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RESEARCH

# The Wear Characteristics of Heat Treated Manganese Phosphate Coating Applied to AlSi D2 Steel with Oil Lubricant

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A B S T R A C T

*Today, in the area of material design conversion coatings play an important role in the applications where temperature, corrosion, oxidation and wear come in to play. Wear of metals occurs when relative motion between counter-surfaces takes place, leading to physical or chemical destruction of the original top layers. In this study, the tribological behaviour of heat treated Manganese phosphate coatings on AISI D2 steel with oil lubricant was investigated. The Surface morphology of manganese phosphate coatings was examined by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) .The wear tests were performed in a pin on disk apparatus as per ASTM G-99 Standard. The wear resistance of the coated steel was evaluated through pin on disc test using a sliding velocity of 3.0m/s under Constant loads of 40 N and 100 N with in controlled condition of temperature and humidity. The Coefficient of friction and wear rate were evaluated. Wear pattern of Manganese phosphate coated pins with oil lubricant, Heat treated Manganese phosphate coated pins with oil lubricant were captured using Scanning Electron Microscope (SEM). The results of the wear test established that the heat treated manganese phosphate coating with oil lubricant exhibited the lowest average coefficient of friction and the lowest wear loss up to 6583 m sliding distance under 40 N load and 3000 m sliding distance even under 100 N load respectively. The Wear volume and temperature rise in heat treated Manganese Phosphate coated pins with oil lubricant is lesser than the Manganese Phosphate coated pins with oil lubricant.*



## 1. INTRODUCTION

The aim of Phosphating treatment is to convert the metallic surface completely into a non-metallic surface. A Phosphating is a chemical conversion treatment which produces a porous surface layer of crystalline phosphate. The primary aim of chemical conversion process is not to increase hardness but confer anti-welding properties although many do also increase the surface hardness [1].Wear may be regarded as the undesirable flow of material from surface .it can be kept within bounds either by controlling the flow of force and energy or by absorbing the flows of force and energy [2]. High carbon high chromium steels are commonly used in applications requiring excellent wear resistance in tool and die making industries. The wear properties of the phosphate coatings are dependent on the surface finish and the material used for the sliding counter face. The thin coating is satisfactory for running against smooth surface whilst the thicker coating is superior against coarser surfaces. Phosphating is highly beneficial when employed under lubricating conditions as less advantage could be found for the phosphating of materials operating under dry sliding conditions [3]. This process involves a reaction between a solution and a metal surface such that the coating derives partly from the solution and partly from the substrate [4]. Phosphate coatings are generally formed by immersing iron (or) steel into an aqueous solution of phosphoric acid and manganese carbonate [5]. Manganese Phosphate coatings are created by chemical conversion and the main component of the film is hureaulite $(Mn\ Fe)_5\ H_2(PO_4)_2$. Due to its economy, speed of operation, excellent corrosion resistance, wear resistance, adhesion and lubricative properties, it plays a significant role in the industries [6-10]. In applications, phosphate coatings may be exposed to high temperature (or) to thermal fluctuations and under such circumstances, the chemical stability of such coatings, especially dehydration behavior, is a great concern [11]. The benefits of manganese phosphate coatings includes an oil retaining capacity which facilitate low friction motion and eliminate scuffing and galling [12]. Manganese phosphate coatings improve the resistance to adhesive wear, and adsorb the lubricant. Phosphating is a process used to produce a crystalline oil-absorbing coating with an excellent wear Resistance. These coatings are applied to facilitate initial running of new parts like piston rings, camshafts, Cylinder liners and gears [13]. Phosphate coatings are to provide wear resistance and aid in cold forming of steel. Andrzej Kozjowski [14] observed that the chemical pretreatment has no practical effect on the dry friction coefficient value, and the friction coefficient decreases as the load increases. The mechanism of dry friction of manganese phosphate coatings is probably similar to that of brittle substance. Hivart [15] claimed that the adhesion of the phosphate coating seems to be an efficient mechanical keying of the phosphate crystals onto the peaks of the metal surface. Rout[16] claimed that Polymanganese coated galvHeat treated steel sheets with 1000 g/m$^2$ oil helps in reduction of coefficient of friction with the die surface from 0.22 to a value of 0.11 indicating superior lubricating property. Hivart [17] conducted test on tribological properties of manganese phosphate Coating and observed that annealing of a phosphate part at temperature up to 700 $^o$C leads to dehydration and modification of coatings. This treatment results in an increase in the ability of the coating to retain the lubricant. Neville [18] observed that Diamond like Coating (DLC) provides inherently lower friction coefficients and the oil with molybdenum dialkyl dithiocarbanate (MoDTC) and Zinc dialkyl dithiophosphate (ZDDP) shows lowest friction in the ferrous system. Psyllaki P.P. [19] conducted test on Pin-on-disc for diamond like carbon coatings and observed that the apparent wear life time of the coating was found to increase when decreasing the normal load applied and with increasing sliding speed and substrate hardness. Bahrami A. [20] conducted test on wear resistance of AISI H13 tool steel and observed that gradual increase in friction coefficient during the initial stage at 98 N loads can be attributed to the in situ surface tempering phenomenon. M. A. Chowdhury et al. [21] observed that the presence of normal load and sliding velocity affects the coefficient of friction considerably. The values of friction coefficient decrease with the increase in normal load for copper-copper, copper-brass, brass-brass and brass-copper pairs.

V. Bria et al. [22] explained that the role of aramide fibers in the composite on increasing the wear resistance of materials while the graphite particles appearing from carbon fibers breaking acts as dry lubricant. From the above literature it could be revealed that manganese phosphate coating is included in the family of wear resistance coatings. The aim of this paper is to compare the wear resistance of manganese phosphate coating with oil lubricant with Heat treated Manganese Phosphate coating with oil lubricant on AISI D2 steel substrate under low and high load condition.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

The AISI D2 steel was used as substrates. The chemical composition of the materials is given in Table 1. The properties of the materials are given in the Table 2.

**Table 1.** Chemical Composition of the AISI D2 tool steel [wt.%] analysed by Optical emission Vacuum Spark Spectrometer.

| **Elements** | C | Si | Mn | Cr | Ni | Mo | V | Ti | S | P | Te |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Percentage** | 1.50 | 0.41 | 0.74 | 12.01 | 0.01 | 1.01 | 0.27 | 0.01 | 0.03 | 0.03 | Balance |

**Table 2.** Mechanical properties of the AISI D2 tool steel.

| | |
|---|---|
| **Tensile Strength ($N/mm^2$)** | 770 |
| **Hardness [$HR_C$]** | 20 |

**Table 3.** Material specification, Hardness and Surface finish for pin and disc.

| **Description** | **Material** | **Hardness HRc** | **Surface Roughness ($R_a$) Microns** |
|---|---|---|---|
| Pin (8 mm dia, 15 mm long) | D2 Steel mill Heat treated | 20 | 0.1 |
| Disc (Dia 60 mm, Thickness 10mm for 40 n load) (Dia 165 mm, Thickness 8 mm for 100 N Load) | D2 Steel Hardened and Tempered | 60 | 0.10 |

## 2.2 Specimen

The materials specification and their initial hardness values for the pin and disc are listed in Table 3.

## 2.3 Treatment

The formulation of coating consists of three basic sequences are: Cleaning, Refining and Phosphating. S. Ilaiyavel et al. [8] already explained the coating procedure Mineralogy and structure of manganese phosphate coating used in this present study.

## 2.4 Heat treatment after the Coating

The coated steel substrate is heated slowly up to 450 $^0$ C and kept for 15 min duration. It is then cooled in the furnace to reach room temperature. The steel substrate is not affected by the heating and furnace cooling. Below 450 $^0$C there was no phase transformation in the high carbon high chromium steel. Figure 1 shows micro graph of heat treated manganese phosphate coated AISI D2 steel. Heating process generates micro voids in the manganese phosphate coatings due to dehydration. These micro voids increase the quantity of oil retention.

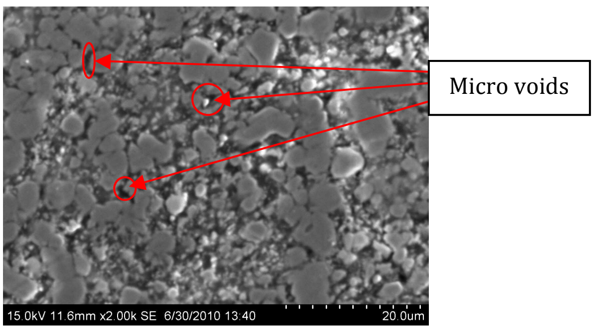


**Fig. 1.** Micro graph of heat treated manganese phosphate coated AlSi D2 steel.

## 2.5 Lubrication

After Phosphating with/without Heating, prior to wear testing the coated pins are dipped into oil lubricant for around 15 to 20 min at room temperature. Lubricating oil creates a thin separating film between surfaces of adjacent moving parts .This minimizes direct contact between them, decreases heat caused by friction and reduces wear. In this experiment 20W40 oil is used as a lubricant. Table 4 shows the properties of the lubricant.

**Table 4.** Properties of Lubricant.

| | |
|---|---|
| Kinematic Viscosity at 100 $^0$ C | 13.5-15.5 |
| Viscosity Index, Min. | 110 |
| Flash point (COC), $^o$C Min. | 200 |
| Pour point, $^o$C Max. | (-)21 |

## 2.6 Wear testing

Wear testing was carried out on a pin on disc type apparatus which has a specific feature for direct loading of cylindrical test pin in vertical contact with surface of high carbon and high chromium steel disc hardened to 60 HRc. The schematic view of wear testing apparatus is shown in Fig. 2. The unit consists of an arm to which the pin is attached. At the bottom is a fixture which accommodates a disk up to 10 mm thickness. The tests were carried out under 40 N and 100 N applied load for sliding velocity of 3 m/s for a constant sliding radius of 15 mm. During testing the tangential force was measured by a set of load cell and monitored by computerized data acquisition system. In all the cases the friction coefficient, wear volume and temperature of the pins were estimated by taking the average values of 3 tests.

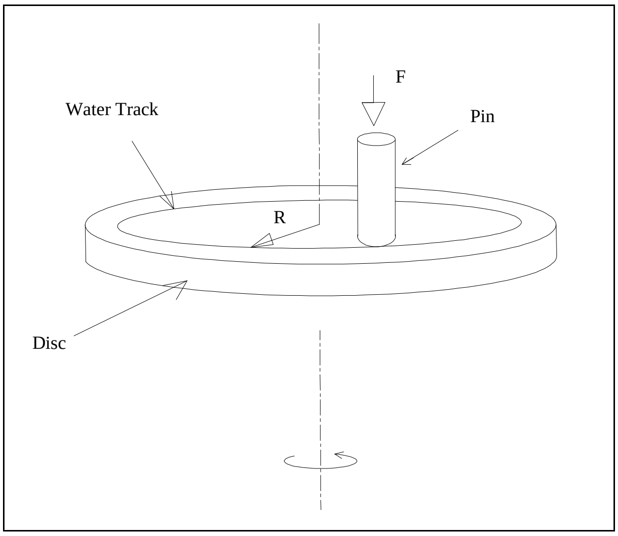


**Fig. 2.** Schematic diagram of pin-on-disk wear apparatus.

## 3. RESULTS AND DISCUSSION

### 3.1 Friction Coefficient

Test procedures were employed to the pin on disc tests at 3 m/s under 40 N and 100 N loads. The Plot of friction coefficient versus sliding distance for 40 N and 100 N of Manganese Phosphate coated with oil lubricant and Heat treated Manganese Phosphate coated with oil lubricant pins are shown in Figs. 3 and 4 respectively. Initially the two types of pins with oil lubricant under 40 N and 100 N loads revealed almost similar coefficient of friction around 0.1, the reason being the oil lubricant which reduces the coefficient of friction to a lower level. Manganese Phosphate coated with oil lubricant pins show an average coefficient of friction 0.1 at their steady state for both 40 N and 100 N. The coating failed after sliding distance of 3100 m for 40 N load and 1050 for 100 N loads respectively. Heat treated Manganese phosphate coated pins with oil lubricant show an average coefficient of friction of 0.1 at their steady state for both 40 N and 100 N. The coating failed after sliding distance of 6800 m for 40 N load and 2900 for 100 N loads respectively. The lower coefficient of friction can be assessed by the ability of the coating to retain the lubricant by means of the micro cracking. Heating process causes micro cracks due to dehydration which generate traps these micro cracks act as an oil reservoir, there by retaining an increased quantity of oil in them. Hence Heat treated manganese phosphate coated pins with oil lubricant maintained low coefficient of friction for longer time, even at higher loads.

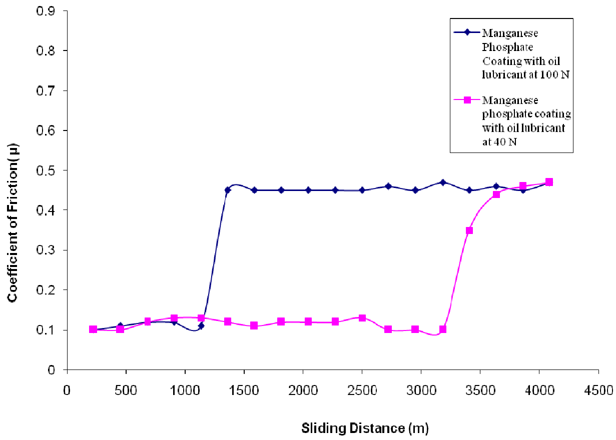


**Fig. 3.** Coefficient of friction vs Sliding distance for Manganese Phosphate coating with oil lubricant.

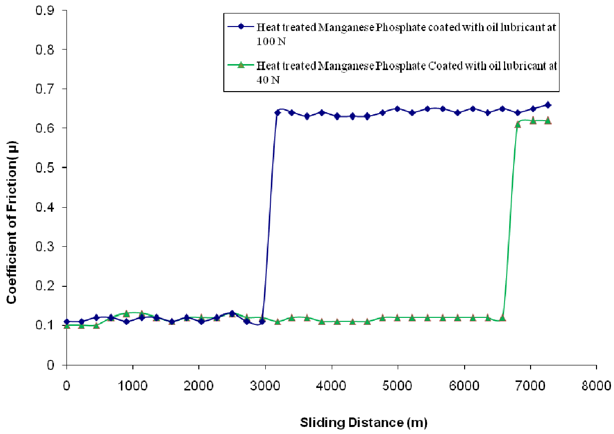


**Fig. 4.** Coefficient of friction vs Sliding distance for Heat treated Manganese phosphate coated with oil lubricant.

### 3.2 Wear volume

The wear volume of Manganese phosphate coated pins with oil lubricant and Heat treated Manganese Phosphate coated pins with oil lubricant is shown in Figs. 5 and 6 at a sliding distance under 40 N and 100N load respectively. When a 40 N load is applied, the wear volume of Pins increases slightly as the time increases. The Wear volume of Manganese Phosphate coated pins with oil lubricant is higher than Heat treated Manganese Phosphate coated pins with oil lubricant. When 100 N load is applied, the wear volume increases more rapidly because of higher load conditions. While 100 N load is applied on Manganese Phosphate Coated pins with oil lubricant they show average wear volume around 6.0 mm$^3$ at 2500 m sliding distance. At the same time Heat treated Manganese Phosphate coated pins with oil lubricant show average wear volume around 1.8mm³. When 40 N load is applied on Manganese Phosphate Coated pins with oil lubricant they show average wear volume around 2.5 mm³ at 6,000 m sliding distance, in similar conditions Heat treated Manganese Phosphate coated pins with oil lubricant show less wear volume around 1.3 mm³ only. The removal of particles accelerates wear while the presence of a lubricant may reduce wear.

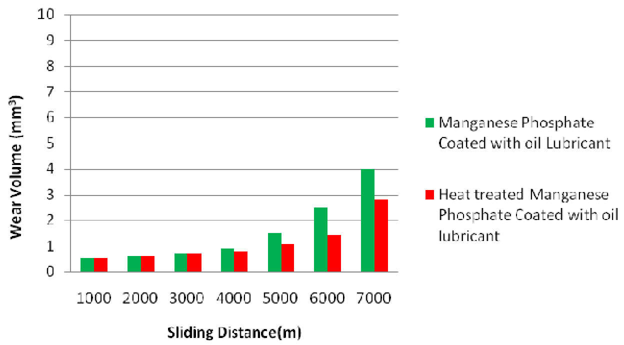


**Fig. 5.** Wear volume vs Sliding distance at 40 N Load.

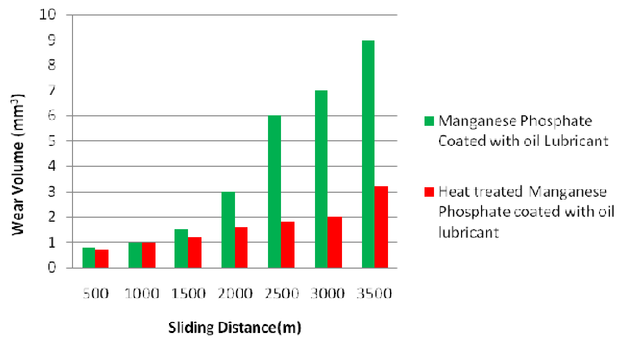


**Fig. 6.** Wear volume vs Sliding distance at 100 N Load.

Manganese phosphate coating significantly retains oil and eliminates scuffing and galling. This in turn reduces wear and helps in lubrication to a great extent. Perry. J. [3] has claimed that Phosphating is not the sole beneficial factor in reducing wear and bringing down the coefficient of friction for it is enhanced by oil lubrication. Wear rate under dry conditions are high and the thin phosphate layer is instantly removed. Micro cracks appear in the crystals, perpendicular to the substrate surface, in the range of 450 ⁰C – 550 ⁰ C, especially due to the dehydration of huralite. These Cracks occurs only due to the loss of water and when the dehydration is complete, the maximum oil retaining capacity is improved.

### 3.3 Temperature

The temperature of the pins was measured in real time with a thermometer at the wear surface of the pins. Figs. 7 and 8 shows a relation between pin temperature and sliding distance with 40 N, 100 N loads at constant speed condition respectively. It is seen that there is rise in pin temperature with sliding distance. It indicates that frictional heating has rising trend with increasing sliding distance. Heat treated Manganese phosphate coating with oil lubricant shows lesser rise in pin temperature because of less friction coefficient and avoiding metal to metal contact.

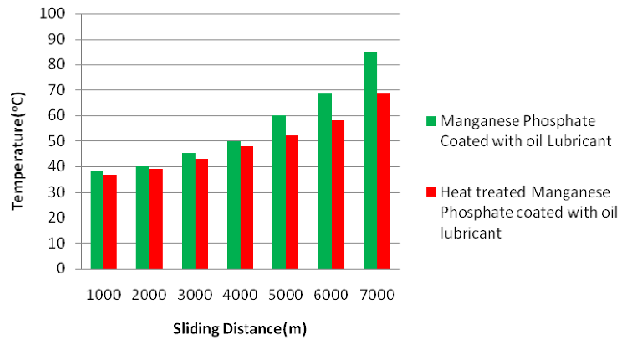


**Fig. 7.** Temperature vs Sliding distance at 40 N Load.

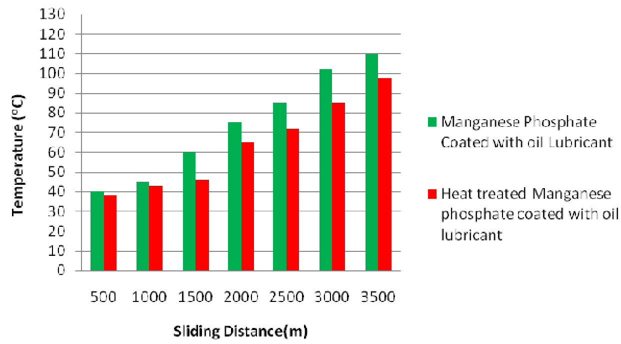


**Fig. 8.** Temperature vs Sliding distance at 100 N Load.

### 3.4 Examination of worn surface

The SEM Images reveal differences in the wear behaviour of the Manganese phosphate coated pins with oil lubricant and Heat treated Manganese phosphate coated pins with oil lubricant on a microscopic scale, under100 N. The best results were found for the Heat treated Manganese phosphate coatings with oil lubricant. It was proved by means of SEM images that the coating itself remain almost unaffected, whereas Manganese Phosphate coating with oil lubricant showed few cracks. It proves that good resistance against sliding wear may be achieved only by an improved oil retaining capacity of manganese phosphate coating. The worn surface of the test pin was examined under Scanning Electron Microscope (SEM) for mode of damage and nature of distortion at the surface. Figure 9 shows the SEM images of the Manganese phosphate coated pins with oil lubricant after 900 sec running at speed 3 m/s under the load 100 N.

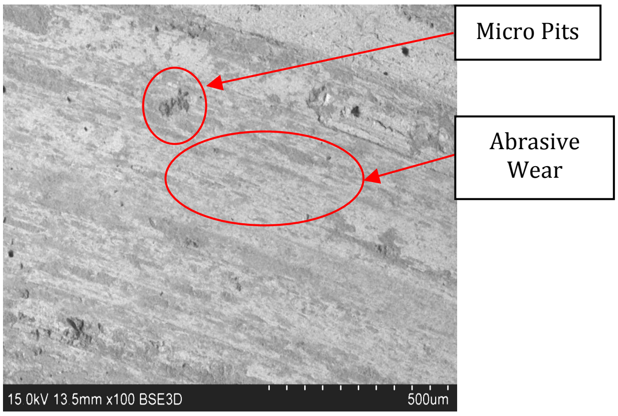


**Fig. 9.** SEM micrograph of Manganese Phosphate coated pin with oil lubricant after wear test under 100 N load.

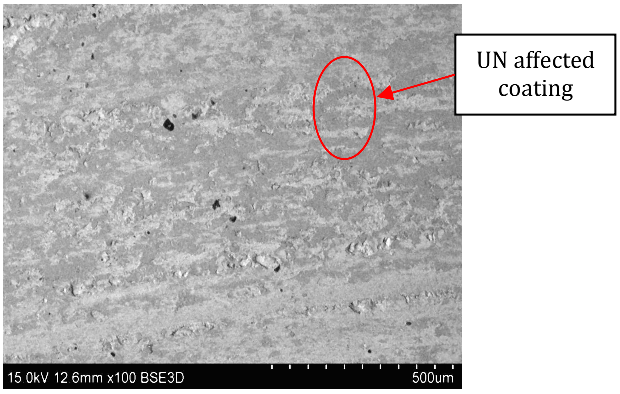


**Fig. 10.** SEM micrograph of Heat treated Manganese Phosphate coated pin with oil lubricant after wear test under 100 N load.

Figure 10 shows SEM image of Heat treated Manganese phosphate coated pins with oil lubricant with fine surface finish and negligible pits. Heat treated Manganese Phosphate Coating was beneficial when used on pins sliding under oil lubrication. The heat treatment helps to release the internal stresswhich were formed during machining and eliminates hydrogen embrittlement. Under these conditions the density and widening of micro cracks increases with temperature. Manganese Phosphate coating behaves like a solid lubricant. It improves wear resistance by providing greasy lubrication. The micro cracks, due to dehydration generate traps and increase the reactive surface. The heat treatment may increase the quantity of oil retained through the micro cracking phenomenon which increases oil retention. Chao-Min Wang et al. [23] investigated that phosphate compound that coated above the steel substrate remained amorphous after heat treatment at 500 °C for a period up to 60 min. The thermal decomposition of the anhydrous phosphate compound occurred at a higher temperature, forming $Mn_3(PO_4)_2$. Oil can react at the grain boundaries of the Heat treated coating to form a beneficial adherent film, increasing the wear resistance under oil lubricating conditions. P.H. Hivart et al. [17] also expressed that the dehydrated and transformed new coating surface has a better reactivity towards lubrication than the initial Huralite.

## 4. CONCLUSIONS

The characteristics of Manganese phosphate coated pins with oil lubricant and Heat treated Manganese phosphate coated pins with oil lubricant were examined under 40 N and 100 N loads using pin on disk apparatus and the results are summarized as follows:

- Initially Manganese phosphate coated pins with oil lubricant and Heat treated Manganese phosphate coated pins with oil lubricant revealed almost the same coefficient of friction around 0.1.
- Heat treated Manganese phosphate coated pins with oil lubricant showed low coefficient of friction and less wear volume as compared to pins coated only with Manganese Phosphate coated pin with oil lubricant.
- Heat treated Manganese phosphate coated pin with oil lubricant maintained coefficient of friction around 0.1 up to sliding distance 3000 m under 100 N load, but only Manganese Phosphate coated pin with oil lubricant shows same coefficient of friction under the same load up to a sliding distance of 1050 m only. Heat treatment helps to retain the oil lubricant for longer time.
- The Wear volume of Heat treated Manganese Phosphate coated pins with oil lubricant is lesser than the Manganese Phosphate coated pins with oil lubricant,

that are 3.1 $mm^3$ ,9 $mm^3$ under 100 N load, with sliding distance 3500 m respectively.

- The temperature rise was high for Manganese Phosphate coated pins. It was low for Heat treated manganese phosphate with oil lubricant, because of lesser friction coefficient and good load carrying capacity.

## Industrial summary

The reasons to coat components in a production situation are to increase tool life, improve the surface quality of the product and increase the production rate. The advantages of Manganese Phosphate coating include high corrosion resistance, oil retaining capacity, hardness, excellent lubricity, high chemical stability and resistance to wear. The substrate metal like high carbon and high chromium steel possesses good abrasion and wear resistance in corrosion environments. .In addition to that Manganese Phosphate coating with oil lubricant reduces the coefficient of friction considerably and improves life and surface quality of the product at lesser cost. A major limitation that needs to be addressed in the research and development of manganese phosphate coating process is that it is applicable only for low load conditions. Heat process increases micro cracks due to dehydration generate traps and increase the reactive surface. This treatment may increase quantity of oil retained. The micro cracking phenomenon increases oil retention. Hence Heat treated Manganese Phosphate coating with oil lubricant may with standard higher load conditions.

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