreme-pressure properties of tribenzyl borate and found that borate films are heterogeneous structures containing both inorganic and organic components. Dong and co-workers found that some borates can form BN, FeB, and Fe₂B on rubbing surfaces.¹ Dong *et al.*¹ and Liu *et al.*⁴ showed the existence of borate adsorption films within the frictional zones. Baldwin⁵ examined the antiwear efficiency of a series of sulphur-containing borates and suggested that the sulphur, not the boron, plays a major role in the antiwear properties of such compounds.

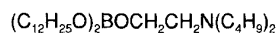
Oil-soluble organometallic compounds have also been used as antiwear lubricant additives.⁶ In the present paper, the antiwear synergism of borates and oil-soluble metal compounds is addressed, and the mechanism of the synergy is discussed.

EXPERIMENTAL

Wear tests were performed on a four-ball machine at 1450 rpm at ambient temperature. GCr15 steel balls (1.00% C, 1.50% Cr, 0.25% Si, and 0.0% Mn; $R_c = 62-65$) with a diameter of 12.7 mm were used. The test times were 10 and 30 min.

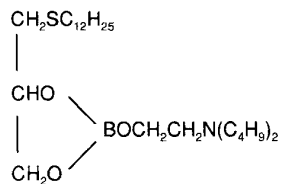
The chemical state of boron on the wear surfaces was analysed using X-ray photoelectron spectroscopy (XPS). The composition of the wear surfaces was examined by an 18 kW rotating anode X-ray diffractometer (XRD); a small quantity of substance can be detected directly with XRD due to the high energy. The topography and elemental compositions of the rubbing surfaces were examined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Before the XPS and XRD analyses, the wear sample was ultrasonically rinsed with hexane and petroleum ether for 10 min.

Paraffin oil was used as the base oil. Two borates,



N,N-di-*n*-butylaminoethyl-didodecyl borate (DBN)

and



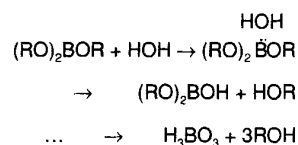
N,N-di-*n*-butylaminoethyl-3-(1'-mercaptododecyl)-1,2-propyl borate (SBN)

J.B. Yao, Q.L. Wang, S.Q. Chen, J.Z. Sun, and J.X. Dong: Borate esters used as lubricant additives

and three oil-soluble metal salts, copper oleate (CuOLE), dibutyl tin dilaurate (SnDBDL), and cadmium diamyldithiocarbamate (CdDDC), were evaluated in this study. The two borate additives have been reported previously.⁶⁻¹⁶

RESULTS AND DISCUSSION:
Hydrolytic stability improvement

The susceptibility of borates to hydrolysis is due to the existence of electron-deficient boron:



where R is an alkyl group. Some methods for improving the hydrolytic stability of borate esters are the following:

1. A hindered phenol inhibits hydrolytic attack on the boron-oxygen bonds.¹⁷
2. The hydrolytic stability is improved by the addition of amine compounds which have non-bonding pairs of electrons. These amines coordinate with the electron-deficient boron atom, preventing hydrolysis.¹⁸
3. The hydrolytic degradation of borates is inhibited by the incorporation of certain diols in the lubricant formulation. They react with the boric acid produced by hydrolysis of borate esters to form stable five-member ring structures.¹⁹

However, these methods do not achieve hydrolytic stability in use. In addition, a series of other problems, such as poor oil solubility and high viscosity, are also encountered.

A new solution to the problem of the hydrolytic stability of borate esters is described here. It can be improved by introducing an aminoethyl group into the molecules of such compounds to form a stable five-member ring structure involving coordination of the nitrogen atom with boron:

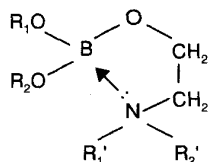
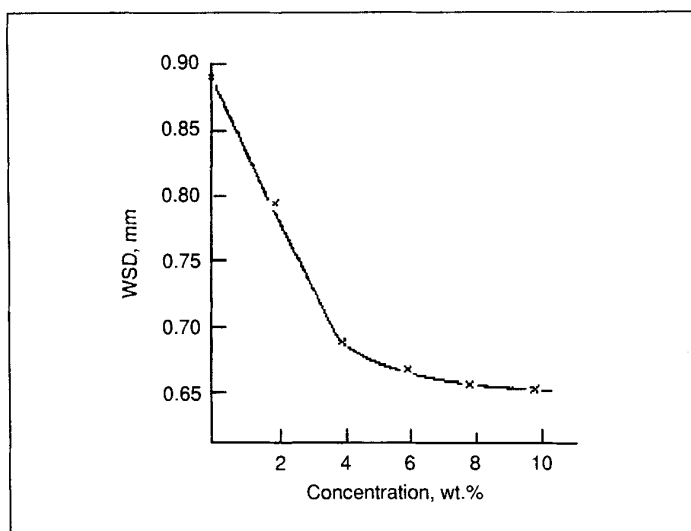


Figure 1 Effect of borate (DBN) concentration on antiwear properties



where R_1, R_2 are the same or different alkyl groups. The larger the attached alkyl groups on the nitrogen, the stronger their electron-donating effect; therefore, the electron density of the nitrogen atom increases. This may enhance the coordination with boron and decrease the possibility of hydrolytic attack on the boron–oxygen bonds, potentially also improving the hydrolytic stability of the borate esters. When the alkyl radicals on the nitrogen, i.e., R_1', R_2' , contain more than three carbon atoms, excellent hydrolytic stability of borate esters is possible.

Antiwear function and mechanism of borates containing nitrogen

The wear tests were performed on the four-ball tester under a load of 392 N. **Figure 1** shows the effect of borate (DBN) concentration on the antiwear properties. The wear-scar diameters (WSDs) were obtained after 10 min duration tests. It was found that the antiwear capacity increases with increasing borate concentration, although this tendency is less significant for concentrations greater than 5.0 wt.%.

To investigate the antiwear mechanism of the borate ester, the surface film on the four-ball wear scar was analysed using XPS. The result is shown in **Figure 2**. The B 1s binding energies on the rubbing surfaces are 192 and 190.3 eV, suggesting the presence of borate ester and boron nitride.^{1,4,20} The

J.B. Yao, Q.L. Wang, S.Q. Chen, J.Z. Sun, and J.X. Dong: Borate esters used as lubricant additives

Figure 2 Binding energy of B 1s on rubbing surface

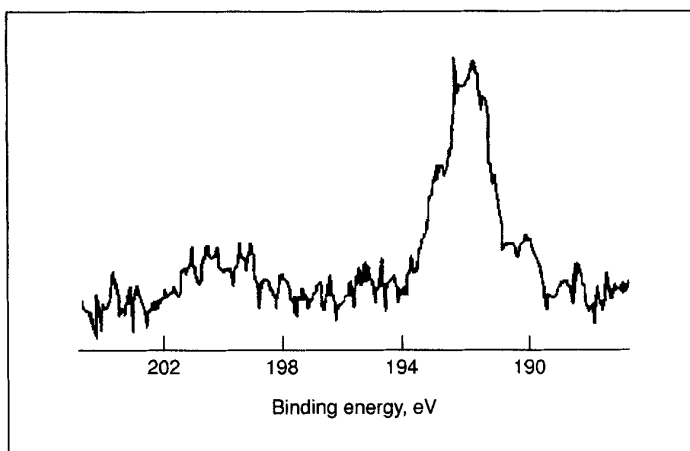


Figure 3 Standard B 1s XPS of boron nitride

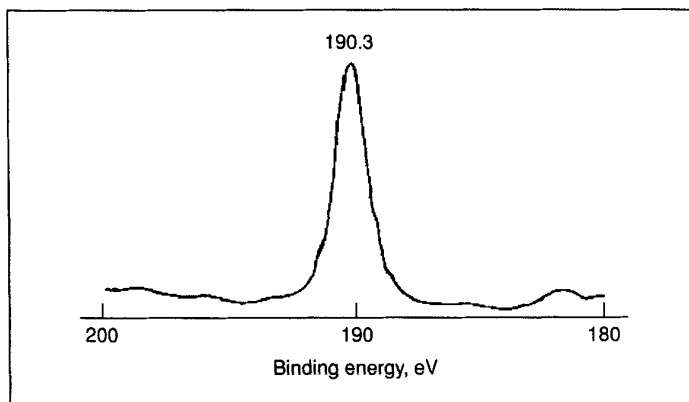
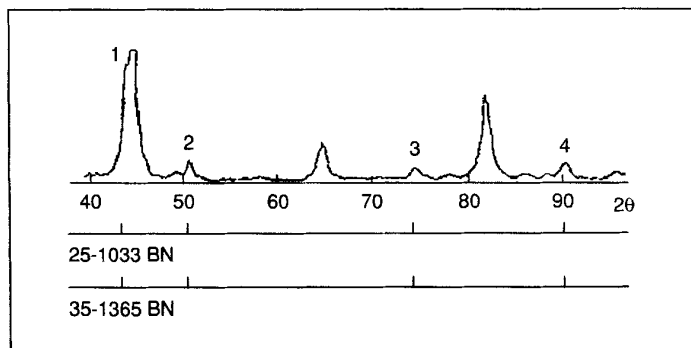


Figure 4 Powder diffraction pattern search/match report



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