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The Impact of Surface Roughness and PTFE/TiF_3/FeF_3 Additives in Plain ZDDP Oil on the Friction and Wear Behavior Using Thermal and Tribological Analysis under Extreme Pressure Condition

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***Abstract*—**The use of titanium fluoride and iron fluoride (TiF_3/FeF_3) catalysts in combination with polutetrafluoroethylene (PTFE) in plain zinc- dialkyldithiophosphate (ZDDP) oil is important for the study of engine tribocomponents and is increasingly a strategy to improve the formation of tribofilm and provide low friction and excellent wear protection in reduced phosphorus plain ZDDP oil. The influence of surface roughness and the concentration of TiF_3/FeF_3/PTFE were investigated using bearing steel samples dipped in lubricant solution at 100°C for two different heating time durations. This paper addresses the effects of water drop contact angle using different surface; finishes after treating them with different lubricant combination. The calculated water drop contact angles were analyzed using Design of Experiment software (DOE) and it was determined that a 0.05 μm R_a surface roughness would provide an excellent TiF_3/FeF_3/PTFE coating for antiwear resistance as reflected in the Scanning electron microscopy (SEM) images and the tribological testing under extreme pressure conditions. Both friction and wear performance depend greatly on the PTFE/and catalysts in plain ZDDP oil with 0.05 % phosphorous and on the surface finish of bearing steel. The friction and wear reducing effects, which was observed in the tribological tests, indicated a better micro lubrication effect of the 0.05 μm R_a surface roughness treated at 100°C for 24 hours when compared to the 0.1 μm R_a surface roughness with the same treatment.

***Keywords*—**Scanning Electron Microscopy (SEM), ZDDP, catalysts, PTFE, friction, wear.

I. Introduction

ZINC DIALKYLDITHIOPHOSPHATE (ZDDP) is the primary antiwear agent in conventional engine oils and is the main source of phosphorus. Environmental regulations have pushed for reduction of phosphorus levels present in engine oils since it is known to cause poisoning and failure of catalytic converters in car exhaust system [1]-[3]. Degradation of ZDDP is a very complex process and much effort has been dedicated to understand its mechanism and interaction with other additives [4]-[7].

To develop a better understanding of the wear mechanisms thermal and tribological analysis were developed using three different surface finishes (0.2μm R_a, 0.1μm R_a, and 0.05 R_a) in the presence of 0. 5 wt. % FeF_3 + 0. 5 wt. % TiF_3 masticated and dispersed catalysts + 2 wt. % PTFE + 0.05 wt. % P (phosphorus) plain ZDDP oil. Bearing steel coupons were dipped in the oil samples at 100°C for 24 or 12 hours and the data collected from measuring the water drop contact angles were analyzed using Design of Experiment software (DOE) to find the optimum solution that will be used in the tribological stages for understanding the possibilities of phosphorus reduction in engine oils. Tribological tests were run under an extreme load of 336 Newton as was optimized by earlier studies [8]-[11].

This study focuses on the catalysts and PTFE influences on the antiwear performance of plain ZDDP oil using idling speed or engine startup of 700 rpm under extreme loading conditions of 336 Newton or 2.6 GPa Hertzian contact pressure. The thermal analysis was a leading indicator for the tribological testing using two different surfaces conditions. Finding catalysts combination that work with PTFE and can concentrate antiwear additives on metal surfaces and hence reduce dependency on ZDDP under a temperature below 120^0C describes the underlying research findings to be discussed in this article.

II. Experimental Details

A secondary ZDDP (7.2 wt. % P) consisting of both basic and neutral forms, two catalysts iron fluoride FeF_3 and titanium fluoride TiF_3 and polytetrafluoroethylene PTFE were used in this study. Several blends were formulated with each antiwear additive for all thermal tests (Table I), and one blend was optimized using DOE with a composition of 0.05 wt. % P (phosphorus) in 100-neutral base oil + 0.5 wt. % FeF_3 + 0.5 wt. % TiF_3 + 2 wt. % PTFE to run the tribological tests. In order to keep the FeF_3 and TiF_3 in solution a dispersing agent (viscoplex from Castrol, NY, USA) was used and subsequently diluted in base oil (solvent neutral-100) up to 20% solid concentrate. The suspended concentrate is, then, added to the oil mixture to give a 0.5 wt. % FeF_3 dilution, and 0.5 wt. % TiF_3 dilutions. The PTFE is solid lubricant dispersed in hydrocarbon oil with 1 to 5 ratios. The oil formulation mixtures were blended in a kitchen aid blender 4 quart capacity with a power rating of 250 Watts for 30 minutes until a homogenous solution was reached.

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The lubricant blends were used to study the effect on bearing steel coupons after 24 or 12 hours treatment at 100^0C. The bearing steel coupons were polished to 0.2μm R_a, 0.1μm R_a, and 0.05 μm R_a respectively. Afterward, differences in surface tension evidenced by water drop contact angle on these coupons after treatments were measured and are shown in Table I. Atomic Force Microscopy was used to observe nano-size droplets of water on steel coupons.

An in-house-made ball on cylinder lubricity evaluator (BOCLE) was used to conduct the boundary lubrication tests for the lubricant blend using a surface roughness of 0.05μm $R_{a,}$ and 0.1μm $R_{a.}$ The surface finish of the rings was examined using a profilometer (Mahr Perthometer M1). The rings were cleaned with acetone and hexane to remove any machining oil that was present. An SAE Timken steel ring (60-62 Rockwell C Hardness (HRC), 60mm OD) was the moving body. A 12.5 mm tungsten carbide ball (79 HRC) was the counter body. A tungsten carbide ball was chosen as the counter surface to ensure that the wear occurred on the test cylinder. The annealing of the steel ball at the contact point resulted in extensive wear and the subsequent reduction of Hertzian contact load was not controlled. With the use of tungsten carbide (WC) ball which has a hardness of 15 Rockwell C higher than the underlying cylinder the Hertzian contact load was kept constant. The cylinders were dipped in the lubricant blend and treated for 24 hours at 100°C, then removed and mounted on the machine and the extra oil were spun to ensure a starved boundary lubrication testing. The WC ball was pressed against the cylinder and the desired load was applied.

Design of Experiment (DOE) factorial software was used to optimize all data, since the traditional approach of examining one factor at a time (OFAT) is time consuming. The limitation of this approach is the large number of experiments that are needed to evaluate products and multifactor interactions to reach high desirability. Using a DOE factorial approach all variables are varied simultaneously in a predetermined fashion and using this approach it is possible to determine how one factor influences the outcome when two or more of the other variables are varied at the same time. In addition it is possible to determine the interaction between several factors simultaneously. The surface morphologies of the wear track on the ring were examined in secondary electron mode using a scanning electron microscope (SEM, JEOL-JSM-IC845A) and the frictional data collected were plotted using Excel software.

III. Results and Discussion

A. Thermal Result

Table I provides a detail description of the water drop contact angle for different concentrations of TiF_3/ FeF_3 catalysts with PTFE and ZDDP oil through different heating times and using several surface finishes. The mechanism of thermal film formation was followed carefully to check the deposition of certain products that can reduce the friction coefficient under extreme contact and enhance antiwear film formation. The surface modification can be just nanometers thick. Since negligible weight is added to the metal with this treatment, this process would have enormous potential on the tribological behavior of engine components and metal to metal surface contact. Water drop contact angle data were part of Design of Experiment software analysis using general factorial since the surface finish was considered at three levels in the experimental design (Table I). Lubricant blends were composed of FeF_3/TiF_3/PTFE at different concentrations blended with 0.05 P% (phosphorus) plain ZDDP oil. The general factorial design was usually set up by identifying the variables to be studied and the ranges over which these variables need to be studied. The set up analyzed the measured outcomes involving water drop contact angles. The response has its own desirability value with respect to each factor, and the change in desirability was a result of factors interactions.

Figs. 1-3 show the optimized conditions of all surface finishes. It is reported that the water drop contact angle was high with a desirability of over 90% when the surface roughness is close to 0.05 R_a. Time duration for temperature treatment at 100°C varied with the water drop contact angle, since it was higher when the treatment was 24 hours for 0.05 R_a and 0.1 R_a surfaces contrary to the treatment for 0.2 R_a surface finish. The optimized lubricant mix was 0.5 wt. % TiF_3, 0.5 wt. % $FeF_{3,}$ 2 wt. % PTFE, and 0.05 P % plain ZDDP oil for all treated surfaces at 100°C. Experiments conducted with the PTFE and catalysts suggest significant modification of the metal surface and the anti-wear additive of FeF_3 + TiF_3 and ZDDP provided better protection especially when 0.05μm R_a surface finish is treated with this lubricant blend for 24 or 12 hours at 100^0C. These results present good argument about the usage of fluorinated catalysts with ZDDP in tribological applications.

The thermal analysis provided proof that the tribological behavior of ZDDP will react faster to the presence of a fluorinated catalysts and PTFE; therefore the probability of forming antiwear resistant film is higher than when ZDDP is used alone. Figs. 4-6 indicated that with higher PTFE concentration and TiF_3/FeF_3 catalysts mix water drop contact angle was increased. It was also reflected in Figs. 4-6 that reduced surface roughness played an important role in enhancing the antiwear resistance film especially when the duration of heating time is increased to 24 hours. The response surface model (Figs. 1-3) presented a 3D view of the water drop contact angle variation with respect to catalysts and PTFE concentrations. The 18 hours time duration did not indicate any significant improvement with respect to the three surfaces considered in the analysis. Some improvement can be observed when you increase the heating time from 12 to 24 hours and optimization of all these variables were achieved using targeted values and desirability techniques in the Design of Experiment software (DOE) as reflected in Figs. 1-3. The design of experiment software ran the analysis simultaneously for all factors and response considered in the model. Evaluation of water drop contact angles were investigated with respect to factor interactions and the final decision outcomes were optimized leading to the calculation of lubricant blend and time duration that will be used to investigate tribological behaviors based on the highest possible desirability. Desirability is used when multi objective optimization is sought. Each factor corresponds to a certain desirability value. The desirability is high when factor interactions contribute positively to the targeted response such as target within range, minimum, maximum. Therefore, desirability will indicate that based on the different factors in the model a maximum water drop, contact angle varies with respect to lubricant blend heating time.

TABLE I
DESIGN OF EXPERIMENT DATA FOR WATER DROP CONTACT ANGLE USING DIFFERENT SURFACE FINISHES AND DIFFERENT LUBRICANT TREATMENTS AT DIFFERENT HEATING TIMES

Tests Run	Factor 1: TiF_3/FeF_3 % concentration: 0.4%-1%	Factor 2: PTFE % concentration: 0.8%-2%	Factor 3: Surface Finish (R_a) 0.05-1-2 (μm)	Factor 4: Heating Time 12-24 (Hour)	Response Water Drop Contact Angle: Degree
1	1	2	0.05	24	121
2	0.4	2	0.2	24	99
3	1	2	0.05	12	104
4	0.4	2	0.1	12	98
5	0.4	2	0.05	12	102
6	0.4	0.8	0.1	24	103
7	1	0.8	0.05	12	98
8	0.4	0.8	0.05	24	100
9	1	2	0.2	24	101
10	0.4	2	0.05	24	102
11	0.4	2	0.2	12	98
12	0.4	0.8	0.2	24	97
13	0.4	0.8	0.1	24	102
14	1	2	0.1	12	116
15	1	0.8	0.1	12	112
16	1	0.8	0.2	12	111
17	1	2	0.1	24	119
18	1	2	0.2	12	111
19	0.4	2	0.1	24	97
20	1	2	0.05	12	104
21	0.4	2	0.2	24	100
22	1	0.8	0.05	24	105
23	1	2	0.2	12	112
24	1	0.8	0.1	12	112
25	1	2	0.05	24	120
26	1	0.8	0.2	12	112
27	0.4	2	0.2	12	98
28	1	0.8	0.1	24	105
29	0.4	0.8	0.1	12	99
30	0.4	0.8	0.2	12	97
31	0.4	0.8	0.05	24	101
32	0.4	2	0.05	24	103
33	1	2	0.1	24	117
34	0.4	0.8	0.2	12	98
35	0.4	2	0.1	24	97
36	1	0.8	0.05	12	97
37	1	0.8	0.2	24	98
38	0.4	0.8	0.05	12	102
39	1	0.8	0.2	24	96
40	1	2	0.1	12	115
41	0.4	0.8	0.1	12	100
42	1	0.8	0.1	24	105
43	1	0.8	0.05	24	105
44	0.4	2	0.1	12	97
45	1	2	0.2	24	101
46	0.4	0.8	0.05	12	103
47	0.4	0.8	0.2	24	98
48	0.4	2	0.05	12	102

Two bearing steel coupons with surface finishes of 0.1 R_a and 0.05 R_a were treated with a lubricant blend that contains 0.5 wt. % TiF_3 + 0.5 wt. % FeF_3 + 2 wt. % PTFE + 0.05 P % plain ZDDP oil and the balance is neutral oil 100 for 24 hours heating time at 100°C. Products deposited on these surfaces are presented in Figs. 7 (a) and (b) using scanning electron microscopy (SEM). These figures show that the entire surfaces are covered with smooth film. There are small and large white patches of stable films shown in Figs. 7 (a) and (b). These SEM images indicate that the films adhere to the surfaces and it is more stable on the 0.05 μm R_a polished surface.

B. Tribological Results

Two tribological tests were run to investigate the friction and wear tracks of these surfaces under extreme loading condition of 336 Newton or 2.6 GPa Hertzian contact pressure and engine idling speed of 700 rpm using a lubricant blend optimized by the thermal treatment and DOE software with a heating time before testing of 24 hours. Fig. 8 depicts the typical progression of friction when 0.5 wt. % TiF_3 + 0.5 wt. % FeF_3 + 2 wt. % PTFE + 0.05 P % plain ZDDP oil was using two different cylinders one with 0.1μm R_a surface finish and the other with 0.05 μm R_a surface finish. Tests were repeated several times and showed a great consistency with error less than 10%. The importance of fluorinated catalysts and PTFE additives along with ZDDP were very significant as indicated in Fig. 8. Low magnification secondary electron micrographs (Fig. 8) of the wear tracks showed that the tribofilms formed on the 0.05 μm R_a surface were distinctive due to smooth surface, with just few scratches when compared to the other tribofilms formed on the 0.1 μm R_a surface. It is clearly evident that there is strong interaction between FeF3/TiF3/PTFE/ZDDP and the 0.05 μm R_a surface that was confirmed by the frictional events and the SEM findings. These results corroborate closely with the thermal results of the water drop contact angle. It is also in accordance with several earlier studies that describe in details the importance of fluorinated catalysts and PTFE [5]-[7], [12].

IV. CONCLUSION

The following conclusions can be drawn from this study:

1. Thermally treated surfaces at 100°C where roughness is optimized using Design of Experiment (DOE) for water drop contact angle analysis and different concentrations of PTFE and catalysts are very important for understanding frictional events and the formation of antiwear resistant film for the protection of components undergoing extreme pressure loading and starved lubrications especially at the cold start of an engine.
2. The performance of ZDDP oil with antiwear fluorinated additives will increase when the surface roughness is reduced and the temperature treatment time is reduced if compared to higher R_a surfaces of 0.2 μm or more.
3. The tribological results of thermally treated surfaces with reduced R_a of 0.05 μm are very significant if compared to a higher R_a surface. It is well reflected in the scanning electron images of the wear tracks and the frictional events of Fig. 8.

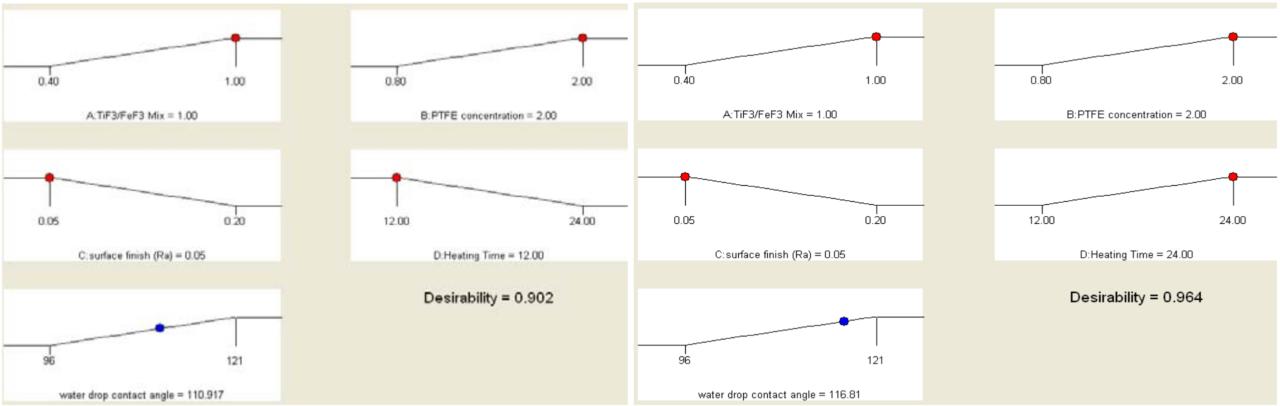

Fig. 1 Optimization of lubricant mix and heating time for 0.05 μm R_a surface roughness evidenced by water drop contact angle

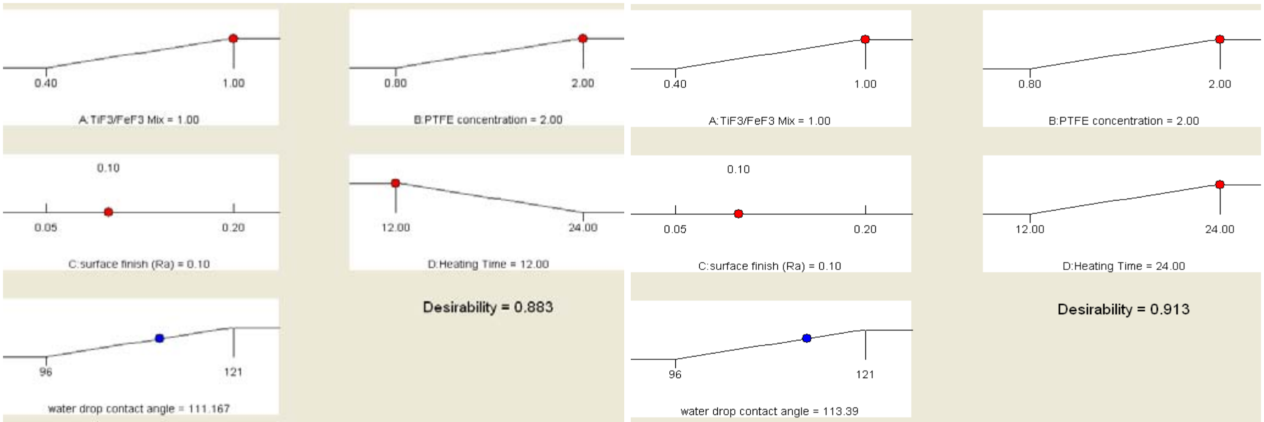

Fig. 2 Optimization of lubricant mix and heating time for 0.1 μm R_a surface roughness evidenced by water drop contact angle

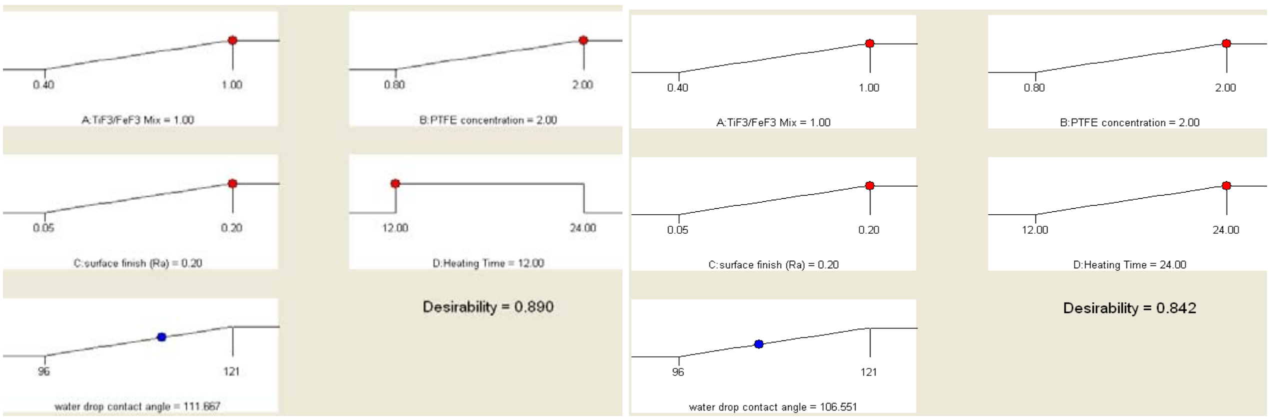

Fig. 3 Optimization of lubricant mix and heating time for 0.2 μm R_a surface roughness evidenced by water drop contact angle

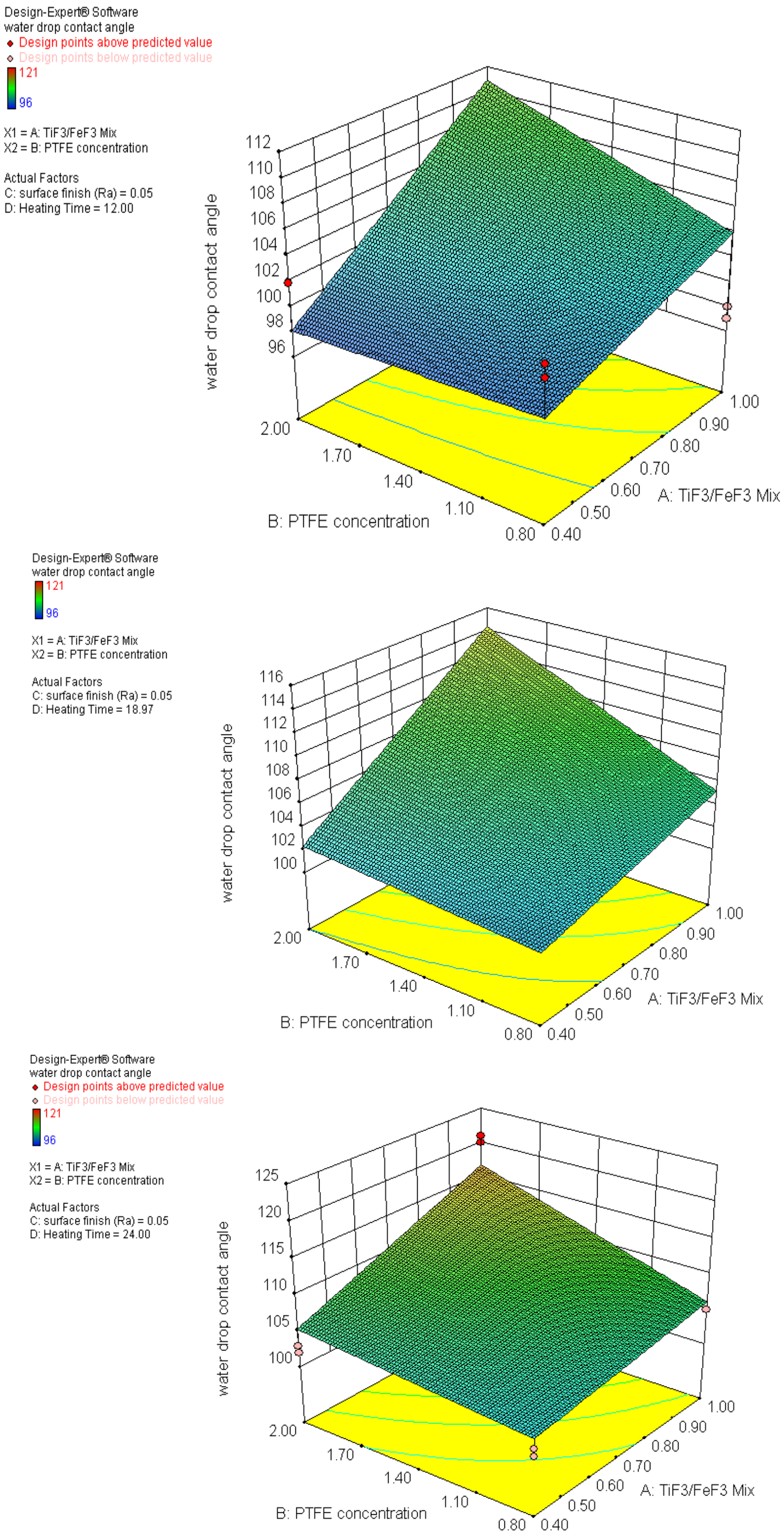

Fig. 4 DOE Response surface Model (RSM) of water drop contact angle for 0.05 µm R_a surface roughness with respect to different heating time of the lubricant at 100°C, different PTFE % concentration and different TiF_3/FeF_3 catalysts % concentration.

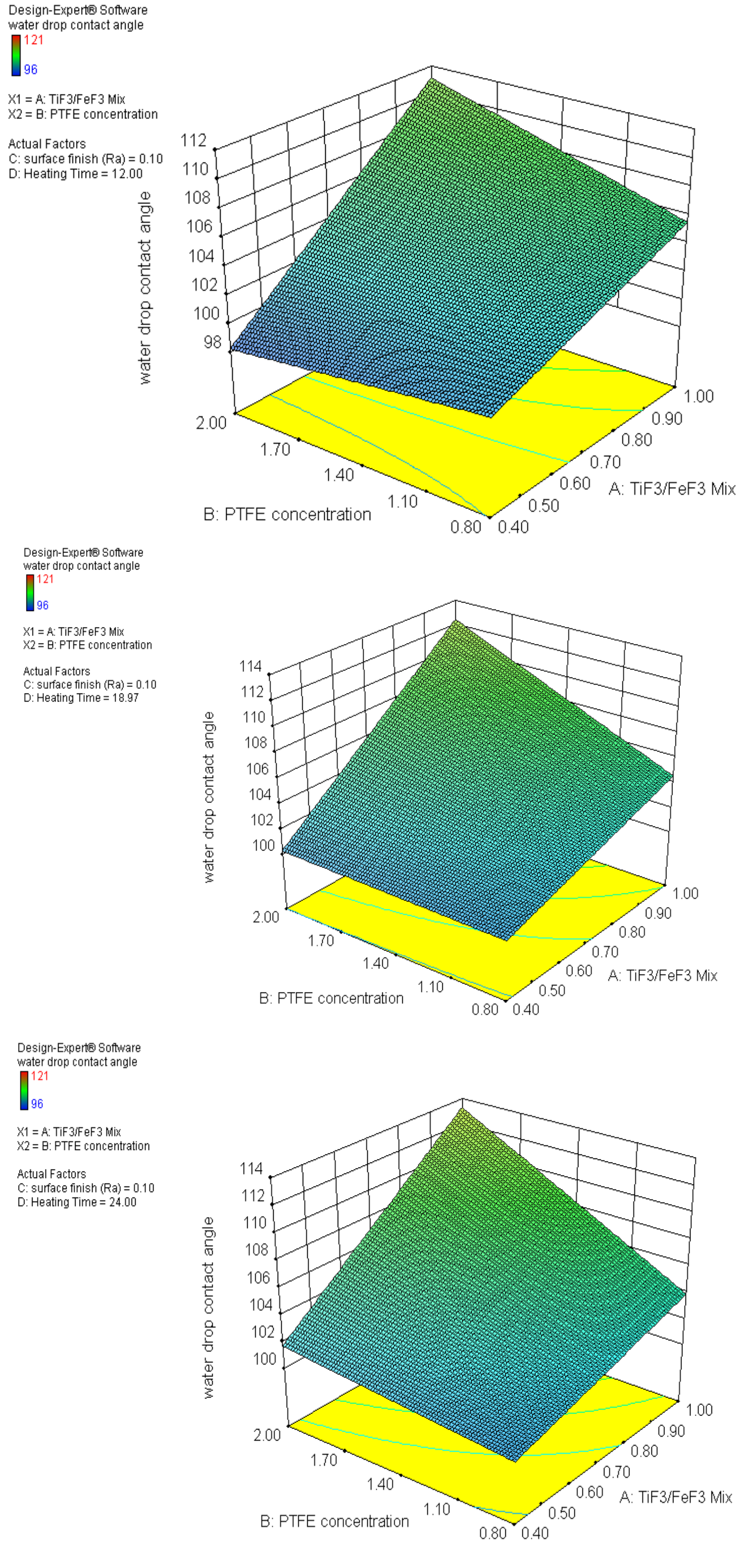

Fig. 5 DOE Response surface Model (RSM) of water drop contact angle for 0.1 µm R_a surface roughness with respect to different heating time of the lubricant at 100°C, different PTFE % concentration and different TiF_3/FeF_3 catalysts % concentration

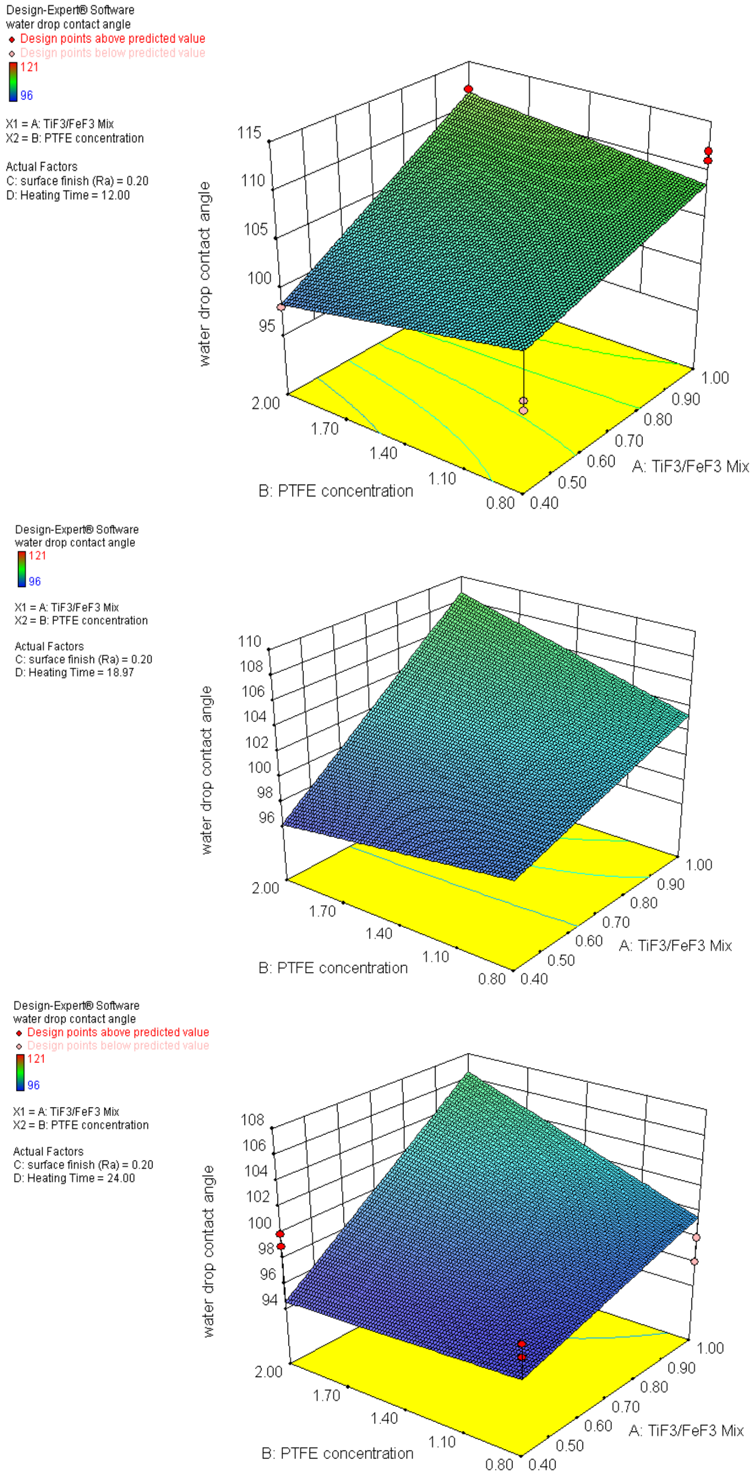

Fig. 6 DOE Response surface Model (RSM) of water drop contact angle for 0.2 µm R_a surface roughness with respect to different heating time of the lubricant at 100°C, different PTFE % concentration and different TiF_3/FeF_3 catalysts % concentration.

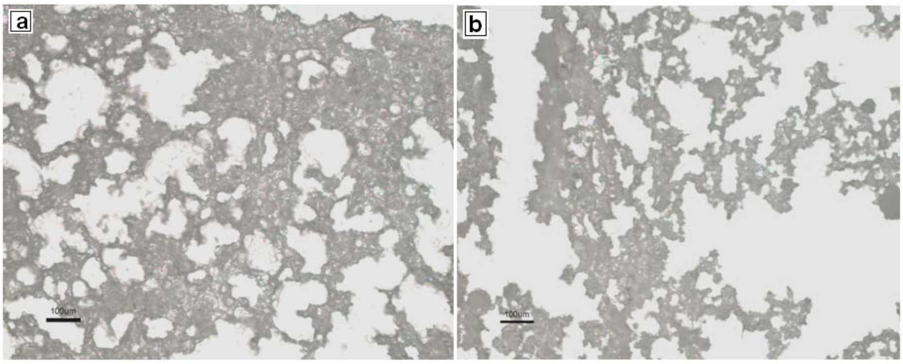

Fig. 7 Scanning Electron Micrograph of PTFE/TiF_3/FeF_3 deposition on 0.1 µm R_a surface roughness (a) and on 0.05 µm R_a surface roughness (b). Bearing steel surfaces were treated for 24 hours at 100°C in 0.05 P % ZDDP + 0.5 wt. % TiF_3 + 0.5 wt. % FeF_3 + 2 wt. % PTFE and the balance 100-neutral base oil

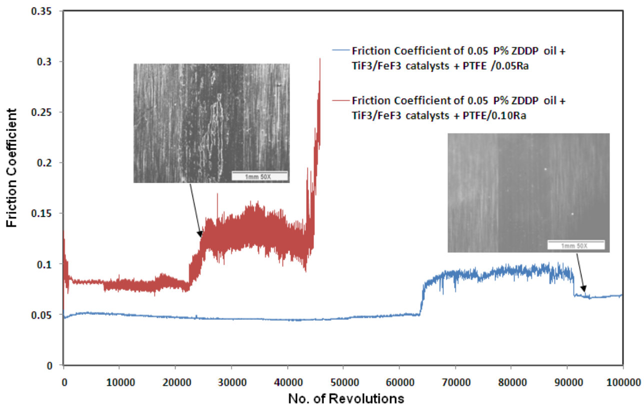

Fig. 8 Tribological behavior of two surface finishes treated with 0.05 P % ZDDP + 0.5 wt. % TiF_3 + 0.5 wt. % FeF_3 + 2 wt. % PTFE and the balance 100-neutral base oil for 24 hours at 100°C under an extreme load of 336 Newton or 2.6 GPa Hertzian pressure

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