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Bismuth Sulfide (Bi₂S₃) as the Active Species in Extreme Pressure Lubricants Containing Bismuth Carboxylates and Sulfur Compounds

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A series of bismuth carboxylates were tested with active and inactive sulfur compounds as extreme pressure (EP) lubricant additives. Wear and load measurements from four-ball tests are reported. Bismuth 2-ethylhexanoate (Bi 2EH), bismuth neodecanoate (Bi NDA) and bismuth naphthenate (Bi Nap) showed excellent EP activity with both active and inactive sulfur compounds (\geq 620 kg four-ball weld load). The mechanism of the EP lubricity was studied using thermogravimetric analysis (TGA), high-temperature X-ray diffraction (HTXRD), and scanning electron microscopy with energy-dispersive Xray spectroscopy (SEM-EDS). The results of these studies support the formation of bismuth sulfide during thermolysis of the bismuth carboxylate-polysulfide mixtures. The structure of bismuth sulfide suggests that interlayer shear occurs and provides lubricity.

KEY WORDS

Extreme Pressure Additives; Bismuth Carboxylates; X-Ray Diffraction (XRD); Thermogravimetric Analysis (TGA); Scanning Electron Microscopy (SEM)

INTRODUCTION

The field of lubricant additives is extremely diverse, with functional types ranging from antiwear to viscosity modifiers used in finished fluids. The demands placed on lubricants in these myriad applications mean that the formulator must include a series of specific additive types to improve performance whether the product is a fluid or grease. Within each additive type, there are also a number of chemistries that can be selected. The choices made are critical in enhancing lubricant properties.

Most lubricants are required to operate under severe boundary lubrication regimes in which there is close contact between metal surfaces. If the correct additive types are not selected, the chances for rubbing and welding can increase, leading to machinery failure.

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Extreme pressure (EP) additives fill the role by providing the needed properties to ensure that applications operating under severe conditions can continue without interruption. The main classes of EP additives have been based on chlorinated, phosphorus-containing (Beiswansen et al. (1)), sulfur-derived (Rohr (2)), and overbased sulfonate materials.

The first three extreme pressure additive types operate at specific temperature ranges in which they react with the metal surface to form iron chloride, iron phosphide, and iron sulfide salts (Beiswansen (1); Rohr (2)). These species produce a boundary that reduces friction, wear, and metal scoring while minimizing the chances of welding. Overbased sulfonates form a colloidal carbonate salt that acts as a barrier between metal surfaces (Cahoon et al. (3)).

A specific type of extreme pressure additive that has been used widely as a solid lubricant is molybdenum disulfide (MoS_2). When coated on a metal surface, this additive reduces the friction and is able to provide good antiwear characteristics (Boozer (4)). When used in oil-based systems under EP conditions, molybdenum coordination compounds deposit MoS_2 in situ. Molybdenum dithiocarbamates are one class of compounds used as EP additives in oil-based systems. Solid MoS_2 is often used in greases. While MoS_2 -based EP additives are highly competent, many people are currently seeking alternatives based on the decreasing availability of such materials. Molybdenum is currently trading at relatively low prices, but the recent tumultuous nature of the price and supply of molybdenum has led many to search for alternative EP additives.

Unfortunately, users of some of these EP additives have been faced with environmental problems and/or cost concerns. Shortchain chlorinated paraffins have the unattractive potential to bioaccumulate, and, as possible carcinogens and aquatic toxins, they pose potentially serious environmental issues (CPIA website, (5)). Additionally, organophosphates are potent neurotoxins and, thereby, pose an immediate and severe threat to humans (ATSDR website (6)). However, of the organophosphates used in the lubricant industry, only ortho-cresol phosphate esters have been classified as neurotoxins.

Bismuth carboxylates are excellent alternatives to the current EP additives. In addition to their EP activity, bismuth carboxylates are environmentally benign. Bismuth is nontoxic and

Base Stock

is currently used in several products requiring human contact and/or ingestion. The most well-known is bismuth subsalicylate, Bi(OH)(salicylate), the main component of prevalent antidiarrheal treatments (National Institutes of Health website (7)). Others include bismuth subnitrate, BiO(NO₃), and bismuth subcarbonate, Bi₂O₂(CO₃), which are used in radiopaque catheters (Drewes and Taylor (8)). Nanotubes of bismuth subcarbonate have shown antibacterial properties (Chen et al. (9)).

In this study, we show that bismuth carboxylates are excellent EP lubricant additives. Using detailed lubricant studies, we provide further understanding of the synergism between bismuth carboxlyates and sulfurized additives for EP lubricants, first shown to exist by Rohr earlier in this decade (Rohr (10)). Characterization of the material resulting from thermolysis of mixtures of bismuth carboxylates and sulfurized additives shows that bismuth sulfide (Bi₂S₃) is generated under EP or high-temperature conditions. We employ solid-state structural tools, such as Xray diffraction (XRD) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), to identify the residue remaining after the bismuth/sulfur mixtures are subjected to EP or high-temperature conditions. The fact that Bi₂S₃ is a layered solid strongly suggests that interlayer shear provides lubricity in the reported tests.

EXPERIMENTAL

All bismuth carboxylates were prepared by the Shepherd Chemical Company. The sulfur compounds were supplied by Arkema Chemical, Rhein Chemie, and Chevron Phillips. The six sulfur compounds are labeled throughout the text and figure captions as Active Sulfur A, B, and C (AS A, B, or C) and Inactive Sulfur A, B, and C (IS A, B, or C).

Samples for EP testing were sent to Petro-Lubrication Testing Laboratories, Inc. in Lafayette, New Jersey. The samples were prepared with 2.5–7.0 wt.% bismuth carboxylate, 0.25–1.0 wt.% sulfur compound, and 82–97.25 wt.% base oil, consisting of Chevron Phillips N100 (Group II) and Bright Stock mixed to an 80 w 90 viscosity (see Table 1). Four-ball tests were performed according to ASTM methods and included ASTM D 2783 and ASTM D 4172. The steel balls from one set of experiments were returned to the Shepherd Chemical Company for further testing.

TGA data were collected on a SDT 2960 (TA Insts., New Castle, DE). Experiments were run from ambient temperature to 800°C under air or nitrogen with a flow rate of 110 mL/min. The samples were 15–25 mg and contained in 300 μ L platinum pans. Temperature-mass points were collected every 7.5 s.

X-ray diffraction data were collected on a d-max 2100 diffractometer (Rigaku Corp., Tokyo). High temperature was provided by a resistive furnace controlled with a PTC-20A. A flow of nitrogen at ~1 L/min was used. The temperature ramp was 10°C/min. After a 30-min hold at 250°C, data were collected in 0.02° 2 θ steps for 8° $\leq 2\theta \leq 80^\circ$. A second data set was collected after an additional hour hold. Simulated diffraction patterns were either derived from d-I lists in the PDF-4+ database (ICDD, Newtown Square, PA) or calculated from published crystallographic parameters, as noted in the text.

Scanning electron microscope images were collected on an ABT-60 (Topcon, Tokyo) using 20 kV accelerating potential and

Group II	Bi NDA (5.0)	AS A (0.4)	PE (1.0)
Group II	Bi NDA (5.0)	IS A (1.0)	PE (1.0)
Group II	Bi NDA (2.5)	IS A (1.0)	_
Group II	Bi NDA (7.0)	IS A (1.0)	_
Group II	Bi NDA (5.0)	AS B (0.25)	_
Group II	Bi NDA (5.0)	IS B (0.75)	_
Group II	Bi NDA (5.0)	AS C (0.25)	_
Group II	Bi NDA (5.0)	IS C (1.0)	_
Group II	Bi 2EH (5.0)	AS A (0.4)	PE (1.0)
Group II	Bi 2EH (5.0)	IS A (1.0)	PE (1.0)
Group II	Bi 2EH (2.5)	IS A (1.0)	_
Group II	Bi 2EH (5.0)	AS B (0.25)	_
Group II	Bi 2EH (5.0)	IS B (0.75)	_
Group II	Bi 2EH (5.0)	AS C (0.25)	_
Group II	Bi 2EH (5.0)	IS C (1.0)	_
Group II	Bi Nap (5.0)	AS A (0.4)	PE (1.0)
Group II	Bi Nap (5.0)	IS A (1.0)	PE (1.0)
Group II	Bi Nap (2.5)	IS A (1.0)	_

Sulfur Cpd

(%)

TABLE 1-SAMPLE BLENDS USED IN THIS WORK

Bi C_v

(% loading)

a 1.1 μ m spot size. X-ray spectra were collected from 0.10 to 20.58 keV in 2048 channels for 30 s with a liquid N₂ cooled Si(Li) detector (EVEX, Princeton, NJ). Count rates were typically ~1460 s⁻¹. For elemental analysis and mapping, 2keV windows (FWHM) were identified around the following peaks: C_{Ka} (0.28 keV), S_{Ka} (2.31 keV), Fe_{Ka} (6.40 keV), and Bi_{La1} (10.84 keV). The EDS images were collected in 256² points with a count time of 0.5 s per point and a cutoff of two counts.

RESULTS AND DISCUSSION

Four-Ball Testing

Several samples, comprised of one bismuth carboxylate loaded at 5 wt.% and one sulfur compound (active or inactive) loaded at 0.4–1.0 wt.% with the remaining 94.0–94.6 wt.% being base-stock (Group II with Bright Stock), were tested using ASTM methods on a four-ball apparatus. The samples were evaluated by ASTM D 2783 and ASTM D 4172 to measure EP and antiwear lubricant properties, respectively. The bismuth carboxylates tested were bismuth 2-ethylhexanoate (Bi 2EH), bismuth naphthenate (Bi Nap), and bismuth neodecanoate (Bi NDA). The sulfur compounds used in the majority of experiments were AS A and IS A. Table 1 shows the test fluid compositions.

The results of the four-ball weld-load tests are shown in Fig. 1. From the data it is obvious that the samples have considerable EP activity against the welding of metal surfaces. The samples all gave a 600 kg or higher weld point, far higher than any of the additives alone. Specifically, we note that neither the bismuth carboxylates nor the sulfur compounds give individual weld points higher than 300 kg (Fig. 2). Phosphate esters are often added to lubricant systems for an enhancement in antiwear (AW) activity. In our systems we saw little to no effect in AW or EP activity when phosphate esters were mixed with bismuth carboxylates and sulfur compounds. The high values of weld points for the

Phosphate Ester

(%)



Fig. 1—Weld-load results from four-ball test, ASTM D 2783. Dark grey = AS A (0.4%); white = IS A (1.0%). All bismuth carboxylates were loaded at 5 wt.%. NDA = neodecanoate; 2EH = 2-ethylhexanoate; Nap = naphthenate; control = only polysulfide.

bismuth carboxylate-polysulfide mixtures support a synergy between the two types of materials. Furthermore, this synergy is indicative of an active intermediate related to bismuth sulfide, Bi_2S_3 .

The effect of bismuth concentration is shown in Fig. 3. Samples were adjusted to 2.5 wt.% bismuth carboxylate and 7.0 wt.% bismuth carboxylate. As expected, lowering the bismuth carboxylate concentration also lowers the weld point for the sample. However, even at 2.5 wt.% bismuth carboxylate loading, the weld points are all near 500 kg, equating to moderate EP activity. Increasing the concentration of bismuth carboxylate gives the maximum value for weld point, 800 kg, the same as the sample with 5.0 wt.% bismuth carboxylate. It should be noted that the samples were tested for scarring as well but showed poor to moderate antiwear properties. This result is anticipated because high wear rates are observed under the severe conditions that require extreme pressure additives (Tysoe and Kotivs (11)).

We also prepared samples with additional sulfur compounds to test the scope of the EP activity (AS B, IS B, AS C, and IS C). The data shown in Fig. 4 offer evidence that the bismuth carboxylates show EP properties regardless of the sulfur source. Despite



Fig. 2—Weld-load results from four-ball test, ASTM D 2783, for the control samples. Black = Bi 2EH loaded at 5.0 wt.%; blocked = phosphate ester loaded at 1.0 wt.%; white = AS A loaded at 0.4 wt.%; striped = IS B loaded at 1.0 wt.%; grey = phosphate ester (1.0 wt.%) plus AS A (0.4 wt.%).



Fig. 3—Weld-load results for varying concentrations of bismuth. White = 2.5% Bi carboxylate, 0.4% AS A; dark grey = 2.5% Bi carboxylate, 1.0% IS A; striped = 7.0% Bi carboxylate, 1.0% IS A. NDA = neodecanoate; 2EH = 2-ethylhexanoate; Nap = naphthenate.

this generality, there was one system that did not perform well in the four-ball test. The combination of Bi 2EH and IS C showed only low levels of EP activity. Further experiments are required to determine the cause for this lack of EP activity. Regardless, it appears that bismuth carboxylates are generally responsive to most forms of sulfur, only requiring the ability to produce free sulfur.

Although mixtures with all of the sulfur compounds show similarly high levels of EP lubricity, there is one case that shows considerably lower wear scarring. Figure 5 shows the antiwear (wearscar width) test results for Bi NDA and Bi 2EH with the different sulfur compounds. The mixture of Bi NDA and IS C gave a wear scar of 0.73 mm, more than 0.1 mm lower than the other mixtures. This value is only 0.15 mm larger than the control with no bismuth carboxylate. Further experiments are necessary to determine why this particular sample has considerably better antiwear properties versus typical bismuth carboxylate-polysulfide mixtures, although it is likely due to a lower concentration of active sulfur in the sample (Speight (12)). However, this set of tests shows



Fig. 4—Weld-load results for sample containing sulfur compounds from different producers. All bismuth carboxylates were loaded at 5 wt.%. Dark grey = AS B (0.25%); white = IS B (0.75%); light grey = AS C (0.25%); striped = IS C (1.0%). NDA = neodecanoate; 2EH = 2-ethylhexanoate; control = polysulfide only.



Fig. 5—Antiwear values (scar-width values) of bismuth carboxylates with different types of sulfurized additives. All bismuth carboxylates loaded at 5 wt.%. Dark grey = AS A (0.4%); striped = IS A (1.0%); light grey = AS B (0.25%); black = IS B (0.75%); blocked = AS C (0.25%); white = IS C (1.0%). NDA = neodecanoate; 2EH = 2-ethylhexanoate; control = polysulfide only.

that antiwear properties may be subtly adjusted while keeping high EP activity simply be changing the sulfur compound in the mixture.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) experiments were undertaken to understand synergism between bismuth carboxylates and sulfurized additives and identify any species formed. A compound that can possibly be generated under the severe boundary lubricant conditions in the 4-ball EP test is bismuth sulfide.

Samples were prepared with sulfur-to-bismuth ratios designed to give the correct stoichiometry for Bi_2S_3 . Although this approach does not use the same ratio as in the samples prepared for the four-ball tests, the experiments were designed to minimize waste and side-product formation. Six samples were investigated, including three bismuth carboxylates mixed with active or inactive sulfur compounds. The samples were then heated to 800° C in an air or a nitrogen atmosphere. Data from Bi 2EH are shown. Bi NDA and Bi Nap showed similar thermal behavior.



Fig. 6—TGA of Bi 2EH + IS A obtained in air. Data collected at 1°C/min. Inset shows closeup of data between 260 and 630°C.



Fig. 7—XRD patterns of the residues obtained from the TGA experiments. Spectra are (from top to bottom) Bi NDA + IS A in nitrogen, Bi 2EH + IS A in nitrogen, simulated pattern for bismuth subsulfate, Bi 2EH + AS A in air, Bi NDA + IS A in air, and simulated pattern for bismuth oxide (bismutite, Bi₂O₃).

Figure 6 shows the TGA data for the experiment performed with Bi 2EH and inactive sulfur (IS A) in air (loading: 21.88 wt.% Bi, 5.03 wt.% S). There is one major loss of mass between 100 and 215°C corresponding to burning of the organic portion of the molecule. The residual mass is in the correct range for the formation of Bi₂S₃ (theoretical: 26.9%, found: 27.4%). There is a second thermal event starting near 300°C and ending near 600°C. This event corresponds to an overall small decrease in residual mass. This is likely due to oxidation to Bi₂O₃ and bismuth subsulfate, Bi₂O₂(SO₄). The X-ray diffraction pattern of the resulting residue shows both materials (Fig. 7). The likely oxidant in this case is atmospheric oxygen, although we cannot rule out internal oxidants derived from the organic carboxylate fragments (vide infra).

Figure 8 shows the TGA data for the experiment performed with Bi 2EH and inactive sulfur (IS A) in a nitrogen environment. The initial thermal event, between 100 and 300°C, is coupled to a loss of mass corresponding to Bi₂S₃ formation (theoretical: 26.9%, found: 26.0%). This event is, again, likely due to thermolysis of the organic portion of the mixture, releasing bismuth cations and "free" sulfur (perhaps as hydrogen sulfide [H₂S], hydrosulfide anion [HS⁻], or even sulfide anion [S²⁻]. Interestingly, the XRD pattern of the residue matches those of Bi₂O₃ and bismuth subsulfate, suggestive of oxidation. The nitrogen atmosphere should eliminate oxygen as the culprit. It is possible that an internal oxidant, such as carbon dioxide (CO₂), is formed



Fig. 8—TGA of Bi 2EH + IS A obtained in a nitrogen atmosphere. Data collected at 1°C/min. Inset shows closeup of data between 200 and 600°C.

from reactive organic fragments evolved during the thermolysis of the carboxylate fragments. Unfortunately, observing these reactive oxidants is beyond the scope of our current capabilities.

Figures 9 and 10 show the analogous TGA data for the experiment performed with Bi 2EH and AS A in air and nitrogen, respectively (loading: 23.65 wt.% Bi; 5.90 wt.% S). The results are similar to those for the inactive sulfur cases, with evidence of Bi₂S₃ formation near 250°C (for air: theoretical: 29.1 %, found: 29.5%; for nitrogen: theoretical: 29.1%, found: 28.1%). Again, we see final products consistent with oxidized species, including Bi₂O₃ and bismuth subsulfate.

The TGA data of the thermolysis reactions between bismuth carboxylates and polysulfides offer two conclusions. The first is that in all cases, Bi_2S_3 is likely the first material formed after thermolysis of the organic portion of the sample. We believe that Bi_2S_3 is, therefore, the species responsible for providing extreme pressure characteristics. Further evidence of the formation of Bi_2S_3 in these systems is given below. Second, a temperature range in which these mixtures will be active for EP lubrication applications can be inferred. The samples are "activated" when Bi_2S_3 is formed, near 250°C. In the TGA experiments, oxidation is complete by 625°C, with the final products being Bi_2O_3 and bismuth subsulfate. It is unknown if the material maintains EP

25 7.8 23 7.6 21 7.4 19 mass (mg) 7.2 17 7 15 13 68 200 300 400 500 600 11 9 7 5 0 200 400 600 800 T (°C)

Fig. 9—TGA of Bi 2EH + AS A obtained in air. Data collected at 1°C/min. Inset shows closeup of data between 200 and 600°C.



Fig. 10—TGA of Bi 2EH + AS A obtained in a nitrogen atmosphere. Data collected at 1°C/min. Inset shows closeup of data between 200 and 600°C.

lubricity once oxidized, but the low end for a temperature range of EP activity for mixtures of bismuth carboxylates and sulfur compounds is 200–600°C. In contrast, sulfurized additives become EP active at a temperature of 600°C. Thus, utilization of bismuth with sulfur compounds confers a more rapid onset of EP activity.

High-Temperature X-Ray Diffraction

The residues obtained from the TGA experiments were all subjected to XRD analysis (Fig. 7). Results consistently showed the presence of Bi_2O_3 (PDF 04-007-1342) and bismuth subsulfate (PDF 01-073-8172) as products in the thermolysis of bismuth carboxylates in the presence of polysulfides. The oxidized species were expected from experiments performed in air, but we were surprised to find similar products from the anaerobic experiments. As stated above, we cannot rule out internal oxidants derived from the organic carboxlyate ligands. Although the residual masses obtained from the TGA data corresponded to initial formation of Bi_2S_3 , we were interested in obtaining further evidence of such an intermediate. We subjected a sample of the Bi 2EH and IS A mixture to a high-temperature X-ray diffraction experiment. The sample is identical to that used in the TGA experiments.



Fig. 11—Upper: XRD pattern of Bi 2EH and IS A heated at 250°C for 30 min. Lower: The simulated XRD pattern of bismuthinite, Bi₂S₃. The off-scale peaks are due to the Pt sample holder.



Fig. 12—SEM/EDS images from the rotating steel ball used in the load-wear test on Bi 2EH and AS A. From left to right: backscattered electron image, false color element maps for: bismuth (red), sulfur (green), carbon (blue), and iron (magenta).

The sample was loaded in the diffractometer and placed under a nitrogen atmosphere. The sample was heated to 250° C and held for 30 min. At this time, a scan was taken, and the sample was heated at 250° C for an additional hour and scanned again. There was no change in the XRD pattern after the additional time at 250° C. Figure 11 shows the HTXRD pattern from the second scan and the calculated pattern for crystalline Bi₂S₃ from the literature (Kyono and Kimata (*13*)). The (3,0,1), (1,0,3), (2,0,3), (2,1,2), (1,0,5), and (3,2,1) Bragg peaks are clearly defined in the experimental pattern. This suggests that bismuthinite, Bi₂S₃, is the major product of thermolysis. Scherrer analysis of the peak widths suggests particle sizes of ~100 nm (Patterson (*14*)).

Scanning Electron Microscopy and X-ray Spectroscopy

Further confirmation of Bi_2S_3 as an intermediate in the thermolysis of mixtures of bismuth carboxylates and sulfur compounds comes from SEM-EDS experiments on the steel balls from the four-ball wear tests. The rotating ball used in the 620 kg test of Bi 2EH and IS A was subjected to SEM analysis. It is important to note that at this load the balls have not seized. It seems reasonable to believe that the active lubricant or its oxidation product exists on this surface. Figure 12 shows the SEM image of the wear scar and the false-color elemental maps. It is most important to note that the bismuth, sulfur, and carbon are spatially correlated, and that the iron is negatively correlated with the others. This result shows that the areas of the test ball that

Fig. 13—The crystal structure of bismuthinite viewed along the crystallographic b axis. Dark grey = bismuth, light grey = sulfur.

were coated with the Bi-S additive slid without scarring. The high levels of bismuth and sulfur observed in the wear scar of the ball support our hypothesis that Bi_2S_3 is the active intermediate in EP additives comprised of bismuth carboxylates and polysulfides.

Description of Bismuthinite Lubricity

The crystal structure of bismuthine consists of twodimensional sheets of Bi_2S_3 . The structure is depicted in Fig. 13. The Jamison parameter has been suggested to be predictive of solid lubricity for crystalline solids (Jamison (15)). It is the ratio of the interplane spacing to the M-Y bond length. Lower values are correlated with better lubricity. For MoS₂, the prototypical solid lubricant, the value is 1.5. In Bi_2S_3 , the ratio is 3.7 Å/2.6 Å, also 1.5. The microscopic lubrication mechanism of MoS₂ is interlayer shear. It seems reasonable to conclude that the same mechanism is in effect for Bi_2S_3 solid lubricants. It is also noted that the melting point of Bi_2S_3 is 775°C (Cubicciotti (16)); thus, this mechanism should be effective under substantial thermal loads.

CONCLUSIONS

We have studied a series of mixtures that include one bismuth carboxylate and one sulfur compound. Four-ball weld load testing shows that inclusion of bismuth salts with sulfurized additives enhances the EP properties of these additives, offering weld load values of ≥ 600 kg for the four-ball EP test with as little as 0.25 wt.% bismuth (2.5 wt.% bismuth carboxylate). The EP properties of these mixtures are due to the synergy of the additives, as neither of these components gives high EP activity alone.

The logical intermediate in these mixtures under severe boundary lubricant conditions is Bi_2S_3 . TGA experiments support initial formation of Bi_2S_3 during thermolysis, before ultimately oxidizing to Bi_2O_3 and bismuth subsulfate, as confirmed by XRD analysis of the resulting residues. Further confirmation of Bi_2S_3 formation came from the HTXRD experiments and the SEM-EDS studies of the rotating ball from the four-ball wear tests. Both sets of experiments showed high levels of Bi_2S_3 in the resulting residues. Based on the cumulative evidence, we believe that Bi_2S_3 is the active species in EP lubricant additives containing bismuth carboxylates and sulfur compounds. The sensibility of this rubric is supported by the favorable Jamison parameter for Bi_2S_3 and supports the interlayer shear model as the mode of lubricity.

Finally, mixtures of bismuth carboxylates and sulfur compounds are excellent EP additives, giving high weld-load values and having active temperature ranges of approximately 200– 600°C. This activation range is significantly lower than that of sulfur compounds alone. Also of note is the lower requisite concentration of sulfurized additives when combined with bismuth carboxylates. This, coupled with bismuth's nontoxic characteristics, combines to give an EP additive with excellent activity, variable antiwear characteristics, and a low environmental impact.

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