

4.3 Alumina B System

Section 4.2 presented investigations into the anti-wear behavior of some new tribomonomers in the relatively high wear rate Alumina A system. In that system, the reference total wear averaged 27 mm³. After exhausting the supply of these alumina specimens, a new batch of 100 disks herein referred to as “Alumina B” was ordered from the same supplier with the same specifications. This new batch however, exhibited much lower reference wear rates in hexadecane. The following sections present the reference wear data for hexadecane and compare the effects of six additives using these Alumina B disks. This Alumina B material system represents the majority of the anti-wear tests of this study and proved a consistent proving ground for the effectiveness of the additives. A few compounds were selected for additional separate studies to explore effective concentration limits, isomerism, and higher loads and speeds. Where available, photomicrographs are included to provide visual information on the nature of the worn areas. First, the reference tests are examined to establish a basis for comparison of additive anti-wear effectiveness.

4.3.1 Hexadecane Reference

The total wear volumes of 30 alumina-on-alumina reference tests with hexadecane at 0.25 m/s, 40 N, and 250 m sliding distance are shown in order of increasing wear volume in Figure 4.3.1.1. The distribution of wear volumes among the first six compared to the latter 24 indicates these results likely come from two distinctly different disk wear materials although all the Alumina B disks are from the same order

and appeared identical upon visual inspection. It is likely that two rods of alumina with different mechanical properties were used to prepare the order of 100 specimens.

Having learned of the large variance between reference wear volumes in the previous Alumina A system, most additive tests were conducted on the reverse side of a reference test disk. This method sought to limit material property variations to the ¼ inch thickness of a disk rather than possible variations between disks from opposite ends of a hot pressed rod.

To simplify evaluation and presentation of additive wear results, an average of the larger grouping of tests in Figure 4.3.1.1 was used as the standard reference wear. Using this average tends to slightly exaggerate the wear reduction for the lower wear disks from this batch of 100. Appendix A contains a table of the wear reductions as calculated based on both a Same Side Reference and a Group Average comparison. Where applicable, the adjusted reductions for tests on these six disks are given in the footnotes.

Figure 4.3.1.2 of disks and Figures 4.3.1.3-5 of balls offer visual documentation of the wear characteristics of the Alumina B System lubricated by hexadecane alone. Porosity made photomacrography challenging and often required experimentation with various ratios and intensities of direct (internal to lens and perpendicular to surface) and indirect (external source and oblique to surface) lighting to obtain a meaningful image. Figure 4.3.1.2 of the disk wear surfaces contrasts the visual effects obtained using both types of lighting with varying intensity. In the top image (a) internal lighting reveals the planarity of the worn asperities as evidenced by the mirror like reflection of the direct internal light perpendicular to the disk. The middle and bottom images reveal an

unremarkable wear surface almost indistinguishable from the unworn surface with the exception of smoother areas appearing more opaque than slightly rougher areas appearing a crystalline white.

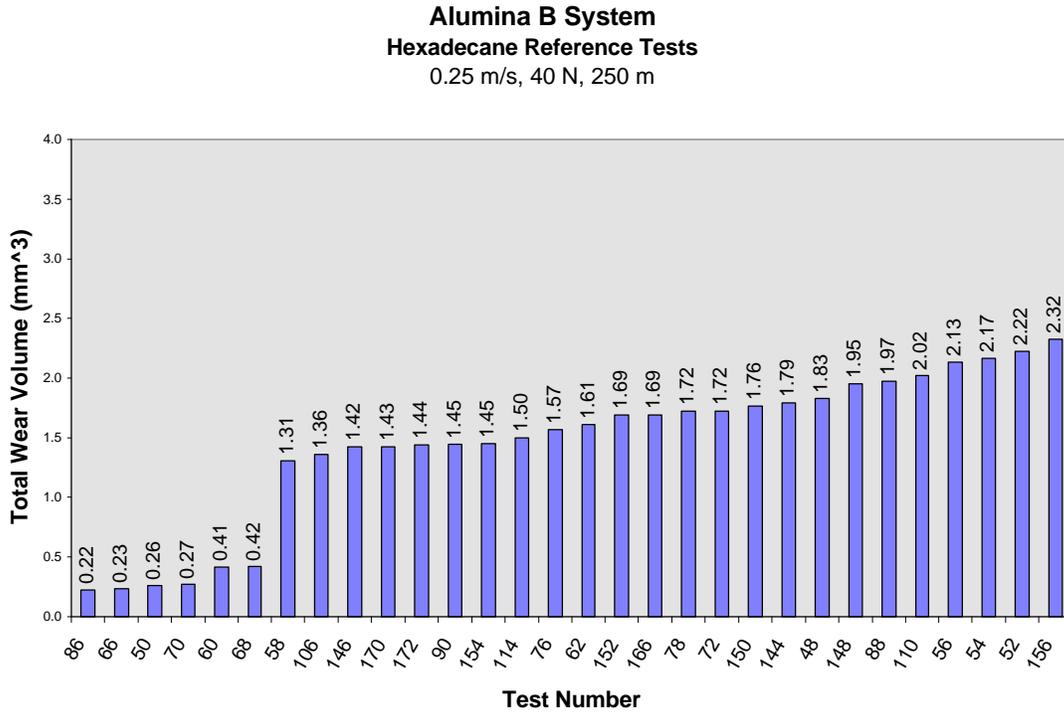


Figure 4.3.1.1 Hexadecane Reference Wear Volumes in Ascending Order for Alumina B System.

Figures 4.3.1.3-5 of ball wear scars from hexadecane reference tests at various magnifications show baseline debris appearances. Indirect lighting better reveals colorations (or lack thereof) in the wear area whereas direct lighting better reveals contour variations in mirror-like reflections of the wear area. The unremarkable wear surfaces for hexadecane reveal uniform circular wear patterns on the balls unlike the earlier two systems. Very little if any wear debris or films appear on either wear surface.



(a) Test 49 disk, 15.75x internal lighting



(b) Test 114 disk, 40x, external lighting

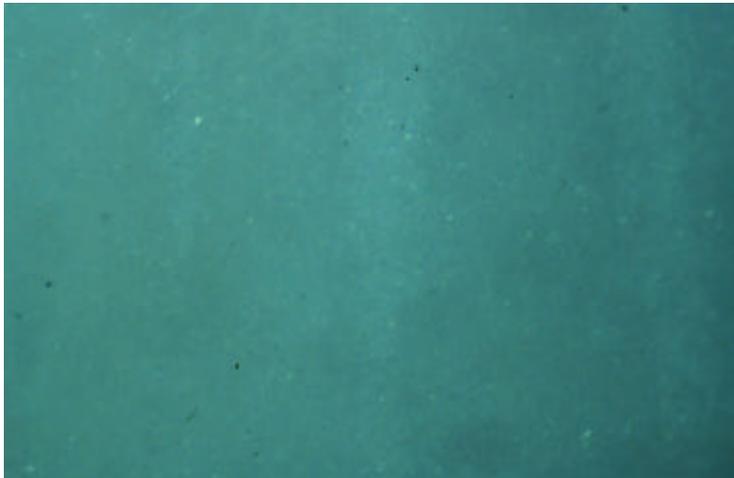


(c) Test 114 disk, 80x, external lighting

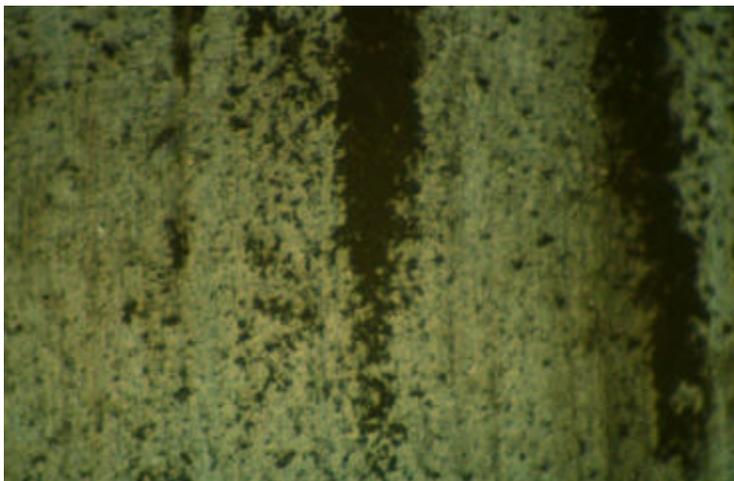
Figure 4.3.1.2 Disk Photomicrographs from Hexadecane Reference Tests.



(a) Test 90 ball, 25x, internal lighting



(b) Test 90 ball, 80x, external lighting

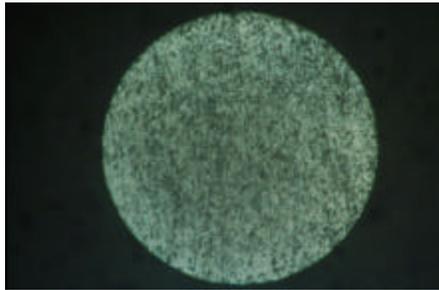


(c) Test 90 ball, 80x, internal lighting

Figure 4.3.1.3 Ball Photomicrographs from Hexadecane Reference, Test 90.

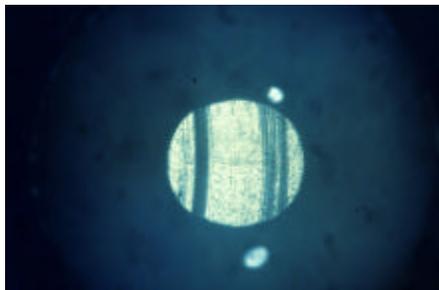


Test 131 ball, 15.75x, int./ext. lighting

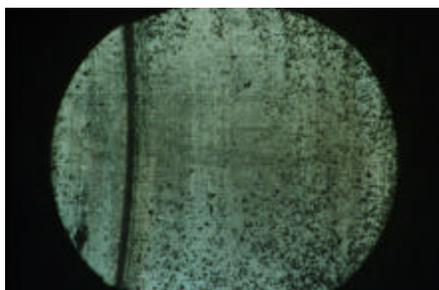


Test 131 ball, 40x, int./ ext. lighting

Figure 4.3.1.4 Ball Photomicrographs from Hexadecane Reference, Test 131.



Test 137 ball, 15.75x, int./ext. lighting



Test 137 ball, 40x, int. + ext. lighting

Figure 4.3.1.5 Ball Photomicrographs from Hexadecane Reference, Test 137.

4.3.2 A-R-B Type Tribomonomers

Testing in the Alumina B system again spanned four groups of anti-wear additive candidates. The first of these groups was the A-R-B type, which consisted of two tribomonomers. The average wear results for two tests of the first compound, an aliphatic amino acid, are compared to the hexadecane reference in Figure 4.3.2.1. Photomicrographs from the two tests are shown in Figures 4.3.2.2–3. The ball wear areas are apparently coated with residual material; however, disk wear areas absorbed both internal and external light possibly masking the presence of thin deposited films.

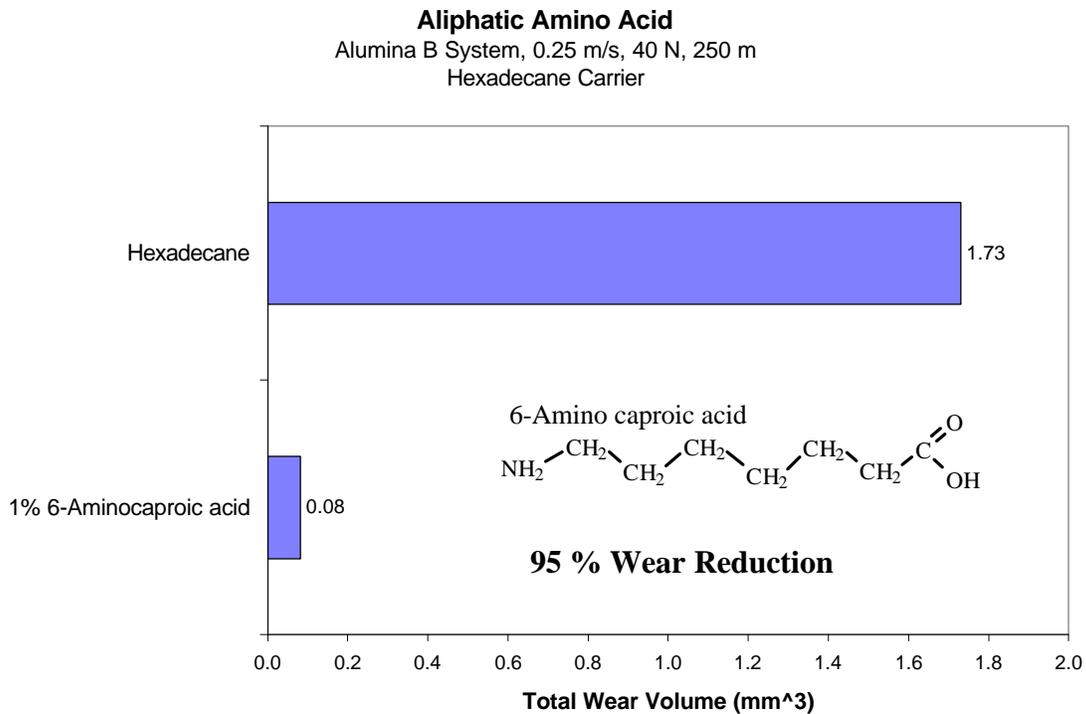


Figure 4.3.2.1 Anti-wear Effect of Aliphatic Amino Acid in Alumina B System.

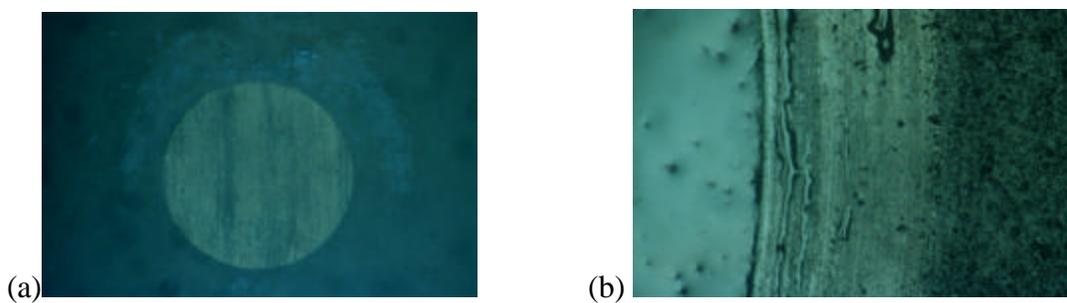


Figure 4.3.2.2 Photomicrographs of 6-Aminocaproic Acid Wear Areas, Test 107 (a) ball, 40x, int. + ext. lighting, after hexane rinse (b) disk, 40x, int. + ext. lighting.

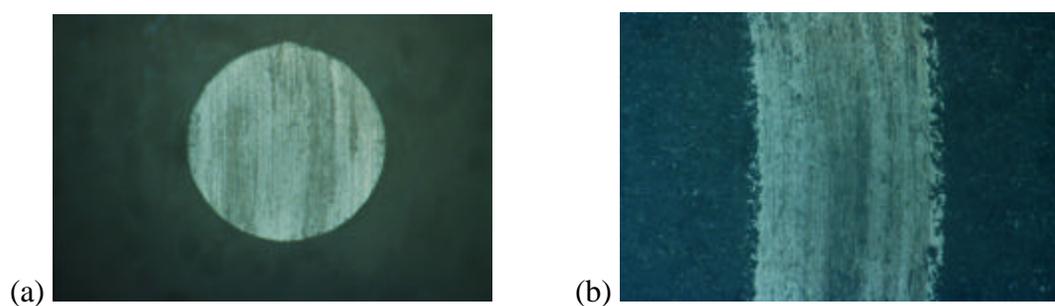


Figure 4.3.2.3 Photomicrographs of 6-Aminocaproic Acid Wear Areas, Test 108 (a) ball, 40x, int. + ext. lighting, (b) disk, 40x, int. + ext. lighting

Similar wear reduction was achieved using an aromatic A-R-B type amino compound with an ester functional group. The wear results for this aromatic amino ester, ethyl-4-aminobenzoate, are graphically and visually illustrated in Figures 4.3.2.4 and 4.3.2.5 respectively. The extremely smooth worn areas appear to be covered by a thin film.

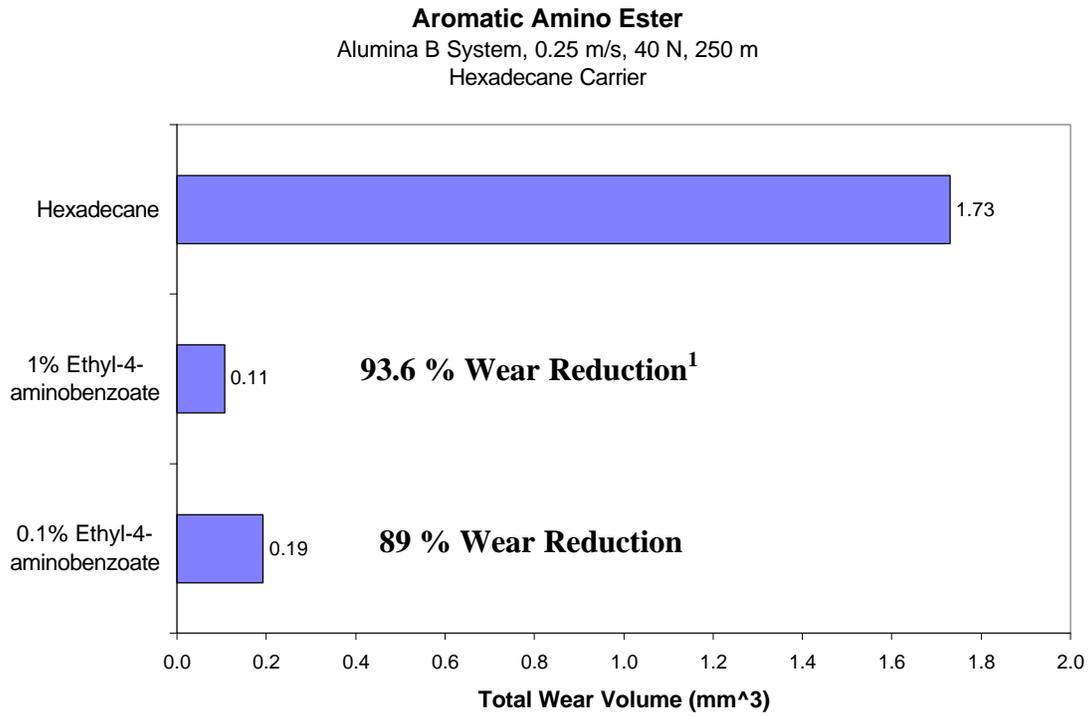


Figure 4.3.2.4 Anti-wear Effect of Aromatic Amino Ester in Alumina B System.

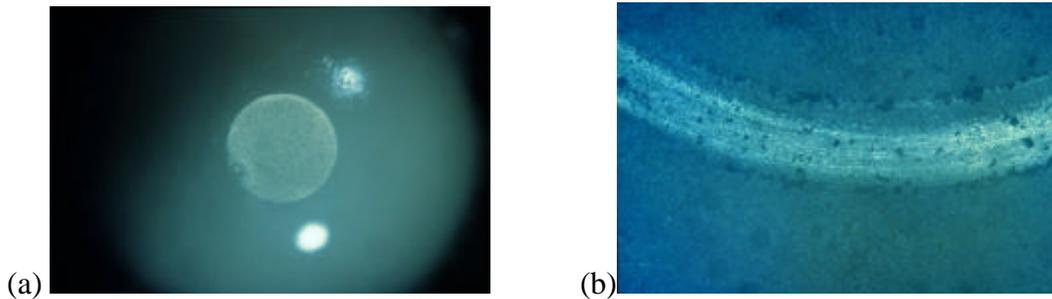


Figure 4.3.2.5 Photomicrographs of Ethyl-4-aminobenzoate Wear Areas after methanol rinse, (a) Test 158 ball, 15.75x, int. + ext. lighting, (b) Test 51 disk, 15.75x, int. + ext. lighting.

¹ 76% when compared to same side reference

4.3.3 A-R-A + B-R'-B Type Compounds

Testing within the second class, A-R-A + B-R'-B, consisted of two groupings of difunctional additive pairs. The first grouping revisited the tert-butyl hydroquinone and dimethyl terephthalate pair. Additionally, variation of the location of the pendant functional group investigated structural isomerism effects on anti-wear performance. Results for three dimethyl phthalate isomers paired with tert-butyl hydroquinone are presented below in Figure 4.3.3.1. Each bar represents an average of two tests, some tests were conducted on the lower wear group of six reference disks slightly inflating the wear reductions. Where applicable, appropriate corrections are given in the footnotes.

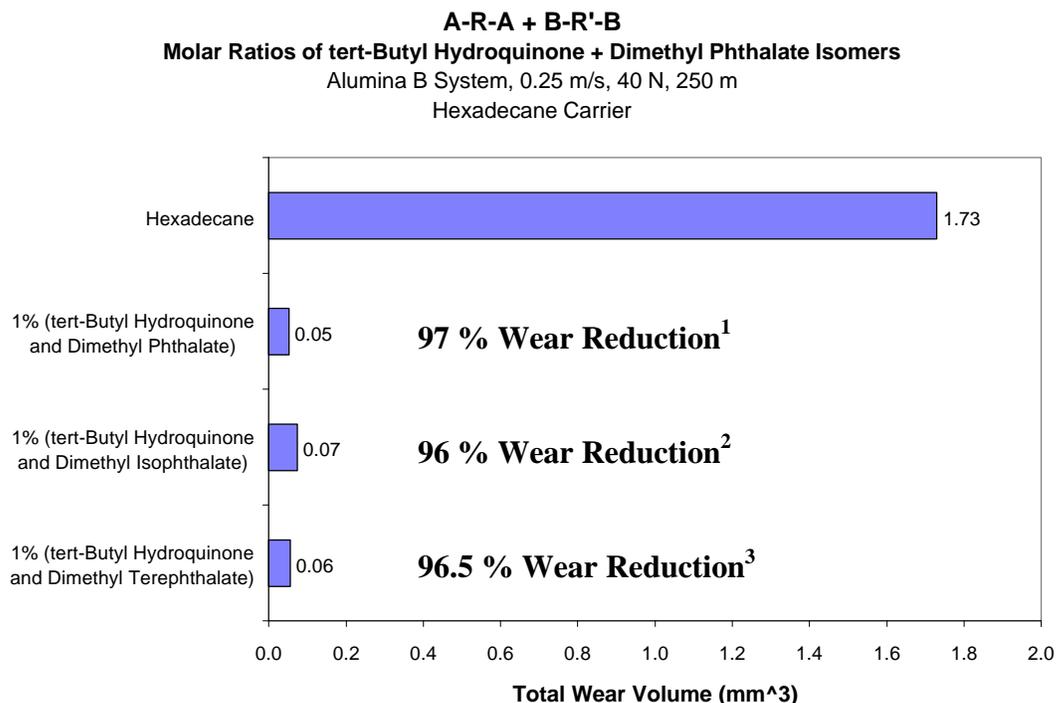


Figure 4.3.3.1 Anti-wear Effects of A-R-A + B-R'-B Compounds Tert-Butyl Hydroquinone and Isomers of Dimethyl Phthalate in Alumina B System.

¹ 89.5% when compared to same side references

² 88% when compared to same side references

³ 84.4% when compared to same side references

The three dimethyl phthalate isomer pairings with tert-butyl hydroquinone resulted in comparable wear reductions. Photomicrographs revealed unremarkable wear surfaces and have been omitted for these compounds.

The second additive pairing in the A-R-A + B-R'-B class was the DuPont Kapton® monomer combination of ODA and BTDA. The excellent anti-wear characteristics of this mixture resulted in over a 98% wear reduction at 1% and 0.1% concentrations by weight as shown in 4.3.3.2

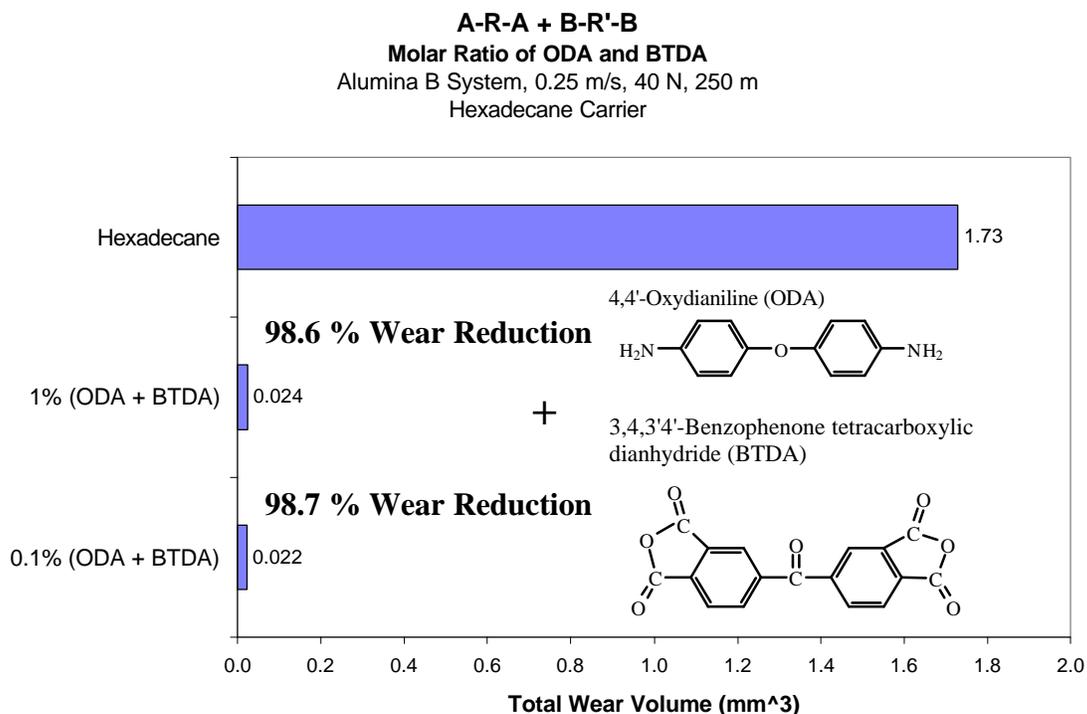


Figure 4.3.3.2 Anti-wear Effect of A-R-A + B-R'-B Compounds ODA and BTDA in Alumina B System.

In contrast to the unremarkable appearance of the previous compounds, the solution of Kapton® monomers resulted in very noticeable and colorful deposits. Figure 4.3.3.3 presents six photomicrographs of balls from wear tests. The photos on the left were taken under external lighting and reflect the colors as they appeared to the naked eye.

Internal direct lighting resulted in the reflective appearance as displayed in photos on the right. Photos (e) and (f) at 80x magnification best revealed deposits that appear similar to a layered wrinkle. This suggests that delamination of the tribochemical debris layer governs material removal from the contact area after run-in. Note the reflections from the debris at the edges of the scar under direct internal lighting. Image (d) shows abraded material extending outside the circular worn area that reflects in the same plane as the wear scar. This extended planar formation of wear debris indicates a formative interaction between the debris and anti-wear additive resulting in a film resilient to abrasion.

A consistent brownish disk wear track is observed in Figure 4.3.3.4. The right side photomicrographs (b) and (d) of Figure 4.3.3.5 demonstrate the smooth nature of the wear track which is not evident under external lighting or to the naked eye. Note that the brown color spans evenly across the width of the wear track. This will later be contrasted to the tracks under more severe operating conditions.

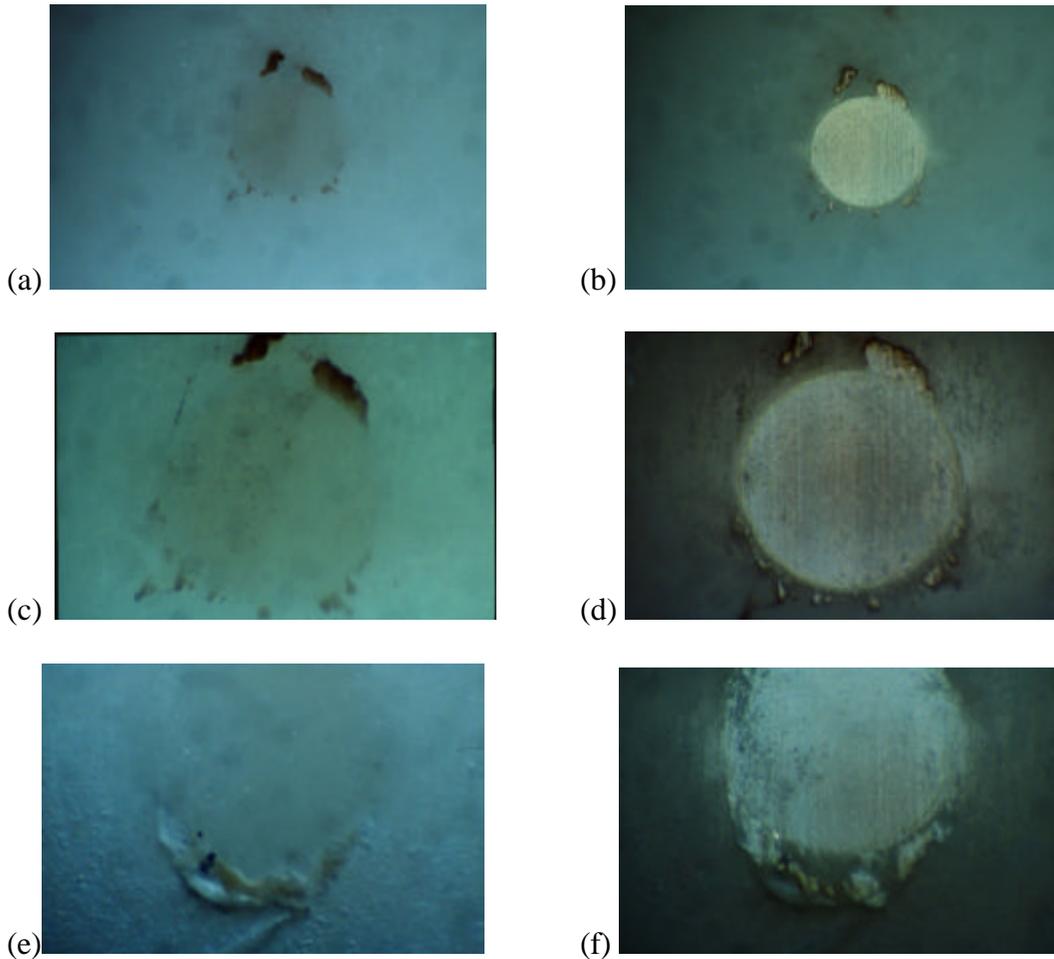


Figure 4.3.3.3 Photomicrographs of ODA+BTDA Ball Wear Areas after methanol rinse, (a) Test 109, 40x, int. + ext. lighting (b) Test 109, 40x, int. + ext. lighting, (c) Test 109, 80x, int. lighting, (d) Test 109, 80x, int. + ext. lighting, (e) Test 115, 80x, ext. lighting, (f) Test 115, 80x, int. lighting.

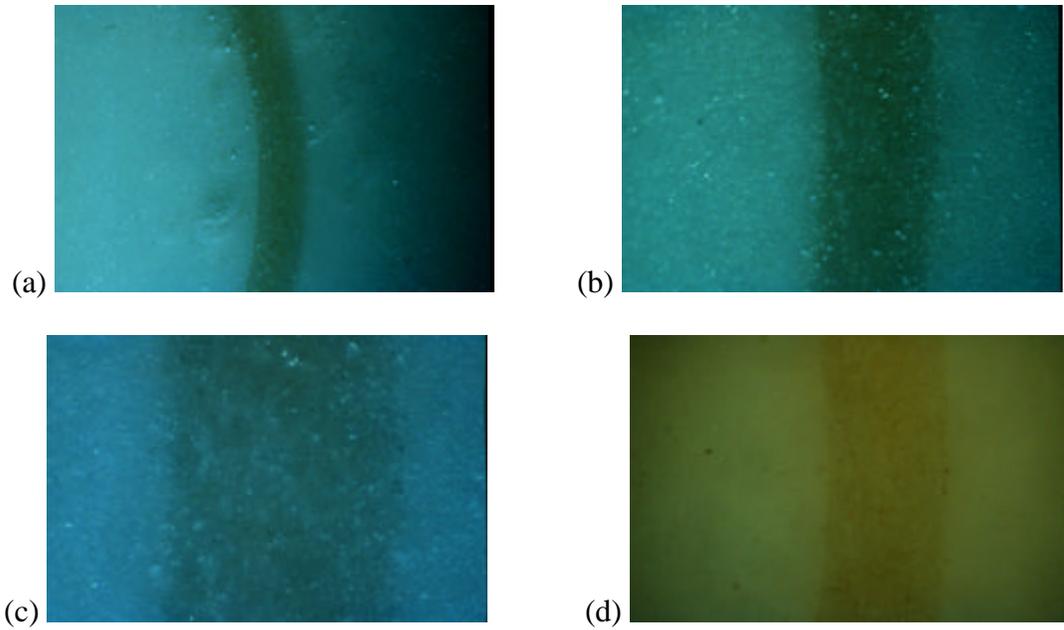


Figure 4.3.3.4 Photomicrographs of ODA+BTDA Disk Wear Tracks after methanol rinse, Test 115 disk (a) 15.75x, ext. lighting, (b) 40x, ext. lighting, (c) 80x, ext. lighting, (d) 40x, int. lighting.

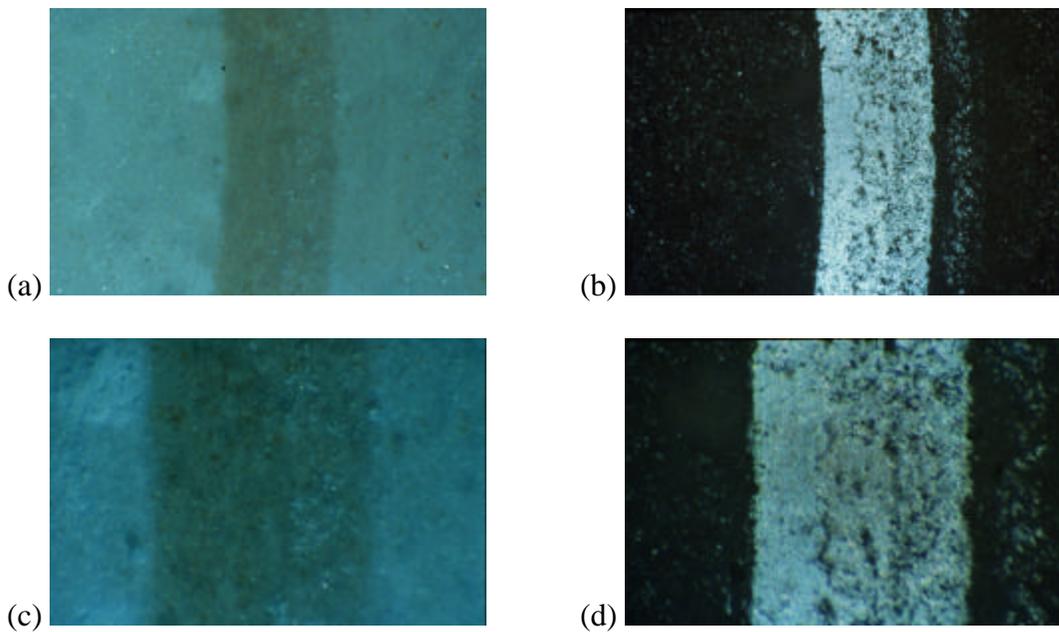


Figure 4.3.3.5 Photomicrographs of ODA + BTDA Disk Wear Tracks, Test 109 (a) 40x, ext. lighting, (b) 40x, int. lighting., (c) 80x, ext. lighting, (d) 80x, int. lighting.

ODA/BTDA AT HIGHER FRICTIONAL HEAT GENERATION

The excellent wear reductions of these compounds warranted further study at higher loads and speeds. Device experimental limitations permitted only a six fold (2x load and 3x speed) increase in heat generation compared to the 16 fold associated with Tritt's [41] work. However, the maximum tested speed of 0.75 m/s approached the 1.0 m/s where earlier compound classes failed to show any anti-wear behavior. Figure 4.3.3.6 shows the most significant and interesting result of this thesis. *Total wear was reduced by over 95% in all cases and by 99% at the most severe conditions.*

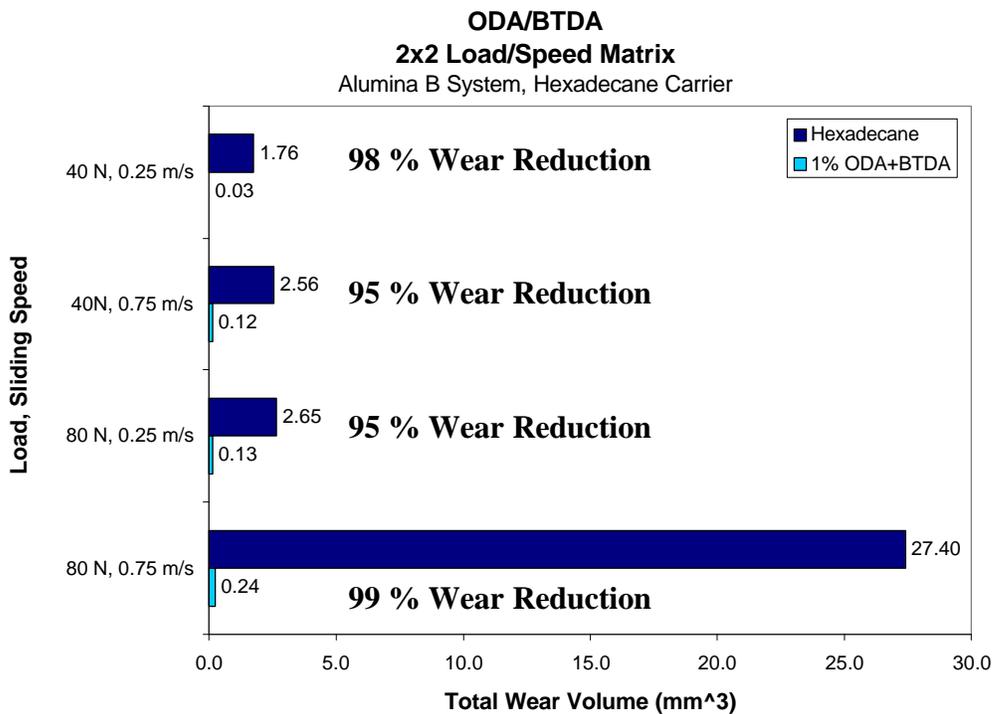


Figure 4.3.3.6 Anti-wear Effect of A-R-A + B-R'-B Compounds ODA and BTDA in Alumina B System 2x2 Load/Speed Matrix.

The colorful and abundant deposits on and near the wear areas in Figures 4.3.3.7 – 8 indicate the significant tribochemical activity of this mixture of compounds. The figures show photomicrographs from the 0.25 m/s tests on the left and 0.75 m/s tests on

the right with load being 40 N on the top and 80 N on the bottom. The most severe test conditions resulted in the most impressive tribochemical phenomena as evidenced by photo (d) in each figure.

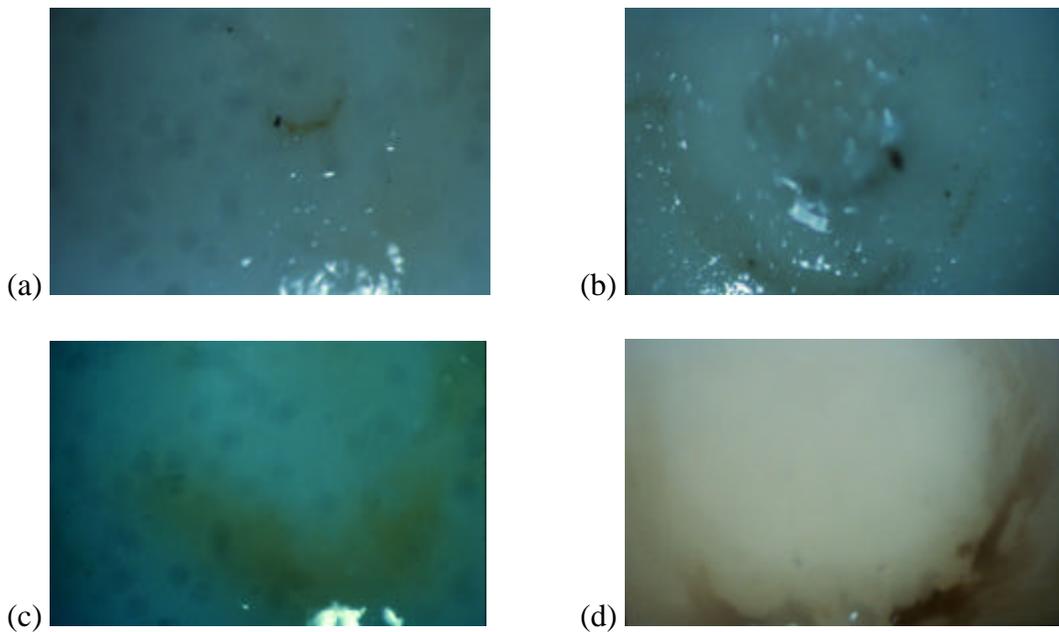


Figure 4.3.3.7 Photomicrographs of ODA + BTDA 2x2 Matrix Ball Wear Areas, (a) Test 115, 40x, ext. lighting, (b) Test 119, 40x, ext. lighting, (c) 40x, ext. lighting, (d) 40x, ext. lighting.

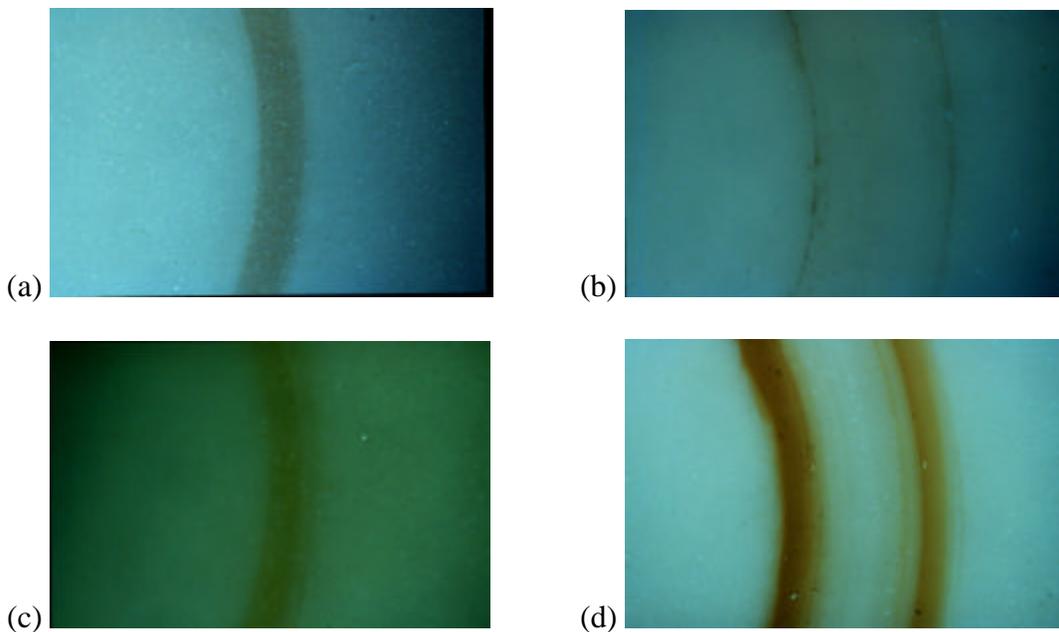


Figure 4.3.3.8 Photomicrographs of ODA + BTDA 2x2 Matrix Disk Wear Tracks, (a) Test 115, 15.75x, ext. lighting, (b) Test 125, 15.75x, ext. lighting, (c) 15.75x, ext. lighting, (d) 15.75x, ext. lighting.

Higher magnification photomicrographs of the disk are presented below in Figure 4.3.3.9. The high speed tests at right show colored debris at the edges of the track. A close look at the disturbed strip of brown pasty deposit in photo (d) strongly supports the definition of tribopolymerization as a phenomena occurring at *or near* the surface.

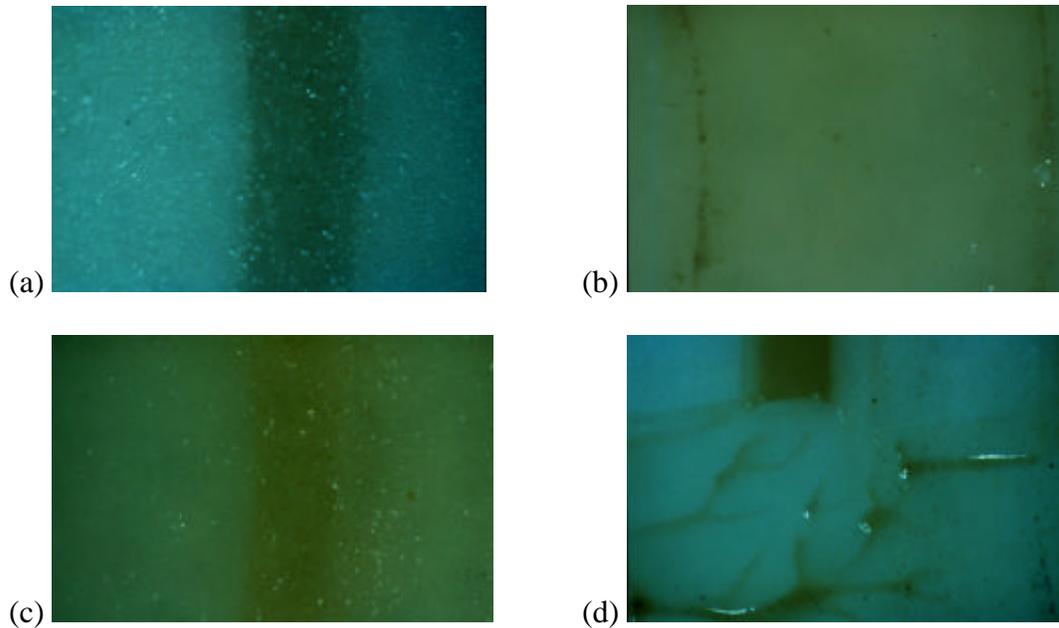


Figure 4.3.3.9 Photomicrographs of ODA + BTDA 2x2 Matrix Disk Wear Tracks, (a) Test 115, 40x, int. lighting, (b) Test 125, 40x, ext. lighting, (c) Test 128, 40x, ext. lighting, (d) Test 123, 40x, ext. lighting.

Photomicrographs of the wear areas in Figure 4.3.3.10 show the similar nature of the films left on the ball. The dark deposits at the leading edge of the ball wear area show the significant amount of tribochemical activity occurring in tests with these effective additives.

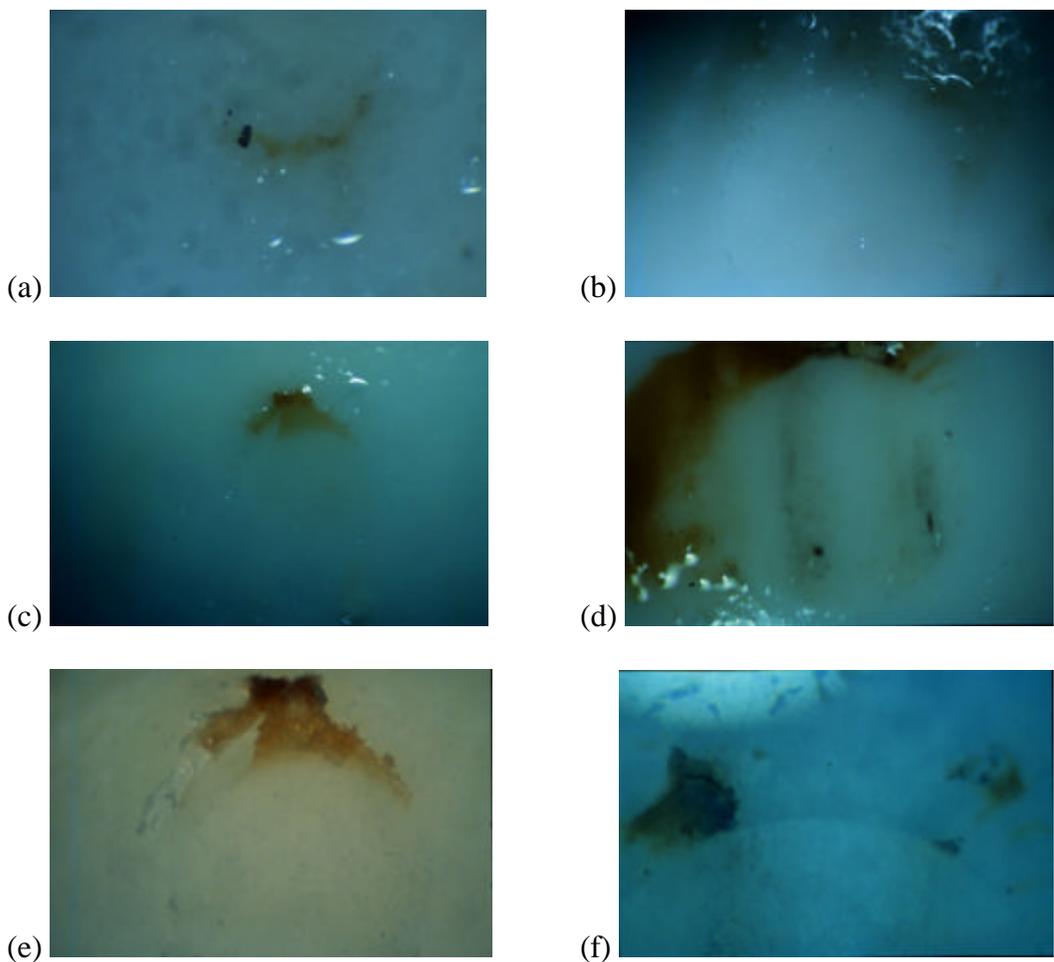


Figure 4.3.3.10 Photomicrographs of ODA + BTDA 2x2 Matrix Ball Wear Areas, (a) Test 115, 80x, int. lighting, (b) Test 125, 40x, ext. lighting, (c) Test 128, 40x, ext. lighting, (d) Test 123, 40x, ext. lighting, (e) Test 128, 80x, ext. lighting, after hexane rinse, (f) Test 123, 80x, ext. lighting after hexane rinse.

4.3.4 Cyclic Amides

Testing in the Alumina B system within the third class, cyclic amides, included separate studies on caprolactam and lauro lactam. Total wear results for the two lactam compounds at the standard conditions are displayed in Figure 4.3.4.1. The lactam with five carbons in the heterocycle, caprolactam, reduced wear at concentrations as low as

0.02 % by weight. Lauro lactam, containing twelve carbons in the ring offered a similar anti-wear effect. Caprolactam is commercially utilized in the manufacture of Nylons. Its commercial abundance and demonstrated effect in the Steel and Alumina A Systems prompted further investigation under more severe operating conditions.

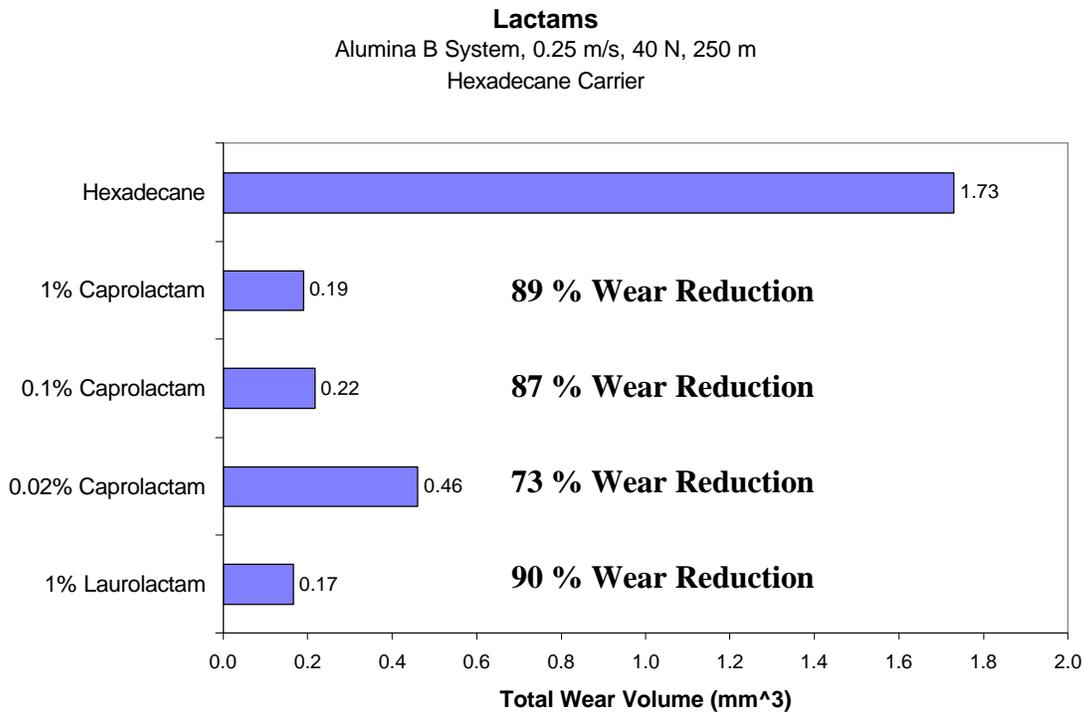


Figure 4.3.4.1 Anti-wear Effect of Cyclic Amide Class in Alumina B System.

CAPROLACTAM AT HIGHER FRICTIONAL HEAT GENERATION

A 2x2 load/speed matrix investigation representing a six fold increase in frictional heat generation was conducted using caprolactam. The wear results in Figure 4.3.4.2 show another breakthrough finding. Caprolactam anti-wear behavior persists up to the worst case conditions of 0.75m/s and 80 N while giving excellent wear reductions at lower conditions.

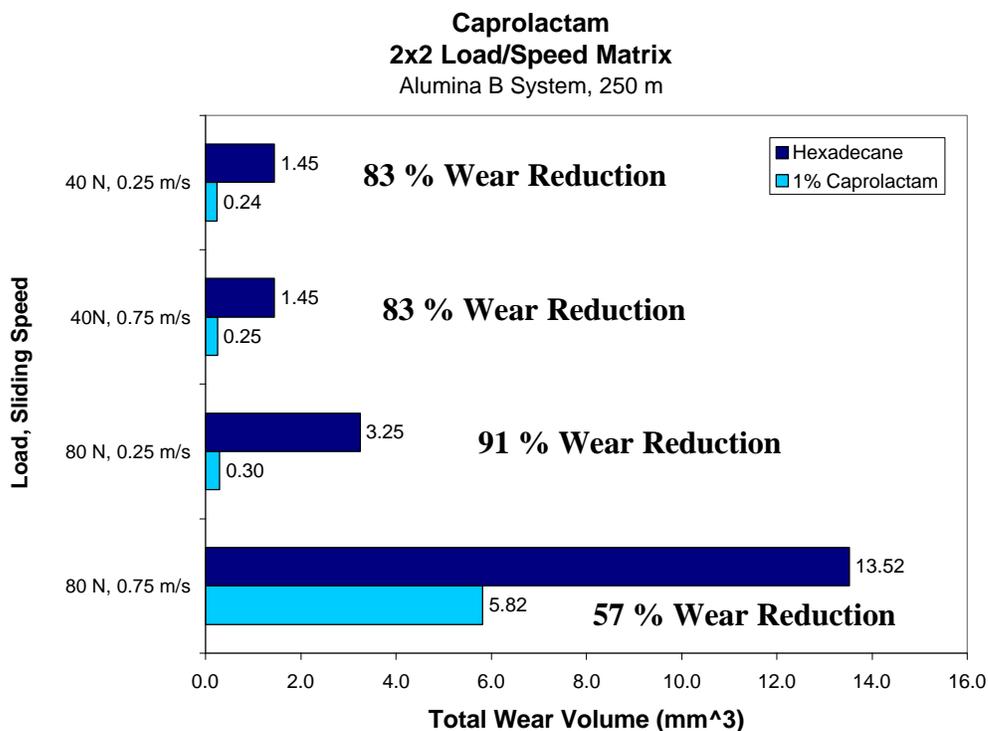


Figure 4.3.4.2 Anti-wear Effect of Caprolactam in Alumina B System 2x2 Load/Speed Matrix.

4.3.5 A-R-A or B-R'-B Compounds Alone

To evaluate the effects of individual additives compared to the synergistic mechanism predicted by tribopolymerization concept, candidates from the third group, A-R-A and B-R'-B compounds, were tested alone. Figure 4.3.5.1 shows the anti-wear behavior for the first A-R-A/B-R'-B pair tested alone. The wear reductions of these compounds acting alone were a significant and unexpected finding. The best of these was tert-butyl hydroquinone with a wear reduction of 98%. This finding revealed anti-wear behavior independent of the synergistic mechanism designed for these compounds and will be discussed later. Photomicrographs of tert-butyl hydroquinone wear areas are given in Figure 4.3.5.2. The higher magnification image (b) using internal lighting shows

a partially reflective surface, indicating that an extremely thin opaque film may be present. The other compounds resulted in unremarkable wear track appearances.

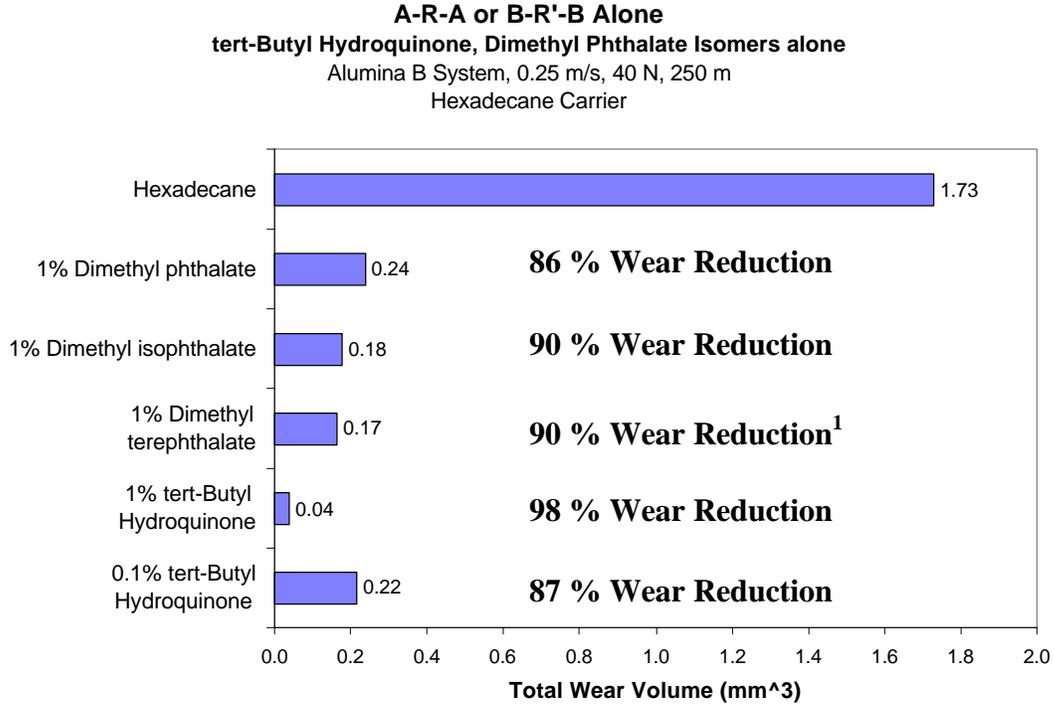


Figure 4.3.5.1 Anti-wear Effect of A-R-A or B-R'-B Compounds Tert-Butyl Hydroquinone and Dimethyl Phthalate Isomers Alone in Alumina B System.

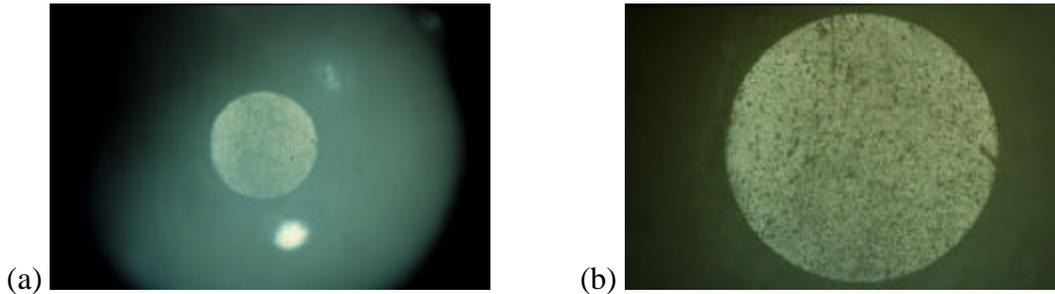


Figure 4.3.5.2 Photomicrographs of Tert-Butyl Hydroquinone Ball Wear, (a) Test 159, 15.75x, int/ext. lighting, (b) Test 159, 40x, int/ext. lighting.

¹ 69% when compared to same side references

Evaluation of additive synergy for the Kapton® compounds ODA and BTDA resulted in a similar unexpected anti-wear finding. Wear results in Figure 4.3.5.3 clearly demonstrate that the anti-wear behavior of this pair is governed by BTDA with an amazing wear reduction of 99%. Photomicrographs of the ODA ball in Figure 4.3.5.4 show an unremarkable wear scar. The noticeably smaller BTDA ball wear scar in Figure 4.3.5.5 images (a) and (b) possesses a slight filmlike appearance. In Figure 4.3.5.5 images (c) and (d) reveal obvious tribochemical changes evidenced by the lightly brown colored BTDA disk wear track.

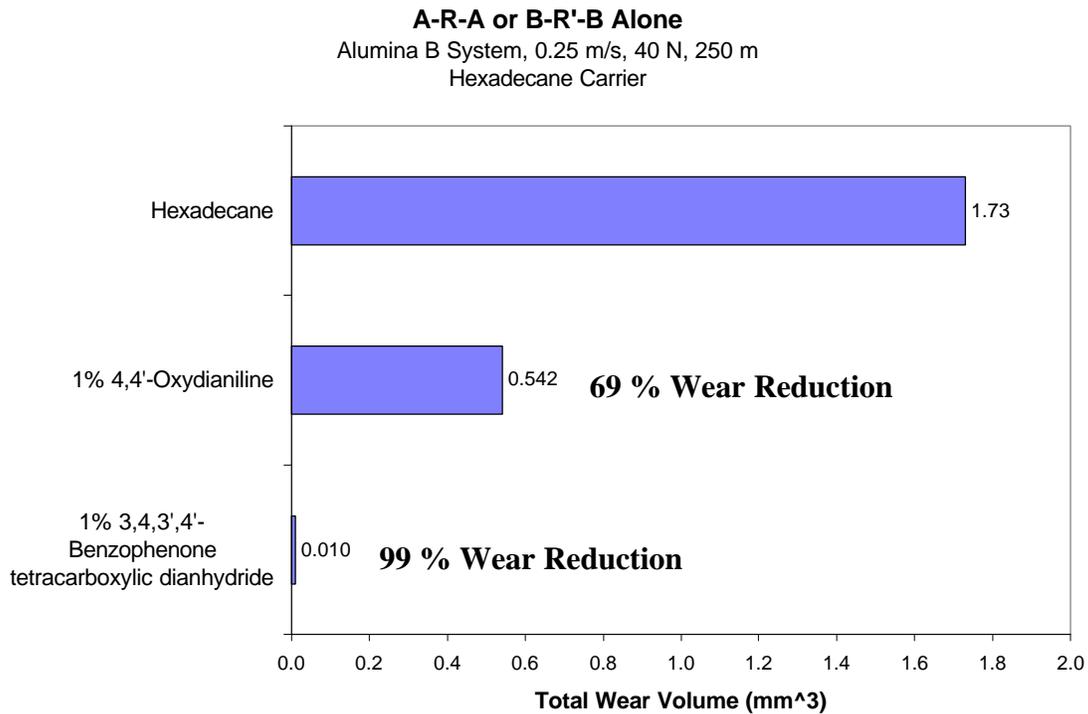


Figure 4.3.5.3 Anti-wear Effects of A-R-A or B-R'-B Compounds ODA and BTDA Alone in Alumina B System.

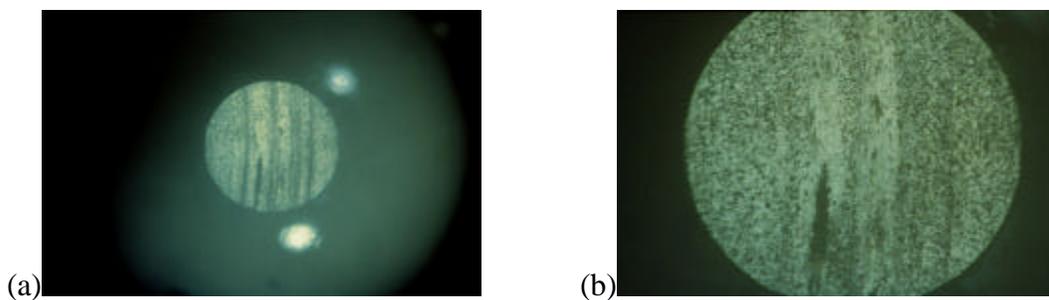


Figure 4.3.5.4 Photomicrographs of ODA Alone, Ball Wear Area, Test 151, (a) 15.75x, int./ext. lighting, after methanol rinse (b) 40x, int./ext. lighting, after methanol rinse.

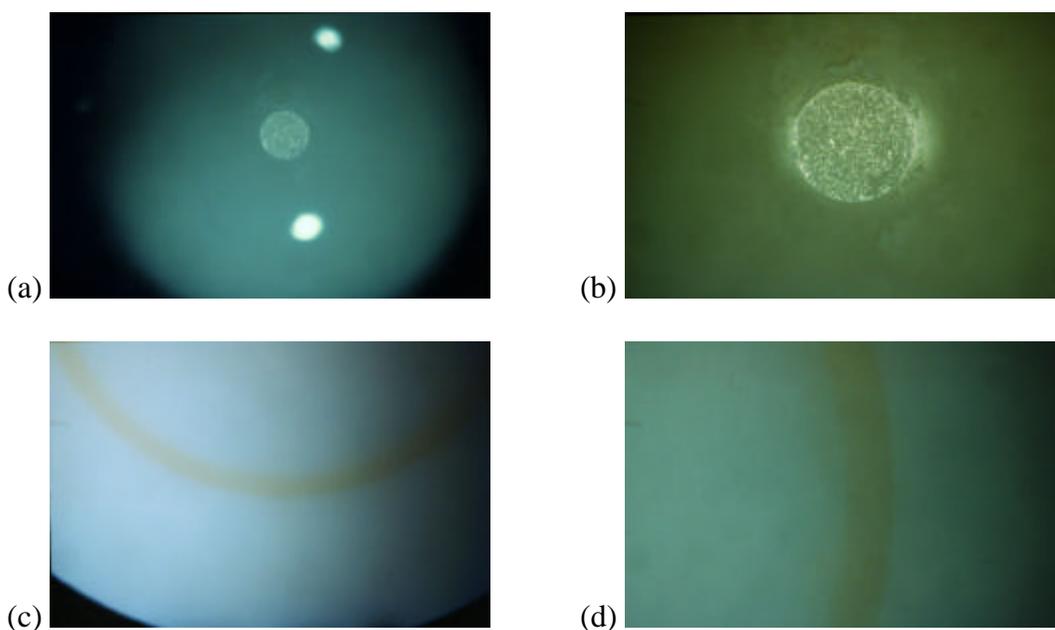


Figure 4.3.5.5 Photomicrographs of BTDA Alone Wear Areas, Test 153, (a) 15.75x, int./ext. lighting., after methanol rinse (b) 40x, int./ext. lighting, after methanol rinse, (c) 7.9x, ext. lighting, (d) 15.75x, ext. lighting.

4.3.6 Other Compounds

Two compounds from Tritt's [40] study that significantly reduced wear at the high and low loads (160 N) under the lower sliding speed of 0.25 m/s were tested in this study on the Alumina B System. The two goals of this separate study were to support earlier findings and to establish a common ground for comparing this study's unique

findings. Significant wear reductions were reaffirmed as shown by the graphical comparison of data in Figure 4.3.6.1. Diallyl phthalate produced no noteworthy deposits. The monoester wear areas did not produce colorful deposits but the consistency was similar to that of caprolactam and BTDA. Figure 4.3.6.2 illustrates this with photomicrographs of ball and disk wear areas.

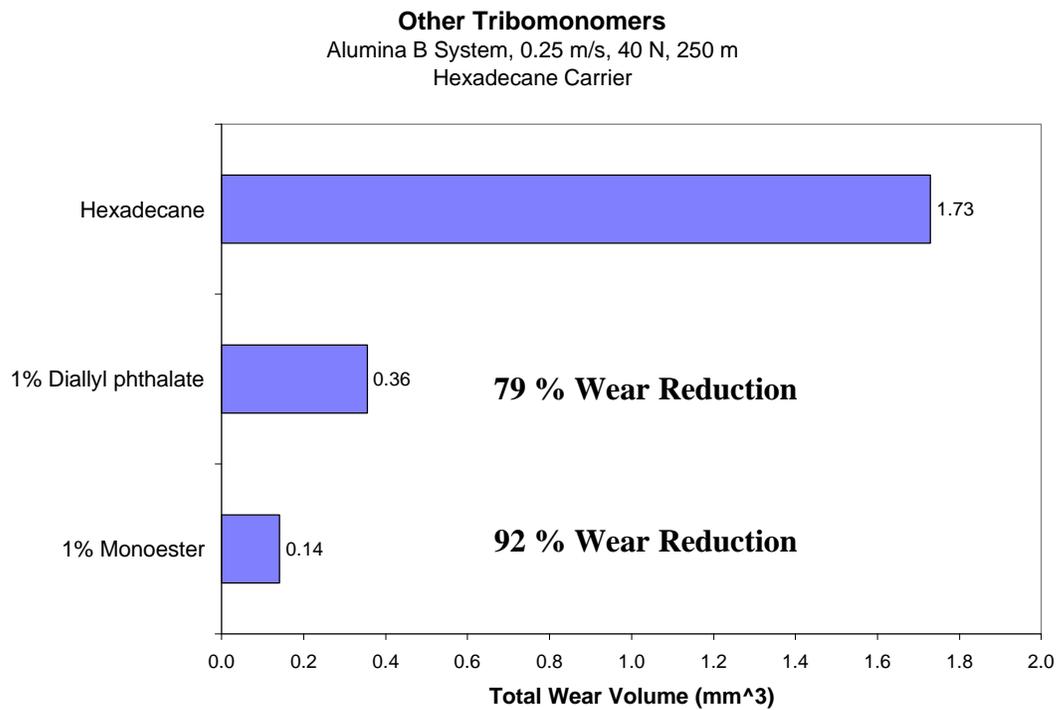


Figure 4.3.6.1 Anti-wear Effects of Other Compounds in Alumina B System.

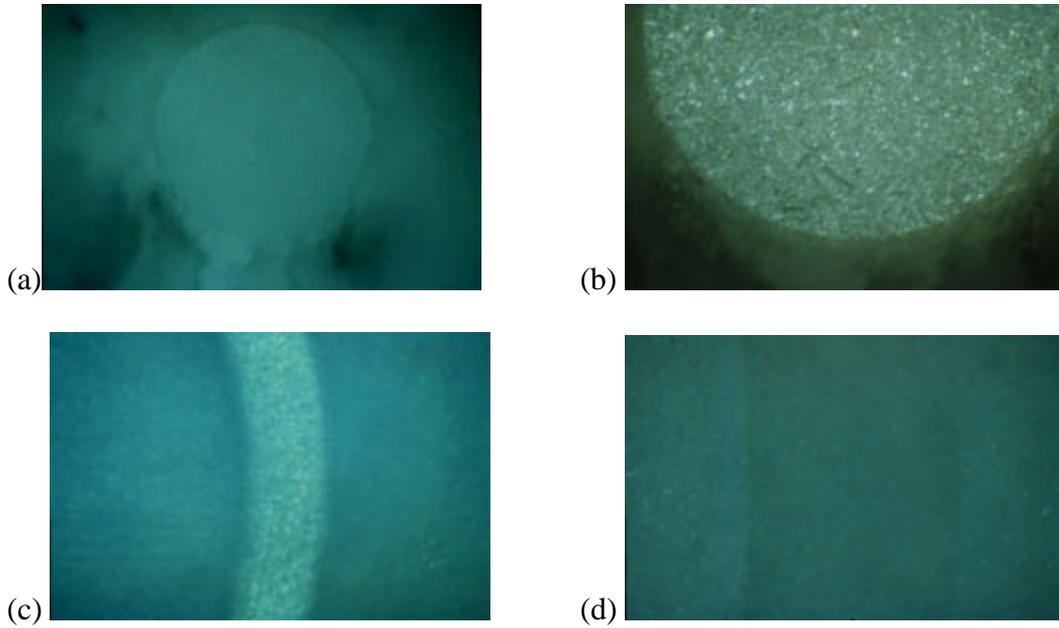


Figure 4.3.6.2 Photomicrographs of Monoester Wear Areas, Test 171, (a) 40x, ext. lighting., after methanol rinse (b) 80x, int./ext. lighting, after methanol rinse, (c) 15.75x, int. lighting, (d) 40x, ext. lighting.

Chapter 5

DISCUSSION

5.1 Objectives

Discussion of results begins with a restatement of the major objectives of this study:

- 1) To continue to use the tribopolymerization concept as an anti-wear approach for ceramics.
- 2) To explore the anti-wear capabilities of new high-temperature tribomonomers with amino and aromatic content.
- 3) To evaluate promising anti-wear behavior and/or economical additives at higher loads and speeds.
- 4) To identify and characterize any tribochemical changes evident in surface films formed from the boundary energy environment.

First the performance of the various classes of molecules as anti-wear additives is summarized by material systems of Steel, Alumina A and Alumina B for the standard test conditions of 40 N, 0.25 m/s and 250 m sliding distance. Next, the surprisingly effective anti-wear behavior of select molecules at higher loads and speeds is discussed. Finally, the performance of individual molecules from the molecular pairs (A-R-A + B-R'-B) is discussed.

5.2 Steel System

Due to the availability and low cost, initial exploratory testing was conducted using steel test specimens. Table 5.1 summarizes how representative new high-temperature additives from each class performed on steel substrates. Most of the new

aromatic compounds tested on steel were the simple A-R-B type where two different functional groups of similar monomers join to form a polymer. Four of the five A-R-B type monomers tested on steel contained acid end groups. Two of these A-R-B compounds contained an amino functional group and two contained a hydroxyl functional group. Both the amino and hydroxyl functional groups performed equally well with the acid. The fifth A-R-B type additive contained an amino group and an ester functional group. This aromatic amino ester, ethyl-4-aminobenzoate, showed comparable wear reduction to the first four. Overall, anti-wear behavior on the steel substrates of the five showed promise within the A-R-B class of tribopolymerization additives.

While the study on steel was a limited exploratory one, several observations from this system merit discussion. A minor trend observed during steel testing was that the longer cinnamic and phenylacetic molecules of the first class provided greater wear reduction (roughly 90% over 50%) compared to the shorter simpler benzoic counterparts. The longer molecules are more flexible and offer less steric resistance to bending and rotation thus providing more functional group interaction and favoring in-situ polymerization. The ester linkage in ethyl-4-aminobenzoate lends higher thermal stability, however anti-wear performance at standard conditions in the steel system did not show marked improvement over the other aromatic compounds.

Observations with the second and third classes of new compounds revealed anti-wear performance comparable to the first class of greater than 90% wear reduction. The A-R-A + B-R'-B pair of tert-butyl hydroquinone and dimethyl terephthalate tested in molar ratios suggested that mixed reactants could yield an in-situ product capable of wear reduction. The cyclic amide caprolactam also gave good wear reduction of over 90%.

These tests demonstrated anti-wear action where the reactive steel substrate may have contributed to the kinetics and/or thermodynamics of film formation. The overall performance on steel showed initial promise for these new additives leading to further tests of the tribopolymerization design concept on ceramic systems.

Table 5.1

Steel System Summary			
Polymerization Class	Molecular Structures	Additive Name	Wear Reduction
A-R-B Type	Aromatic hydroxy acids	4-hydroxy benzoic acid	58%
		4-hydroxy cinnamic acid	96%
	Aromatic amino acids	4-amino benzoic acid	56%
		4-amino phenylacetic acid	93%
	Aromatic esters	Ethyl-4-aminobenzoate	94%
A-R-A + B-R'-B Type	Aromatic diester + Aromatic dihydroxy	Dimethyl terephthalate + Tert-butyl hydroquinone	94%
Ring Type	Cyclic amide	Caprolactam	94%

5.3 Alumina A system

Moving from the steel system to the ceramic systems offered a new proving ground for the new classes of additives. The significantly greater reference total wear volume of 27 mm³ in Alumina A compared to 0.84 mm³ observed with steel gave opportunity to demonstrate potential savings under a drastically higher material removal

rate and inert substrate. Table 5.2 summarizes testing across the classes on the Alumina A system.

Three compounds from the A-R-B class underwent testing, an aromatic amino acid, an aromatic amino ester, and an aromatic hydroxy ester. Similar to findings in the steel system, each A-R-B additive offered some wear reduction. However, in the Alumina A system the additive containing the ester functional group, ethyl-4-aminobenzoate, drastically outperformed both the additive with the acid group, 4-amino benzoic acid (99.7% versus 33% wear reduction), and the aromatic hydroxy ester methyl-4-hydroxybenzoate (99.7% versus 83% wear reduction). The lower thermal conductivity of alumina tends to drive the surface temperature higher. The comparison between these functional groups differs from the Steel system comparison suggesting the aromatic additive with the ester and amino functional groups may show enhanced anti-wear performance at the higher surface temperatures in the Alumina A system.

Similar to the steel system results, the second and third classes of new compounds gave excellent anti-wear performance of greater than 90% wear reduction. The A-R-A + B-R'-B pair of tert-butyl hydroquinone and dimethyl terephthalate yielded an impressive wear reduction of 99.9%. The cyclic amide caprolactam gave an equally remarkable wear reduction of 99.8%.

The overall performance of the additives from each class in the Alumina A system further reinforced the success of the tribopolymerization design concept for high-temperature anti-wear additives found in the Steel system. Extended and expanded anti-wear performance of selected promising additives was found from tests using the Alumina B system summarized next.

Table 5.2

Alumina A System Summary			
Polymerization Class	Molecular Structures	Additive Name	Wear Reduction
A-R-B Type	Aromatic amino acid	4-amino benzoic acid	33%
	Aromatic amino ester	Ethyl-4-amino benzoate	99.7%
	Aromatic hydroxy ester	Methyl-4-hydroxy benzoate	83%
A-R-A + B-R'-B Type	Aromatic diester + Aromatic dihydroxy	Dimethyl terephthalate + Tert-butyl hydroquinone	99.9%
Ring Type	Cyclic amide	Caprolactam	99.8%

5.4 Alumina B system

Continued testing on the second ceramic system offered more evidence of the anti-wear potential of selected additives from each class. The Alumina B material system exhibited much lower wear rates than the first alumina material system (1.73 mm^3 compared to 27.1 mm^3 reference averages). Further exploration at standard conditions (40 N, 0.25 m/s, 250 m) continued within the three classes as shown in Table 5.3.

Additives gave excellent wear reductions averaging over 90% across the six candidates.

Within the A-R-B class, ethyl-4-aminobenzoate continued to perform well reducing wear by 93%. The aliphatic amino acid, 6-aminocaproic acid, is closely related

to the cyclic amide caprolactam. This aliphatic structure performed essentially equal to the cyclic form thus demonstrating that the basic anti-wear behavior starts with the amino acid composition.

Two formulations from the A-R-A + B-R'-B class and one from the cyclic amide class also resulted in excellent wear reductions. The tert-butyl hydroquinone and dimethyl terephthalate combination gave a wear reduction of 97%. Not tested in earlier systems, the Kapton® compounds ODA and BTDA gave a wear reduction of 98%. The interesting films formed in-situ and the high temperature stability of the commercial Kapton® film warranted exploratory testing at higher loads and speeds which is discussed later. As in the steel and first alumina system, caprolactam demonstrated excellent anti-wear action by reducing wear 89%. Due to its commercial availability and good solubility, caprolactam was also selected for exploratory testing at higher loads and speeds.

Table 5.3

Alumina B System Summary			
Polymerization Class	Molecular Structures	Additive Name	Wear Reduction
A-R-B Type	Aliphatic amino acid	6-aminocaproic acid	95%
	Aromatic amino ester	Ethyl-4-amino benzoate	93%
A-R-A + B-R'-B Type	Aromatic diester + Aromatic dihydroxy	Dimethyl terephthalate + Tert-butyl hydroquinone	97%
	Kapton® monomers	ODA +BTDA	98.6%
Ring Type	Cyclic amides	Caprolactam	89%
		Lauro lactam	90%

5.5 Parametric studies

The results from these three material systems represent substantial findings on the anti-wear capability of new high-temperature additives at 1 % by weight in hexadecane for the standard conditions of 40 N, 0.25 m/s, and 250 m sliding distance. Extensions to the successful exploratory findings included four parametric studies. These were conducted to investigate: 1) filtering and lower concentrations, 2) individual performance of the A-R-A and B-R'-B pairs, 3) effect of ring size for the cyclic amide and 4) performance of caprolactam and Kapton ® compounds at higher loads and speeds.

Several compounds were tested after filtering or at lower concentrations in the high wear Alumina A system. The successful ethyl-4-aminobenzoate underwent filtering to remove cloudy particulates visible in the solution with hexadecane. The filtering resulted in a slight decrease in wear reduction from 99.7% to 80%. A filtered dimethyl terephthalate and tert-butyl hydroquinone solution resulted in a nearly identical wear reduction of 99.8% compared to the 99.9% reduction at 1% by weight. Similarly, a filtered caprolactam solution compared equally to the 1% solution at 99.6% versus 99.8% wear reduction. The filtered solutions removed the cloudiness or particulate suspensions thus eliminating the potential of a solid film lubricant effect. Due to low solubility of most of the compounds in hexadecane at room temperature the true concentrations of the filtered solutions were not known, but definitely less than 1% suspensions.

However, in the low wear Alumina B system, the Kapton ® compounds and caprolactam were tested using measured lower concentrations without filtering. The Kapton ® compounds ODA and BTDA at 0.1% by weight gave an almost identical wear reduction of 98.7% compared to the 98.6% of the 1% by weight solution. Solutions of

caprolactam at 0.1% and 0.02% by weight gave 87% and 73% wear reductions respectively compared to the 89% of the 1% by weight solution. The initial concentration and rate of depletion of additives must be considered for any system application and would require further testing. These results from studying the filtered and lower concentrations of additives demonstrate substantial material savings provided from very low concentrations in a carrier fluid.

The second parametric study investigated the effect of ring size within the cyclic amide class. Laurolactam, containing an amide group with a 12 carbon ring was tested and compared to the highly successful caprolactam which contains the amide and a 5 carbon ring. The resulting 90% wear reduction of lauro lactam suggested that ring size was less important than the core functionality within the ring – the amide bond – which is capable of breaking to form polymers in the contact zone. The linear 6-aminocaproic acid has similar molecular composition to caprolactam but does not need to undergo an initial ring-opening step to polymerize. As expected, this structure gave comparable wear reduction to the lactams showing that the tribochemistry favors ring-opening anti-wear action via tribopolymerization.

The third parametric study investigated individual molecules of the two pairs from the A-R-A + B-R'-B class. Testing revealed two significant findings. First, the isomeric variations of dimethyl – phthalate, - isophthalate, and - terephthalate, had little effect on wear reduction as all isomers fell within the range of 96-97% wear reductions when paired with tert-butyl hydroquinone. Second, dimethyl phthalate, dimethyl isophthalate, and dimethyl terephthalate reduced wear when tested alone by 86%, 90% and 90% respectively. Further, tert-butyl hydroquinone alone reduced wear by the same order as

the combinations at 98% compared to 97%. This suggests that tert-butyl hydroquinone provided the superior boundary layer protection at the root of the wear reductions in all tests. The Kapton® monomers underwent similar individual testing resulting in evidence of superior wear reduction from the BTDA molecule of the pairing. The ODA additive alone reduced wear by 69% while BTDA by itself produced a 99% wear reduction. These findings support that the initial surface interaction plays an important role in wear reduction and that tribopolymerization may sometimes occur in more than one step.

The fourth and most important parametric study tested the Kapton® compounds and caprolactam at higher loads and speeds. Previous work by Tripathy [23] and Tritt [40] showed various trends presented here for discussion. Part of Tripathy's work presented again in Figure 5.1 found that diallyl phthalate and monoester demonstrated the best trends of increasing wear reduction with increasing load at the low sliding speed of 0.25 m/s. It is of some interest to note that of the five compounds tested in Tritt's work only diallyl phthalate had aromaticity and only the monoester had a cyclic component.

Tritt's work, summarized in Table 5.4, found speed to be the limiting factor in anti-wear behavior with only one of the six compounds reducing wear at 1.00 m/s and only slightly at 13%. A common ground for this body of work was established by testing earlier compounds. Diallyl phthalate and monoester tested at the 40 N and 0.25 m/s conditions yielded wear reductions in the current study of 79% and 92% respectively. The same test conditions in Tritt's previous study produced comparable reductions of 95% and 93% for these two compounds. In the current study, testing limitations allowed for only twice the load and three times the speed of standard conditions.

Effect of Load on Relative Wear for Several Tribomonomers

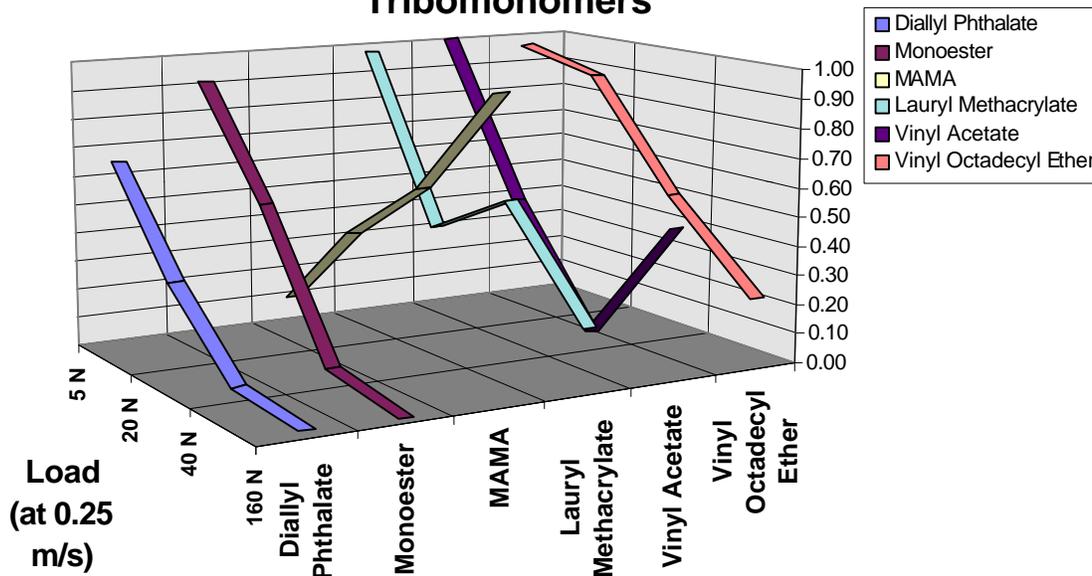


Figure 5.1 Effect of Load on Relative Wear for Several Tribomonomers

These conditions provided a 2x2 matrix of load and speed affording 1x, 2x, 3x, and 6x the frictional heat generation whereas Tritt's study extended to 16x the baseline conditions. However, the maximum sliding speed of 0.75 m/s approached the 1.0 m/s limit found by Tritt. The results of Table 5.5 are the most interesting and significant of the study. At the most demanding conditions, caprolactam reduced wear by 57% while the ODA/BTDA combination reduced wear by a remarkable 99%. The striking anti-wear performance of the ODA/BTDA pair was accompanied with striking visual evidence of tribochemical activity as seen in the colorful deposits presented in Chapter 4. Caprolactam's performance was accompanied by a noticeable wear debris layer but no colorful films. Thus, both anti-wear additives reacted from the liquid phase on or near the surface as desired and predicted by the tribopolymerization model.

Table 5.4

High Speed High Load Results: Tritt's Study [40]				
Additive Name	Wear Reduction			
	Load (N)			
	L(40)	L(40)	H(160)	H(160)
	Speed (m/s)			
	L(.25)	H(1.00)	L(.25)	H(1.00)
Diallyl Phthalate	95	13	97	0
Monoester	93	-47	98	-8
MAMA ¹	37	-84	-10	-6
Lauryl Methacrylate	44	-131	78	-22
Vinyl Acetate	93	-81	49	-38
Vinyl Octadecyl Ether	48	-118	76	-1
Relative Frictional Heat Generation	1x	4x	4x	16x

Table 5.5

High Speed High Load Results: Current Study				
Additive Name	Wear Reduction			
	Load (N)			
	L(40)	H(80)	L(40)	H(80)
	Speed (m/s)			
	L(.25)	L(.25)	H(.75)	H(.75)
Caprolactam	83	91	83	57
ODA/BTDA ²	98	95	95	99
Relative Frictional Heat Generation	1x	2x	3x	6x

The success of these two additives at 0.75 m/s partially fills a gap left by earlier additives on tribopolymerization effectiveness between sliding speeds of 0.25 m/s and 1.0 m/s. The high temperature design potential of these additives seems to correspond with good anti-

¹ Methyl 2-Acrylamido 2-Methoxy Acetate

² 4,4'-Oxydianiline and 3,4,3',4'-Benzophenone tetracarboxylic dianhydride

wear behavior as desired. The outstanding wear reduction for the ODA/BTDA pair was originally intended for synergistic polymerization requiring both compounds. However, BTDA clearly provided superior boundary protection at standard conditions and may alone explain the success at higher loads and speeds. The tribochemistry of the brown film observed with the combination does not rule out a synergistic polymer.

X-ray Photoelectron Spectroscopy (XPS) of the disk wear surface shows evidence of tribochemical reaction that corresponds with the visual evidence. XPS offers surface chemical composition information in the form of atomic concentrations up to a depth of 50 μm . Figure 5.2 compares the relative surface concentrations of several atoms present outside the disk wear track of an ODA/BTDA test to that inside the wear track. The most significant result is the comparison of the aluminum atomic (Al^{2p3}) concentrations outside versus inside the wear track. This reflects the difference between what is absorbed to the surface and what is tribochemically present at the wearing surface. The tribochemically altered disk wear track shows a 10% reduction in aluminum, a 17% decrease in oxygen, a 25% increase in carbon and double the atomic concentration of nitrogen compared to the unaltered surface. This is evidence of a durable film protecting the alumina surface that has been tribochemically composed of carbon and nitrogen atoms from the additive molecule just as predicted by the tribopolymerization concept.

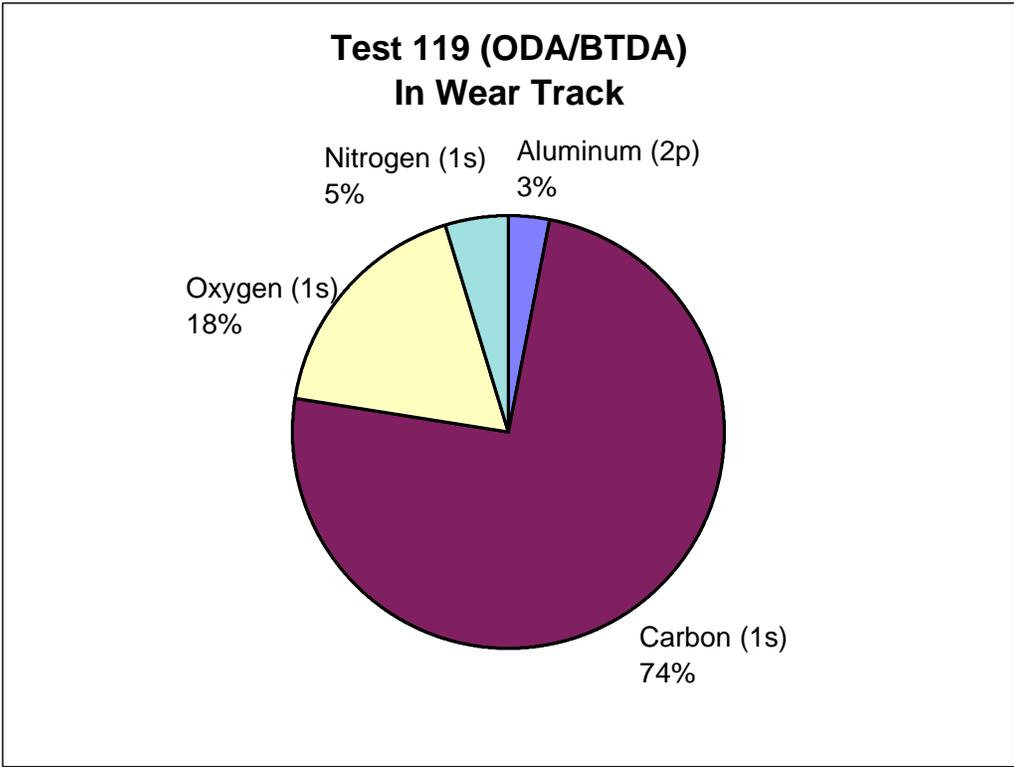
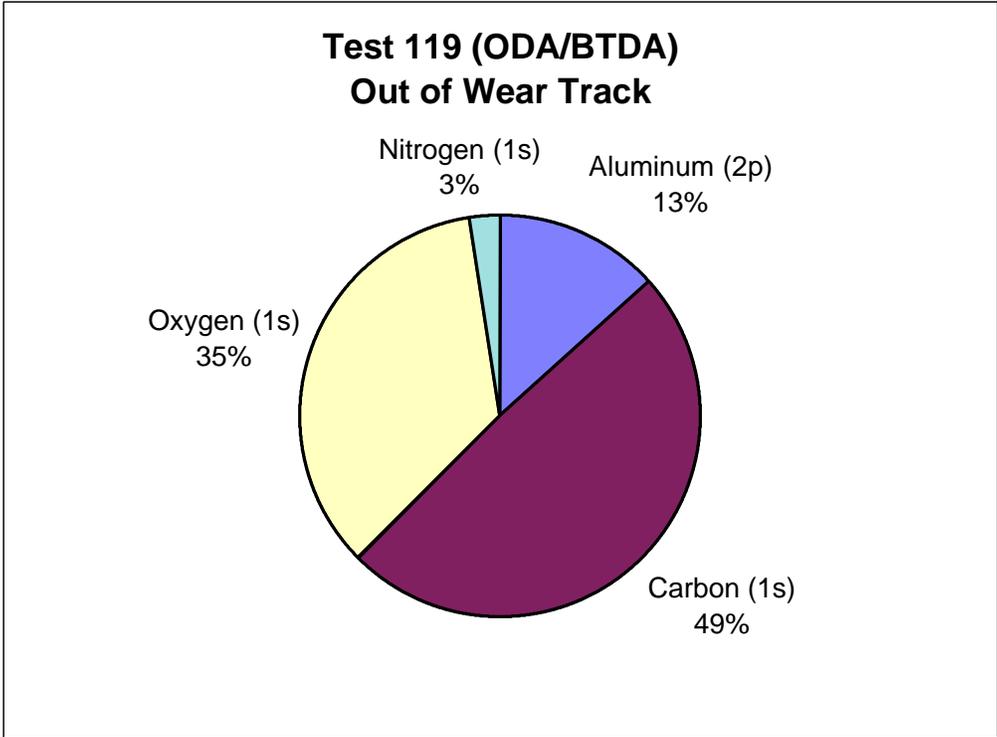


Figure 5.2 XPS Results from ODA/BTDA Surfaces

Chapter 6

CONCLUSIONS

- 1) Three new classes of high temperature tribopolymerization compounds containing nitrogen and/or aromaticity tested for anti-wear effects at concentrations of 1% by weight or less in hexadecane showed significant wear reductions at the standard conditions of 0.25 m/s, 40 N, 250 m in three distinct material systems demonstrating continuing success of the tribopolymerization approach to boundary lubricant design.
- 2) Exploratory testing in a steel system followed by two ceramic systems offered diverse conditions for investigating anti-wear behavior. The first alumina system (A) had an average reference wear of 27 mm³ whereas the lower wear system's (B) average was only 1.73 mm³. The majority of testing was conducted in the Alumina B system, where same side reference testing reinforced the wide variation in reference results found in earlier systems. In both alumina systems, compounds from each class demonstrated outstanding anti-wear behavior by consistently reducing wear volumes by one order of magnitude.
- 3) The most promising A-R-B type compound, an aromatic amino ester (ethyl-4-aminobenzoate) yielded significant wear reductions (94%, 99.7%, 93%) in all three material systems.
- 4) The A-R-A + B-R'-B pairing of tert-butyl hydroquinone and dimethyl terephthalate yielded significant wear reductions (94%, 99.9%, 97%) in all three material systems.
- 5) The A-R-A + B-R'-B pairing of Kapton® compounds ODA and BTDA yielded the best anti-wear performance in the Alumina B system at 99% wear reduction.

- 6) The cyclic amide, caprolactam, yielded significant wear reductions (94%, 99.8%, 89%) in all three material systems.
- 7) Individual compounds from the A-R-A + B-R'-B group were tested alone at 1% weight concentration in hexadecane with an alumina-on-alumina system. Dimethyl phthalate isomers (para-, iso-, and tere-) each reduced wear by 85 to 90% while tert-butyl hydroquinone reduced wear by over 95%. ODA reduced wear by greater than 65% while BTDA showed a reduction of over 99%.
- 8) Compounds from two classes demonstrated anti-wear effects in a 2x2 matrix of higher speeds and loads representing up to a six-fold increase in frictional heat generation. At the most demanding conditions of 0.75 m/s and 80 N caprolactam reduced wear by over 50% while the ODA/BTDA combination reduced wear by a remarkable 99%.
- 9) Visible brown debris/reaction films evident whenever BTDA was in the lubricant solution demonstrate the substantial tribochemical activity behind the wear reduction.
- 10) Photomacrography evidence of debris adhesion and/or thin films on and near wear areas correlated with effective anti-wear behavior of additives.
- 11) XPS analysis of an ODA/BTDA disk wear track tribochemical changes showed a 10% reduction in aluminum, a 17% decrease in oxygen, a 25% increase in carbon and double the atomic concentration of nitrogen. This is evidence of a durable film composed of atoms from the additive molecules that protects the alumina surface.

Chapter 7

RECOMMENDATIONS

- 1) Extended and in-depth testing of the new classes of tribopolymerization additives is warranted. Study of the effects of load, speed and temperature would be invaluable contributions to the tribopolymerization knowledge base.
- 2) Additives such as the ones demonstrated here offer great promise in anti-wear applications. Similar compounds should be sought and explored to further investigate which molecular attributes are responsible for anti-wear behavior.
- 3) These additives should be evaluated in other ceramic material systems to test the anti-wear behavior under different tribochemistry.
- 4) Vapor-phase lubrication studies should be conducted with the new additives for evaluation and comparison of anti-wear behavior to Smith's and others' work.

References

1. Dowson, D., History of Tribology, Longman Group Lmtd., New York, [1979].
2. Katz, R. N., "Opportunities and Prospects for the Application of Structural Ceramics," Structural Ceramics, *Treatise on Materials Science and Technology*, Vol. **29**, J. B. Watchman, Jr. ed., Academic Press Inc., Boston pp 1-26 [1989].
3. Bratt, R. C., 2nd European Symposium on Engineering Ceramics, F. L. Riley, ed., Elsevier, London, p 230, [1989].
4. Graham, Edgar E., Makki, James F., "Ceramic Article Having Wear Resistant Coating," U.S. Patent 5139876, Issued Aug 18, 1992.
5. Griffith, Michael J., "Combination Thermal Barrier and Wear Coating for Internal Combustion Engines," U.S. Patent 5413877, Issued May 9, 1995.
6. Kawamura, Hideo, "Ceramic Engine," U.S. Patent 5063881, Issued to Isuzu Motors Limited, Nov 12, 1991.
7. Habeeb, J. J. Blahey, A. G., and Rogers, W. N. "Wear and Lubrication of Ceramics," Tribology: Friction, Lubrication and Wear: 50 Years, On, *Proc. of the Intitution of Mechanical Engineers*, Imech, C132/87, London, pp 555-564 [1987].
8. Studt, P., "Influence of Lubricating Oil Additives on Friction of Ceramics Under Conditions of Boundary Lubrication," *Wear*, **115**, pp. 185-191 [1987].
9. Sasaki, S., "The Effect of Surrounding Atmosphere on the Friction and Wear of Alumina, Zirconia, Silicon Carbide, and Silicon Nitride," *Wear of Materials* [1989], K. C. Ludema, ed. ASME, New York, pp 409-417; *Wear*, **134**, pp 185-200 [1989].
10. Tsunai, Y. and Enomoto, Y., "Tribochemistry of Silicon Based Ceramics in Alcohols," *Proc. 8th Int'l Symp. On Alcohol Fuels*, Tokyo, pp 715-721, [1988].
11. Jahanmir, S. and Fischer, T.E., "Friction and Wear of Silicon Nitride Lubricated by Humid Air, Water, Hexadecane and Hexadecane + 0.5 Percent Stearic Acid," *Tribology Trans.*, **31**, pp 32-43 [1988].
12. Tsunai, Y. and Enomoto, Y. "Tribochemical Wear of Silicon Nitride in Water, n-Alcohol and Their Mixtures," *Wear of Materials* 1989, K. C. Ludema, ed., ASME, New York, pp 369-374 [1989].
13. Fischer, T. E., Anderson, M. P., Jahanmir, S. and Salher, R., "Friction and Wear of Tough and Brittle Zirconia in Nitrogen, Air, Water, Hexadecane, and Hexadecane Containing Stearic Acid," *Wear*, **124**, pp 133-148 [1988].

14. Klaus, E. E., Phillips, Y. S., Lin, C., Wu, N. L. and Duda, Y. L., "Structure of Films Formed During the Deposition of Lubrication Molecules on Iron and Silicon Carbide," *Tribology Trans.*, 33, pp 25-32 [1990].
15. Wu, W. T., Duda, Y. L. and Klaus, E. E., "Lubrication Studies with Alumina-on-Alumina, Steel-on-Steel, and Steel-on-Alumina Bearing Systems," *J. Am. Ceram. Soc.*, 73, pp 2247-2254 [1990].
16. Habeeb, Jacob J., Blahey, Alan G., Rogers, William N., "Method of Reducing the Wear of Metal and Ceramic Surfaces," U.S. Patent 4826612, Issued to Exxon Research and Engineering Company, May 2, 1989.
17. Wedeven, Lavern D. "Method for Broad Temperature Range Lubrication with Vapors," U.S. Patent 5584360, Issued Dec 17, 1996.
18. Rosado, Lewis, et al. "Lubrication by Sublimation," U.S. Patent 5327998, Issued July 12, 1994.
19. Lauer, James L, Dwyer, Scott R, "High Temperature Lubrication by Carbon Continuously Replenished by Surface Reaction with Carbonaceous Gases. Comparison of Metallic (Ni) and Ceramic (Si₃N₄) Surfaces." Rensselaer Polytechnic Inst, Troy, NY, USA. SAE-Trans. v 99 Sect 4, p 258-264 [1990].
20. Ahsley, Steven, "Lubricating Ceramic Engines with Exhaust," *Mechanical Engineering*. Vol. 14, No. 10, p 72-73, Oct 1992.
21. Braza, J. F., Cheng, H. S., Fine, M. E., Gangopadhyay, A. K., Keer, L. M., and Worden, R. E., "Mechanical Failure Mechanisms in Ceramic Sliding and Rolling Contacts", *Tribology Transactions*, Vol. 32, No. 1, pp. 1 -8, [1989].
22. Jahanmir, S. and Fischer, T. E., "Friction and Wear of Silicon Nitride Lubricated by Humid Air, Water, Hexadecane and Hexadecane + 0.5 Percent Stearic Acid," *Tribology Trans.*, 31, pp 32-43 [1988].
23. Tripathy, B. S., "A New Approach to Ceramic Lubrication: Tribopolymerization," Ph.D. Dissertation, Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, August, [1994].
24. Furey, M.J., "The Formation of Polymeric Films Directly on Rubbing Surfaces to Reduce Wear", *Wear*, 26, pp. 369-392 [1973].
25. Furey, M. J., "The *in situ* Formation of Polymeric Films on Rubbing Surfaces," *Proc. In't'l Colloq. Polymers and Lubrication*, Brest, Centre National de la Recherche Scientifique, Paris, No. 133, pp 393-404 [1975].

26. Furey, M. J. and Kajdas, C., "Tribopolymerization," 4th Int'l Tribology Conf. Budapest, Hungary, Sep 22-24 [1987].
27. Furey, M. J., Kajdas, C., Ward, T.C. and Hellgeth, J. W., "Thermal and Catalytic Effects on Tribopolymerization as a New Boundary Lubrication Mechanism," Plenary Lecture (MJF), 5th *International Congress on Tribology*, Helsinki, Finland, June 12-15, 1989; also published in *Wear*, 136, pp. 85-97 [1990].
28. Furey, M. J., and Kajdas, C., "Tribopolymerization as an Anti-Wear Mechanism," *Symp. on Surface Science Applications and Advances in Tribology*, Division of Colloid and Surface Chemistry, 201st National Meeting., American Chemical Society, Atlanta, GA, April 14-19 [1991].
29. Furey, M. J., "Tribopolymerization: A Novel Approach to Ceramic Lubrication," Proc. of the 4th Int'l Symp. on Ceramic Materials and Components for Engines, R. Carlsson, T. Johansson and L. Kahlman, eds., Elsevier Applied Science, London pp. 1211-1218 [1992].
30. Furey, M. J., and Kajdas, C., "Tribopolymerization as a Lubrication Mechanism for High-Energetic Contacts of Solids,- 6th *Int'l Tribology Colloq.*, Technische Akademie Esslingen, Esslingen, Germany, Jan.12-14 [1988].
31. Furey, M. J., and Kajdas, C., "Models of Tribopolymerization as an AntiWear Mechanism," *Proc. of the Japan Int'l Tribology Conf.*, Nagoya, Oct. 29 - Nov.1, Vol.11, pp 1089-1094 [1990].
32. Furey, M. J., "Tribology", *Encyclopedia of Material Science and Engineering*, Editor-in-Chief M. B. Bever, Pergamon Press, Oxford, pp. 5145-5157 [1986].
33. Furey, M. J., and Kajdas, C., "The Planned Formation of Polymeric Films on Rubbing Surfaces to Reduce Wear," 61st *Colloid Surface Science Symposium*, American Chemical Society, The University of Michigan, Ann Arbor, 21-24 June [1987].
34. Furey, M. J., Kajdas, C., and Kempinski, R., "Tribopolymerization as an Anti-Wear Mechanism: Surface Interactions with Dimer Acid/Glycol Derivatives," 200th *Amer. Chem. Soc. National Meeting*, Div. of Colloid and Surface Chemistry, Paper COLL 23, Washington DC, August 26-31, [1989].
35. Marin-LeFleche, P., Kajdas, C., Furey, M. J., Ward, T. E., and Heligeth, J. W., "A Study of Tribopolymerization Under Fretting Contact Conditions," 200th *Amer. Chem. Soc. National Meeting*, Div. of Colloid and Surface Chemistry, Paper COLL 26, Washington DC, August 26-31, [1989].
36. Furey, M. J. and Kunc, J. F., "A Radio Tracer Approach to the Study of Engine Valve Train Lubrication," *Lubrication Engineering*, pp. 302-309, July [1958].

37. Marin-LaFleche, P., "A Study of Tribopolymerization Under Fretting Conditions," MS Thesis, Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, May [1990].
38. Marin-LaFleche, P., Kajdas, P., Furey, M. J., Ward, T. C., and Heligeth, J. W., "A Study of Tribopolymerization Under Fretting Contact Conditions," *Proc. of the 8th Int'l Colloq. Tribology -- "Tribology 2000"* Esslingen, Germany, Jan 14-16, Vol. 1 [1992].
39. Smith, J. C., "Ceramic Lubrication: Vapor Phase Tribopolymerization and A New High Speed, High Load Pin-on-Disk Machine," MS Thesis, Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, February 1994.
40. Tritt, B.R., "Tribopolymerization: Ceramic Lubrication Under High Loads and High Speeds," MS Thesis, Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, January, 1995.
41. Nakayama, K., Masmimoto, H., and Fakuda, Y., "Triboemission From Aluminum Oxide Film in Atmosphere," *Proc. Japan Int'l Tribology Conf.*, Nagoya, pp 1141 - 1146 [1990].
42. Nakayama, K., Masmimoto, H., "Triboemission from Various Materials in Atmosphere," *Wear*, 147, pp 335-343 [1991].

Jeffrey Joseph Valentino: VITA

The author was born on August 13, 1970 in Pittsburgh Pennsylvania to Mr. Ralph Allen Valentino and Mrs. Anne Power Valentino. He received his Bachelor of Science in Mechanical Engineering from Virginia Polytechnic Institute and State University in July of 1992. After one year of graduate school he worked as an assistant volleyball coach at Bethel Park High School, then served one year as an environmental engineer for URS Consultants of Virginia Beach before returning to Virginia Tech in 1995 to continue his Master's studies. Upon completion of the MS degree, he will continue to work for the United States Army Tank-automotive and Armaments Command (USATACOM) in Warren, Michigan.