ผลของสารยับยั้งการกัดกร่อนในสารหล่อลื่นสำหรับอุตสาหกรรมอิเล็กทรอนิกส์

นางสาวณัฐกฤตา ไหมพูล

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECT OF CORROSION INHIBITORS IN LUBRICANT FOR ELECTRONIC INDUSTRY

Miss Natclitta Maipul

จุฬาลงกรณ์มหาวิทยาลัย
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A Thesis Submitted in Partial Fulfillment of the Requirements
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ณัฐกฤตา ไหมพูล : ผลของสารยับยั้งการกัดกร่อนในสารหล่อลื่นสำหรับอุตสาหกรรมอิเล็กทรอนิกส์ (EFFECT OF CORROSION INHIBITORS IN LUBRICANT FOR ELECTRONIC INDUSTRY) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.สุคคเณศ ตุงคะสมิต, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.ดวงกมล ตุงคะสมิต, 54 หน้า.

พอลิเมอร์และเอสเทอร์ของกรดไขมันของ พอลิหนึ่งบิวทีนไพโรลิโดน และ โพรพิลีนไกลคอล โมโนสเตียเรท ที่มีคุณสมบัติเหมาะสมได้รับการตรวจสอบและถูกใช้เป็นสารยับยั้งการกัดกร่อนสำหรับการป้องกันการหลุดออกของวัสดุที่อยู่ในหัวอ่าน-เขียน ระหว่างกระบวนการขัด ในการผลิตฮาร์ดดิสไดร์ฟ พฤติกรรมการกัดกร่อนของวัสดุแม่เหล็กไฟฟ้า (IrMn) ที่มีความอ่อนไหวต่อการถูกกัดกร่อนมากที่สุดในหัวอ่าน-เขียน ศึกษาด้วยวิธีโพเทนชิออไดนามิก โพลาไรเซชัน (potentiodynamic polarization) พบว่า อัตราการกัดกร่อนของสารหล่อลื่นที่ถูกปรับแต่งด้วย พอลิหนึ่งบิวทีนไพโรลิโดน และ โพรพิลีนไกลคอล โมโนสเตียเรท มีค่า 0.086 และ 0.084 อังสตรอมต่อนาที ตามลำดับ ขณะที่สารหล่อลื่นมาตรฐานมีอัตราการกัดกร่อน 0.111 อังสตรอมต่อนาที นอกจากนี้ได้ศึกษาการหลุดออกของอะตอม โดยใช้เทคนิคอินดักทีฟลี คัปเปิลพลาสมา แมสสเปคโทรสโกปี (ICP-MS) พบว่าสารหล่อลื่นที่ถูกปรับแต่งด้วย พอลิหนึ่งบิวทีนไพโรลิโดน และ โพรพิลีนไกลคอล โมโนสเตียเรท ส่งผลต่อการหลุดออกของโลหะเท่ากับ 3-7 ไมโครกรัมต่อลิตร ขณะที่สารหล่อลื่นมาตรฐานส่งผลต่อการหลุดออกของโลหะ เท่ากับ 4-15 ไมโครกรัมต่อลิตร จากผลการวิเคราะห์แสดงให้เห็นว่า สารยับยั้งการกัดกร่อนดังกล่าวช่วยลดอัตราการกัดกร่อนของวัสดุในหัวอ่าน-เขียนได้ดี เมื่อเทียบกับสารหล่อลื่นมาตรฐานชนิดไกลคอล นอกจากนี้ค่าสภาพนำไฟฟ้าและสมบัติความเป็นกรด-เบส ของสารหล่อลื่นที่ถูกดัดแปลงได้รับการตรวจสอบและวิเคราะห์ นอกจากนี้ทำการตรวจสอบการสร้างชั้นสาร (layer) บนผิวด้วยหมู่ฟังก์ชัน ที่ทำหน้าที่ปกป้องพื้นผิววัสดุ ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) พร้อมทั้งศึกษาพารามิเตอร์ที่แสดงสมรรถนะทางไฟฟ้า จากการทดสอบควอไซด์สแตติก (QST) และการทดสอบการขัด พบว่า สารยับยั้งการกัดกร่อนดังกล่าวช่วยให้กระบวนการขัดดีขึ้น ในกระบวนการผลิตจริง โดยไม่ส่งผลต่อคุณภาพและประสิทธิภาพของหัวอ่าน-เขียน ดังนั้นในงานวิจัยนี้ได้เสนอ โพรพิลีนไกลคอล โมโนสเตียเรท และ พอลิหนึ่งบิวทีนไพโรลิโดน เป็นสารทางเลือกลำดับที่ 1 และ 2 ตามลำดับ เพื่อเป็นสารเติมแต่งเพิ่มเติมในการป้องกันการกัดกร่อนของวัสดุอิริเดียมแมงกานีส ในกระบวนการผลิตหัวอ่าน-เขียน ในฮาร์ดดิสไดร์ฟ

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สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2560 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5772259123 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: CORROSION INHIBITOR / HARD DISK DRIVE (HDD) / LUBRICANTS / POLYMER FILM COATING

NATCLITTA MAIPUL: EFFECT OF CORROSION INHIBITORS IN LUBRICANT FOR ELECTRONIC INDUSTRY. ADVISOR: ASST. PROF. SUKKANESTE TUNGASMITA, Ph.D., CO-ADVISOR: DUANGAMOL TUNGASMITA, Ph.D., 54 pp.

The selected functional polymers and fatty esters of poly)1-butene pyrrolidone) (PP) and propylene glycol monostearate (PG) were investigated and applied to use as the corrosion inhibitors for protecting material removal during read/write head lapping processes in hard disk drive (HDD) production. Potentiodynamic polarization measurement was used to study their corrosion behaviors against antiferromagnetic materials (IrMn) which are the most sensitive materials in the head structure. Corrosion rate of PP- and PG-modified lubricants were 0.086 and 0.084 Å/min, respectively, while standard lubricant was 0.111 Å/min. Moreover, the leaching out of metallic atoms was investigated by using inductively couple plasma mass spectroscopy (ICP-MS). Leaching out of metallic atoms was in range 3-7 µg/L for PP- and PG-modified lubricant but, standard lubricant was 4-15 µg/L. The results showed that corrosion rate can be reduced compared to the standard glycol-based lubricant. The conductivity and acid-base properties of the modified lubricants were also measured and analyzed. Scanning electron microscopy (SEM) showed that the protection of those inhibitors came from the formation of protective thin layer over the surface by their functional groups. Furthermore, the electrical performance parameters from quasi static test (QST) and lapping test indicated a better lapping performance, without losing quality and electrical performance of the slider. We propose that PG and PP are the 1st and 2nd choice of additional additives in corrosion protection of IrMn material in HDD slider fabrication process.

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Co-Advisor's Signature ....

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LIST OF ABBREVIATIONS

Å	Angstrom unit
AlTiC	Aluminium titanium carbon
A/cm^2	Ampere/square centimeter
cm	centimeter
CMC	Critical micelle concentration
cP	Centipoise
E_{corr}	Corrosion potential
HDD	Hard disk drive
hr	Hour
i_{corr}	Corrosion current density
ICP-MS	Inductively coupled plasma mass spectroscopy
IrMn	Iridium manganese
kV	Kilovolt
M	Molar
mg KOH/g	Milligram Potassiumhydroxide/gram
min	Minute
mL	Milliliter
mm	Millimeter
mmol	Millimolar
MRR	Magneto resistive resistance
N	Neuton
nm	Nanometer
QST	Quasi static test
RF	Radio frequency
rpm	Round per minute
SEM	Scanning electron microscope
TBN	Total base number
THB	baht
V	Volt

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µL	Microliter
µg/L	Microgram/liter (ppb)
µs/cm	Microsiemens/centimeter
∆%MRR	Percent delta magneto resistive resistance
%wt	Percent by weight

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CHAPTER 1

INTRODUCTION

1.1 Background

In hard disk drive (HDD) fabrication industry, the capacities and level of qualities excellence have been developed continuously. The read-write head or slider is one of the most important parts in HDD that must be improved for higher capacity in storing data [1-2]. Lapping process is a process in production that can be used to obtain a specific surface roughness and finishing of the part. It also reserved for products that demand very tight tolerances of flatness, parallelism, and thickness. [3-5]. For modern higher capacity data storage, very high precision lapping during the fabrication processes is required due to the complexity of the slider nanostructure. In final lapping process, the ethylene glycol based lubricant is normally used to control the properties of the slider surface and enhancing efficiency of the lapping process. They reduce friction and heating during the process. The lapping lubricant consists of several additives such as surfactant, viscosity index improver, antistatic agent and corrosion inhibitors. The chemical reactions from these additives are the major cause of some sensitive materials removal on the slider surface by chemical corrosion. There are several material layers in the slider for encouraging reading and writing data in HDD, but the interested material in this research is IrMn. It is the new material that was detected as a sensitive material that easy to corrode. Therefore, efficiency and life time of read-write heads in the HDD were decreased [6].

This research focuses on the additives in the lapping lubricant as corrosion inhibitor that protect material atoms (especially metallic atoms) in the HDD reader components which were removed due to corrosion in slider lapping process. The performance of corrosion inhibitor strongly depends on the ability to get adsorbed on the sensitive material surface. It was found that some polymer-based corrosion inhibitor can protect the material surface by the function of their functional groups that interact with surface atoms. This group of polymer has been used throughout the industrialized world as corrosion inhibitor for protecting corrosion of metal [7-9]. Poly(1-butene pyrrolidone) (PP), poly(4-vinylpyridine N-oxide) (PVO), polyoxyethylene (20) stearate (PO) and propylene glycol monostearate (PG) were applied as functional polymer- and fatty ester-based corrosion inhibitors for this purpose. Because they represented as the corrosion inhibitors which can form protective layer by functional groups for protective corrosion. They are also friendly to environment, no toxic, not expensive and not easily biodegradable in metal [9]. They have been widely used as emulsifier, dispersant and surface cleaner [10]. Moreover, they can use as corrosion inhibitions for mild steel and several metals [11-17]. Therefore, these inhibitors were carefully studied for an extra additive in the glycol-based lapping standard lubricant to protect corrosion occurrence on some sensitive materials in HDD slider during lapping process.

The corrosion behaviors and lapping performance of all inhibitor modified lubricants were characterized and investigated to optimize the modified lubricant for highest corrosion protection, and improve any impact on sliders in lapping process.

1.2 Literature review

In 2009, Saviour studied the corrosion inhibition of mile steel by polyvinylpyrrolidone (PVP) and polyethyleneimine (PEI) as inhibitors. These polymers function as corrosion inhibitor due to their ability to form complexes through their functional groups with metal ions which occupy large area. Polarization measurements showed that both PVP and PEI are effective for the inhibition of mild steel in acid media. PVP was also found to function as an inhibitor by blocking the active sites on the cathodic and anodic regions [11].

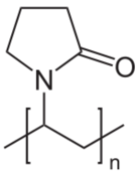

Figure 1.1 The molecular formula of polyvinyl pyrrolidone (PVP) $(C_6H_9NO)_n$ [11]

In 2012, Al Juhaiman et al. studied the prevention of carbon steel (CS) in 0.1 M NaCl at pH 7 and pH 8 by using polyvinyl pyrrolidone (PVP) as polymer corrosion inhibitor. Their results suggested that PVP can form film coating on metal surface by functional group of oxygen. From the electrochemical results found that corrosion rate of carbon steel was decreased from 318 (mg/cm^2.hr) to 251 (mg/cm^2.hr) at pH 7 and 402 (mg/cm^2.hr) to 253 (mg/cm^2.hr) at pH 8 when compared to the metal which no adding corrosion inhibitor. These polymers have also been reported as effective corrosion inhibitors because of their high molecular weight. Moreover, they have large repeating units of polymer that may cover more area on the target surface and form polymer complex, which lead to anticorrosion property [12].

In 2012, El Ayyoubi et al. studied the using of Poly (4-vinylpyrridine-g-polyethylene-oxide) as corrosion inhibitor for protecting iron in 1 M NaCl. They found this corrosion inhibitor can protect metal by adsorption of nitrogen and oxygen functional groups on metal surface. From electrochemical results, the solution which added corrosion inhibitor gave the corrosion rate 0 (mg.cm^2/h) while solution which no added corrosion inhibitor gave 0.405 (mg.cm^2/h). Increasing of corrosion inhibitor's concentration also affect more efficiency of corrosion prevention [13].

In 2015, Moses and saviour studied the corrosion inhibition effect of polypropylene glycol (PPG) with and without the additional iodide ions at mild steel in 0.5M H_2SO_4 solution. The results showed the efficiency of PPG as corrosion inhibitor for protecting mild steel in acid environment. PPG can absorb on mild steel surface by physisorption and chemisorption as PPG combined to iodide ions. Potentiodynamic polarization results also showed that PPG behaved as mixed type inhibitor but under anodic control when combined with iodide ions [14].

In 2015, Karthikaiselvi and Subhashini reported corrosion prevention results of polymethylaniline and polyvinylpyrrolidone copolymer at carbon steel in 1 M HCl solution. Each corrosion inhibitor can protect corrosion of metal but polymethylaniline not dissolve in water. Polyvinylpyrrolidone was added for help dissolving in water of polymethylaniline. The results showed corrosion rate more decreased when concentration of corrosion inhibitor were increased. They can protect metal by film formation of functional groups of these polymers [15].

In 2015, Shunli et al. developed superhydrophobic coating for aluminium metal in acid-based solution by using myristic acid or tetradecyltetradecanoate as corrosion inhibitor. From the results found that this corrosion inhibitor is a versatile inhibitor such

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as help to protect corrosion, self-cleaning, anti-icing and separate oil and water. Superhydrophobic value was 155.2±0.5° [16].

In 2015, Dinodi and Nityananda investigated efficiency of stearate, palmitate and myristate (long chain carboxylate) as corrosion inhibitors in 0.1 M Na_2SO_4 and NaCl solution by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). From the results found that they can protect corrosion of magnesium alloy (ZE41) by adsorption of its functional groups on metal surface [17].

1.3 Objective

Investigated and studied the corrosion prevention in read-write head by using polymer as corrosion inhibitors for lapping process in hard disk drive production.

1.4 Scopes of work

1.4.1 Formulate modified lubricants and test their properties.

1.4.2 Characterize the modified lubricants using:

- Potentiodynamic polarization measurement to investigate corrosion rate.
- ICP-MS to study leaching out trend of metal with times.
- SEM to investigate morphology and propose mechanism.
- Fluorescence spectroscopy to determine CMC for proposed mechanism.
- Lapping test and QST to check the actual work of modified lubricants in lapping process.

1.4.3 Select the best corrosion inhibitor from properties and performance results.

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CHAPTER 2

THEORY

2.1 Slider lapping process

2.1.1 Slider head

The HDD sliders were obtained from a chip fabricated wafer, as shown in Figure 2.1. Each wafer contains about 50,000 individual sliders. Each slider/head consists of varieties of materials such as Al_2O_3-TiC (AlTiC) as slider substrate, nickel-iron (NiFe) for magnetic shield layer, cobalt-iron (CoFe) for the writer layer, Iridium manganese (IrMn) layer as antiferromagnetic for arrangement of magnetic direction field, etc.

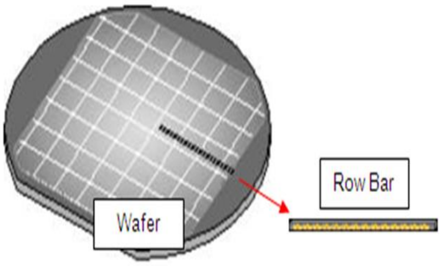

Figure 2.1 Wafer plate [18-19]

2.1.2 Lapping Process

Figure 2.2 illustrated the actions on the slider during lapping process. This lapping process is another important part in a slider fabrication process. It consists of five steps are wafer loading, grinding, rough lapping, final lapping, and cleaning. In this work, the final lapping process was focusing. This process is provided a very smooth surface. The slider that passed through the lapping process should have dimension, surface roughness, surface topography, as well as magnetic property that match the design criteria and can be assembled to make products as shown in Figure 2.3. There are many process parameters involved in the finishing quality of this process. It is very important and necessary to measure and control those parameters that affect lapping process, especially the lubricant, which plays the most important role in the process.

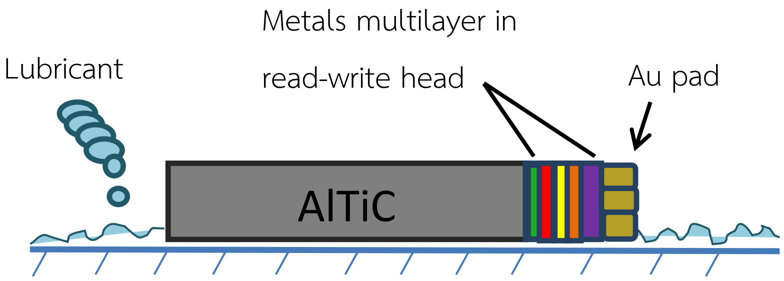

Figure 2.2 Simulation lapping process of read-write head

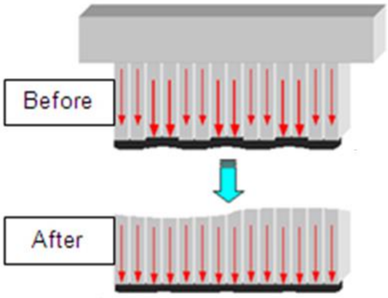

Figure 2.3 Surface topography of slider between before and after lapping process [19]

2.2 Lubricants

Lubricant can be referred to the materials (any forms) used for the purpose of diminishing friction and wear to help tools and machines work effectively by minimizing the contact area between the surfaces of materials [6]. Some lubricants can form surface coating layer, which help to prevent reactions with oxygen. They can also have chemical ingredients that suppress reactions of reactive substances before reacting with the material surfaces. There are several types with various grades according to the viscosity. The ideal properties of lubricant are as follow:

- Provide lubrication or reduce friction as much as possible.
- Provide good cooling.
- No oxidation.
- The viscosity does not change at high temperatures.
- High flash point.
- Lowest temperature of flow stops.

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In this work, the lubricant consisted of ethylene glycol as based lubricant (90%) and approximately 10% of additives.

2.2.1 Ethylene glycol

Ethylene glycols (EG) based lubricant does not only help in controlling of lapping process and prevent material from over polished, but it also helps increasing the material removal rate by corrosion which make surface soften and easier to be polished by mechanical lapping. From the literatures, it was reported that pure ethylene glycol gave the most corrosive properties and reduced when additives are added [6].

2.2.2 Additive

Additives are chemical compounds added to EG-based lubricant to enhance its properties and performance. The functional additives, such as anti-wear additive, viscosity index improver, surfactant, dispersant, detergent and corrosion inhibitor were added in EG based-lubricant [6].

2.3 Corrosion in materials

Corrosion occurs from the destructive attack of metals or materials by chemical or electrochemical reaction with the environment. Metals which are damaged from chemical and physical corrosion are called corrosion-erosion, corrosive wear or fretting corrosion. Principles of corrosion are that metal produces electrons and hydrogen ions receive electrons showed in Figure 2.4 which was described in type of corrosion reaction part [20].

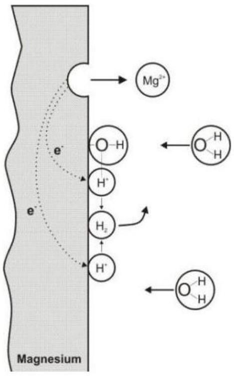

Figure 2.4 Corrosion diagram [21]

Corrosion is a redox reaction (equation 2.3). The two reactions of redox are oxidation for anode and reduction for cathode that are showed in equation 2.1 and 2.2, respectively.

$$Mg \longrightarrow Mg^{2+} + 2e^- \qquad (2.1)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (2.2)$$

$$Mg + 2H^+ \longrightarrow M^{g2+} + H_2 \text{ (gas)} \qquad (2.3)$$

2.3.1 Corrosion reaction

The corrosion reaction consists of main 2 reactions [22].

2.3.1.1 Anodic reaction

Anodic reaction occurs in an electrochemical cell at the anode. Positive electron is flowed off of the anode in electrolyte solution (oxidation) and then received by cathode. Anodic reaction can cause the corrosion occurrence. For example in equation 2.4, metallic iron can produce ferrous ions by the anodic reaction [22].

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad (2.4)$$

Moreover, in a solution with higher pH, the anodic reaction produces a surface film of ferric oxide according to reaction as showed in equation 2.5 [23].

$$2Fe + 3H_2O \longrightarrow Fe_2O_3 + 6H^+ + 6e^- \qquad (2.5)$$

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2.3.1.2 Cathodic reaction

In corrosion processes the most common cathodic reaction is the electrochemical reduction of dissolved oxygen. Hydrogen atom is reduced to their atoms and formed hydrogen gas when these ions react with electrons in the cathode according to the equation 2.6 and 2.7. Cathodic reaction also can cause the corrosion occurrence [22].

$$2H^{+} + 2e^{-} \longrightarrow H_2 \qquad (2.6)$$

$$Fe^{2+} + 2H^{+} \longrightarrow Fe^{2+} + H_2 \qquad (2.7)$$

2.3.2 Types of corrosion inhibitors

Corrosion inhibitor is the functional additive which added to a medium solution for protecting corrosion of metal or materials. Types of corrosion inhibitor can be divided from their mechanism, or chemical nature. In this work, we have investigated the performance of corrosion inhibitor as polymer and fatty ester inhibitors by studying their functional groups mechanism [24].

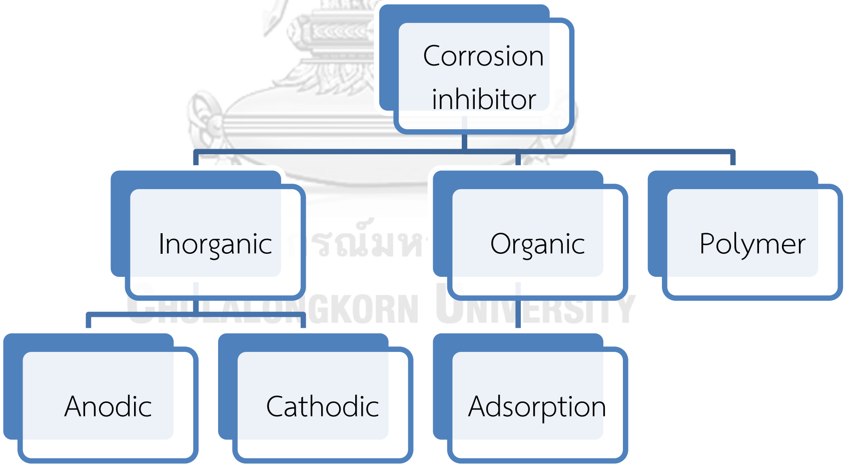

Figure 2.5 Types of corrosion inhibitor [24]

Table 2.1 Example of corrosion inhibitors [24]

Mode of action	Examples	
Adsorption	Amines	RNH_2
	Thiourea	NH_2CSNH_2
	Benzoate	$C_6H_5COO^-$
Passivating	Nitrite	NO_2^-
	Chromate	CrO_4^{2-}
	Calcium plumbate	Ca_2PBO_4
Surface layer	Phosphate	$H_2PO_4^-$
	Silicate	$H_2SiO_4^{2-}$
	Hydroxide	OH^-

2.3.2.1 Anodic inhibitor

Anodic inhibitor is a substance that can form a protective film on the specimen surface by decreasing anodic reaction and encouraging the normal reaction of metal surface passivation such as chromate, nitrate, tungstate and molybdate [24].

2.3.2.2 Cathodic inhibitor

Cathodic inhibitor can protect corrosion in 2 ways. These are slowing the cathodic reaction or precipitating on cathodic areas in order to increase the impedance of the surface and also confine the distribution of reducible species to the surface. Examples of cathodic inhibitor such as polyphosphates, phosphonates, Zn ion, etc [24].

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2.3.2.3 Organic inhibitor

Organic inhibitor can be used to prevent the corrosion by an adsorption mechanism. It can form a thin film that covers and blocks the surface from the corrosion environment, or by retarding the electrochemical processes. The mechanism of organic inhibitor is shown in Figure 2.6. These compounds adsorb and form a covalent bond on the metal surface and cover the entire surface area of the corroding metal with a thick film by the adsorption of positively or negatively charged soluble organic compounds. Examples of organic inhibitor are, thiourea and amino and its derivatives, propargyl alcohol, phosphates, etc [25].

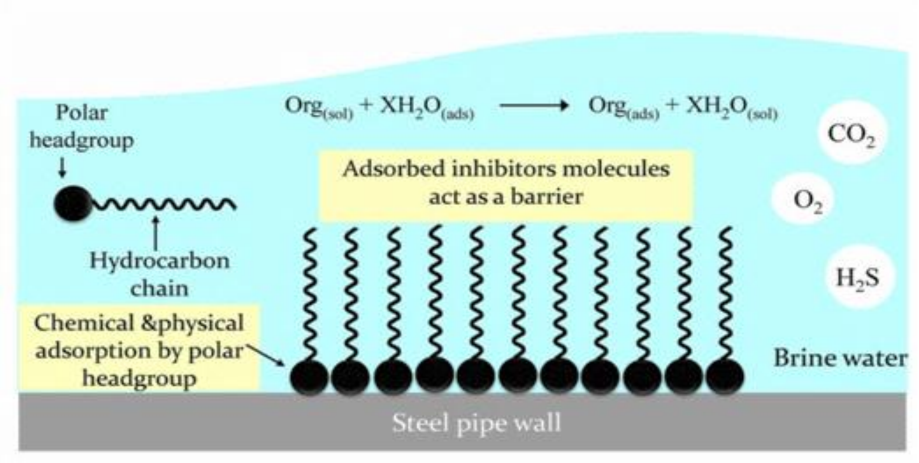

Figure 2.6 Mechanism of organic inhibitor [26].

Moreover, there are several researches used organic corrosion inhibitors for preventing corrosion of metal as shown in Table 2.2.

Table 2.2 Example of organic inhibitors [25]

Alloy	Environmental	pH	Inhibitor	Concentration	Efficiency
Aluminium	3% NaCl	6.3	Laurusnobilis L. oil	50 ppm	89.9
Cu-10Al-5Ni Alloy	3.5% NaCl	-	N-acetylcysteine	6mM/L	87.6
Copper	0.5M HCl	-	Chitosan	8 chitosan	92.0
Copper	1M HCl	-	Cysteine	18 mM	84.13

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2.3.2.4 Polymers as corrosion inhibitors

Polymers have been reported in several researches that they can be used as corrosion inhibitor for protecting metal through their functional groups. They can create complexes with metal ions to form a thin layer, coating on surface. This thin layer depends on the functional group, nature of metal surface and number of adsorption active center in the molecule, as shown in Figure 2.7. The advantages of using polymers as corrosion inhibitor are environmental friendly, non-toxic, less expensive and slow degradable, which allow for their long time storage [27].

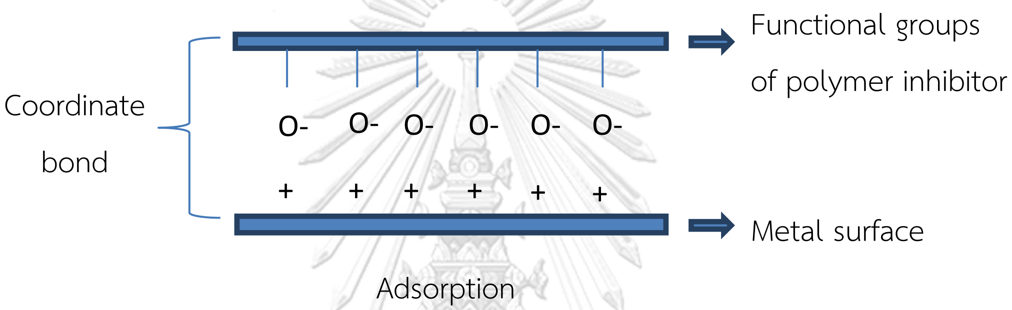

Figure 2.7 Adsorption mechanism of polymer corrosion inhibitor [28]

2.4 Characterization of modified lubricants

2.4.1 Potentiodynamic polarization

Polarization measurement is used to investigate the corrosion behavior of metal and its environment using kinetic principles. Potentiodynamic polarization curves can be obtained from this measurement. Generally, the corrosion of metal is an electrochemical process. The dissolution of metal in the environment can be represented by the electrochemical reaction. From the potentiodynamic polarization curves, several important parameters can be extracted. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) are estimated by the method of logarithm-polarization of tafel extrapolation as seen in Figure 2.8. The results will be plotted on a logarithm scale. At the intercept of tafel slope, Y is log i_{corr} and X is E_{corr}. Corrosion rate (CR) can be determined from equation 2.8 [29].

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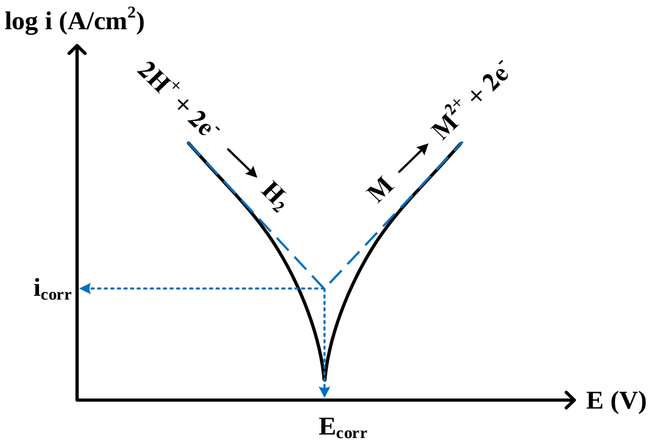

Figure 2.8 Potentiodynamic polarization curve including tafel slope, corrosion potential and corrosion current density [29]

$$CR = \frac{0.13 \times i_{corr} \times EW}{p} \tag{2.8}$$

When, CR = Corrosion rate (mm/year)

i_{corr} = Current density (A/cm^2)

EW of IrMn = equivalent weight of metal = 3.123×10^{-4}

p of IrMn = density of metal (g/cm^3) = 62.07 g/cm^3

2.4.2 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS is an analytical technique to determine the multiple elements in same sample by inductively coupled plasma. A plasma source is scanned to atomic elements, ionizing of sample is achieved. Then, these ions are separated and quantified by mass spectrometer. The advantages of the ICP-MS technique are high resolution, lower detection limits of most elements, which are in ppb (parts per billion = μg/L) and ppt (parts per trillion = ng/L) [30-31].

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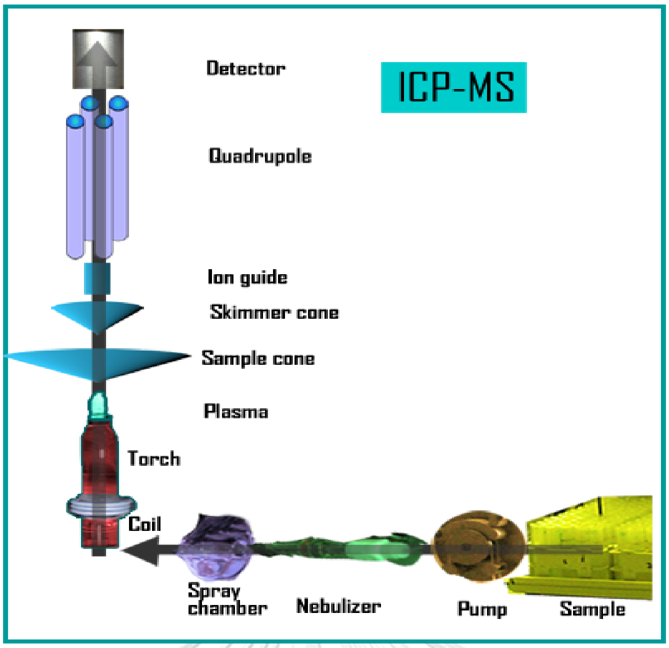

Figure 2.9 ICP-MS structure [30]

2.4.3 Scanning electron microscope (SEM)

In this work, scanning electron microscope was used to study the surface morphology of samples by using electron beams interactions with surface atoms to produce a surface topography. Electron beam generates different kinds of signals, such as secondary electrons, backscattered electrons, and characteristic X-ray, which is detected from detector. It is known that the high-performance instrument of SEM produces high resolution about 10-20 Å. As electron beam is scanned across the specimen, ionization occurrence will happen near the surface of sample [32].

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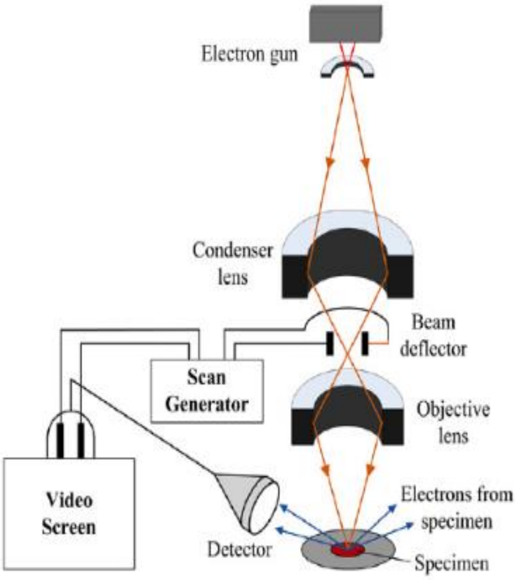

Figure 2.10 Schematic diagram of the SEM working principle [33]

2.4.4 Fluorescence spectrometry

Fluorescence spectrometry is a technique to investigate the unique qualities and concentration of a corrosion inhibitor in ethylene glycol solution by absorbing the UV radiation. That causes the molecule to be excited and vibrated within the molecule, from the ground state to excited state. This behavior is called exciting energy. The molecules that moving to high energy level, are not stable. The energy then releases and falls into the lower energy level. The energy of molecule is released from the first excited energy level to the ground state level, causing the emission of photons to form the fluorescence spectrum at specific energies of the substance as shown in Figure 2.11. The advantages of this measurement are fast, simple and inexpensive. Wavelengths of beam are varying between 180 to 800 nm through a sample cuvette [34].

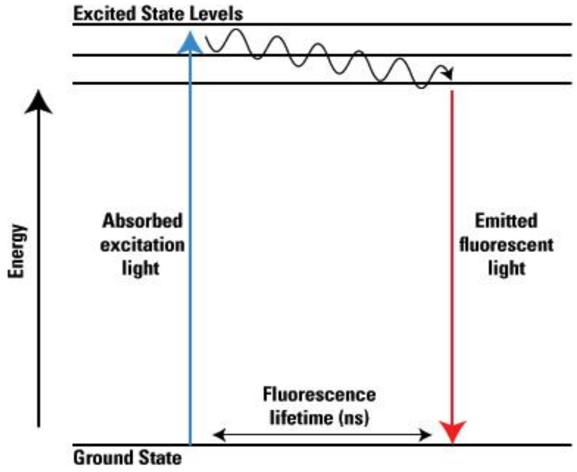

Figure 2.11 Ground state Vs excited state of an atom from fluorescence principle [35]

2.4.4.1 Critical micelle concentration (CMC)

Micelle is a structure of surfactant molecule that consists of hydrophobic and hydrophilic parts. Hydrophilic is the head region that contact with aqueous solution and hydrophobic is the tail region in the micelle center which is non-polar molecule as shown in Figure 2.12. Critical micelle concentration is defined as the concentration of surfactant which begins to form the micelle. Some surfactant or polymer can arrange as micelle by theirs ion molecules [36].

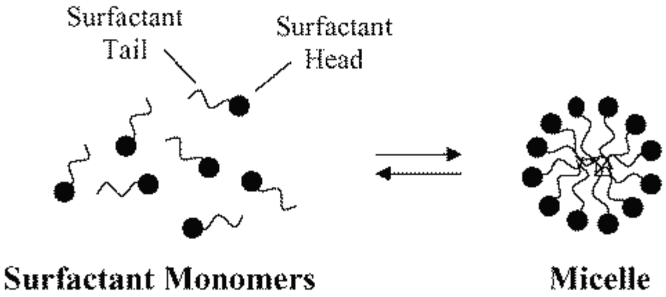

Figure 2.12 Micelle forming models for a spherical micelle of sodium dodecyl sulfate [37]

2.4.4.2 CMC determination

Fluorescence spectrometry has been used widely to determine the cmc value. In general, pyrene is used as fluorescent probes because it is sensitive to the polarity of aqueous solution [25]. The pyrene spectrum exhibits the intensity ratio of the first at 373 nm and third at 383 nm vibronic peaks. The intensity ratio of the first and third peaks is very sensitive to the environment. The I1/I3 can be used as a sensitive indicator of the polarity of the pyrene [38-39]. Figure 2.13 describes how CMC value can be extracted. At the initial measurement, the micelle has not yet formed due to low concentration of corrosion inhibitor. As the concentration is increased, micelle then can be formed. Thus, the point between below and above break point is the concentration of sample that start to form micelle [39].

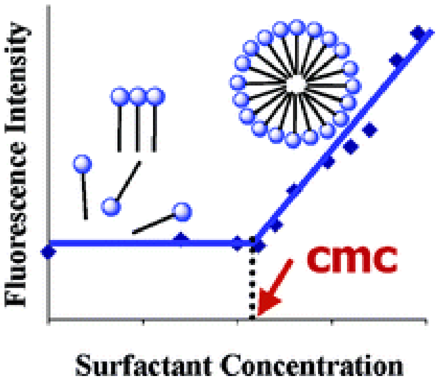

Figure 2.13 Graph over the relationship between surfactant concentration and fluorescence intensity [39].

The CMC calculation can be calculated in %wt of corrosion inhibitor following equation 2.9 [39].

$$C = \frac{10\ dx}{m} \qquad (2.9)$$

When, c = concentration (M) was obtained from CMC measurement.

d = density of EG (1.11 g/cm^3)

x = %wt of corrosion inhibitor

m = MW of corrosion inhibitor

2.4.5 Lubricant performance test in actual production

2.4.5.1 Final lapping test

The lapping machine polishes slider with the lubricant until it reaches design criterion. Then lap time was measured. The baseline lap time is approximately 2 minutes. The shorter the lap time, the better the productivity is. Therefore, it is important to optimize the processing conditions to minimize the lap time [6].

2.4.5.2 Quasi-static test (QST)

QST is a measurement to analyze the electrical performance of MR reader in a slider. The key parameter that is monitored in the lapping process is MRR. MRR or Magneto resistive resistance is a measurement of resistance across the shield of the MR element. The data is used to analyze the electrical performance of the reader. Low MRR values or low resistance across the shield of the MR element can be used to indicate some bridging or smearing of the shield causing high electrical conductivity. This parameter is used to screen out sliders with poor electrical performance from the lapping process [6].

2.4.5.3 Tribology

The science of tribology has been developed for understanding friction, wear and lubrication of the interaction between the surfaces in relative motion. If any material is being moved by any force, friction and wear will occur. Wear is the main problem of reducing the efficiency of equipment. Therefore, friction must be controlled by using lubricant for reducing wear occurrence. A normal force (F_N) is applied on a ball then wear is investigated from contacting of the ball with the surface, and the data was detected by sensor as seen in Figure 2.14. The data is converted by tribometer software to coefficient of friction (COF) [40]. COF can be calculated by using the following equation 2.10 [41].

$$F_z = \mu F_N \tag{2.10}$$

Where, F_z = measured tangential friction force (N)

F_N = applied normal force (N)

μ = coefficient of friction (COF)

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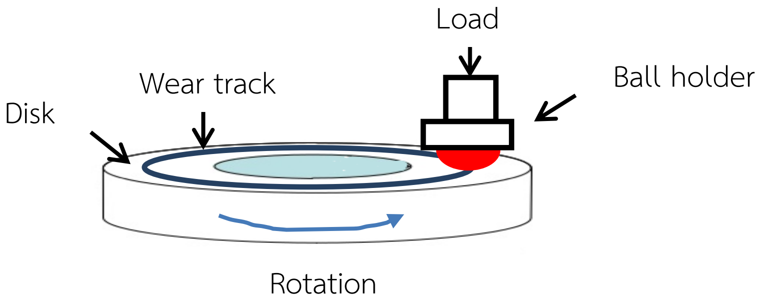

Figure 2.14 Schematic of the ball-on-disk wear tester.

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CHAPTER 3

EXPERIMENTS

3.1 Materials and chemicals

3.1.1 Materials

3.1.1.1 Slider bars (Western Digital (Thailand) Co., Ltd.)

3.1.1.2 IrMn coupon (Ir 21%, Mn 79%) (Western Digital Thailand Co., Ltd.)

3.1.2 Chemicals

3.1.2.1 Ethylene glycol (EG) (Innovative Organics Company)

3.1.2.2 Poly(1-butene pyrrolidone) (PP) (Ashland Inc.)

3.1.2.3 Propylene glycol monostearate (PG) (Chemipan Corporation)

3.1.2.4 Polyoxyethylene 20 stearate (PO) (Chemipan Corporation)

3.1.2.5 Poly(4-vinylpyridine N-oxide) (PVO) (Ashland Inc.)

3.1.2.6 Tetradecyltetradecanoate (Ashland Inc.)

3.1.2.7 Vinylpyrrolidone/3-dimethylaminopropyl-methacrylamide (Ashland Inc.)

3.1.2.8 Glacial acetic acid (Merck, 99%)

3.1.2.9 Perchloric acid (Merck, 70-72%)

3.1.2.10 Potassium hydrogen phthalate (Merck, 99%)

3.1.2.11 Chlorobenzene (Merck, synthesis grade)

3.1.2.12 Nitric acid (Merck, 65%)

3.1.2.13 Manganese standard for ICP (Aldrich)

3.1.2.14 Iridium atomic absorption standard solution (Aldrich, 1000 μg/mL in 10% wt HCl)

3.1.2.15 Pyrene (TCL, 99%)

3.1.2.16 Ethanol (Merck, analysis grade)

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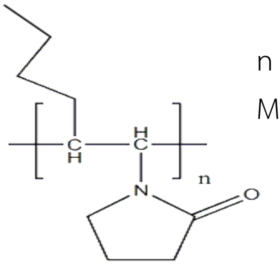
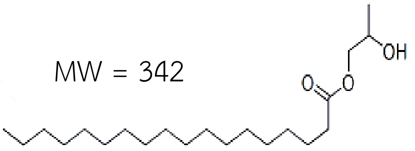
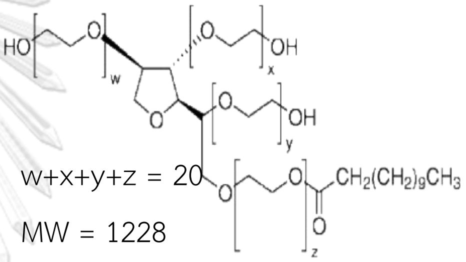
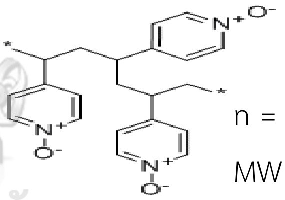
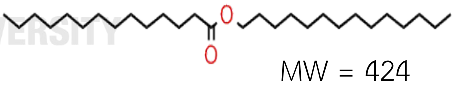
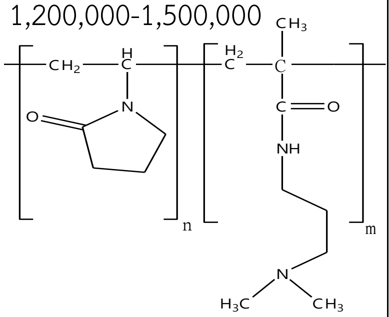
Table 3.1 Chemical structures of high potential selected 6 corrosion inhibitors

Corrosion inhibitors	Type	Structure
1. Poly(1-butene pyrrolidone) (PP)	Polymer	 n = 264 MW = 22000
2. Propylene glycol monostearate (PG)	Fatty ester	MW = 342 
3. Polyoxyethylene (20) stearate (PO)	Polymer	 w+x+y+z = 20 MW = 1228
4. Poly(4-vinylpyridine N-oxide) (PVO)	Fatty acid	 n = 546 MW = 200,000
5. Tetradecyl tetradecanoate (Myristic acid)	Copolymer	 MW = 424
6. Vinylpyrrolidone /3-dimethylaminopropyl methacrylamide (DMAPMA)	Polymer	MW = 1,200,000-1,500,000 

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3.2 Modification of lubricants

The modified lubricants were prepared by adding normal additives and each corrosion inhibitor as an extra additive into the standard glycol-based lubricant (SL) at 4 different concentrations. For each corrosion inhibitor, the concentration was added as 0.01, 0.03, 0.06 and 1.0 %wt of the standard glycol- based lubricant, shown in Table 3.2. These modified lubricants were then characterized and tested for their performance in the lapping processes, compared to standard lubricant (SL).

Table 3.2 Compositions of modified lubricants and standard glycol-based lubricant

Lubricants	EG (%wt)	Additives (%wt)	Corrosion inhibitors (%wt)	Mixed lubricants (%wt)
SL	93.118	6.882	0.00	100
PP-modified lube	93.108	6.882	0.01	100
	93.088	6.882	0.03	100
	93.058	6.882	0.06	100
	93.018	6.882	0.10	100
PG-modified lube	93.108	6.882	0.01	100
	93.088	6.882	0.03	100
	93.058	6.882	0.06	100
	93.018	6.882	0.10	100
PO-modified lube	93.108	6.882	0.01	100
	93.088	6.882	0.03	100
	93.058	6.882	0.06	100
	93.018	6.882	0.10	100
PVO-modified lube	93.108	6.882	0.01	100
	93.088	6.882	0.03	100
	93.058	6.882	0.06	100
	93.018	6.882	0.10	100

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3.3 Characterizations of modified lubricants

3.3.1 Fundamental properties of modified lubricants

3.3.1.1 pH and conductivity values

pH and conductivity values of all the modified lubricants were measured by using SevenExellence^{TM} Metter Toledo pH/conductivity meter. All concentrations of each inhibitor-modified lubricant were measured for both values to compare with SL.

3.3.1.2 Total base number (TBN)

TBN was measured by using auto titration T50 with LiCl in EtOH glass electrode, following the ASTM D2896. This measurement gives the information on basicity of lubricants, expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of lubricant sample (mg KOH/g). Normally, lubricants contain basic additives which are designed to react with and neutralize acids, preventing damage to engine parts, including corrosion of metallic surface. 1 g of each modified lubricant (for all concentrations) was dissolved in 40 mL of chlorobenzene and 20 mL acetic acid, and then titrated with standardized 1% perchloric acid in 99% glacial acetic acid. The obtained values were compared to SL.

3.3.1.3 Viscosity

Viscosity was measured by Anton Parr - Physica MCR 301 rheometer, in order to estimate how lubricant spread on lapping plate and how lubricant stay between work piece and lapping plate during lapping process. PP- and PG-modified lubricants at concentration of 0.06 %wt were investigated and compared to SL.

3.3.2 Corrosion studies

3.3.2.1 Potentiodynamic polarization measurement

Potentiodynamic polarization measurement were carried out using a potentiostat/galvanostat (EG&G Model 273) controlled by Nova-19 software. This measurement is aimed for studying the corrosion behaviors between the modified lubricants and the surface of IrMn metal, in order to select the optimized concentration of each corrosion inhibitor in comparison with the standard glycol-based lubricant. The potentiodynamic measurement was measured at 0.00122 step potential, 0.002 v/s scan rate and -1, 0.6 V potential range. The corrosion tests were performed with a standard three electrode cell. Ag/AgCl electrode, platinum sheet and IrMn coupon were used as reference, counter and working electrodes, respectively as shown in Figure 3.1. The measurements were done by using the modified lubricants as electrolyte. Before each experiment, IrMn coupon was immersed in test solutions for 15 min in order to reach steady state and all the experiments were repeated three times. All concentrations of each modified lubricant were determined and compared to SL.

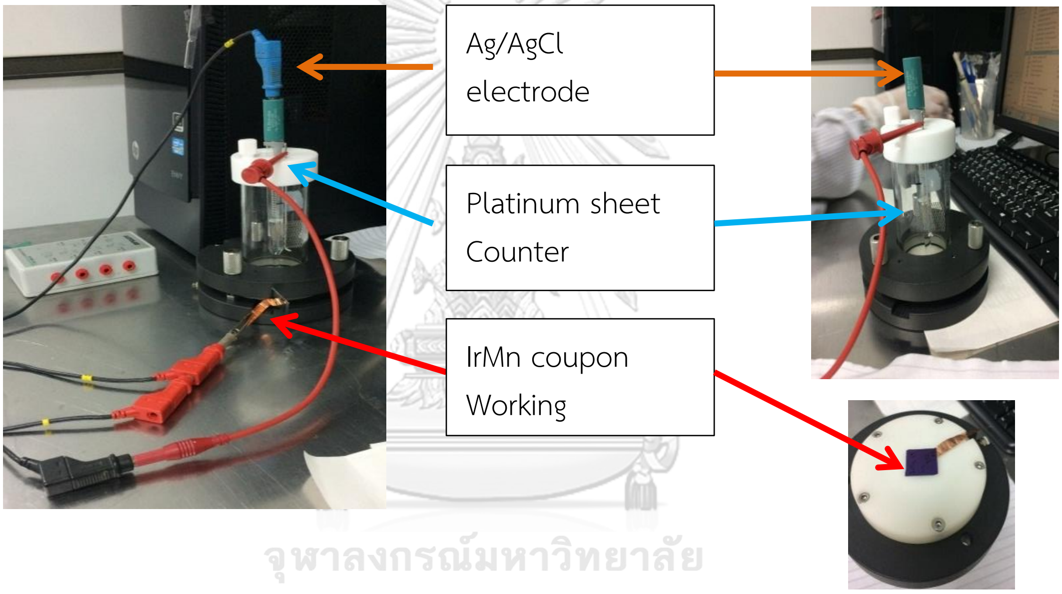

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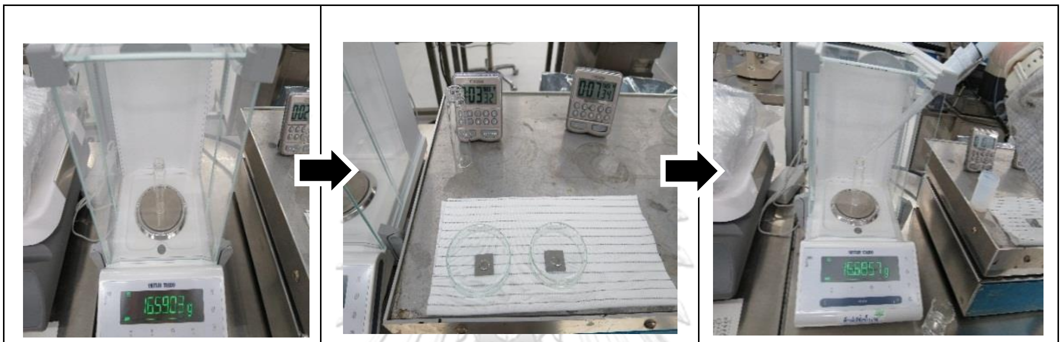
Figure 3.1 Equipment setup of polarization test

3.3.2.2 Leaching out of metal measurement

To verify and measure the time-dependent leaching out of each metal, inductively coupled plasma-mass spectrometer (ICP-MS: Agilent model 7500 ce), was utilized. The collision/reaction cells were adopted for removing spectral interferences in ICP-MS. The operating condition was at ICP RF power of 1500 W, with an ultrapure grade carrier (argon, 99.99% pure) flow rate 0.9 L/min, and a nebulizer pump speed of 0.1 rps.

For calibration of the instrument, solutions of single element ICP-MS standard iridium and manganese used as internal standard ranging from 5-300 µg/L are 0.5, 1, 5, 10, 50, 100 and 300 µg/L, respectively. They were prepared by using 1% HNO_3. All standard solutions were fresh prepared before the ICP-MS analysis by diluting the stock solution in 5% v/v HNO_3. For sample preparation, the modified lubricants were dropped on IrMn coupon for 100 µL then pipette 70 µL back to vial and top up with 1% HNO_3 acid 5 mL, as illustrated in Figure 3.2



Weight vial (Blank)

Drop PP- and PG-modified lubricants 100 µL

Pipette sample 70 µL back to vial + top up with 1% HNO_3 5 mL

Figure 3.2 Preparation of samples for ICP-MS measurement

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3.3.3 Protective thin layer formation

3.3.3.1 Scanning electron microscopy (SEM)

In order to investigate the morphology and mechanism of corrosion inhibitors, a scanning electron microscope (Jeol JSM 6400), operated at an accelerating voltage of 5.0 kV was utilized. The IrMn specimens of 1x1 cm were immersed in PP modified lubricant compared to PG-modified lubricant at concentration 0.06 %wt for 1 hr.

3.3.3.2 Fluorescence spectroscopy

For confirming the protection mechanism of corrosion inhibitors, critical micelle concentration (CMC) was determined by fluorescence spectrometer measurement. The dye which used as fluorescence probe was pyrene. Pyrene solution $5\text{x}10^{-5}$ M was prepared by dissolving in ethanol. In the measurement, pyrene excitation wavelength was 337 nm and emission wavelength was 375 and 392 nm, which coincided to the first (I_1) and third (I_3) vibration peak [37]. The excitation and emission slit widths were set at 5 nm. For preparing the stock solution of samples, pure PP- and PG-corrosion inhibitors were diluted with EG solution at different concentrations. To prepare mixing samples for fluorescence measurement, stock solutions of samples were added into EG solution and pipette to quartz cell. Figure 3.3 showed the preparation protocol of samples for this measurement.

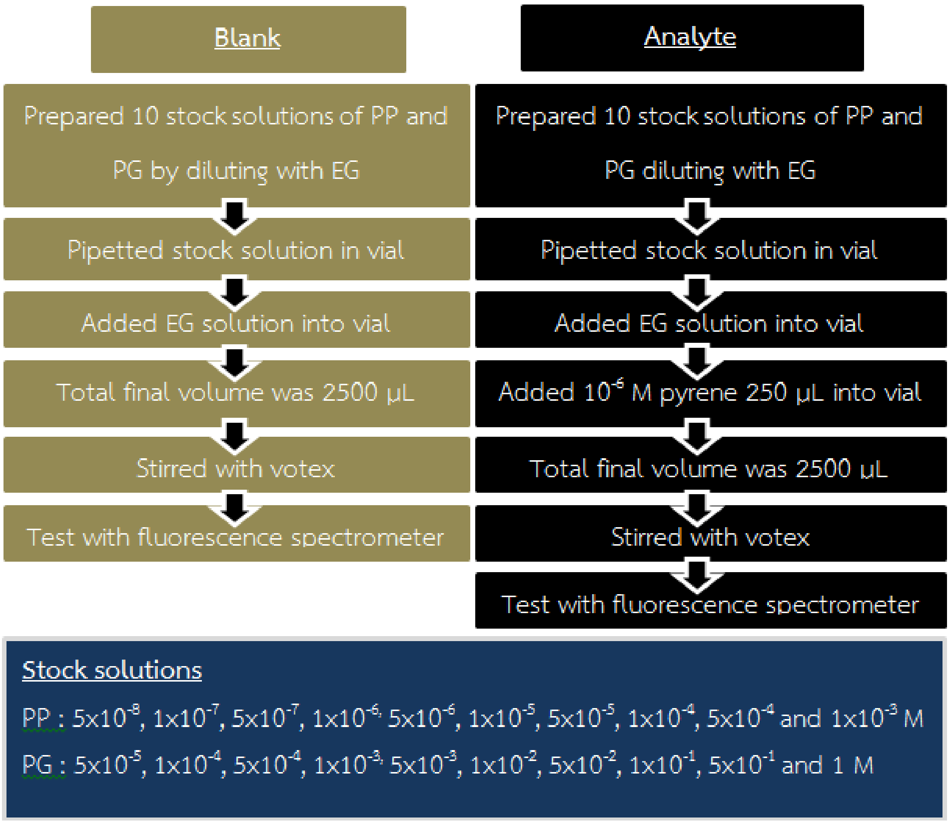

Figure 3.3 Diagram for preparing sample for CMC measurement

3.3.4 Lubricant performance test in actual production

3.3.4.1 Lapping test

Lapping time is the data that obtain from lubricant testing with actual machine in production line. PP- and PG-modified lubricants at 0.06 %wt were analyzed by final lapping ASL 200 machine, as shown in Figure 3.14. The slider lapping was setup to the rotational speed of plate at 10 rpm which attached with Sn-Bi lapping plate. This machine polishes slider until it reaches design criteria. Shorter lap time value is better the productivity. However, the quality of the surface finishing is also matters.

Figure 3.4 Final lapping machine ASL 200

3.3.4.2 Quasi static test (QST)

Quasi static test or QST is a tool to analyze the electrical performance of magnetic signal reader in slider. It is used as a guidance to screen out sliders with poor electrical performance of magnetic head. The Δ%MRR (magneto resistive resistance) can be obtained from this QST. The data were compared and calculated between before and after lapping process. These Δ%MRR values can be referred as corrosion occurrence and electrical stability of the sliders, incorporated with the surface finishing by modified lubricants. Basically, the Δ%MRR can be determined from equation 3.1. The analysis was done by using jmp 7.0.1 software package.

$$\Delta\%\text{MRR} = \frac{\text{MRR after lapping} - \text{MRR before lapping}}{\text{MRR before lapping}} \times 100 \qquad (3.1)$$

Figure 3.5 QST machine

3.3.4.3 Tribology

For study the effects of the modified lubricant to wear and friction between contacting of two surfaces would also be examined by tribometer UMT-2, CETR. AlTiC disk with a diameter of 76.23 mm were used as a rotating disk and AISI 304 stainless steel ball with a diameter of 6.35 mm were used as a sliding ball. Sliding velocity at 3600 mm/min and normal load force 0.5 N were performed for investigated coefficient of friction.

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Figure 3.6 Tribometer UMT-2, CETR [42]

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Fundamental properties of modified lubricants

From solubility test in EG of all selected inhibitors, the results showed that tetradecylester and polyvinyl pyrrolidone dimethylacrylamide could not dissolve in EG based lubricant because of their large molecular size. There were 4 corrosion inhibitors that will be studied in this research. The fundamental properties of those modified lubricants were measured such as pH, TBN, conductivity and viscosity to compare with standard lubricant (SL).

4.1.1 Acid-base properties

4.1.1.1 pH values

The pH values of modified lubricants were closed to each other, which in range about 8.50 - 8.60 as shown in Table 4.1. Their pH values were slightly higher than SL, which around 8.40. The values of all modified lubricants were affected by basicity of some chemicals. Moreover, the total base number (TBN) measurement was carried as another test method to measure the acid-base value of the modified lubricants.

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Table 4.1 pH values of modified lubricants compared to SL

Concentrations of corrosion inhibitors	pH				
	SL	PP-modified lube	PG-modified lube	PO-modified lube	PVO-modified lube
0.00	8.40	-	-	-	-
0.01	-	8.57	8.56	8.58	8.64
0.03	-	8.55	8.55	8.62	8.62
0.06	-	8.56	8.55	8.52	8.56
0.10	-	8.56	8.54	8.49	8.57

4.1.1.2 Total based number values (TBN)

TBN of modified lubricants were measured and related to pH values. We found that the TBN values of all 4 modified lubricants were slightly increased when increased the concentration of corrosion inhibitor. The TBN value of SL was at 3.72 mg KOH/g which was less than all modified lubricants significantly, as shown in Table 4.2.

Acid-base properties can be described a trend of corrosion occurrence. More acidity of modified lubricants tends to provide high corrosion occurrence. From pH and TBN results, all modified lubricants tend to increase basicity, compared to SL. This can be due to the corrosion inhibitors may induce a little basicity from their chemical structures. The structures of PP, PG, PO and PVO have one position of double bond oxygen atoms that can be generated to O^- charge. Therefore adding corrosion inhibitor caused an increasing basicity, and affecting corrosion occurrence trend of all modified lubricants are decreased. These might help to extend the lifetime of the machine that use in production line and decrease acidity from other additives [6].

Table 4.2 Exhibit TBN values of modified lubricants compared to SL

Concentrations of corrosion inhibitors	TBN (mg KOH/g)				
	SL	PP-modified lube	PG-modified lube	PO-modified lube	PVO-modified lube
0.00	3.72	-	-	-	-
0.01	-	23.01	23.13	22.82	21.62
0.03	-	23.20	23.30	22.86	22.09
0.06	-	23.31	23.32	22.86	22.83
0.10	-	23.33	23.34	23.06	22.89

4.1.2 Conductivity

The conductivity value affects almost directly to the corrosion rate. It can be indicated a trend of corrosion. Corrosion occurrence has been trending upward if lubricant has high conductivity value. From Table 4.3, It showed that the conductivity values increased as the concentration of corrosion inhibitor was increased. PP- and PG-modified lubricants have conductivity values less than PO-, PVO-modified lubricants and SL. For PP, this is because the functional group of PP is hard to ionize. For PG, it has one OH group that can be ionized in lubricant. In contrast, PO and PVO tended to increase the conductivity and have also higher values than SL. This may be due to PO contained high OH groups that can be ionized to H^+ and affect the lubricant conductivity.

Table 4.3 Conductivity values of modified lubricants and SL

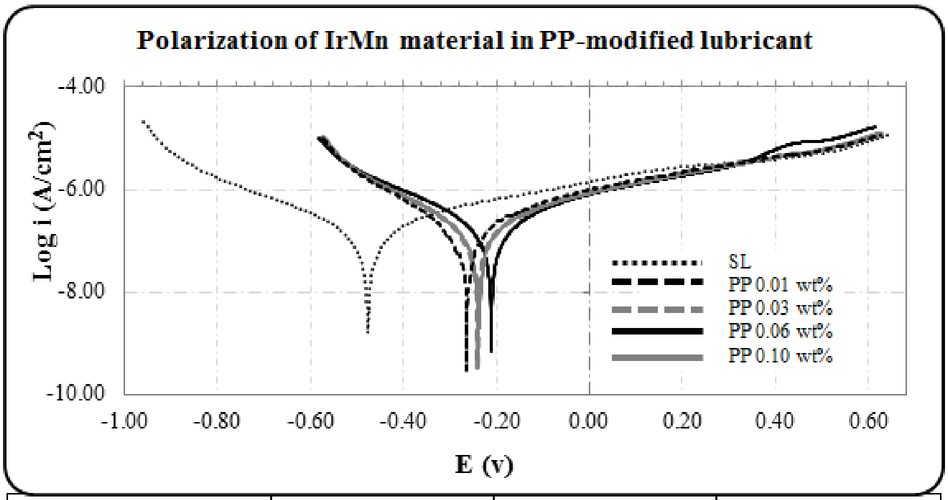
Concentrations of corrosion inhibitors	Conductivity (μs/cm)				
	SL	PP-modified lube	PG-modified lube	PO-modified lube	PVO-modified lube
0.00	126.43	-	-	-	-
0.01	-	112.73	114.8	118.93	126.03
0.03	-	113.10	115.5	122.10	129.47
0.06	-	114.80	117.23	136.03	138.90
0.10	-	115.00	117.73	140.50	147.17

4.2 Corrosion studies

4.2.1 Potentiodynamic polarization test

The optimum concentration of each corrosion inhibitor was obtained from potentiodynamic polarization curves from IrMn reference sample in each concentration of modified lubricants. In general, the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) are used to determine the corrosion occurrence. That is the higher E_{corr}, the harder to corrode and the low i_{corr} gives a slow corrosion rate. All modified lubricants: PP, PG, PO and PVO were investigated and the results showed as follow.

4.2.1.1 PP-modified lubricant



Concentrations of PP	i_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (Å/min)
0.00 (SL)	2.25 x10^{-7}	-0.476	0.111
0.01	1.88 x10^{-7}	-0.273	0.092
0.03	1.80 x10^{-7}	-0.248	0.088
0.06	1.76 x10^{-7}	-0.212	0.086
0.10	1.78 x10^{-7}	-0.247	0.088

Figure 4.1 Potentiodynamic polarization curves of PP-modified lubricant, compared to SL

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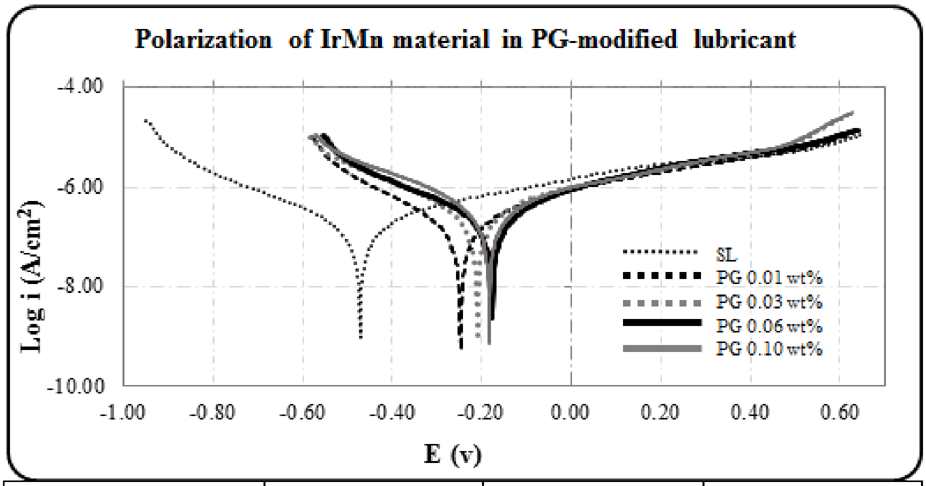
From Figure 4.1, it was found that PP-modified lubricant in all concentrations can protect IrMn material better than standard glycol-based lubricant. However, the corrosion rates of all PP concentrations were slightly closed to each other, but the E_{corr} value of PP-modified lubricant at 0.06 %wt was the highest, which means that it provided the best corrosion for IrMn material in this aspect. Therefore, optimum concentration of PP in PP-modified lubricant was at 0.06 %wt.

4.2.1.2 PG-modified lubricant



Concentrations of PG	i_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (Å/min)
0.00 (SL)	2.25×10^{-7}	-0.476	0.111
0.01	1.67×10^{-7}	-0.250	0.082
0.03	1.84×10^{-7}	-0.218	0.090
0.06	1.71×10^{-7}	-0.194	0.084
0.10	1.72×10^{-7}	-0.199	0.084

Figure 4.2 Potentiodynamic polarization curves of PG-modified lubricant, compared to SL

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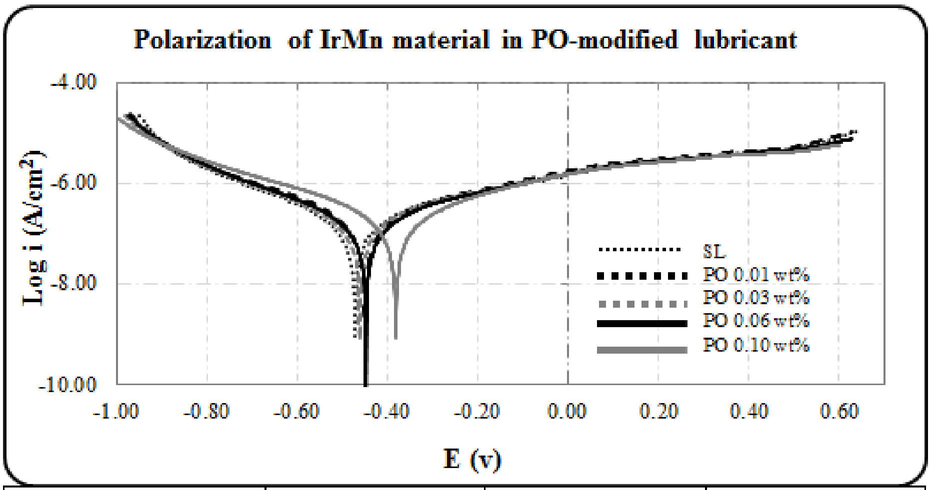
From Figure 4.2, the polarization result indicated that PG-modified lubricant in all concentrations can also protect IrMn material better than SL, since they have better i_{corr}, E_{corr} and corrosion rate values than SL. As we considered each concentration, they were slightly closed. PG-modified lubricant with PG at 0.06 %wt gave the highest E_{corr}, as the optimum condition for this case.

4.2.1.3 PO-modified lubricant



Concentrations of PO	i_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (Å/min)
0.00 (SL)	2.25×10^{-7}	-0.476	0.111
0.01	1.96×10^{-7}	-0.484	0.096
0.03	1.95×10^{-7}	-0.475	0.096
0.06	1.91×10^{-7}	-0.451	0.094
0.10	1.98×10^{-7}	-0.375	0.097

Figure 4.3 Potentiodynamic polarization curves of PO-modified lubricant, compared to SL

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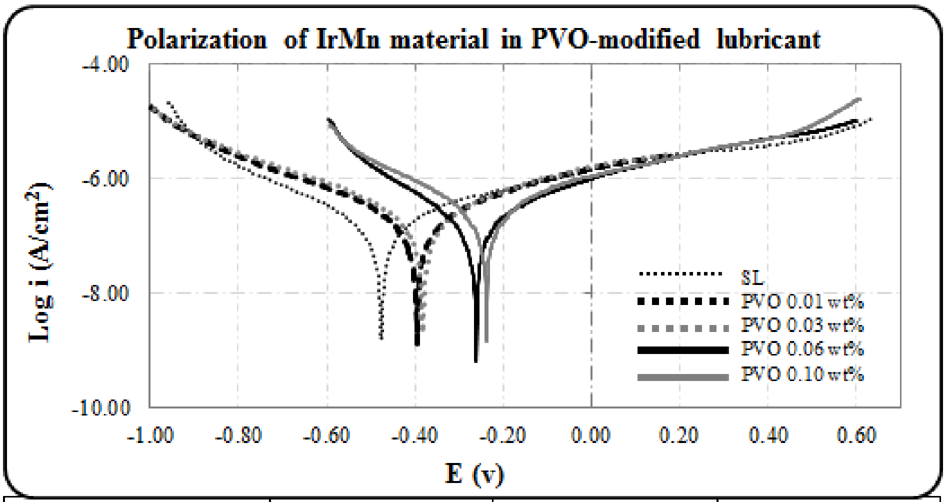
For PO-modified lubricant shown in Figure 4.3, it was found that the i_{corr} values of all modified lubricants were increased, as compared to SL. Nonetheless, the corrosion potential (E_{corr}) of each concentration was slightly closed to each other. The obtained result indicated that the E_{corr} values of PO-modified lubricants were increased upon additional concentration of corrosion inhibitors and 0.1 %wt of PO gave the highest E_{corr} value. Therefore, optimum concentration of PO-modified lubricants was at 0.1 %wt of PO.

4.2.1.4 PVO-modified lubricant



Concentrations of PVO	i_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (Å/min)
0.00	2.25 $\times10^{-7}$	-0.476	0.111
0.01	1.75 $\times10^{-7}$	-0.399	0.081
0.03	1.77 $\times10^{-7}$	-0.391	0.087
0.06	1.78 $\times10^{-7}$	-0.276	0.088
0.10	1.80 $\times10^{-7}$	-0.259	0.088

Figure 4.4 Potentiodynamic polarization curves of PVO-modified lubricant, compared to SL

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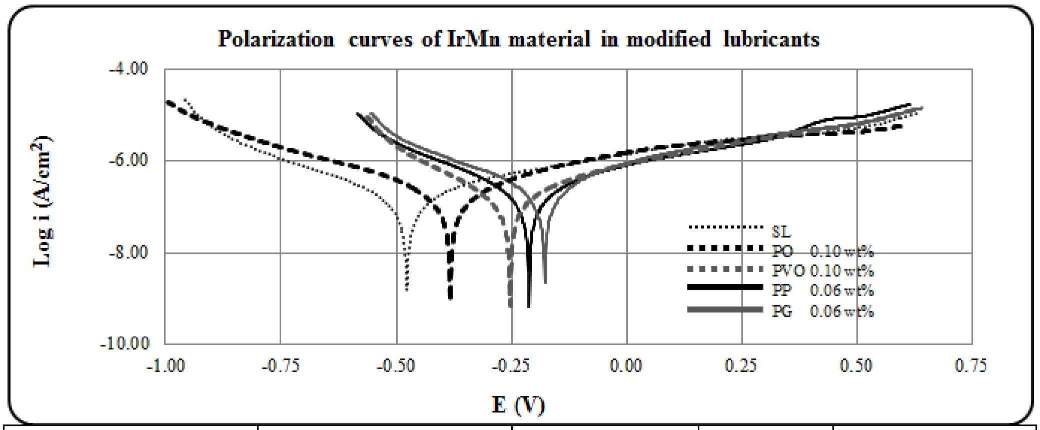
The E_{corr} values of PVO-modified lubricants as seen in Figure 4.4 also increased upon the concentration of the corrosion inhibitors. They can also help to protect the surface from corrosion better then SL due to their high E_{corr} values.

From all the results regarding the corrosion issue, PP- and PG-modified lubricants at 0.06 %wt were selected as the candidate lubricants for further investigations due to their high E_{corr} values (hard to corrode) and low I_{corr} (slow corrosion rate). They indicated the sign to protect corrosion better than PO, PVO-modified lubricants and SL as shown in Figure 4.5 because PP and PG corrosion inhibitors influenced some properties of modified lubricant.



Modified lubricants	Optimum concentration	i_{corr} (A/cm^2)	E_{corr} (V)	Corrosion rate (Å/min)
SL	-	2.25 x10^{-7}	-0.476	0.111
PP-modified lube	0.06	1.76 x10^{-7}	-0.212	0.086
PG-modified lube	0.06	1.71 x10^{-7}	-0.194	0.084
PO-modified lube	0.10	1.98 x10^{-7}	-0.375	0.097
PVO-modified lube	0.10	1.80 x10^{-7}	-0.259	0.088

Figure 4.5 Electrochemical parameters and optimum concentrations obtained from polarization curves for IrMn coupons immersed in difference concentration of modified and standard glycol-based lubricant

4.2.2 Leaching out of metal trend

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ICP-MS was performed to analyze and study the leaching out of Ir and Mn materials from IrMn coupons by vary dropping time 3 times: 5, 10 and 15 minutes, respectively. PP- and PG-modified lubricants at concentration 0.06 %wt were used for this measurement. The result was then analyzed and compared to SL. Form Table 4.4, the range of Mn %RSD was between 0.2 - 2.13% while the Ir %RSD was between 0.51 - 0.61%. These values were under the acceptable range. Generally, the acceptable %RSD should not over than 4% RSD [43]. The minimum concentration of an analysis was about 0.5 μg/L and standard calibration curve was in range 0.5-300 μg/L. Measured concentration of both metals are showed in Table 4.4. In all cases, we found the Ir concentrations was below 1 μg/L while the Mn concentration was about 3-15 μg/L.

Table 4.4 Detected quantity of Ir and Mn metals by ICP-MS (µg/L)

Lubricants	Dropping times (min)	Mn (in HNO_3)		Ir (in HNO_3)	
		Concentration (µg/L)	%RSD	Concentration (µg/L)	%RSD
SL	5	3.99	0.64	0.37	0.51
	10	7.87	0.83	0.61	2.13
	15	14.98	0.74	0.88	4.61
PP-modified lube	5	3.34	0.76	0.17	3.13
	10	4.42	1.16	0.26	2.88
	15	7.02	1.97	0.48	4.61
PG-modified lube	5	4.8	0.2	0.08	3.8
	10	6.06	2.13	0.11	4.24
	15	6.89	1.84	0.17	3.07

From Figure 4.6, showed the data from table 4.4 we found that the magnitude of Mn and Ir materials loss is a function of dropping time. By increasing of dipping time, it can increase the leaching out of Ir and Mn from the IrMn material. Moreover, it was found that Mn can be detected more than Ir, due to the composition of IrMn in the test specimen was about 4:1 (Mn79% and Ir 21%). The results indicated that PP- and PG-modified lubricants affect leaching out of Ir and Mn element less than SL. When compared protective leaching out performance of metal between PP- and PG-modified lubricants, PP-modified lubricant can protect Mn leaching out better than PG-modified lubricants at 5 minutes of dropping time, while Ir leaching out results, PG-modified lubricant was the best inhibitor for protecting corrosion. According to the results, we selected PP-modified lubricant as the best corrosion inhibitor because it can protect more Mn leaching out at lower time. This may be due to the important function of their functional groups. However, both corrosion inhibitors can form protective layer, coating on the specimen surface, which can be seen from electron micrographs.

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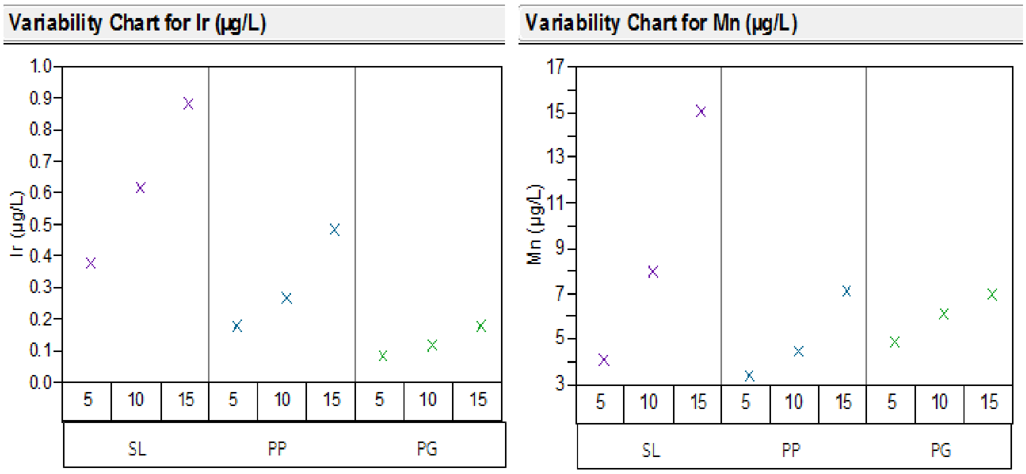

Figure 4.6 Variability charts for measured Ir and Mn materials, after dropped with PP- and PG-modified lubricants on the surface at different dropping times (5, 10 and 15 minutes, respectively).

4.3 Protective thin layer formation

4.3.1 Morphology analysis

The surface morphology analysis was done by using SEM to study the protective mechanism of PP and PG corrosion inhibitors. IrMn specimens were exposed to PP- and PG-modified lubricants for 1 hr before dried and investigated by SEM. The surfaces were compared with the as-grown IrMn coupon. The surface protective mechanism of both inhibitors can be proven from electron micrographs. It can be seen that there was thin layer of protective films coated on IrMn surface, as shown in Figure 4.7-b and Figure 4.7-c. The corrosion protection behavior of PP- and PG-modified lubricants can be explained by its chemical structure. PP can hydrolyze in neutral solution, which produced a positive charge on the nitrogen atom and a negative charge on the oxygen atom [44-45]. On the other hand, PG has OH group that can deprotonate H atom to OH group of glycol and becomes O^- charge. These two corrosion inhibitors also have oxygen atom with negative charge which can adsorb on metal surface with positive charge of metal, as shown in Figure 4.8 [12-13].

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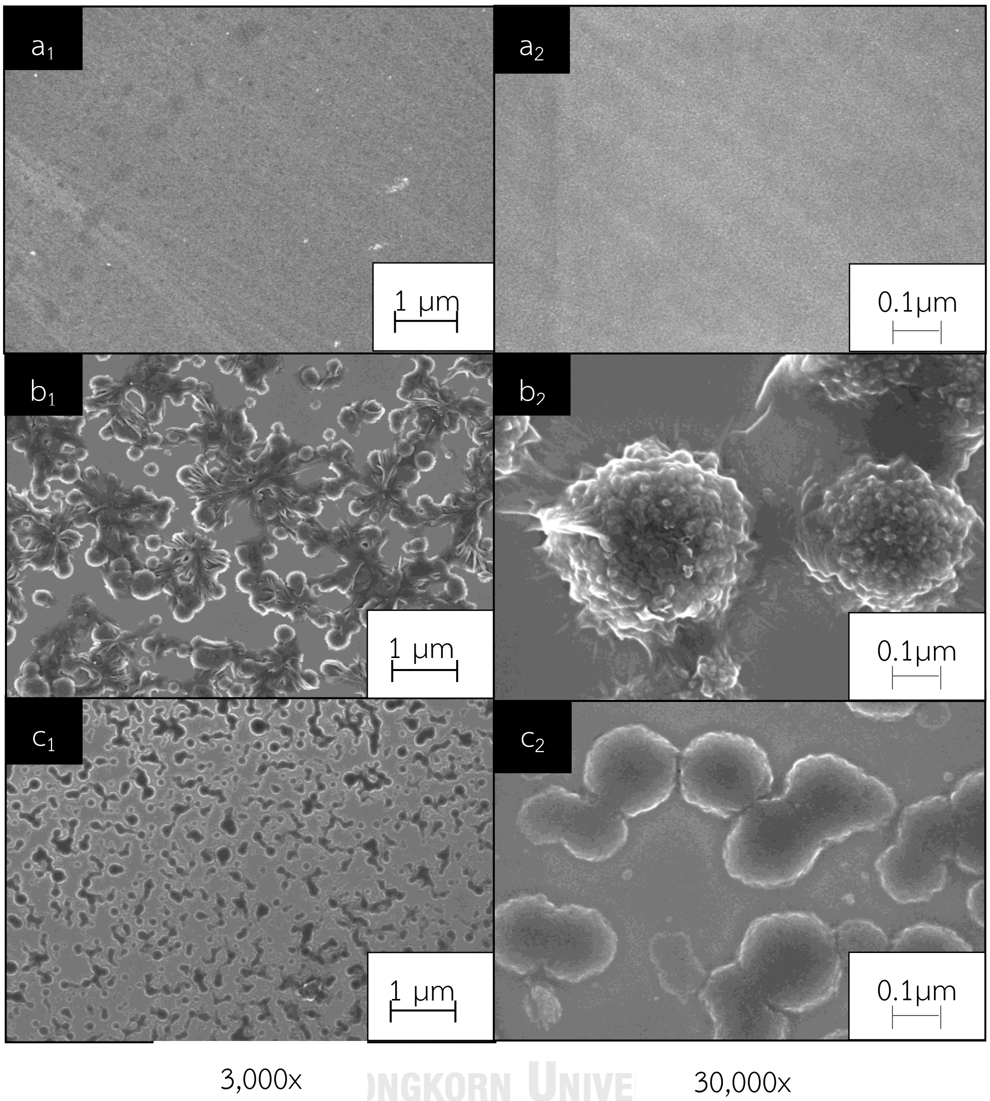

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Figure 4.7 SEM images (magnification: 3,000x and 30,000x) of IrMn a) no dipped. b) dipped in PP-modified lubricant and c) dipped in PG-modified lubricant

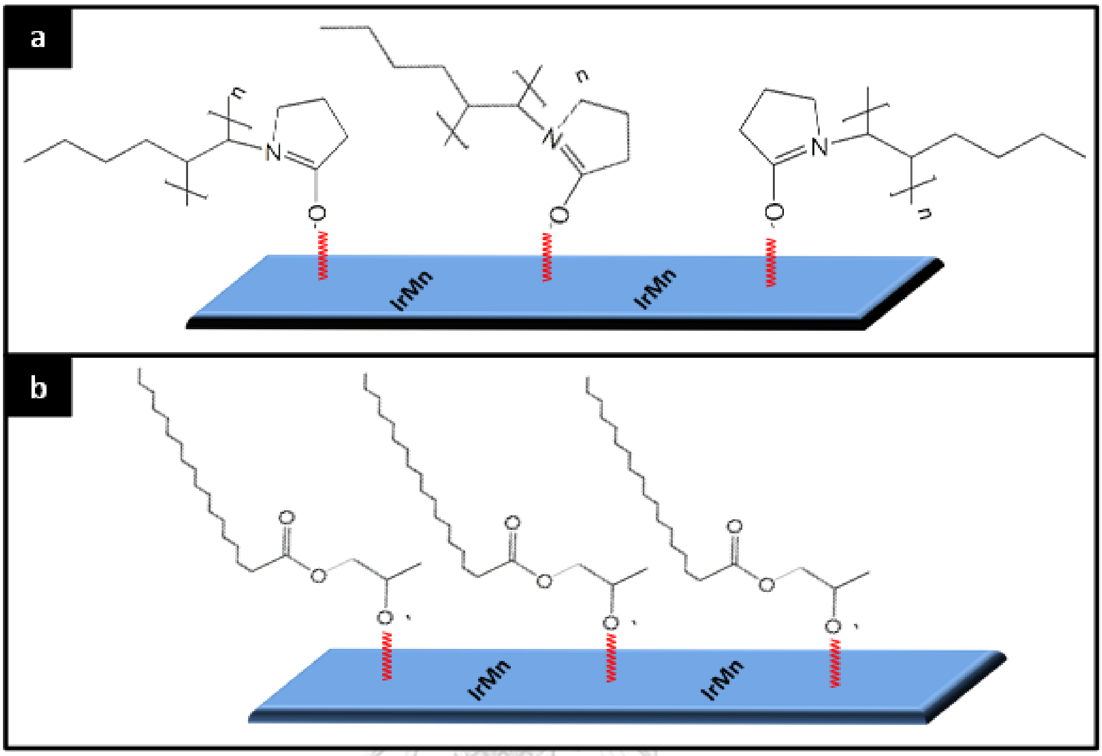


Figure 4.8 Schematic presentation of selected functional a) PP and b) PG inhibitors which adsorbed on IrMn surface by partial charging effect.

4.3.2 Critical micelle concentration analysis

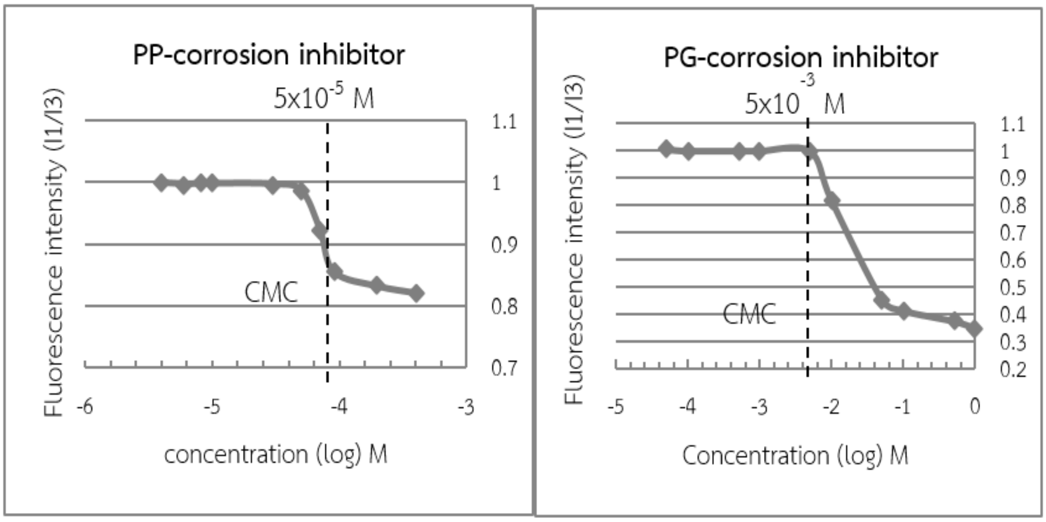


Figure 4.9 Fluorescence intensity of 1x10^{-6} M pyrene with different concentration of modified lubricants in EG solution

To confirm the protective mechanism of PP and PG inhibitors, CMC measurement was performed by using fluorescence spectrometry. Figure 4.9 shows a plot of fluorescence intensity vs. log concentration of both PP and PG-corrosion inhibitors. From the results, PP and PG inhibitors started to form micelle at concentration 5×10^{-5} M and 5×10^{-3} M, respectively. If convert these CMC values result to %wt in standard glycol-based lubricant, found that PP formed micelle at concentration 0.1 %wt, while PG was 0.15 %wt. But, the concentration of PP and PG used as corrosion inhibitor in standard glycol-based lubricant was only 0.06 %wt. Therefore, it can be assumed that PP and PG inhibitors were not protect corrosion by micelle formation. Both inhibitors can adsorb on IrMn surface by individual functional group interaction, along with the thin layer formation on the surface to protect the corrosion. Moreover, this research calculated the molecular size of PP and PG micelle, molecular size of PP is 829.20 Å and 25.64 Å for PG.

4.4 Lubricant performance test in actual process

4.4.1 Lapping time

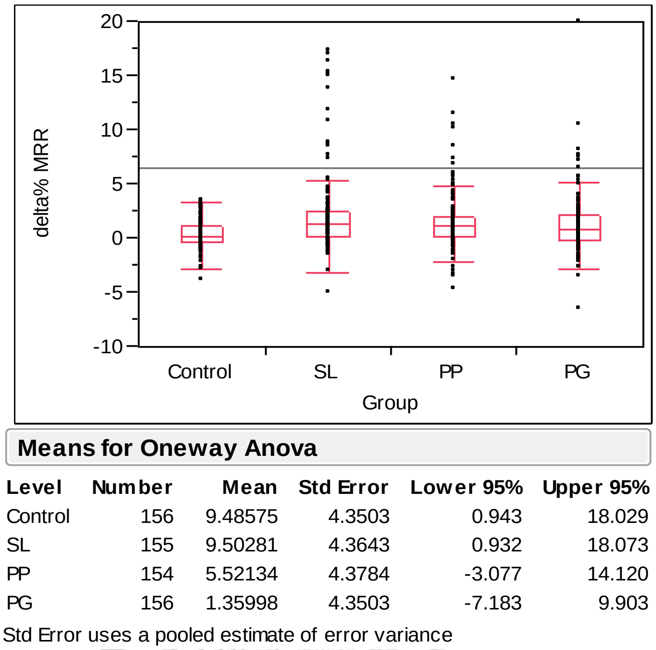
Lapping test results using PP and PG in the modified lubricants gave the lapping time about 1.49 and 1.47 minutes, respectively. Normally, the lapping time in the slider production should not longer than 2 minutes. The average lapping time using the standard lubricant is about 1.54 minute. The test result was as expected because PP and PG in modified lubricant provided the viscosity values about 19.05 and 19.59 cP, respectively, and which not significantly different from standard lubricant (19.95 cP), as shown in Table 4.5. From the results, it can be explained that PP- and PG-modified lubricant can be used in lapping process because they obtained lapping time in defined criterion.

Table 4.5 Viscosity and lapping time values of PP- and PG-modified lubricants at 0.06 wt% compared standard glycol-based lubricant

Lubricants	Viscosity (cP)	Number of sliders	Mean of lapping time (min)	SD
SL	19.95	443	1.54	0.44
PP-modified lube	19.59	445	1.49	0.44
PG-modified lube	19.05	446	1.47	0.44

4.4.2 QST

QST technique was selected to investigate the performance of the sliders, after be lapped in the process using the modified lubricants. In HDD production industry, extracted data from QST is very important. In other words, QST data is the parameter that can be used to screen out the low performance of slider by checking the distributions of the QST data. The industry has been tried to decrease them. Data has more distributions, which means that low performance of slides. The delta %MRR (magneto resistive resistant) values before and after lapping with PP- and PG-modified lubricants are shown in Figure 4.10. From the results, found that both modified lubricants of PP- and PG help to decrease distributions of the Δ%MRR data better than SL, which more distribute in PG-modified lubricant. Moreover, Δ%MRR values can be described corrosion occurrence. Low Δ%MRR value indicated that during the lapping process, lubricant affects low corrosion occurrence because magnetic resistance of sliders before and after lapping with modified lubricants are slightly difference. From the results, it can be summarized that PG-modified lubricant affects lower corrosion occurrence than PP-modified lubricant and SL.



Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Control	156	9.48575	4.3503	0.943	18.029
SL	155	9.50281	4.3643	0.932	18.073
PP	154	5.52134	4.3784	-3.077	14.120
PG	156	1.35998	4.3503	-7.183	9.903

Std Error uses a pooled estimate of error variance

Figure 4.10 Δ%MRR of PP- and PG-modified lubricants at 0.06 %wt compared to standard glycol-based lubricant from QST (oneway analysis from jump program)

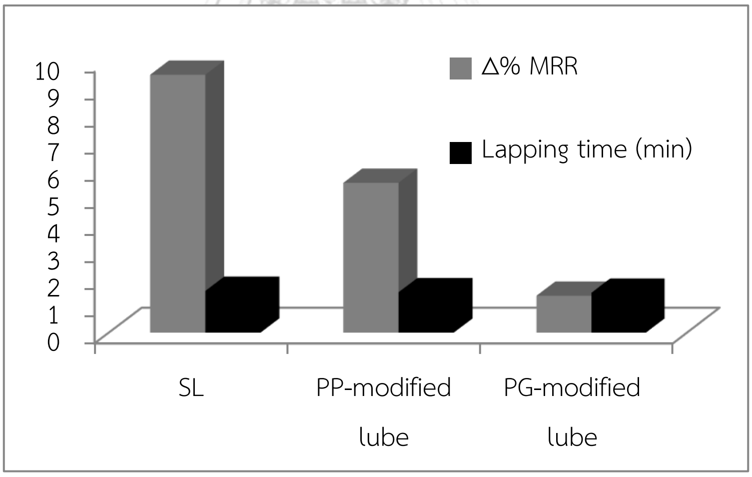


Figure 4.11 Δ%MRR and lapping time values of SL compared to PP- and PG-modified lubricants at concentration 0.06 %wt

From Figure 4.11, Δ%MRR of PP- and PG-modified lubricants were approximately decreased by 3 times of standard glycol-based lubricant whereas the lapping times were not different. This indicates the PP- and PG-modified lubricants are not only help to protect material removal from corrosion, but also have no side effect to the lapping time in the lapping process.

Moreover, to confirm the performance of these modified lubricants can be used in line production, tribological property of EG based lubricant was measured by tribometer, compared to SL (without adding corrosion inhibitor). This method is a simulation of final lapping process. The results exhibited that these additional corrosion inhibitors help to protect the wear occurrence. Coefficient of friction (COF) of corrosion inhibitor added lubricant that was 0.0068 while COF of SL was 0.0516 which is not significantly different. Therefore, we can be summarized that adding additional corrosion inhibitor in modified lubricants have no effect to COF values or friction occurrence.

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CHAPTER 5
CONCLUSIONS AND SUGGESTION

The polymer type and fatty ester type corrosion inhibitors were investigated to use as additional additive for corrosion protection in glycol-based lubricant during HDD heads lapping process. PP and PG corrosion inhibitors at concentration 0.06 %wt were selected as the best corrosion inhibitors for protecting IrMn materials in slider because of their corrosion protection performance. Both of them gave the lower corrosion rate and affected hard corrosion of IrMn material, compared to standard lubricant. However, PG provided corrosion rate less than PP inhibitor about 2.38 % so PG inhibitor is the best additive in case of protecting IrMn corrosion. On the other hand, the studying on leaching out of each material indicated that PP can protect Mn materials (which is the major component material in IrMn coupon) better than PG and standard lubricant. Therefore, in case of each material leaching out, PP inhibitor is the best corrosion inhibitor in this aspect. The functional group of the selected inhibitors (PP and PG) can be adsorbed on the surface of antiferromagnetic test material, IrMn by partial charging effect and formed protective thin layer over the surface.

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In slider fabrication for HDD, the data from QST measurement is very important parameters for checking the performance of slider after through the lapping process by observing the distribution data. PP and PG inhibitors exhibited their performance to decrease the failure distribution which obtained from QST measurement. That means, these modified lubricants can be used as alternated lubricants in the production, without losing quality and electrical performance. However, as consider the economic point of view, the price of standard lubricant is 417.89 baht/Liter while, the price of standard lubricant which added PG inhibitor is 417.99 bath/Liter and 419.21 baht/ Liter for lubricant added PP inhibitor. From the price comparison, it shows that the prices of PP- and PG modified lubricants increase very little form standard lubricant but the benefit that the industry will received that is, decreasing of the cost because of waste decreasing from production.

Finally, compare overall both price and performance, we proposed PG as the best corrosion inhibitor for protecting IrMn materials in slider during lapping process because it has many benefit as follows:

1. PG inhibitor gave the lower corrosion rate and better corrosion, compared to PP inhibitor and standard lubricant by 2.38 % and 32.14%, respectively.
2. PG inhibitor gave the 0.02 seconds lower lapping time than PP inhibitor and 0.07 seconds standard lubricant.
3. PG inhibitor decreased the variation of test result from QST measurement which is the impact that the industry has been tried to decrease better than PP inhibitor and standard lubricant.

Finally, we have summarized the properties and abilities on corrosion protection of PP-and PG-modified lubricants, compared to standard lubricant as in Table 5.1

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Suggestions

- To confirm the composition and functional groups of protective layers formed on the material surface. Raman spectroscopy is suggested for this study.

Table 5.1 The properties and all the results of PP and PG corrosion inhibitors for protecting IrMn materials in slider.

Properties		SL	PP-modified lube (0.06%)	PG-modified lube (0.06%)
EG		93.118	93.058	93.058
Additives		6.882	6.882	6.882
Corrosion inhibitor (PP)		-	0.06	-
Corrosion inhibitor (PG)		-	-	0.06
pH		8.40	8.56	8.55
TBN (mg KOH/g)		3.72	23.31	23.32
Conductivity (µs/cm)		126.43	114.80	117.23
Lapping time (min)		1:54	1:49	1:47
Corrosion rate (Å/min)		0.111	0.086	0.084
Viscosity (cP)		19.95	19.59	19.05
Leaching out of IrMn	Mn (µg/L)	3.90-14.98	3.34-7.02	4.80-6.98
		-	PP protected Mn leaching out better than PG	
	Ir (µg/L)	0.37-0.88	0.17-0.48	0.08-0.17
		-	PG protect Ir leaching out better than PP	
Cost (THB)		417.89/ Liter	419.21/Liter	417.99/Liter

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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

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