LUBETECH

NO.10

MEETING THE NEEDS OF MODERN INDUSTRIAL GEAR OILS

Lubrizol observe lubricants based on sulphur-phosphorus chemistry provide greater protection and performance.

Industrial gear oils operate under more diverse conditions and applications than automotive gear oils. The gears can be as large as 10 meters in diameter and incorporate spur, bevel, helical and spiral bevel designs in an endless variety of configurations. Industrial gear oils typically must function in the presence of large quantities of water, which can cause rust, corrosion and a loss of protection. These oils also are used in highly contaminated environments. To make matters worse, modern gearboxes have been downsized and operate at higher speeds and loads, resulting in higher operating temperatures.

To meet the demands of today's industrial gear drives, a lubricant must meet a variety of performance requirements. The minimum performance requirement for industrial gear oil is heavy-duty extreme pressure (EP) performance combined with rust, corrosion and oxidation resistance in the presence of water, scale and heat. A higher, premium level of performance adds thermal stability and cleanliness to the baseline requirements. Top-tier performance includes durability requirements such as high temperature EP protection, extended demulsibility and foam inhibition in the presence of contaminants. Compatibility with various mineral and synthetic base fluids is also a concern.

Two important trends in the development of industrial gear oils are:

- Increased emphasis by end users on reducing costs. They are demanding longer lubricant life, which reduces maintenance and disposal costs.
- Design changes to improve efficiency. Today's smaller gearboxes operate at higher speeds and loads, resulting in higher operating temperatures.

They also have smaller oil capacities, so less lubricant is available to cool the equipment and suspend contaminants.

The United States Steel (USS) 224 Specification for Non-lead, EP Industrial Gear Oils is one of the most widely recognised specifications in the U.S. industry. It was written and released in the early 1980s to address the use of sulphur-phosphorous formulations. The American Gear Manufacturers Association (AGMA) upgraded its AGMA 250.04 enclosed gear oil specification shortly after USS 224 was released.

Recently, Lubrizol developed new additive technology to improve the performance of modern industrial gear oils.

GEAR TEST RESULTS

Tests	Commercial Oil	New Oil	Requirements
4-Ball Wear Scar Diameter (mm)	0.29	0.29	0.35 max
4-Ball EP Weld Load (kg)	250	250	250 min
4-Ball EP LWI (kg)	55.1	60.5	40 min
Timken OK Load (lb)	80	75	60 min
Copper Strip Corrosion (ASTM D130)	1A	1A	1B min
Turbine Oil Rust			
A - Distilled Water	Pass	Pass	Pass
B - Synthetic Water	Pass	Pass	Pass
S-200 Viscosity Increase (%)	3.7	4.88	6.0 max
ASTM D 1401 Demulsibility @ 82°C			
Oil-Water-Emulsion (ml)	40/40/0 (20)	40/40/0 (10)	
ASIM D 2711 Demulsibility @ 82°C			
Water in Oil (%)	1	0.2	2
Total Free Water (ml)	84.6	84.1	80
Emulsion (ml)	0	0.1	1
ASIM D 2711 Demulsibility @ 54°C			
Water in Oil (%)	2.3	1.6	
Total Free Water (ml)	79.5	81.4	
Emulsion (ml)	0.1	0.1	

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The capabilities of new chemistry were evaluated by comparing the performance of an oil formulated with the new additive with those of a commercially available oil. Performance was investigated in the following USS 224 tests:

- **Gear Protection** Four-Ball Wear (ASTM D 4172), Four-Ball EP (ASTM D2783), Timken Test (ASTM D 2782)
- **Corrosion and Oxidation-**(Copper Strip) Corrosion (ASTM D 130), USS $-200 Oxidative Thickening, Turbine Oil Rust (ASTM D 665)
- **Demulsibility** - Demulsibility (ASTM D 1401 and ASTM D 2711)

The commercial oil has proven field performance and is widely used in the industry. The new oil is a cost-effective alternative with improved demulsibility while maintaining good load carrying capacity and wear protection. These properties were produced with an alternative sulphur-phosphorous chemistry and rebalancing of the formulation.

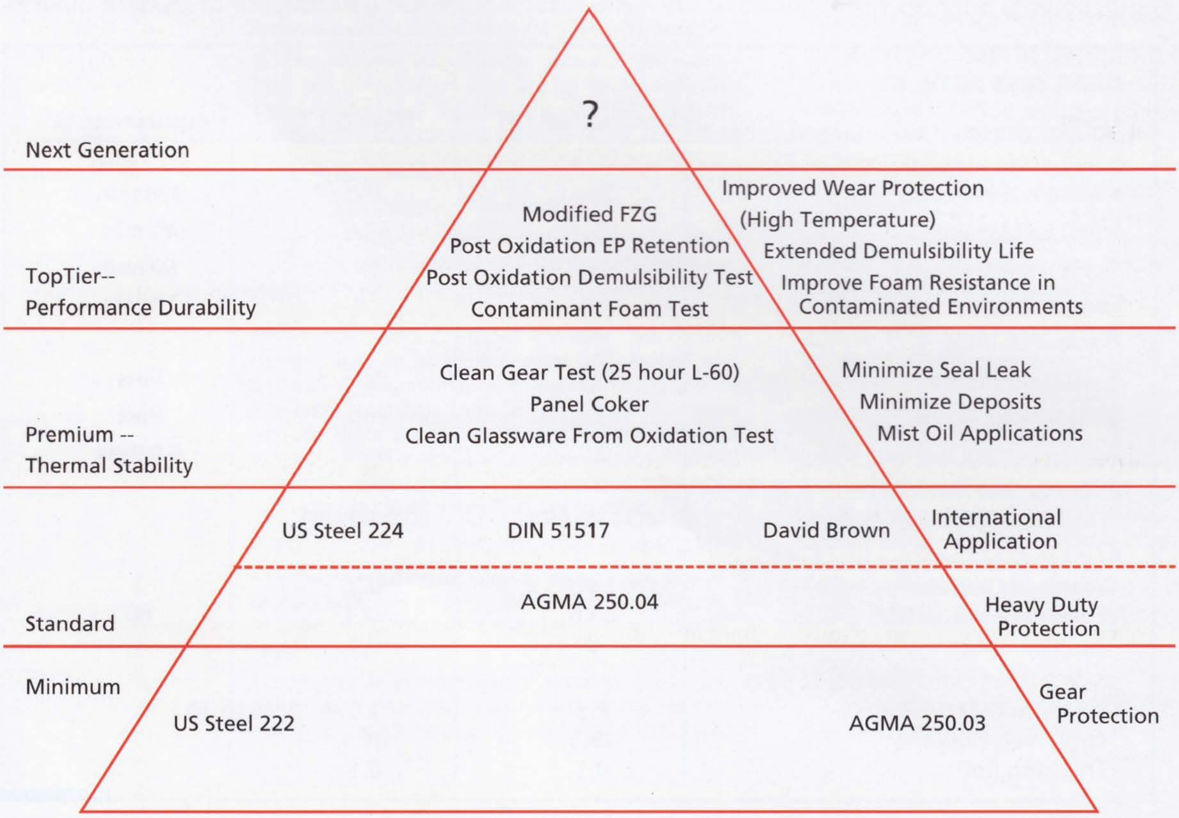
As shown in the table, Four-Ball Wear, Four-Ball EP and Timken test results for the new gear oil are similar to those of the commercially available oil. Wear scar diameter was 0.29 mm, which is well below the 0.35 mm required by USS 224. Load Weld Index (LWJ) was higher than that of the commercial oil. The Timken load was 75 lb, which is above the minimum specified by USS 224. The results indicate that the new oil can protect gears in the field.

Copper strip, USS 200 and turbine oil rust tests show that both oils passed the corrosion and oxidation tests, indicating that the new oil can provide good corrosion and oxidation performance. Finally, in the ASTM D 1401 test, the new oil completely separated water within 10 minutes, while the commercial oil required 20 minutes. This indicates better demulsibility performance for the new oil.

The ASTM D 2711 test evaluates the resistance to water mixing and the promotion of rapid water separation. Both oils performed well even though the new oil provided slightly better performance. In addition, the new oil performed better than the commercial oil at 54°C, a temperature reportedly of interest to the steel industry.

Article courtesy of The Lubrizol Corporation.

INDUSTRIAL GEAR OIL PERFORMANCE PYRAMID



DESIGNER SURFACES FOR TITANIUM COMPONENTS

INTRODUCTION

Titanium and its alloys are particularly attractive for use in situations requiring a high strength to weight ratio, for example in aerospace and automotive, particularly motorsport applications. The metal and associated alloys not only have low density allied to high tensile strength, but have good resistance to corrosion under normal conditions, and excellent bio-compatibility. One may well ask why these materials are not therefore in much more widespread use than at present. This is mainly because titanium alloys are characterised by, especially in sliding situations, poor tribological properties, including high and unstable friction coefficients, severe adhesive wear, susceptibility to fretting wear, and a strong tendency to seize. This poor tribological behaviour of titanium can be attributed to the electron configuration, crystal structure and ineffectiveness of lubricants. Furthermore, titanium and its alloys can exhibit poor corrosion resistance in some aggressive environments, such as high temperature reducing acids and a susceptibility to crevice corrosion in hot chloride solutions.

However, there is ever increasing interest in the applications of titanium alloys in such sectors as chemical, off-shore, biomedical, automotive, performance sports, power generation and general engineering in which tribological and corrosion behaviour are often major concerns for titanium component designers. Much work has therefore been carried out in investigating ways of overcoming the tribological and environmental limitations of titanium alloys, thus realising their full benefit in various applications. Since the tribological and environmental limitations of titanium and its alloys are closely related to their inherent surface nature, problems may be overcome only by changing the nature of the surface i.e. surface engineering i.e."the design and modification of the surface and substrate together of a component, as a system, to give cost effective performance enhancement of which neither is capable on its own (Bell, 1991)".

Surface engineering has proved to be a most promising way to enhance the surface-related performance of titanium and its alloys by producing designed surfaces with economically viable technically enhanced performance. This contrasts with earlier approaches which merely endeavoured to use one of a number of existing techniques to solve or alleviate problems arising from inadequate material selection or design. Developments in the surface engineering of titanium alloys during the past few years have targeted tribological property improvement, corrosion resistance enhancement, and/or achievement of a synergistic combination of both improved tribological performance and elevated corrosion resistance in an alloy.

THE THERMAL OXIDATION PROCESS

A novel surface engineering process based on thermal oxidation, designated the TO process, has recently been successfully developed. This thermochemical process effectively improves the tribological behaviour of titanium alloys under light to moderate loads without deteriorating the good corrosion resistance. A typical cross-sectional structure of Ti6Al4V specimen treated using the proprietary TO treatment comprises a thin outer rutile oxide layer (~2μm), overlying the oxygen diffusion zone (~20μm).

Friction coefficient profiles of untreated and TO treated material obtained by using a WC ball sliding against the Ti6Al4V disc show marked differences. The friction trace of the untreated material fluctuates widely throughout the whole testing period, indicative of the 'stick-slip' adhesive behaviour of titanium and its alloys when sliding against most engineering materials. The friction trace of the TO treated material shows significantly reduced and stable friction values.

This friction-reducing effect of TO treated material is ascribed to the following mechanisms. Firstly, it is generally accepted that plastic deformation between contacting surfaces makes an important contribution to wear and friction. Significant reduction in friction and wear is anticipated if the contacts between surfaces are predominately elastic. Previous work on characterisation of surface mechanical properties using a nano indentation technique shown that the TO treatment effectively limits the degree of plastic deformation. As a consequence, a high degree of elastic contact can be anticipated, which favours low adhesion between the contacting surfaces and hence low friction.

Secondly, slightly oxygen-deficient rutile (TiO_{2-x}) behaves as a low shear strength, lubricious oxide due to its particular crystallographic shear (CS) plane. Work has now shown that the TO treatment induced oxide is most likely to be slightly oxygen-deficient or substoichiometric ($TiO_{1.95}$). Thus, there is a good reason to believe that the observed low friction of TO treated material may, to some extent, be related to the slightly oxygen-deficient or substoichiometric rutile. In short, both of the above mechanisms in terms of low plastic deformation and the low shear strength of rutile formed in the TO process are involved, to a varying degree, in reducing friction of Ti6Al4V alloy.

In lubricated sliding-rolling wear tests involving TO treated and untreated Ti6Al4V, it was shown that the untreated material is characterised by a very high wear rate (2.76×10^{-3}mg m^{-1}), which may be associated with the preferential transfer of Ti6Al4V onto the steel counterpart. The wear surface of the untreated material was very rough,

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with typical adhesive wear features evidenced by numerous adhesive craters and deep ploughing grooves. Clearly, untreated titanium can not be used under rubbing conditions even with oil lubrication and a low sliding to rolling ratio.

In contrast, the wear rate of the TO treated specimen ($1.57x10^{-3}$mg m^{-1}) was dramatically reduced by more than 2 orders of magnitude over the untreated material and it was even lower than that of the hardened steel counterpart ($1.61x10^{-4}$mg m^{-1}) by a factor of more than 10.

Scuffing is a form of severe sliding wear characterised by unacceptably high friction and a high degree of surface damage, which is associated with local solid-state welding between the rubbing surfaces under high duty operating conditions. The anti-scuffing capacities of untreated and TO treated material were evaluated by obtaining the critical load-to-failure during the stepwise loading process of oil lubricated sliding wear tests

The untreated material, sliding against a hardened En19 steel wheel under oil lubrication, showed a strong tendency to scuffing. On the other hand, the TO treated material (with oxide) had an excellent anti-scuffing capacity, involving three orders of magnitude improvement over that of the as-received material.

This desired anti-scuffing capacity conferred by TO treatment could be ascribed to the favourable lubrication condition promoted by the surface oxide layer. This is largely because the surface rutile layer possesses a high ionic factor, which promotes high wettability of polar lubricants, thus enhancing lubrication conditions.

PALLADIUM TREATED THERMAL OXIDATION PROCESS

Another simple and effective surface modification technique, namely palladium-treated thermal oxidation (PTO), has been developed in the present research towards recently for corrosion resistant titanium designer surfaces.

Both TO treated and PTO treated CP Ti exhibit superior corrosion resistance to untreated material either in immersion testing or in electrochemical testing, although the PTO treated material is significantly superior. It is believed that the excellent corrosion resistance of both the TO and PTO treated titanium in boiling HCl solutions mainly results from the protective surface oxide layers formed during the TO and PTO treatments because they are essentially inert and resistant in this environment. The significantly increased lifetime for the protective surface layer breakdown of the PTO treated material over the TO treated material may be attributed to the following factors: (1) the beneficial effect of palladium on the formation of protective surface layers by modifying the structure, morphology and composition of the layers and/or (2) the existence of palladium close to the coating/substrate interface, which may increase the passivating ability of pinholes and improve coating adhesion at the layer/substrate interface.

Tribological characterisation of TO and PTO treated titanium specimens also revealed that PTO treated titanium and its alloys gives higher critical load over TO treated materials. Thus titanium designer surfaces with a synergistic combination of both high tribological performance and elevated corrosion resistance can be achieved.

OXIDATION BOOST DIFFUSION PROCESS

Although both TO and PTO processes have proved to be effective surface engineering techniques for enhancing the tribological as well as corrosion properties of titanium and its alloys, the load bearing capacity of either TO or PTO treated titanium alloys is not high enough to withstand the high stresses encountered in such general engineering components as bearings and gears, and thus deep case hardening is necessary. It is not possible to increase the depth of the surface modified layer by further use of high temperatures and/or long times without causing severe stratification or scaling. Consequently, a new oxygen boost diffusion (OD) process has been developed for deep case hardening of titanium and its alloys. However, although OD treated titanium alloys exhibited significantly improved abrasive resistance over untreated materials, their sliding wear resistance was only marginally increased. This is presumably due to the fact that OD can increase hardness via oxygen interstitial solid solution hardening, but metallurgical compatibility would be hardly changed. Consequently, a novel duplex system combining low friction, high wear resistance diamond-like coating (DLC) with OD deep case hardening has been designed.

A total hardened case of about 300 µm, twenty times that of the hardened layer produced during TO or PTO treatment, was successfully achieved following the optimised OD treatment. Amorphous hydrogenated carbon a-C:H or DLC containing a small amount of titanium was deposited on the OD treated Ti6Al4V using a rf-reactive sputtering system. To overcome the main problem encountered with the deposition of DLC at low temperature, i.e. poor coating adhesion to the substrate, a graded layer, Ti/TiN/TiCN/TiC, between the substrate and the DLC layer was used.

The outstanding stress-resisting performance can be attributed to the optimised design of the duplex system. The compositionally graded intermediate layer, Ti/TiN/TiCN/TiC, eliminates interfacial cracking and leads to a homogenisation of the stress distribution in the coating under local loading, thus high adhesion is achieved.

Therefore, a duplex treatment is essential in achieving a high load bearing capacity. In summary, this novel duplex system can effectively extend the service conditions for titanium components in terms of a high sliding ratio and / or higher loads, and thus it could be an important step towards titanium designer surfaces.

These processes, together with a full list of references, are described in detail in Issue 6, Volume 50, 'Industrial Lubrication and Tribology'.

David Margaroni