

**ENHANCING THE PERFORMANCE AND/OR DURABILITY OF
CERTAIN WET FRICTION MATERIALS**

This invention relates to improving the frictional performance and/or the durability-performance of mechanical apparatus having frictional surfaces that operate while in contact with an oil-based lubricant or functional fluid. Frictional materials that operate in this manner are sometimes referred to hereinafter as "wet service friction materials".

More particularly, this invention relates to ways of improving the durability and performance of friction materials containing 10% or more of fibrous aramid polymers where the friction materials are exposed to an oil-based lubricant and/or functional fluid during usage.

Fibrous aramid polymers such as poly(para-phenyleneterephthalamide) are useful as components in the manufacture of friction materials such as plates, linings, rings and other frictional surfaces which come in contact with oil-based lubricants and/or functional fluids during actual service conditions.

It has previously been observed that a glaze tends to develop over the surface over wet service friction materials. The polishing of such glaze can markedly diminish the effectiveness of the friction surface. Moreover, pieces or chunks of the glaze can break away from the surface and thereby destroy the integrity and greatly impair the durability of the friction surface.

So far as is known, no satisfactory explanation heretofore existed for the cause of such glaze formation or ways by which its formation can be controlled, if not eliminated.

This invention is based, in part, on the discovery of the cause of the glaze problem, and in part on the discovery of a highly effective solution to this problem. In addition, pursuant to this invention it is now possible to achieve excellent long-term performance and durability in mechanical apparatus which utilizes wet service friction materials.

In the first place, it has now been discovered that the glaze that develops on the surface of wet service friction materials is caused by thermal decomposition of various additives present in oil-based lubricant or functional fluids. Friction

surface temperatures measured at 320°C and higher were found in many cases to cause such decomposition and analyses of the resultant glazes provided confirmation of this discovery.

Secondly, it was found that phosphorus-containing ashless (i.e., metal-free) dispersants unlike many other dispersant or detergent additives have sufficient thermal stability to resist such thermal decomposition. Thus not only do such additives not contribute appreciably to the formation of glaze on the wet service friction surface, but they keep the surface free of excessive deposits and thereby can enable friction modifiers to interact with the original friction surface and perform their intended function.

Still further, this invention involves the discovery that by utilizing a phosphorus-containing ashless dispersant with wet service friction materials having frictional surfaces comprising 10% or more of aramid fibers, excellent long-term frictional performance and/or durability can be achieved. For best results, the oil-based lubricant or functional fluid containing the phosphorus-containing ashless dispersant is devoid of metal-containing components such as zinc dithiophosphates, and contains at most 100 ppm of alkali and/or alkaline earth metal detergent additives such as calcium phenates or the like. In short, the lubricants or functional fluids used are preferably "ashless" or "substantially ashless".

In one of its embodiments this invention provides, in combination, friction means having at least one friction surface in contact with an oil-based lubricant and/or functional fluid wherein the friction surface comprises at least 10, preferably at least 15, more preferably at least 20, still more preferably at least 25, and most preferably at least 30 percent by weight of fibrous aramid polymer, and wherein the oil-based lubricant and/or functional fluid contains a minor amount of at least one oil-soluble or oil-dispersible phosphorus-containing ashless dispersant. Such combinations of wet service friction materials and oil-based lubricants and/or functional fluids cooperate to achieve results that cannot be achieved by other combinations of such materials.

In particular, pursuant to this invention, the excellent strength and frictional properties of aramid fiber-containing friction surfaces that operate while wet with oil are, in a sense preserved by using an oil that contains a phosphorus-containing

ashless dispersant. In the absence of a phosphorus-containing ashless dispersant in the oil, a heavy glaze can readily develop on the friction surface and thereby greatly impair the performance of the clutch, transmission, torque converter, wet brake, limited slip differential, synchronizer, or like mechanical apparatus in which
5 such friction material is used. But with the presence in the oil of a phosphorus-containing ashless dispersant, the formation of such glazed friction surface is prevented or at least greatly inhibited for long periods of time during which the friction surface can perform as it was intended and designed to perform.

Another embodiment of this invention resides in a method of improving
10 the frictional performance and/or frictional durability of a friction surface of a wet service frictional material which comprises supplying or using as the friction material a material in which the friction surface has at least 10, preferably at least 15, more preferably at least 20, still more preferably at least 25, and most preferably at least 30 percent by weight of fibrous aramid polymer, and supplying or using as the
15 lubricant or functional fluid for such frictional material, an oil-based lubricant or functional fluid containing a minor friction-performance enhancing and/or friction-durability enhancing amount of at least one oil-soluble or oil-dispersible phosphorus-containing ashless dispersant.

Other embodiments will appear in the ensuing description and appended
20 claims.

Figures 1 through 8 are plots of test data obtained with 8 different automatic transmission fluids. Two of the figures present data obtained by the practice of this invention.

Figure 9 is a plot of torque versus time for a single engagement in the
25 friction tester used in generating the data plotted in Figures 1-8. Figure 9 also defines visually the midpoint and peak torques which are plotted in Figures 1 through 8.

As is apparent from the foregoing, this invention in one of its aspects comprises providing apparatus equipped with a wet service frictional material
30 containing at least 10% by weight of aramid fibers, and providing and/or employing as factory fill and/or service fill lubricant and/or functional fluid for said apparatus, a lubricant and/or functional fluid comprising oil of lubricating viscosity and a minor

amount of an oil-soluble or oil-dispersible phosphorus-containing ashless dispersant.

The apparatus involved in this embodiment is typified by a wet brake system, a manual transmission, an automatic transmission, a torque converter, a limited slip differential, and vehicles equipped with such apparatus. Examples of vehicles which commonly included apparatus include automobiles, trucks, vans, buses, tractors, motorcycles, mopeds, farm machinery, military vehicles (e.g., tanks and self-propelled artillery), earth moving equipment, road building equipment, and cranes.

As is well known in the art, aramid fibers are manufactured fibers in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide (-CO-NH-) linkages are attached directly to two aromatic rings. Two well-known aramid polymers are poly(para-phenyleneterephthalamide) and poly(meta-phenyleneisophthalamide). Hundreds of chemical variations of aramid fibers exist, but at the present time these two aramid polymers are the most important commercially. The developer of such polymers, E.I. duPont de Nemours & Company, produces and sells poly(para-phenyleneterephthalamide) products under the KEVLAR trademark, and poly(meta-phenyleneisophthalamide) products under the NOMEX trademark. Highly useful fibers for use in the manufacture of friction surfaces used in the practice of this invention include, but are not limited to, KEVLAR® 49 aramid fibers and KEVLAR® 29 aramid fibers. It will of course be appreciated that this invention is not limited to aramid fibers made by any particular manufacturer or by fibers based on aramid polymers made by any particular manufacturer. The only requirement is that the fibers or fibrils are produced from at least a major proportion of a fiber-forming long-chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings.

Among the highly desirable properties of aramid fibers for use in the fabrication of friction surfaces are their high strength, high toughness, high wear resistance, non-abrasiveness, high thermal stability, low density, low electrical and thermal conductance, and their dimensional stability and non-softening characteristics at elevated temperatures. Another advantage is their high strength to weight ratio.

The aromatic polyamides are generally prepared from aromatic diamines and di-acid chlorides. The reaction can be carried out as an interfacial polymerization or in a mutual solvent such as dimethylacetamide, N-methylpyrrolidinone, hexamethylphosphorus triamide or tetramethylurea. Even
5 these amide solvents are not suitable for higher molecular weight polymers without the addition of lithium or calcium salts, which increase solubility by complexation to the amide carbonyls of the polymer. The HCl produced in the reaction of acid chlorides is usually neutralized by LiOH or CaO. After the desired molecular weight is achieved, the solid polymer is filtered from the slurry and redissolved
10 in concentrated H_2SO_4 . The extremely high-modulus fibers are spun from a lyotropic liquid crystalline solution in H_2SO_4 . Such fibers are highly crystalline, decompose at temperatures above $500^\circ C$ without melting and have remarkable tensile strength.

As noted above, the friction surface comprises at least 10% by weight of
15 a fibrous aramid polymer. However as much as 30% or more can be present. In general, the higher the amount, the more preferable the surface for use. While various other components can be utilized in forming the finished friction surface, the following types of components are preferred:

a) Particulate fillers such as barium sulfate, graphite, silica, Wollastonite,
20 molybdenum disulfide, magnesium oxide, metal powder (copper, zinc, aluminum, brass, and iron), kyanite, sodium carbonate, calcium carbonate, gypsum, calcium oxide, zeolite, powdered polytetrafluoroethylene, calcium stearate, lime, zirconium stearate, serpentine, calcium titanate, aluminum phosphate, talc, antimony sulfide, cryolite, copper oxide, dolomite, and many others. A preferred material is
25 diatomaceous earth. Another preferred material is particulate glass.

b) Reinforcing fibers such as fibrous glass, cellulose fibers, metal fibers (e.g., steel or brass), graphite fibers, rock wool fibers, rayon fibers, ceramic fibers, or nylon fibers. Use of fibrous glass is preferred.

c) Resinous binders such as cashew-derived resins (e.g., Cardolite ^(RTM) D-10, FF1080, FF1600 and NC-300 resins; Cardolite Corporation), melamineformaldehyde
30 resins, and Novolac resins. The preferred binders are phenolformaldehyde resins.

d) Resin modifiers such as natural and synthetic rubbers, and silicones.

The proportions of these components will of course vary
5 depending upon the identity and number of the particular
components used. Such matters are nevertheless, well-known
to those skilled in the art of manufacturing friction
materials for use in "wet" service applications.

A particularly preferred friction material for use in
10 the practice of this invention is SD 2050 friction material
under development by Borg-Warner which upon microscopic
inspection and chemical analyses appears to contain 30% by
weight of aramid fibers (apparently KEVLAR® fibers),
diatomaceous earth filler, fibrous and/or particulate glass
15 and a polymerized phenol-formaldehyde resinous binder.

Phosphorus-containing ashless dispersants which can be
used in the oil-based lubricant and/or functional fluid,
and methods for their production are described, for
example, in U.S. Pat. Nos. 3,403, 102; 3,502,677; 3,511,780;
20 3,513,093; 4,615,826; 4,648,980 as well as in GB 1,153,161
and GB 2,140,811. Preferably the phosphorus-containing
ashless dispersant is comprised of at least one phosphorus-
containing alkenyl succinimide of an alkylene polyamine.
The dispersant used pursuant to this invention can, and
25 preferably does, also contain boron. Patents describing
phosphorus-and boron-containing ashless dispersants are
U.S. Pat. Nos. 4,857,214 and 4,338,205.

Particularly preferred additive formulations for preparing oil-based lubricants and functional fluids for use in the practice of this invention are the HITEC^(RTM) 410 and 420 series of additives produced and sold in the United States by Ethyl Petroleum Additives, Inc. These additive packages contain ashless dispersants which contain both phosphorus and boron. Preferably the ashless dispersant is a phosphorus-and boron-containing alkenyl succinimide of a mixture of polyethylene polyamine having an average overall composition falling in the range of diethylene triamine to pentaethylene hexamine. Recommended dosage levels for natural and synthetic base oils fall in the range of 5 to 25 percent by weight based on the total weight of the finished oil blend. Another phosphorus-containing ashless dispersant package that can be used is available from Exxon Chemical Company, Paramins Division, as Paranox^(RTM) 445 additive.

Some of the advantages realized by the practice of this invention are illustrated by the results of a series of tests. In these tests a number of commercially available automatic transmission fluids were subjected to severe repetitive testing and analyzed for frictional profiles and clutch plate surface composition for evidence of additive decomposition.

In these tests, an SAE #2 Friction Test Machine from Greening Associates

(RTM)

with standard HEFCADT fixtures described in the DEXRON[®]/II specification was used for the repetitive engage-disengage testing. Computer control and data acquisition are integral to the system. The clutch packs consisted of three clutch plates lined with Borg-Warner ^(RTM)SD 2050 friction material alternating with four steel reaction plates. Flywheel and motor inertia amounting to 0.449 kg·m² with an initial motor speed of 3600 rpm gave a total system energy of 32 kJ. The pneumatic apply pressure was checked hourly and adjusted to maintain an engagement or stopping time of 0.80 ± 0.03 s. Fluid from a 25-l reservoir at a bulk temperature of $105 \pm 2^\circ\text{C}$ was circulated over the clutch pack at 2 l/min. Torque, rotational speed and apply air pressure were sampled and recorded at 1 ms intervals during each engagement. The cycle time was 30 s. Each test was run for 20,000 cycles or until the midpoint dynamic friction dropped to 80% of its value at 200 cycles.

As regards analyses, standard Inductively Coupled Plasma (ICP) and sulfur analysis techniques were used to determine elemental composition of the various fluids. Additional analyses were performed by FT-IR, ¹³C and ³¹P NMR to determine additive types. The used clutch plates were evaluated visually prior to Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis. (Note in this connection, Postek, M.T., Editor; Scanning Electron Microscopy, Ladd Research Industries, 1980). For these operations, the clutch plates were cut into 1 cm sections and coated with 200Å of carbon to minimize electrical charging during analysis. The analysis is considered to penetrate to a depth of 1 μ. The semi-quantitative analysis excluded carbon (C) and oxygen (O) from the calculations of surface composition, which were 90-95% of the surface, in order to emphasize elements distinctive to additives. Limitations of the EDS analysis are that nitrogen (N) cannot be distinguished from carbon in these samples and that boron (B) cannot be detected.

In the SEM-EDS analyses, the clutch plates were examined to assess any changes caused by the friction testing or by the fluids. As a reference, an unused plate was also examined, and SEM micrographs at 50- and 200-fold magnifications were obtained in order to obtain a clear visual picture of the surface appearance of the plates before and after the tests.

Interface temperature measurements were also made in the course of these tests. A Marlin J-type thermocouple probe of diameter 0.51 mm was inserted into a 0.56 mm hole drilled radially into an outer tang of an inner steel reaction plate. The lead wires emerging from the head were immobilized with epoxy and silicone rubber at two places. The thermocouple probe was attached to a Yokagawa 3655E Analyzing Recorder for periodic measurements independently of the SAE #2 machine's control and data acquisition system. The small mass of the probe and large mass of the reaction plates ensured rapid response time for temperature measurement.

10 The testing conditions employed for friction durability were rather severe, dissipating twice the energy of a DEXRON®-II HEFCADT during each engagement. Figure 1 shows a plot of torque versus time for a single engagement and visually defines the midpoint and peak torques. The repetitive testing was conducted on each fluid for 20,000 cycles or until the midpoint dynamic coefficient
15 of friction fell to 80% of the value at 200 cycles.

Two techniques were used for evaluating how much the friction surface had changed during testing. One technique followed the decrease in level of certain elements present in the friction material but not contributed by fluids. For example, silicon and zinc are on the surface of the new plate, but do not result from fluid decomposition (except in two cases where zinc is in the fluid). To the extent that
20 levels of these elements decrease, a new surface layer from additive is covering them over. The second technique is to follow the increase of elements present in fluid over levels present on a new plate. Phosphorus is not present on the surface of a new clutch plate but is present in all of the automatic transmission fluids used
25 in these tests.

In all, eight different automatic transmission fluid (ATF) compositions were tested. The elemental analyses of each such ATF, coded A through H, are summarized in Table 1 wherein values are in ppm from standard ICP and sulfur analysis techniques.

Table 1. New Fluid Analysis of the ATFs Tested

ELEMENT	FLUID							
	A	B	C	D	E	F	G	H
Ca	825	8	15	2	740	770	22	27
Mg	3	1	8	2	8	3	3	4
Zn	291	2	7	500	11	6	1	1
P	177	316	336	525	171	165	271	299
B	200	<10	<10	155	177	164	113	126
S	2000	1350	1550	2500	4100	2100	2300	600
Si	8	0	0	0	5	6	9	7

The types of ATF compositions involved in these tests were as follows:

Fluid A - A factory-fill and service fill ATF recommended for use by one large volume car manufacturer.

Fluid B - A factory-fill and service fill ATF recommended for use by another large volume car manufacturer.

Fluid C - A factory-fill and service fill ATF recommended for use by a third large volume car manufacturer.

Fluid D - A factory-fill ATF employed by a fourth large volume car manufacturer; a fluid which uses zinc dithiophosphate as the primary antiwear agent.

Fluid E - A factory-fill ATF employed by still another large volume car manufacturer; a fluid which contains calcium sulfonates, and as antiwear agents, phosphites and sulfurized phosphites.

Fluid F - A fluid that is not commercially-available but which was formulated with the same additive package as Fluid E in a poly-alpha-olefin (PAO) base oil rather than in a solvent-refined mineral oil. A similar synthetic ATF is available commercially with DEXRON®-II, MERCON®^(RTM) and Allison C-4 approvals.

Fluid G - A commercially-available ATF with DEXRON®-II, MERCON® and Allison C-4 approvals; a fluid based on HiTEC® 410 ATF additive

package (Ethyl Petroleum Additives, Inc.) which includes a phosphorus- and boron-containing succinimide.

Fluid H - A commercially-available ATF with DEXRON®-II, MERCON® and Allison C-4 approvals; a fluid which is based on the same additive package as Fluid G, but in a poly-alpha-olefin (PAO) base oil without polymeric viscosity index improver.

It will be recalled that each test involved use of wet clutch plates in which SD 2050 friction material, a friction material under development by Borg-Warner, was used as the friction surface, and that therefore each fresh friction surface comprised approximately 30% by weight of fibrous aramid polymer. Accordingly, the tests conducted with Fluids G and H represent the practice of this invention. The tests conducted with Fluids A through F are comparative tests and do not constitute the practice of this invention because none of Fluids A through F contains a phosphorus-containing ashless dispersant.

Table 2 provides a brief overall summary of the results obtained in each of these eight tests. In Table 2, the number of cycles at failure are given along with a description of the physical appearance of the clutch plates after testing.

Table 2. Durability of Tested ATFs and Clutch Plate Appearance.

FLUID	CYCLES TO FAILURE*	APPEARANCE OF USED CLUTCH PLATES
A	10,000	Black, highly glazed, cracked; 10-15% of friction material flaked off; reaction plates are medium to dark gray
B	9,300	Black, shiny regions mixed with textured regions; reaction plates have black and iridescent discoloration
C	2,300	Black, shiny and glazed; reaction plates have dark brown discoloration
D	2,300	Grayish-brown, shiny, glass-like surface; reaction plates are light gray
E	15,900	Black, shiny and glazed; reaction plates are medium to dark gray
F	15,200	Black, shiny and glazed; reaction plates have mottled dark discoloration
G	down 15% at 20,000	Blackened, textured, non-shiny surface; reaction plates are light gray
H	down 4% at 20,000	Blackened, textured, non-shiny surface; reaction plates are light gray

* Failure is defined as a 20% decrease in the coefficient of midpoint dynamic friction from the value at 200 cycles.

Figures 1 through 8 are plots of midpoint dynamic torque (corresponding to dynamic friction conditions), and peak torque (corresponding to static friction conditions), for each ATF composition A through H, respectively. In most cases, the peak torque increasingly diverges from the midpoint torque throughout the test. An arrow on most traces indicates the failure point by the 20% fade criterion. It can be seen that two fluids (C and D) failed at 2,300 cycles, two (Fluids A and B) failed at 9,000 to 10,000 cycles, and two (Fluids E and F) failed at 15,000 cycles. Only the two compositions representing the practice of this invention (Fluids G and H) survived beyond 20,000 cycles without failure.

Table 3 summarizes the elemental analyses of the used clutch plates after completion of the test run and also sets forth for comparison the elemental analysis of each plate prior to the test run. Values shown in Table 3 are in weight percent, omitting carbon, oxygen, nitrogen and boron.

Table 3. Elemental Composition from EDS Analysis of New and Used Clutch Plates

ELEMENT	FLUID								
	NEW PLATE	A	B	C	D	E	F	G	H
Si	65.2	9.7	7.6	26.3	8.2	22.1	17.7	58.7	34.9
Ca	12.8	7.8	2.0	2.2	1.3	11.8	26.3	7.9	5.0
S	5.7	27.7	22.4	20.0	10.9	26.2	22.8	8.8	9.7
Zn	4.6	12.1	2.4	---	45.4	---	---	3.6	---
Cl	3.7	---	2.3	---	---	1.2	---	---	---
Al	3.0	---	---	---	0.7	3.0	---	1.3	---
Fe	2.6	---	1.7	28.4	1.2	3.4	0.6	3.9	2.0
Mg	1.5	---	---	---	---	---	---	---	---
K	0.9	---	---	---	---	---	---	---	---
P	---	5.8	14.8	14.7	31.7	2.5	13.8	12.5	30.5
Cu	---	37.0	46.9	8.4	0.6	29.7	18.8	3.3	17.9
TOTAL	100	100	100	100	100	100	100	100	100

Interpretations of the data obtained in the tests are as follows:

Fluid A shows highly friction-modified behavior when new, with the peak torque somewhat lower than the midpoint dynamic torque. As this severe testing continues past 4,000 cycles, the static friction at low sliding speeds rises as reflected by the peak torque. The used plates appear very shiny and black with small cracks in the surface. Perhaps 10-15% of the friction material has flaked off of the plates. SEM micrographs show a vastly altered surface with much residue surrounding the fibers of the friction material. The new fluid analysis reveals substantial levels of calcium (Ca), zinc (Zn), phosphorus (P) and sulfur (S), from calcium sulfonate, zinc oleate, organic phosphites and sulfurized phosphite. All of these elements are present above trace levels on the new top layer of the glazed plate. Recall that the content calculations omit carbon, oxygen, nitrogen and boron. Within these constraints, however, copper (Cu) dominates the used plate at 37 wt%, followed by S, 27.7 wt%, Zn at 12.1 wt%, and P at 5.8 wt%. This dominance is interpreted as chemical attack of the fluid on the copper of the system heating element or brass

fittings and subsequent incorporation into the developing glaze. The sulfur level in the glaze is higher than average for this group of fluids, suggesting the use of thermally labile sulfur compounds. Zinc is probably added to the top layer as well. The decrease in silicon (Si) content indicates concealment of the original surface.

5 Fluid B survives about as long as Fluid A in durability, but generates a different kind of glaze during use. The large difference between the peak and dynamic torque levels shows this fluid to be the least friction-modified fluid in the group. The new fluid analysis shows phosphorus and sulfur as the major elements revealing of additive chemistry. The antiwear additive was determined to be a
10 sulfurized phosphate ester or amine salt. The low level of metals results in a low-ash fluid. The appearance of the used plate is a mixture of textured surface with shiny, glazed regions. The surface is greatly altered as shown by SEM micrographs with large areas of fluid-derived residue, which is flattened and worn. Analysis of the residue reveals copper at 46.9%, sulfur at 22.4% and phosphorus at 14.8%
15 by weight of the surface glaze. Again, a low level of silicon in the top layer signifies extensive coverage of the original surface by fluid-derived residue. This fluid resulted in the highest level of copper, which again is apparently removed by chemical dissolution. Although Fluid B has the lowest level of sulfur in the new fluid, it concentrates in the glaze about as much as with the other fluids.

20 Fluid C. After a short break-in period, the peak and midpoint torques are fairly similar for 1,000 cycles, but quickly diverge. The midpoint coefficient of friction failed at 2,300 cycles. The new fluid analysis reveals chiefly phosphorus and sulfur from sulfurized phosphites, but no significant levels of metals, therefore qualifying as low ash. The used plate appeared black and glazed. SEM views of
25 the surface have a very different appearance than a new plate. The major elements found in the glaze by EDS are sulfur, phosphorus and iron. This fluid is the only one of the eight resulting in an iron level on the used plate indicative of wear or chemical attack on steel with collection in the glaze.

30 Fluid D gave a torque plot showing a modest level of friction modification which diminishes rapidly during the test. The failure point was reached after only 2,300 cycles. The used plates have a brown, glassy glaze. SEM micrographs show one of the highest degrees of change from a new plate, with the original surface

completely obliterated by residue. White areas in the micrographs are interpreted as indicating sites of the most intense localized heating, with cooler, surrounding areas being deeper and further away from the steel reaction plate. Qualitative EDS analysis reveals high levels of sulfur and phosphorus but moderate zinc. These decomposition products are directly attributable to the ZDDP in the fluid. The reduction in silicon and calcium from new plate levels demonstrates the extensive coverage by fluid-derived residue.

Fluid E. During friction testing, this fluid begins with a high degree of friction modification and lasts longer than Fluids A through D. The peak torque rises throughout the test as the dynamic torque slowly drops until failure at 15,900 cycles. The used plates appear black and shiny. SEM micrographs of the used plates display some individual fibers, but there is clearly some residue surrounding each discernable fiber. EDS analysis shows the major components on the glazed plate to be sulfur, consistent with the known additives, and copper. The calcium level is about the same as on a new plate as are chlorine, aluminum and iron, indicating that some original surface is exposed. A small amount of phosphorus is present as well, but this is judged to be minor compared to the levels of other additive-derived products. The high level of copper present in the glazed surface is not as high as with Fluids A or B.

Fluid F was formulated in PAO to allow comparison between mineral oils, which may contain various nitrogen and sulfur compounds, and a pure synthetic hydrocarbon, known for superior oxidative and thermal stability. The friction test results are very similar to those of Fluid E, with the same degree of friction modification and the same durability, 15,200 cycles to failure. The used plates are black and glazed. SEM micrographs show some similarities to those of Fluid E, with exposed fibers interspersed with decomposition residue. The levels of silicon exposed and of sulfur deposited are the same with Fluids E and F. Phosphorus and calcium levels are higher and the copper level is lower with F, although measurement errors leave these comparisons suspect. Overall, these two fluids give similar performance, suggesting no friction durability benefit from blending this additive system with PAO base fluids. The tendency to leave a residue is due to the additive package.

Fluid G is a low-ash fluid. The moderate level of friction modification evident at the beginning of testing is maintained for about 6,000 cycles, before a modest divergence in torque levels occurs. At the end of 20,000 cycles, the midpoint coefficient of friction had dropped only 15%. The used plates were blackened but not shiny or glazed. By SEM, at two different magnifications, the plates show a great similarity to new plates with many individual fibers distinctly visible. There is no discernable residue around the fibers or other components of the friction material. The fibers are, however, considerably flattened and worn from the severe testing, but no changes attributable to the fluid are evident. The high silicon level indicates the least coverage by residue of any tested fluid. The similarity of calcium, sulfur, zinc, aluminum and iron to new plate levels confirms this analysis. Phosphorus is the only substantial addition to the surface along with a minor amount of copper. The relatively small difference between midpoint and peak torque levels at the end of testing shows that the friction modifiers still have access to the surface of the friction material.

Fluid H, based on the same additive package as Fluid G, but formulated in a PAO base fluid without polymeric viscosity index improver, began testing with the same spread between midpoint and peak torques as did Fluid G, and suffered the smallest change of any fluid tested. After 20,000 cycles, the coefficient of dynamic friction had decreased by only 4%. The used plates were, again, blackened but not glazed. As with Fluid G, the only changes evident by SEM are from mechanical wear and polishing. The high level of silicon with calcium, sulfur and iron levels similar to those resulting from Fluid G suggest a largely original surface. The somewhat higher level of phosphorus and copper as compared to Fluid G did not affect the friction durability adversely. The additive package used in Fluids G and H is the least harmful to friction materials during severe testing, and shows improved durability on changing the base fluid to PAO.

The similar low levels of sulfur residues for Fluids G and H shows that the sulfur-containing additives common to both fluids do not decompose in a harmful manner. Mineral oils commonly contain 1000 to 4000 ppm of sulfur but the solvent-refined paraffinic oil contributes no more sulfur to the clutch plate surface than does PAO, a sulfur-free hydrocarbon. These observations led to the conclusion that sulfur compounds in solvent-refined mineral oils do not deposit substantial residues in this test. Therefore, additives are implicated in Fluids A through F as the cause of deposition of the significant levels of sulfur on the clutch plates during this testing.

In all cases the measured effects of friction-modifying additives in ATFs are diminished by changes on the clutch plate surfaces. The durability of the initial frictional profile varies inversely with the degree of change suffered by the clutch plates. The greater the surface alteration (Fluids A through D) the shorter the useful life. Less alteration is accompanied by better durability (Fluids G and H). That changes occur on the friction surfaces and not in the bulk fluid was demonstrated by Low-Velocity Friction Apparatus (LVFA) measurements on used fluids. All showed friction modification characteristics comparable to new fluids.

To rule out fluid oxidation as the reason for the differences between fluids or changes in durability other used fluid analyses were performed. Virtually no changes in IR absorbance at 1723 cm^{-1} or in the total acid number (TAN) were observed in the fluids. In spite of 100 or more hours at 105°C , there is no evidence of significant oxidation. We conclude that the observed differences are due only to thermal decomposition of additives on the hot friction surfaces.

Temperatures were measured at the center of an inner steel reaction plate of 1.78 mm thickness during runs of two fluids, A and F. This method was considered adequate to establish a lower limit for the interface temperature, since the temperature will drop as the heat diffuses from the surface to the center of the cooler reaction plate where the thermocouple is located. Between cycles 55 and 100 of Fluid A the temperature was 364°C . With Fluid F, the temperature was $320\text{--}324^\circ\text{C}$ between cycles 100 and 2000, and $331\text{--}334^\circ\text{C}$ at cycles 4000 to 4016. Plots of temperature versus time during single engagements of the test with Fluid F displayed the rapid time response of the system. The maximum temperature

is generated during the 0.8 second of engagement, and then exponential cooling is observed until the applied pressure is released. Cooling occurs with a different exponential rate until the clutch pack begins spinning for the next engagement which brings the temperature down to the bulk fluid temperature of 105°C.

5 Illustrative lubricant and functional fluid compositions suitable for use in the practice of this invention are presented in the following Examples wherein all parts and percentages are by weight. The polyisobutenyl succinimide contains both phosphorus and boron and is formed substantially as described in Example 1A of U.S. Pat. No. 4,857,214.

10 Examples 1 through 4 illustrate preferred compositions using either solvent refined mineral oil base oils (e.g., 100 solvent neutral mineral oil with a viscosity at 100°C of 4 cSt), or PAO-based fluids (e.g., a blend of 80% ETHYLFLO^(RTM) 4 PAO fluid -- available from Ethyl Corporation -- with a viscosity at 100°C of 4 Cst and 20% of diisodecyl adipate; or 95% of ETHYLFLO 4 PAO fluid and 5% of dibutyl
15 phthalate).

EXAMPLES 1-4

Components	Ex. 1	Ex. 2	Ex. 3	Ex. 4
P- & B-contg ashless dispersant	3.772	3.772	3.772	3.772
Ethomeen T-12 (RTM)	0.10	0.10	0.10	0.10
20 Sul-Perm 10S (RTM)	0.48	0.48	--	--
HiTEC® 314 additive	0.04	0.04	0.04	0.04
Antifoam agent	0.06	0.06	0.06	0.06
Naugalube 438L (RTM)	0.26	0.26	0.26	0.26
OLOA 216C (RTM)	0.05	0.05	0.05	0.05
25 Octanoic acid	0.05	0.05	0.05	0.05
Tomah PA-14 (RTM)	0.05	0.05	0.05	0.05
Pluronic L-81 (RTM)	0.01	0.01	0.01	0.01
Mazawet 77	0.05	--	0.05	--
PC 1244	0.03	--	0.03	--
30 Diluent oil	1.76	1.84	2.24	2.32
TC 9825 or TLA 5010	3.50	3.50	3.50	3.50

Examples 5 through 8 illustrate preferred additive packages especially suitable for use in hydrocracked mineral oil base oils (e.g., 100 neutral mineral oil with a viscosity at 100°C of 4 Cst).

EXAMPLES 5-8

	<u>Components</u>	<u>Ex. 5</u>	<u>Ex. 6</u>	<u>Ex. 7</u>	<u>Ex. 8</u>
5	P- & B-contg ashless dispersant	3.772	3.772	3.772	3.772
	Ethomeen T-12	0.10	0.10	0.10	0.10
	Sul-Perm 10S	0.48	0.48	--	--
	HiTEC® 314 additive	0.04	0.04	0.04	0.04
10	Antifoam agent	0.06	0.06	0.06	0.06
	Naugalube 438L	0.26	0.26	0.26	0.26
	OLOA 216C	0.05	0.05	0.05	0.05
	Octanoic acid	0.05	0.05	0.05	0.05
	Tomah PA-14	0.05	0.05	0.05	0.05
15	Pluronic L-81	0.01	0.01	0.01	0.01
	Mazawet 77	0.05	--	0.05	--
	PC 1244	0.03	--	0.03	--
	Diluent oil	1.76	1.84	2.24	2.32
	Panasol AN-3N (RTM)	2.00	2.00	2.00	2.00
20	TC 9825 or TLA 5010	3.50	3.50	3.50	3.50

Examples 9 through 12 illustrate preferred additive packages especially suitable for use in PAO-based fluids containing no viscosity index improver (e.g., a blend of 80% of ETHYLFLO 6 PAO fluid -- available from Ethyl Corporation -- with a viscosity at 100°C of 6 Cst and 20% of diisodecyl adipate; a blend of 95% of ETHYLFLO 6 PAO fluid and 5% of dibutyl phthalate; a blend of 85% of ETHYLFLO 6 PAO fluid and 15% of di-n-octyl phthalate; a blend of 95% of ETHYLFLO 8 PAO fluid -- available from Ethyl Corporation -- with a viscosity at 100°C of 8 Cst and 5% of dibutyl phthalate; or a blend of 80% of ETHYLFLO 8 PAO fluid and 20% of diisodecyl adipate).

EXAMPLES 9-12

<u>Components</u>		<u>Ex. 9</u>	<u>Ex. 10</u>	<u>Ex. 11</u>	<u>Ex. 12</u>
	P- & B-contg ashless dispersant	3.772	3.772	3.772	3.772
	Ethomeen T-12	0.10	0.10	0.10	0.10
5	Sul-Perm 10S	0.48	0.48	--	--
	HiTEC® 314 additive	0.04	0.04	0.04	0.04
	Antifoam agent	0.06	0.06	0.06	0.06
	Naugalube 438L	0.26	0.26	0.26	0.26
	OLOA 216C	0.05	0.05	0.05	0.05
10	Octanoic acid	0.05	0.05	0.05	0.05
	Tomah PA-14	0.05	0.05	0.05	0.05
	Pluronic L-81	0.01	0.01	0.01	0.01
	Mazawet 77	0.05	--	0.05	--
	PC 1244	0.03	--	0.03	--

15 In accordance with conventional practice, various other known components can be present in the oleaginous compositions in order to provide the properties engendered by use of such known additives. Thus any additive can be included so long as (a) it is compatible with and soluble or at least capable of existing as a shelf-stable dispersion in the finished oleaginous liquid composition, (b) it does not contribute to the presence of more than 100 ppm of metal in the finished oleaginous liquid composition, and (c) it does not adversely affect the viscometrics or stability desired in the finished oleaginous composition or otherwise adversely impair the performance of the finished composition.

25 Described below are illustrative examples of the types of conventional additives that are often employed in the lubricant or functional fluid compositions.

Seal performance (elastomer compatibility) improvers such as dialkyl diesters typified by (a) the adipates, azelates, and sebacates of C₈-C₁₃ alkanols (or mixtures thereof), and (b) the phthalates of C₄-C₁₃ alkanols (or mixtures thereof), or combinations of (a) and (b) are often used. Examples of such materials include 30 the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid. Also useful are aromatic hydrocarbons of suitable viscosity such as Panasol AN-3N; products such as Lubrizol (RTM) 730; polyol esters such as Emery 2935, 2936, and 2939 esters from the Emery Group

(RTM)

of Henkel Corporation and Hatcol 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corporation.

The compositions may contain one or more antioxidants, e.g., one or more phenolic antioxidants, aromatic amine antioxidants, sulphurised phenolic antioxidants, and organic phosphites, among others. Examples include 2,6-di-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), mixed methylene-bridged polyalkyl phenols, 4,4'-thiobis(2-methyl-6-tert-butylphenol), N,N'-di-sec-butyl-p-phenylenediamine, 4-isopropylaminodiphenyl amine, phenyl- α -naphthyl amine, and phenyl- β -naphthyl amine.

Corrosion inhibitors comprise another type of common additive used in the finished oils. Examples include dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type currently available from various commercial sources, include the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Other useful corrosion inhibitors include the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, and hexadecenylsuccinic anhydride. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and aminosuccinic acids or derivatives thereof.

Foam inhibitors are likewise typically used in the finished oils. These include silicones, polyacrylates, surfactants.

Copper corrosion inhibitors constitute another class of additives often used in the finished oils. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercapto benzothiazole, 2,5-dimercapto-1,3,4- thiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-(bis-hydrocarbyldithio)- 1,3,4-thiadiazoles.

Friction modifiers can be used, such as aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphonates, and aliphatic thiophosphates, wherein the aliphatic group usually contains above eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia.

Metal-containing detergents such as calcium phenates, magnesium phenates, calcium sulfonates, magnesium sulfonates can also be used. However, as noted above, if an oil-soluble or oil-dispersible phenate or sulfonate is used it should be proportioned such that the finished fluid contains no more than 100 ppm of metal, and preferably no more than 50 ppm of metal.

Still other components that can be present include lubricity agents such as sulfurized fats, sulfurized isobutylene, dialkyl polysulfides, and sulfur-bridged phenols such as nonylphenol polysulfide. Dyes, pour point depressants, viscosity index improvers, air release agents, and many other known types of additives can also be included in the finished oil compositions used in the practice of this invention.

In selecting any of the foregoing optional additives, it is of course important to ensure that the selected component(s) are soluble or stably dispersible in the oleaginous liquid, are compatible with the other components of the composition, and do not interfere significantly with the properties, such as the viscosity and/or shear stability properties, desired in the overall finished oleaginous composition.

In general, the additive components are employed in the oleaginous liquids in minor amounts sufficient to improve the performance characteristics and

properties of the base fluid. The amounts will thus vary in accordance with such factors as the viscosity characteristics of the base fluid employed, the viscosity characteristics desired in the finished fluid, the service conditions for which the finished fluid is intended, and the performance characteristics desired in the finished fluid. However, generally speaking, the following concentrations (weight percent) of the components (active ingredients) in the base fluids are illustrative:

	<u>Typical Range</u>	<u>Preferred Range</u>
P-containing dispersant	0.2 - 15	0.5 - 5
10 Seal performance improver	0 - 30	2 - 20
Antioxidant	0 - 1	0.25 - 1
Corrosion inhibitor	0 - 0.5	0.01 - 0.1
Foam inhibitor	0 - 0.01	0.0001 - 0.005
Copper corrosion inhibitor	0 - 0.5	0.01 - 0.05
15 Friction modifier	0 - 1	0.05 - 0.5
Lubricity agent	0 - 1.5	0.5 - 1
Viscosity index improver	0 - 10	0 - 4
Dye	0 - 0.05	0.015 - 0.035

Although additives such as those mentioned above may be included, the only requirements as regards the oil are that the oil must contain a phosphorus-containing dispersant which optionally (and preferably but not necessarily) also contains boron, and that the oil composition be suitable for its intended usage. The remainder of the components in the finished oil of lubricating viscosity are matters well within the skill and expertise of lubricant manufacturers and their additive suppliers.

It will be appreciated that the individual components can be separately blended into the base fluid or can be blended therein in various subcombinations, if desired. Ordinarily, the particular sequence of such blending steps is not critical. Moreover, such components can be blended in the form of separate solutions in a diluent. It is preferable, however, to blend the components used in the form of an additive concentrate such as the HiTEC® 410 and 420 series of additives of Ethyl

Petroleum Additives, Inc. or Paranox 445 additive of Exxon Chemical Company (Paramins Division), as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

- 5 As used in the foregoing description, the term "oil-soluble" is used in the sense that the component in question has sufficient solubility in the selected base oil in order to dissolve therein at ordinary temperatures to a concentration at least equivalent to the minimum concentration required to achieve the results or effect for which the additive is used. Preferably, however, the solubility of such component
- 10 in the selected base oil will be in excess of such minimum concentration, although there is no requirement that the component be soluble in the base oil in all proportions. As regards the term "oil-dispersible", those skilled in the art are well aware that certain useful additives do not completely dissolve in base oils but rather are used in the form of stable suspensions or dispersions in the oil. Oils containing
- 15 such dispersed additives of can also be employed in the practice of this invention provided such oils do not significantly interfere with the performance or usefulness of the composition in which they are employed. Given a choice, it is preferable to use any oil in which all components thereof are oil-soluble, but this is not a requirement in the practice of this invention.



CLAIMS

1. In combination, friction means having at least
5 one friction surface in contact with an oil-based lubricant
and/or functional fluid, said friction surface comprising
at least 10 percent by weight of fibrous aramid polymer
comprising a fiber-forming long-chain synthetic polyamide
in which at least 85% of the amide linkages are attached
10 directly to two aromatic rings, said oil-based lubricant
and/or functional fluid containing a minor amount of at
least one oil-soluble or oil-dispersible metal-free
phosphorus-containing dispersant.
- 15 2. A combination according to claim 1 wherein said
friction means comprises at least one clutch plate or ring
operatively encased within an automatic transmission;
wherein said surface is comprised of at least 15 percent by
weight of fibrous aramid polymer; wherein said surface is
20 further comprised of (a) particulate filler, (b) fibrous
and/or particulate glass, and (c) at least one polymerised
resinous binder; wherein said oil-based lubricant and/or
functional fluid is a formulated automatic transmission
fluid; and wherein said dispersant is comprised of at least
25 one phosphorus-containing alkenyl succinimide of an
alkylene polyamine.



3. A combination according to claim 1, wherein the fibrous aramid polymer is poly(p-phenyleneterephthalamide).

5 4. A combination according to claim 3 wherein said friction means comprises at least one clutch plate or ring operatively encased within an automatic transmission; wherein said surface is comprised of (a) said at least 20 percent by weight of poly(p-phenyleneterephthalamide) in
10 the form of fibers or fibrils, (b) particulate filler, (c) fibrous and/or particulate glass, and (d) one or more polymerised resinous binding materials, said components (a), (b), and (c) being held in place at least in part by said component (d); wherein said oil-based lubricant and/or
15 functional fluid is a formulated automatic transmission fluid; and wherein said dispersant is comprised of at least one phosphorus-containing alkenyl succinimide of an alkylene polyamine.

20 5. In an automatic transmission which includes an automatic transmission fluid, and at least one member having a friction surface engageable by another surface, at least a portion of said friction surface coming into contact with said fluid during operation of said
25 transmission, the improvement pursuant to which (i) said friction surface is composed of at least 10 percent by weight of one or more fibrous aramid polymers, comprising a fiber-forming long-chain synthetic polyamide in which at



least 85% of the amide linkages are attached directly to two aromatic rings, and (ii) said transmission fluid comprises a major amount of oil of lubricating viscosity and a minor amount of at least one oil-soluble metal-free phosphorus-containing additive.

6. The improvement according to claim 5 wherein said additive is a phosphorus- and boron-containing dispersant.

7. In an automatic transmission which includes an automatic transmission fluid, and at least one member having a friction surface engageable by another surface, at least a portion of said friction surface coming into contact with said fluid during operation of said transmission, the improvement pursuant to which (i) said friction surface is comprised of (a) at least 20 percent by weight of poly(p-phenyleneterephthalamide) in the form of fibers or fibrils, (b) particulate filler, (c) fibrous and/or particulate glass, and (d) one or more polymerized resinous binding materials, said components (a), (b), and (c) being held in place at least in part by said component (d); and (ii) said transmission fluid comprises a major amount of oil of lubricating viscosity and a minor amount of an additive complement which includes at least one oil-soluble metal-free phosphorus-containing additive.

8. The improvement according to claim 7 wherein said particulate filler comprises diatomaceous material; wherein



said component (d) comprises at least one phenol-formaldehyde resin; and wherein said additive consists essentially of a phosphorus- and boron-containing alkenyl succinimide of a mixture of polyethylene polyamines having
5 an average overall composition falling in the range of diethylene triamine to pentaethylene hexamine.

9. A method of improving the frictional performance and/or frictional durability of an automatic transmission
10 which comprises (i) providing as a frictional member within said transmission, a member having at least its friction-bearing surface composed of (a) at least 10 percent by weight of at least one fibrous aramid polymer comprising a fiber-forming long-chain synthetic polyamide in which at
15 least 85% of the amide linkages are attached directly to two aromatic rings, (b) particulate filler, and (c) at least one cured resinous binder material; and (ii) providing as a functional fluid for the operation of said transmission, a formulated automatic transmission fluid
20 containing a minor friction-performance enhancing and/or durability-enhancing amount of at least one metal-free phosphorus-containing dispersant.

25 10. A method as claimed in claim 9 wherein said friction-bearing surface is composed of at least 20 percent by weight of at least one aramid polymer in the form of fibers or fibrils.