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Formation and Frictional Properties of Boundary Lubricating and Surface-Modified Layers at Elevated Temperatures

Abstract

The influence of heating on the properties of lubricating layers formed on steel by inactive and chemically active lubricant components has been studied by electrical probe methods. Model experiments combining X-ray photoelectron spectroscopy analysis and measurements of friction and electrical characteristics in static and dynamic point contact have shown the approach to be promising in separate studies of the properties of the physically adsorbed layer (A-layer) and chemisorbed layer (D-layer) of deposits.

It has been confirmed that D-layers can be formed on metal surfaces at moderate temperatures ($T \sim 200^{\circ}$ C) by both active additives and inactive components of mineral oil. Zinc dialkyldithiophosphate additives provide higher load-bearing capacity of the A-layer compared to pure mineral oil and can form D-layers on steel at relatively low temperatures (of about 100°C). Lubricating layers with different physicomechanical and frictional properties can be formed depending on the chemical origin of the lubricating medium and the temperature regime.

Keywords boundary lubricating layer, contact conductivity, electrical probe methods, ZnDTP additives, load-bearing capacity

Nomenclaturearadius of contact spotEbinding energyffriction coefficient H_{η} microhardness (hardness test similar to Vickers, at load
50 g and pyramid apex angle 136°)Ipeak intensityPload

- p contact pressure
- R_{a} mean average arithmetic profile deviation
- R_c contact resistance
- $R_{\rm s}$ constriction resistance
- S area of load-bearing contact spot
- T temperature
- t time
- ρ electrical resistivity

INTRODUCTION Friction under the boundary lubrication regime is known to be accompanied by lubricant adsorption on the mating surfaces, lubricant transformation in the friction zone resulting from mechanical and thermal action, and interaction of active lubricant decomposition products with the surfaces. As a result, three types of layers (films) can be formed on the mating surfaces:¹⁻⁵

• a physically adsorbed layer (A-layer) with special physical properties, consisting of molecules of the base oil and/or additives

• a resin-like layer of deposits formed predominantly by degradation products of the base oil and additives (D-layer)

• a chemically modified layer (M-layer) on the base metal formed as a result of direct reactions between additives and metal.

So far, the investigation of boundary lubrication mechanisms has often been reduced to a definition of the role of A-, D-, and M-layers in friction behaviour at varying operating parameters. Certain difficulties are encountered in this case, especially at elevated temperatures leading to oxidation of contacting surfaces and lubricants. On the one hand, it is difficult to control the thickness and continuity of A-layers under conditions of dynamic contact; on the other hand, despite successes achieved in studying structure, both the structure and thickness of D- and M-layers and their mechanical and friction properties are insufficiently investigated. It should be noted that the properties of D-layers and their role in boundary lubrication have been studied to a lesser degree.

Electrical contact resistance measurements can give important additional information on the interface formation

under boundary lubrication.⁶⁻⁸ For multiple contacts, the estimations are mainly qualitative because the interpretation of results is rather complex. In the case of nominal point contacts, quantitative estimations concerning thickness, continuity, and load-bearing capacity of layers are, however, possible.⁸

In the present work electrical probe methods have been used to study deposits formed by oils on hot metal surfaces. Measurements of friction and electrical characteristics of the deposits in both static and dynamic contact using electrical probing, in combination with the analysis of surface products formed, have been carried out. Major attention has been given to the mechanical and friction properties of D-layers formed on steel by inactive and chemically active components of oils under various temperature conditions.

EXPERIMENTAL: Test equipment and samples

A microtribometer (MTT),⁹ which ensures smooth normal loading, reciprocating sliding at low speed following the probeplane scheme, and simultaneous monitoring of friction coefficient (*f*) and contact resistance (R_c), was used. The traditional four-point circuit was used for R_c measurements at 50 mV voltage drop in open contact. The upper limit of the circuit sensitivity was 10⁷ Ω .

The probes were chromium steel (IIIX-15) balls of 2 mm radius. Polished plates (manganese steel 65 Γ , $R_a = 0.06 \mu$ m, $\rho = 3 \times 10^{-7} \Omega$ m) served as flat samples. Some of the plates were thermally oxidised (air, $T = 200^{\circ}$ C, t = 7.2 ks).

Medical Vaseline oil (VO) and VO containing zinc dialkyldithiophosphate ((RO)₂PSS)₂Zn (ZnDTP) additive (0.65 wt.%) were used as lubricants. Analytically pure ZnDTP was prepared under laboratory conditions. The alkyl groups were *n*butyl groups with chain length of C₄. The zinc content was 11.9 wt.% and no –SH groups or excess zinc oxide were present. The oil drop was lightly rubbed into the flat plate with subsequent exposure to air (t = 7.2 ks) at room and elevated (100 and 200°C) temperatures. The latter was done to simulate, respectively, mild and moderate thermal effects on a thin oil layer on a metal surface (direct chemical reactions between dialkyldithiophosphate and steel¹⁰ are not observed at less than 200°C).

Specimen treatment	Etching time (min)	C 1s		0 1s		Fe 2p	
		E (eV)	l (counts s⁻¹)	E (eV)	l (counts s⁻¹)	E (eV)	l (counts s⁻¹)
Initial	5	284.6	41	532.1 530.1	18 688	712.3 710.5	495 552
Initial with VO treated at 200°C	2	289.1 284.6	19 76	531.8 530.1	257 638	718.9 710.5	309 476
Oxidised with VO + ZnDTP treated at 100°C	-	284.6	589	533.2 531.8 530.1	76 102 63	716.5 715.2 711.8 708.8	46 48 58 32
	1	288.5 286.6 284.6	39 68 234	533.0 531.4 530.1	139 259 302	719.7 716.7 710.5 709.8	171 167 266 154
Oxidised with VO + ZnDTP	_	288.5 284.6	44 452	534.3	62	713.6 709.5	43 36
treated at 200°C	1	287.9 286.4 284.6	46 73 230	531.5 530.1	389 183	716.7 712.1 710.5 709.3	112 130 139 126

Table 1 XPS analysis (spectral observations) of surface layers

Electrophysical	The layers formed were studied at room temperature. During
probing of layers	the experiments the following values were recorded:

• $R_{c}(P)$ dependences to assess the load capacity of the layers

• f and R_c within the first sliding cycle to characterise the friction properties of the layers

• f(n) and $R_c(n)$ dependences at given P to examine the wear resistance of the layers.

The above-mentioned experiments along with analysis were also performed after the steel plates, on which the D-layer was fixed, had been washed with organic solvents.

The $R_c(P)$ dependences were obtained by determining R_c at various points of the plane at each load step (within 0.1–2 N)

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Specimen treatment	Etching time (min)	Zn 2p		S 2p		P 2p	
		E (eV)	l (counts s⁻¹)	E (eV)	l (counts s⁻¹)	E (eV)	I (counts s⁻¹)
Initial	5						
Initial with VO treated at 200°C	2						
Oxidised with VO + ZnDTP treated at 100°C	-						
	1					134.7 133.1	11 14
Oxidised with VO + ZnDTP	-	1022.7	141	169.2	15	133.1	16
treated at 200°C	1	1022.7	463	169.4	18	133.1	29

Table 1 (continued) XPS analysis (spectral observations) of surface layers

with subsequent statistical processing of the data. Elastic deformation was mainly maintained at the above conditions. The calculated contact parameters dependent on load³ were the following: contour area radius $a = 11-30 \mu m$, contact area S = $(0.4-2.8) \times 10^{-10} m^2$, mean contour pressure p = 260-700 MPa, and constriction resistance $R_s = 13.5-5.0 m\Omega$. The majority of experiments on friction and wear resistance were performed at constant load P = 0.2 N with parameters of original Hertzian contact: $a = 14 \mu m$, p = 330 MPa, $R_s = 10.7 m\Omega$. After thermal treatment, the plates were rinsed in organic solutions and the chemical composition of the surfaces was

lutions and the chemical composition of the surfaces was analysed using X-ray photoelectron spectroscopy (XPS). An ES 2401 electron spectrometer was used at a pass energy of



> 1253.6 eV and a photoelectron exit depth of 1.0–1.5 nm, with resolving power of 0.1 eV. Mg K_{α} radiation as the excitation source and the binding energy of C 1s at 284.6 eV as a reference. In a number of cases, depending upon the sample type, additional cleaning of the surface by etching in argon for 1-5 min was done. The analysis of the spectra employed previously published data.¹¹

The position and intensity of Fe and O peaks (Table 1) show **RESULTS AND** that the original plate surfaces are covered with oxide (Fe_2O_3) **DISCUSSION:** and some adsorbed oxygen could also be detected. Free ferrous peaks were not detected even after etching for 5 min. This means, taking into account the value of the photoelectron exit depth, that the oxide film was not less than 1.5 nm thick.

> The experimental contact resistance R_c for the initial polished plates, and more so for the thermally oxidised plates, is greater by a few orders of magnitude than the calculated constriction resistance R_s (Figure 1(a)). This means that the oxide films do not rupture at normal loading, especially at small loads.

> The results obtained at sliding (Figure 2(a)) were similar to those derived earlier¹² for a reciprocating spherical

Unlubricated

contact



slider on base metals. The physically adsorbed surface layer (moisture, oxygen, solvents, etc.) and oxide films are wearing out in the first sliding cycles. The emergence of metal microspots and adhesion growth result initially in a decrease in R_c and an increase in f(n < 10). Further intensification of seizure and pile-up of oxidised wear products in the contact zone lead to a sharp increase in friction as well as high and unstable R_c . The friction coefficient level of about 0.4–0.5 and the 'stick-slip' effect indicate surface layer failure and transition to

adhesive wear. The number of sliding cycles $n_{\rm cr}$ at which such a level is reached at given P can characterise the system wear resistance. As can be seen (**Figure 2(a)**), $n_{\rm cr} = 15-20$ for unlubricated contact at P = 0.2 N.

Lubrication with VO The VO layer does not practically change the contact conductivity at normal loading (**Figure 1(a)**). Oil is easily squeezed out from the contact clearance and the A-layer thickness is too small to add substantially to the contact resistance (the latter is determined predominantly by the oxide film resistance).⁹

In spite of the low load-bearing capacity of A-layers, once applied, VO ensures the boundary lubrication regime for a long time until the lubricant becomes depleted on the friction track (Figure 2(a)). During the first 40-50 cycles of sliding, the gradually increasing f value reaches 0.12-0.15 and R_{c} decreases from 10-20 to $0.5-1 \Omega$ (Figure 2(a), curve 2). At further sliding, the contact characteristics can preserve such a level for hundreds of cycles. This is consistent with previous data¹³ showing that the life of a once-applied layer of lubricant without additives can be quite long, depending on the lubricant nature, its thickness and susceptibility to tribopolymerisation, replenishment conditions, etc. The A-layer properties in such a case govern friction behaviour. The contact characteristics, however, become similar to those of the unlubricated case (Figure 2(a), curve 1) after washing away the VO, which removes the A-layer.

The results were the same both at normal loading and at sliding after VO heat treatment at 100°C. This means that Alayer properties change slightly and the D-layer does not form at these temperatures. Remarkable changes, however, were found in samples treated at 200°C. R_c was higher than the upper limit of the circuit sensitivity $-10^7 \Omega$ at both static (**Figure 1(b)**, curve 1) and dynamic (**Figure 2(b)**, curve 1) contact. Measured f (**Figure 2(b)**), which at the start of sliding was much higher than with unheated VO (**Figure 2(a)**), increases further, reaching 0.4–0.5 in a few tens of cycles. Typically, the 'stick-slip' effect does not appear in this period.

The $R_c(P)$ dependences for both initial and oxidised plates show essentially a decrease in R_c after washing (**Figure 1(b**), curves 2 and 3), but greater by 1--2 orders of magnitude compared with unlubricated plates. Since additional growth of

oxide film on the oxidised plates could not occur during thermal treatment, this means the presence of some residual adherent layer on the steel. The D-layer detected ensures quite low friction ($f \approx 0.1$) and contact conductivity ($R_c \approx 50 \Omega$) at the start of sliding (**Figure 2(b**), curve 2). During $n \sim 40-50$, fgradually increases up to 0.12–0.15 and R_c decreases to $\sim 1 \Omega$, i.e., becomes typical for unlubricated contact when the adsorption layer is worn out (**Figure 2(a**), curve 1). So, the simultaneous rapid rise of f and R_c at further sliding also confirms the complete removal by wear of the D-layer.

It is known¹⁴ that mineral oils without antioxidants have an upper temperature limit of about 150–170°C imposed by oxidation where the oxygen supply is unlimited. The effects of oxidation are to produce aldehydes, asphaltenes, acidic components, and insoluble oxidation products, which are much more active compared to paraffins. This brings about changes of colour, viscosity, friction, and other properties of oil, and also lacquering and tarry deposits. Hence, the explanation of the results is based on the assumption of intensive oil oxidation.

The volume oxidation of the oil is confirmed by its colour change after heat treatment – it becomes brown. XPS analysis (**Table 1**) of samples after washing shows an increase of the oxygen peak at a binding energy of 531.8 eV and the appearance of a carbon peak at 289.1 eV. According to Nefedov¹¹ this indicates an increase in the number of oxygen–carbon bonds (CO and CO₂ groups) that is typical for oil oxidation products.

A layer of insoluble degradation products (D-layer) is formed on the steel surface due to chemisorption of chemically active oxidation products. The D-layer prevents metal contact and to some extent improves the frictional properties. This layer is quite thin and probably discontinuous since Fe_2O_3 peaks are attenuated a little (**Table 1**). Oxidation products increase oil viscosity, and also the load-bearing capacity of the Alayer, but reduce the lubricity. The results obtained show that the influence of the former process (change of A-layer physical properties) on the contact parameters is the main one.

Lubrication with ZnDTP-containing VO

- Compared with VO without additive, VO + ZnDTP after exposure at room temperature increases R_c to some extent, giving lower and stable f (see overleaf, **Figures 3(a)**, curve 1, and **4(a)**, curve 1). After plate washing, the f(n) and $R_c(n)$ dependences are qualitatively similar to those for the unlubricated



contact (**Figure 2(a)**, curve 1) although with lower f and higher R_c at the start of sliding and slightly higher wear resistance ($n_{cr} = 30-40$). It is evident that the A-layer, including physically adsorbed ZnDTP molecules, shows higher loadbearing capacity, lubricity, and adhesion to the surface compared to that formed by pure VO. Precision measurements of the mechanical and friction properties of an adsorbed ZnDTP layer with a surface force apparatus¹⁵ gave a similar conclusion. At the same time, as discussed elsewhere,¹⁶ ZnDTP molecules are not densely packed on the surface when physically adsorbed. Therefore, only a small amount of additive is kept on the surface after washing, as the data from the present tests indicate.

VO + ZnDTP heat treatment at 100°C results in a small reduction of R_c and f (**Figures 3(a)**, curve 2, and **4(a)**, curve 2). This might be explained by the formation of a more condensed A-layer due to the elevated temperature. The probe sliding on the washed plate has, however, shown that both the A-layer and the D-layer influence the contact behaviour (**Figure 4(b**), curve 1). Starting from 0.07–0.08 (n = 1), f increases slowly up to 0.09 (n = 40), while R_c decreases from 50 to less than 1 Ω . This points to the presence of a protective film on the steel surface, which is thin (low R_c), wear resistant (n_{cr} is not reached in 50 sliding cycles at P = 0.2 N), and has low shear strength (low



f). Note the absence of such a layer for the case of VO without additive for the same heat treatment.

XPS shows (**Table 1**) that, for the samples not etched in argon, the Fe_2O_3 peaks practically disappear, the carbon content is increased, and a significant intensity of the peaks of oxygen-containing groups is retained. After etching for 1 min, low-intensity phosphorus peaks appear together with traces of

sulphur and zinc. The oxygen peak at a binding energy of 533.0 eV corresponding to P–O bonds becomes more intense. The position of the peaks in the spectra indicates that phosphorus is bonded with, in particular, oxygen and sulphur.¹¹

The contact resistance and XPS data indicate that the Dlayer average thickness is 1.5–2 nm. It is obvious that its formation can be attributed to the presence of additive in the oil. It is known¹⁶ that ZnDTP does not decompose at about 100°C. In parallel with physisorption, ZnDTP chemisorption and participation in oxidation reactions are possible, with the formation of $((RO_2)_2PSS)_2$ disulphide, elemental sulphur, and some other reaction products.¹⁷

The role of the additive in D-layer formation becomes still more important at temperatures sufficient for its thermal decomposition. Comparison of the contact characteristics for samples of pure VO and VO + ZnDTP thermally treated at T =200°C confirms this. As seen from **Figures 1(b)**, curve 1, and **3(b)**, curve 1, the contact conductivity of the oil with additive is higher than that for the case with no additive. The relation changes, however, for washed plates (**Figures 1(b**), curve 2, and **3(b**), curve 2). This means that a thicker D-layer is formed in the case of additive being present. In contrast to VO without additive (**Figure 2**), VO + ZnDTP gives a very low initial friction coefficient (f = 0.06), which increases only slightly in the course of sliding, while R_c decreases gradually to $10^4 \Omega$ (**Figure 4(b**)). It is important to note that there is almost no change in contact parameters after plate washing.

The D-layer formed is thicker and also more wear resistant in comparison to the layers generated by VO without additive ($T = 200^{\circ}$ C) and VO + ZnDTP ($T = 100^{\circ}$ C). So, $n_{\rm cr}$ values for D-layers recorded at P = 0.5 N are about 25–30, 5–10, and 15–20, respectively.

Layer probing for the case of VO + ZnDTP shows that there is no large increase in oil viscosity or essential change in the A-layer physical properties, as is observed with VO without additive. Visual observation of the samples also confirms that base oil oxidation is not significant, as in the case with VO without additive. This fact is not unexpected since ZnDTP is a good antioxidant.¹⁴

XPS of samples with VO + ZnDTP treated at 200°C indicates a decreased content of oxygen and iron, whereas the

phosphorus content increases and characteristic peaks of other additive elements – sulphur and zinc – appear. The additive element concentration in the surface layer increases after ion etching, i.e., the D-layer composition is inhomogeneous through the thickness. The atomic abundance ratio Zn:P:S also changes through the thickness. After etching for 1 min the ratio (normalised to [Zn] = 1) is 1:1.3:0.6. This is a rather typical result,¹⁰ showing the decreased relative content of sulphur in the layer compared to the original additive (the atomic ratio in original ZnDTP is 1:2:4).

XPS shows that sulphur is bonded, but no iron sulphide (FeS) is detected. This indicates that there are no direct reactions between ZnDTP and the metal surface during heat treatment. Such reactions are possible when steel is heated to a temperature exceeding 600°C.¹⁰ At temperatures of about 200°C, zinc dithiophosphates decompose thermally, producing hydrogen sulphide, mercaptans, olefins, and a variety of sulphur- and phosphorus-containing compounds. The latter form a deposit (D-layer) on the surface due to chemisorption and interaction with each other. Besides ((RO₂)₂PSS)₂ disulphide, the layer can include various thiophosphorus species such as (RO)₂PSSR, (RS)₃PS, and (RS)₃PO.¹⁷ Bonded sulphur and phosphorus in the boundary layer can essentially reduce friction.¹⁸ This circumstance can improve the wear resistance and friction properties of the protective film after heat treatment. The film exerts the determining influence on the contact characteristics in the case under investigation.

CONCLUSION

Model experiments combining XPS analysis and measurements of friction and electrical characteristics in static and dynamic point contact have shown the approach to be promising for separate studies of the properties of the physically adsorbed layer (A-layer) and chemisorbed layer (D-layer) of deposits.

Confirmation has been obtained that D-layers can be formed on a moderately hot metal surface $(T \sim 200^{\circ}C)$ by chemically active additives and also inactive components of mineral oil. Such a layer consists mainly of oil oxidation products; it can increase the load-bearing capacity at normal loading, but its friction and wear-resistance properties are not good.

ZnDTP additives provide a higher load-bearing capacity of the A-layer compared to pure mineral oil and can form Dlayers on steel at relatively low temperatures (of about 100° C), at which neither direct reactions with the metal surface nor thermal decomposition of the additive occur. Increasing the surface temperature above the additive decomposition temperature results in an increase of the D-layer thickness and an improvement of its friction and wear-resistance properties.

D-layers formed by ZnDTP at moderate temperatures (of about 200°C) are very thin (a few nanometres), but they can effectively separate contact surfaces owing to their good loadbearing capacity and friction and wear-resistance properties. It is essential that D-layers can be formed on steel surfaces independent of the extent of oxidation. An important function of ZnDTP additives is their antioxidative properties which prevent a decrease of the A-layer lubricity.

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