ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SILANIZATION PROCESS AS TEMPORARY CORROSION PROTECTION FOR HIGH PRESSURE RESISTANT COMPONENTS IN DIESEL INJECTION SYSTEMS

M.Sc. THESIS

Duygu ŞADILLIOĞLU

Advanced Technologies Department

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Thesis Advisor: Prof. Dr. Mustafa Ürgen

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

DİZEL ENJEKSİYON SİSTEMLERİNDE YÜKSEK BASINCA DAYANIKLI BİLEŞENLER İÇİN GEÇİCİ KOROZYON DAYANIMI SAĞLAYAN SİLANLAMA PROSESİ

YÜKSEK LİSANS TEZİ

Duygu ŞADILLIOĞLU
521091040

İleri Teknolojiler Anabilim Dalı

Malzeme Bilmi ve Mühendisliği Programı

Tez Danışmanı: Prof. Dr. Mustafa ÜRGEN

HAZİRAN 2012

Duygu Şadıllıoğlu, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **521091040**, successfully defended the **thesis** entitled "**SILANIZATION PROCESS AS TEMPORARY CORROSION PROTECTION FOR HIGH PRESSURE RESISTANT COMPONENTS IN DIESEL INJECTION**" which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Mustafa ÜRGEN** İstanbul Technical University	.....
Jury Members :	**Doç. Dr. Kürşat KAZMANLI** İstanbul Technical University	.....
	Doç.Dr. Gökhan Orhan İstanbul University	.....

Date of Submission : 04 May 2012
Date of Defense : 08 June 2012

To my family,

FOREWORD

This thesis was written for my master degree in Department of Advance Technologies at Istanbul Technical University. The research was executed as an internship at Robert Bosch Diesel Systems in Bursa and handled as one of the surface technology research project of Technical Function Department. The intent of the thesis is to understand mechanism of the silane coating and to examine major step (hydroxylation) of silane coating process.

I would like to thank my supervisor, Prof. Dr. Mustafa Ürgen for all the input and thoughts about the subject and of being great guidance during the development of this thesis; Dr. Nils Lippmann and Dr. Azra Martin of being so helpful with their practical support, vision, and advise during my research and experiments. I would like to express my gratitude to the employees of Robert Bosch. Finally, I would like to thank Prof. Dr. Seniha Güner, Research Asst. Beril Akıncı, Research Asst. Faiz Muhaffel and Mehmet Mümtaz Dokur for their help and support at characterization phase.

May 2012

Duygu ŞADILLIOĞLU
Metallurgy and Material Science
Engineer

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ABBREVIATIONS

RBTR	**:** Robert Bosch Turkey
CR	**:** Common Rail
EU	: European Union
MnS	: Manganese Sulphide
VOCs	: Volatile Organic Compounds
-OH	: Hydroxyl groups
OH^-	: Hydroxyl ions
Si-OH	: Silanol bonds
Me-OH	: Metallo-hydroxide
Me-Si-O	: Metallo-siloxane
Si-O-Si	: Siloxane
BTSE	: Bis-1,2-(triethoxysilyl)ethane
γ-**APS**	: Aminopropyltriethoxysilane
SST	: Salt spray test
DI	: Deionized

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SILANIZATION PROCESS AS TEMPORARY CORROSION PROTECTION FOR HIGH PRESSURE RESISTANT COMPONENTS IN DIESEL INJECTION SYSTEMS

SUMMARY

Diesel Injector parts must have temporary corrosion resistance from the beginning of the production until assembly at the engine customer. On the other hand, increasing demands on fuel efficiency and emission reduction require elevated operating pressure. As to the elevated operating pressure, components require higher fatigue resistance in modern diesel injection systems. Phosphate coating, which is actually applied for temporary corrosion protection, will not more fulfill the requirements for elevated fatigue resistance due to surface imperfection caused by the process.

Silane coating, a new technology performed with organo-silane polymers does not affect fatigue resistance negatively as well as provides adequate corrosion resistance to the components. It is a non-toxic and environmentally friendly process, since the process is conducted in alkaline baths. Since activation and passivation are not required, corrosion protection is achieved with fewer process steps and shorter treatment times. Hereby, less chemical, water and energy consumes in comparison with other similar coatings. However, it requires some crucial pre-treatment prior to silane coating like hydroxylation. Silane reacts at room temperature with hydroxides present on the metal surface and forms strong covalent bonds with the metal substrate after curing (drying) at appropriate temperature.

In this study, effect of hydroxylation step investigated deeply to understand its relationship with corrosion protection. In this frame, parts were hydroxylated in solutions at different chemicals, concentration, time and temperature. Afterwards, the influence of the hydroxylation solution concentration, time and temperature was characterized and corrosion performance of silane coated parts was evaluated. In this thesis, mainly used characterization techniques are Salt Spray Test, Contact Angle Measurement, and Copper Decoration Method.

SST results showed that the part hydroxylated in commercial hydroxylation chemical had better corrosion resistance compared to part hydroxylated in NaOH solution. It is believed that the difference between NaOH and commercial chemical occurred due to rich content of wetting and oxidizing agents in commercial chemical. To understand the importance of hydroxylation step, untreated sample and coated sample without hydroxylation were compared. It is clear that without hydroxylation, silane does not bond to the substrate effectively. Contrary to expectations the 30°C temperature difference in hydroxylation, did not cause a big difference at corrosion resistance performance. Finally, considering the hydroxylation concentration and time; it is observed that under experimented values increasing duration is more effective than increasing concentration on corrosion resistance. As optimized value; 4,5% concentration and 255 seconds hydroxylation

parameters give good corrosion resistance performance as well as higher concentration and time values.

The contact angle results highlighted that all the silane coated parts are hydrophobic with angle 105° more or less. There was only small differences between silane parts that hydroxylated at different parameters; for example the part hydroxylated in 4,5% Gardoclean for 255 seconds is a little more hydrophobic with an average angle 107°, as the part hydroxylated in 1% Gardoclean for 30 seconds with an average angle 104°. With increasing concentration of hydroxylation solution from 1% to 8% the hydrophobicity was not affected in a great extend. Duration of hydroxylation is more influential parameter on corrosion resistance than hydroxylation concentration as parallel to SST result. According to residence time of droplets on silane coated samples, the contact angles decreased as expected. These results proved that again silane coating is a porous structure and only provides short-term corrosion resistance. When silane coated parts and only hydroxylated parts were compared; hydrophilic hydroxylated surface could be clearly noticed. By means of hydrophilic Me-OH groups, the hydroxylated surfaces have averagely 30° contact angle value. In comparison of the samples hydroxylated in different chemicals; it was obvious that hydroxylation in commercial chemical yields higher contact angle. As SST result, it was considered that the difference between NaOH and commercial chemical occurred due to content of rich wetting and oxidizing agents in commercial chemical.

The copper decoration method was performed in order to evaluate homogeneity and porosity of the samples. After the decoration test, the silane coated parts showed no obvious discoloration. However, the importance of hydroxylation step could be easily seen; intensive copper-precipitates and discoloration were observed on the untreated sample and coated sample without hydroxylation step.

DİZEL ENJEKSİYON SİSTEMLERİNDE YÜKSEK BASINCA DAYANIKLI BİLEŞENLER İÇİN GEÇİCİ KOROZYON DAYANIMI SAĞLAYAN SİLANLAMA PROSESİ

ÖZET

Dizel enjektör sistemlerinde, parçaların ilk üretim noktasından sevkiyat için montajına ve müşteride motora monte edilinceye kadar geçici korozyon dayanımına ihtiyaç duyulmaktadır. Yakıt verimliliği ve CO_2 emisyonlarının azaltılmasına ilişkin artan talepleri de karşılamak amacıyla modern dizel enjeksiyon sistemlerinin daha yüksek basınçlarda çalışması ve bunun için de daha yüksek yorulma dayanımına sahip olması gerekmektedir. Mevcut durumda, dizel enjeksiyon sistemlerinde geçici korozyon koruması için uygulanan fosfat kaplama, metal yüzeyinde sebep olduğu yenikler sebebiyle daha yüksek yorulma dayanımı gerektirecek yeni nesil ürünlerde yapılan denemeler sonucunda olumlu sonuçlar vermiştir. Fosfat kaplama kimyasalların metal yüzeyinde sebep olduğu malzeme yenikleri, özellikle yüksek basınç altında çalışma esnasında çatlaklara, sızdırmalara hatta kırılmalara sebep olmaktadır. Ayrıca fosfat kaplama kimyasallarının çevre ve insan sağlığına yönelik olumsuz etkileri de göz önüne alındığında, günümüz çalışma şartları ve yasal gerekliliklerine pek de ayak uyduramadığı bilinmektedir. Fosfat kaplamanın bu gibi olumsuz etkileri nedeniyle yüksek basınç enjeksiyon uygulamaları için alternatif yöntemlere yönelinmiştir.

Fosfat kaplamanın alternatifi olarak geliştirilen polimerik silan kaplama, yorulma direncini olumsuz etkilemediği gibi parçalara yeterli korozyon dayanımı da sağlamaktadır. Proses; fosfat kaplama gibi asit karakterli olmadığından fosfata kıyasla toksik olmayan, çevre dostu bir işlemdir. Fosfat kaplamaya göre daha az proses adımından oluşup daha az kimyasal, süre ve enerji tükettiğinden daha düşük maliyetli süreç ile istenilen özellikler elde edilir.

Silan kaplama prosesi temelde beş ana adımdan oluşmaktadır, sırasıyla; yağ alma, hidroksilleme, durulama, silanlama ve kürleme. Otomotiv endüstrisinde uygulanan her kaplamada olduğu gibi ilk önce yüzeyden yağı ve çapakları uzaklaştırmak için yağ alma işlemi yapılır. İkinci adım; alkali solüsyon içerisinde gerçekleşen kimyasal bir süreç olan hidroksilleme sırasında yüzeyde Me-OH grupları oluşturarak Si-OH grupları ile bağ kurmaya hazır başlangıç noktaları elde edilir. Durulama adımı; özellikle silan solüsyonunun pH değişimini önlemek amacıyla, hidroksilleme solüsyonundan silanlama solüsyonuna kimyasal taşınımını engellemek için yapılır. Silanlama adımında parçalar, önceden uygun oranlarda hazırlanan ve uygun pH'a getirilip yeterli süre hidroliz edilen silan solüsyonuna daldırılarak Me-OH grupları üzerinden Si-OH gruplarının tutunmasını sağlayacak sürede bekletilir. Bu esnada Me-OH grupları ile Si-OH grupları birbirine hidrojen bağlarıyla bağlanmış olur. En son adım olan kürleme işlemi ise metal parçaları belirli sıcaklık ve sürede kurutarak yüzeydeki uçucu bileşenlerin ayrılması ve polimerizasyonunun tamamlanması için yapılmaktadır. Böylelikle kovalent bağlı silan film tabakası elde edilmiş olur.

Bu çalışmada, silan kaplama metoduna ilişkin yeterli bilgi, tecrübe birikiminin sağlanması ve ayrıca hidroksilleme adımının korozyon dayınımına etkisinin araştırılması amaçlanmıştır. Bu çerçevede metal altlıklar; farklı kimyasal, konsantrasyon, süre ve sıcaklık değerlerinde hidroksillenmiştir. Daha sonra, farklı sıcaklık, süre ve konsantrasyonda hidroksillenen parçalar karakterize edilerek silan kaplı parçaların korozyon performansı değerlendirilmiştir. Silan kaplanmış veya hidroksillenmiş metal altlıkların deneysel olarak incelenmesi esnasında; Tuz Püskürtme Testi, Temas Açısı ve Bakır Dekorasyonu karakterizasyon teknikleri kullanılmıştır.

Tuz püskürtme testinde parçalar, 20°'lik açı ile 35°C'de, 5 saat boyunca 50±5g/l tuz içeren tuz buharına maruz bırakılmıştır. Test sonrasında parçalar fotoğraflanarak Bosch kontrol talimatına göre değerlendirilmiştir. Bu tez çerçevesinde, parçaların pas derecesi (Ri)'nin değerlendirmesi, Bosch N42 AP 013 (izin verilebilir korozyon değeri Ri $\leq$ 3) standardına bağlı kalarak yapılmıştır.

Tuz püskürtme testi sonuçları, ticari kimyasal solüsyonunda hidroksillemenin, NaOH solüsyonunda hidroksillemeden daha etkin olduğunu göstermiştir. Ticari kimyasal ile NaOH arasındaki bu farkın; ticari kimyasal içeriğindeki zengin ıslatıcı ve oksitleyicilerden kaynaklandığı düşünülmektedir. Hidroksilleme adımının önemini anlamak için hiç kaplanmamış ve hidroksilleme işlemi görmeden silan kaplanmış parça karşılaştırıldı. Tuz püskürtme testi sonrası parçalardaki benzerlik, hidroksilleme işlemi olmadan silanın yüzeye etkin bir biçimde bağlanmayıp, korozyon dayanımı sağlamadığı ve neredeyse hiç kaplanmamış parça ile aynı Ri değerine sahip olduğunu göstermiştir. Beklenenin aksine, hidroksilleme sıcaklığındaki 30°C'lik bir değişiklik, korozyon dayanımında büyük bir farka sebep olmamıştır.

Hidroksilleme konsantrasyonu ve süresi göz önüne alındığında ise; artan hidroksilleme süresinin, artan hidroksilleme solüsyonu konsantrasyonuna göre korozyon dayanımında daha etkin olduğu görülmüştür. Deneysel değerler içerisinde optimize edilmiş değerler olarak; %4,5 konsantrasyon ve 255 saniye hidroksilleme parametreleri, yüksek konsantrasyon ve süre değerleri kadar iyi korozyon dayanım performansı göstermiştir.

Kontak açısı ölçümlerinde hafif faz olarak hava, ağır faz olarak ise saf su kullanılmıştır. Damlacık hacmi olarak 5µl uygulanmış ve açı ölçümleri yüzeyde 10 saniye, 120 saniye ve 600 saniye kalma süresi sonunda ölçülmüştür. Üçer tekrarlı yapılan ölçümlerde, süreye bağlı olarak damlacıkların davranışı izlenerek parça yüzeylerinin hidrofobikliği/ıslatabilirliği değerlendirilmiştir.

Kontak açısı ölçümleri sonucu tüm silan kaplı parçaların yaklaşık 105° açıda ve hidrofobik özellikte olduğu görülmüştür. Farklı parametrelerde hidroksillenmiş silan kaplı parçalar üzerinde sadece küçük farklılıklar bulunmaktadır; örneğin %4,5 Gardoclean içerisinde 255 saniye sürede hidroksillenmiş parça, %1 Gardclean içerisinde 30 saniye hidroksillenmiş ortalama 104° parçaya göre 107°'lik ortalama açıyla biraz daha hidrofobiktir. Hidroksilleme solüsyonu konsantrasyonunun %1'den %8'e artmasıyla hidrofobik özellik çok büyük ölçüde etkilenmemiştir. Tuz püskürtme sonucuna paralel olarak, hidroksilleme süresi, hidroksilleme konsantrasyonuna göre korozyon dayanımı üzerine daha etken parametre olarak bulunmuştur.

Damlacıkların silan kaplı parçalar üzerinde kalma süresine bağlı olarak, beklenildiği üzere temas açısında düşüş gözlenmiştir. Bu sonuç, silan kaplamanın porozlu bir yapıda olduğunu ve sadece kısa dönemli korozyon dayanımı sağlamada etkin olduğunu kanıtlamıştır. Silan kaplı parçalar ve sadece hidroksillenmiş parçalar karşılaştırıldığında hidrofilik hidroksil yüzeyi fark edilmektedir. Hidrofilik Me-OH grupları sayesinde yüzey 30°'lik temas açısına sahiptir. Farklı kimyasallarda hidroksillenmiş parçalar karşılaştırıldığında; ticari hidroksilleme kimyasalının daha yüksek temas açısı sağladığı bulunmuştur. Tuz püskürtme test sonucunda da olduğu gibi, NaOH ve Gardoclean kimyasalları arasındaki bu farkın, ticari kimyasal olan Gardoclean içeriğindeki zengin ıslatıcı ve oksitleyici içeriklerden kaynaklandığı düşünülmektedir.

Diğer bir karakterizasyonu yöntemi olan bakır sülfat dekorasyonu ise kaplamaların homojenliğini değerlendirmek amacıyla yapılmıştır. Test sonrasında silan kaplanmış parçalar arasında belirgin bir renklenme/homojensizlik olanaklar dahilinde saptanmamıştır. Buna rağmen, hidroksilleme işlemi yapılmadan kaplanmış parça ile hidroksilleme yapılıp kaplanmış parçalar arasındaki fark gözlenmiştir. Hidroksilleme işlemi yapılmadan kaplanan parçada yoğun bakır çökeltilerine rastlanılmıştır.

1. INTRODUCTION

Higher pressures, lower fuel consumption and reduced exhaust-gas emissions have made the diesel engine economical, clean and powerful in automotive industry. For these reasons, demands for diesel-engine systems are continuously increasing. Increasing demands forces diesel engine manufacturers for new and better technologies in diesel injection systems.

One of the advanced fuel-injection systems in diesel technology is the common-rail fuel-injection system (Figure 1.1). The main advantage of the common rail system is its ability to vary injection pressure and timing over wide scales. This is achieved by separating pressure generation (in the high-pressure pump) from the fuel-injection system (injectors). The system modules of an engine control unit and a common-rail fuel-injection system (Figure 1.2) consists of the following main component groups [1]:

- The low-pressure stage, consisting of the fuel-supply system components
- The high-pressure system, consisting of components such as the high-pressure pump, fuel rail, injectors, and high-pressure fuel lines
- The electronic diesel control, consisting of system modules, such as sensors, the electronic control unit, and actuators

Injectors in a common rail (CR) (Figure1.3) diesel injection system are connected with the rail by short high-pressure fuel lines [2]. An injector primarily consists of an injection nozzle, injector body, control valve and control chamber.

For fuel efficiency and emission reduction demands, injectors require more development studies in diesel systems. Demands require higher operating pressure and thus higher fatigue resistant components. Recent generation injectors with solenoid valve for passenger cars that are produced in RBTR already reach an inlet pressure of 1800 bar however pressure levels will reach up to 2200 bar in the upcoming CR generations.

Figure 1.1: Common rail injection system [3]

In recent years, CO_2 emission is one of the important issues that is directly related with the diesel injectors performance. As shown in Figure 1.4 there are some legal regulations of some countries and EU. However, EU regulations permit max. 130 g/km CO_2 emission today, this value has to be decreased more sharply within the next years.

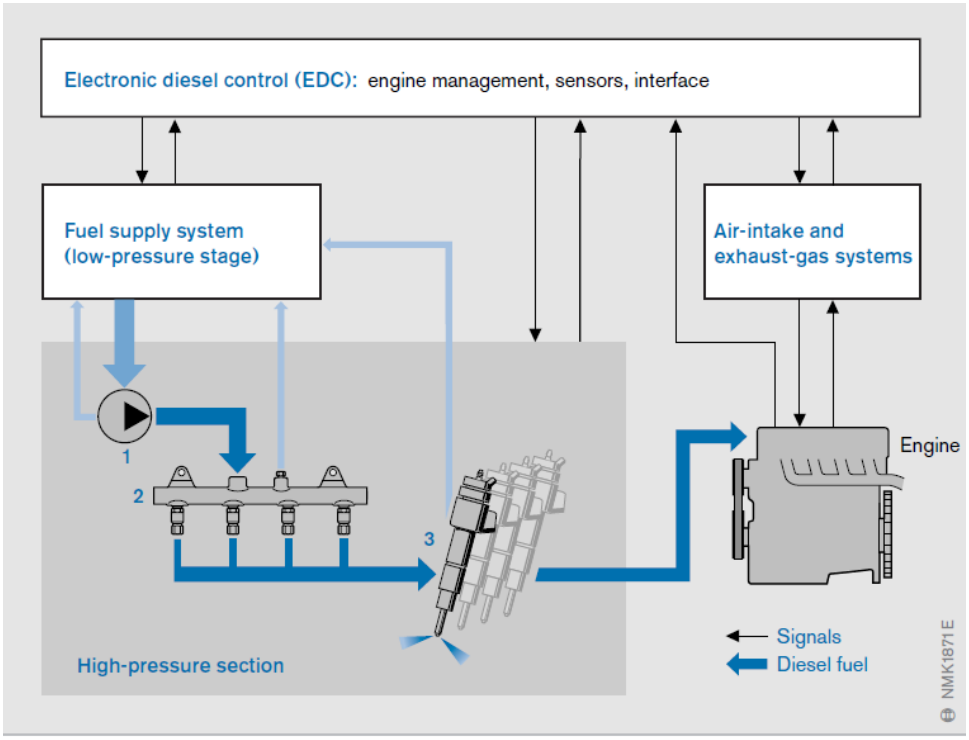


Figure 1.2: System modules of an engine control unit and a common-rail fuel-injection system. 1. High-pressure pump, 2. Fuel rail, 3. Injectors [1].

Figure 1.3: Common rail injector [2]

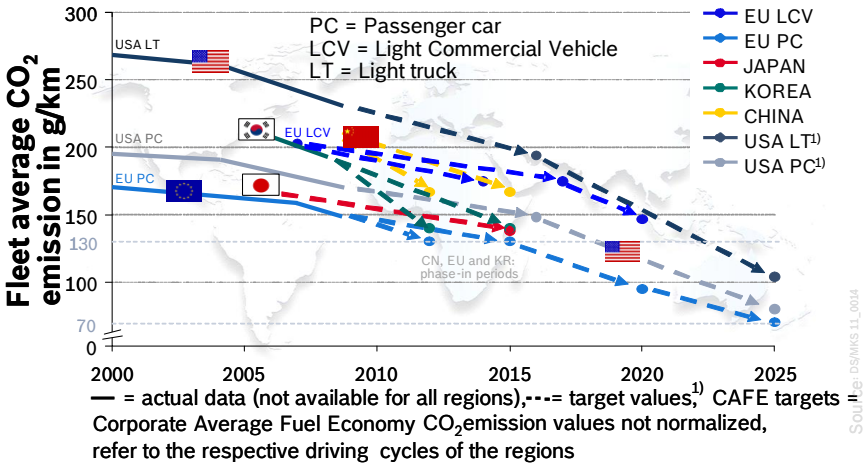


Figure 1.4: Legal Regulations in CO_2 emission [4].

Reduction of CO_2 emission is directly related with effective combustion. Effective combustion requires elevated working pressure for efficient vaporization so that less fuel is consumed as summarized in Figure 1.5. The consumption of fuel is 5.4 l/100 km currently and by 2020, it is targeted to be reduced below 3.6 l/100 km in diesel cars as seen in Figure 1.6.

For these reasons, especially in the upcoming years, fatigue resistance of the injectors should be enough to operate at higher-pressure levels. Thus, with less fuel consumption and CO_2 emission, intended operation of the injectors could be achieved.

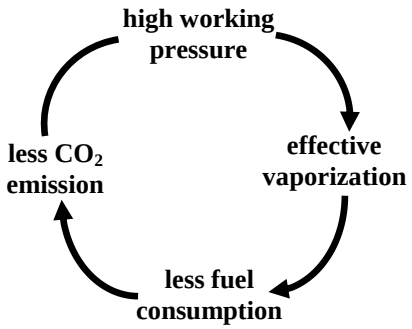


Figure 1.5: CO_2 emission and working pressure relation.

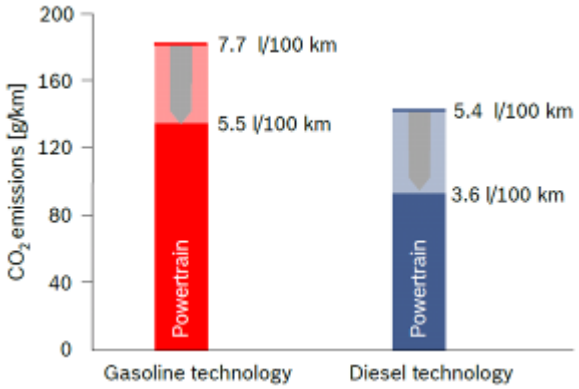


Figure 1.6: CO_2 emission according to fuel consumption [4].

1.1 Purpose of the Thesis

This thesis focused on the investigation of silane coating process (silanization), which is applied without any additional treatment like painting and sealing, to achieve an adequate corrosion resistance for the production and shipment periods of injectors.

Silane usage and developments as adhesion promoter have been investigated over the years. However about usage and developments as corrosion protective coating there are a few studies. Therefore, to achieve a profound knowledge about silanization as corrosion protective coating; the dependency between hydroxylation parameters and corrosion properties are investigated in the frame of this thesis.

1.2 Background

Temporary corrosion resistance of injector body is required in the production line, for the duration of its storage and shipment time until the injector is fitted in the vehicle.

Phosphate coating, which is currently applied for temporary corrosion protection in RBTR, will no more fulfill the requirements for elevated fatigue resistance. Acidic process in phosphate coating causes selective dissolution of material and they lead to pickling edges on the substrate surface as seen in Figure 1.7. Pickling of the injector body surface causes pitting; this occurs i.e. by dissolution of manganese sulphide (MnS) and seems like notches on the surface. Cracks may occur around the areas also may result in leaks between high-pressure zone and low-pressure zone of the injector system [5].

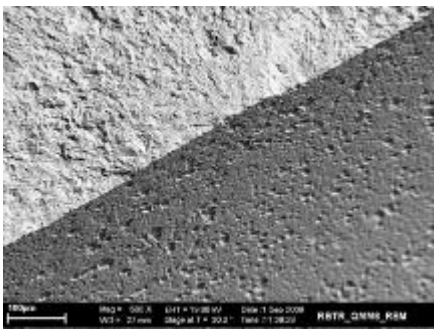


Figure 1.7: Pickling notches on the phosphate coated surface [4].

During the operation of the injector, the fuel could flow with great pressure fluctuations between fuel supply line and injector nozzle because of leakage. Because of this, the injectors cannot perform its function fully and can lead to negative impacts during usage in the engine.

It is targeted that silane coating is going to be applied as a substitute of present phosphate coating for high-pressure applications, which is recently known as corrosion resistant protective coatings [6] for metals.

2. BASICS of SILANE COATING

2.1 Properties of Silane

Toxicological and environmental profile of some coating's (e.g. phosphating, chromating) chemistry has led to develop more preferred chemistries for protection of metals against corrosion [7]. Actually, silanes are known just as adhesion promoters between organic polymers and mineral substrates for many years. The silane may function as (1) a finish or surface modifier, (2) a primer, or (3) an adhesive [8] in surface treatment technology. Since only a few years, silane coatings have emerged to improve corrosion performance as a promising candidate for replacement of conversion coating of metals.

There are many studies regarding to silane molecules as adhesion promoters between metallic substrates and organic coatings that used for corrosion protection [9]. Many tests have shown that silanes provide excellent corrosion protection as well as paint adhesion for metals as chromates do [10]. However, there are not enough studies of silane directly used as corrosion protective coating without any top coating.

Due to lack of active corrosion protection, silane coating is not preferred directly for long-term corrosion resistance. Silane cannot play any active role when the corrosion processes start to damage the surface. During corrosion attack, the cathodic reactions release hydroxyl ions that increase the pH, inducing the decomposition of the silica network. Hereby, degradation processes are accelerated and the barrier effect is lost [11]. Because of this limitation, silane coating without any top coating can be only used for short-term corrosion protection.

Corrosion protective layer is obtained by wetting metal surface using an aqueous solution containing monomeric silane derivatives [5]. Subsequent to wetting, the monomers form polymers during curing of the metal parts.

2.1.1 Environmental concern and aspects

Silane coatings are currently demanded research area due to need of green technology in the metal finishing industries. Silane chemicals are stable, non-toxic, and environmentally friendly chemicals. Chrome coating, phosphate coating and similar conversion coatings have been known as toxic and carcinogenic, and thus their use and waste are regulated heavily by most environmental legislation. These legislations have forced many companies to seek water-based solutions for their corrosion protection needs [12].

On the other respect, energy costs can be discussed in the field of environmental aspects, too. In phosphate coating, the bath must be permanently heated up to approximately 55°C whereas room temperature is sufficient for silane coating [13]. In addition, silane technology needs fewer treatment baths compared to phosphate coating because the activation and passivation steps are no longer required.

2.1.2 Chemistry of silane

In literature, monomeric silicon chemicals are known as silanes and if a silane contains at least one silicon-carbon bond (e.g. Si-CH_3), it is called an organo-silane. Organo-silanes, hereafter shortly called silane, are available in two groups in terms of their solubility; alcohol-based and water-based. Alcohol based silanes require a large amount of organic solvents such as ethanol or methanol while preparation of the silane solutions. The need of alcohol for preparation of silane solution obviously poses a major obstacle in industrial systems. Especially due to legal restriction about VOCs due to flammability and human safety concern [10]. Concerning water-based silanes; they are free of VOCs since only de-ionized water is needed for silane solution preparation [14]. For this reasons, demands for water-based silanes are increasing day by day in industrial systems.

Their general molecular structure is R-Si$(OX)_3$. X is an alkyl (C_nH_{2n+1}) chain, also OX groups are hydrolysable groups such as methoxy (OCH_3), ethoxy (OC_2H_5), acetoxy ($OCOCH_3$), amine or chlorine that reacts with inorganic materials like metals, glass and silica [15, 16, 17]. R group can be non-functional or functional group. If R group contains an organo-functional group (can be Cl, F, CH_3 or C_2H_5), it enables to bond with organic resins and polymers and is preferable as an adhesion promoter.

Also the presence of some Si-alkyl groups in the molecular structure of silanes ensures low surface tension and good wetting properties [18, 6].

Silanes are normally stored in non-hydrolyzed state. Before application, to have sufficient Si-OH groups to interact with the metal substrate, silanes must be hydrolyzed according to 2.1 and 2.2 reactions. After some degree of hydrolysis in water, the hydrophilic Si-OH groups [19] occur in the silane solution. As van Ooij et al. pointed out, the silane solutions become workable once sufficient number of silanols generated [20]. In addition, Michele Fedel expressed that, only the hydrolyzed silane solution can lead to formation of strong covalent bonds with the metal substrate so it is necessary to have effectual numbers of Si-OH groups to interact with the metal substrate [9].

Hydrolysis

$$R-Si(OX)_3 + 3H_2O \quad \leftrightarrow \quad R-Si(OH)_3 + 3XOH \qquad \textbf{(2. 1)}$$

Condensation

$$R-Si(OH)_3 \quad \leftrightarrow \quad R-Si-O-Si-R + 3H_2O \qquad \textbf{(2. 2)}$$

Commercially important reactions can be mainly divided into two categories: hydrolysis and condensation like in the 2.1 and 2.2 reactions. The reactions proceed depending on the nature of the organo-silanes, age of the solution, water availability, pH, concentration and the surface to be coated. These factors also directly affect quality of silane films [9-6].

After a certain degree of hydrolysis of silane in water [21], the silane molecules contain hydrophilic Si-OH that are ready to react with metal surface also with each other. Xu Man [19] stated that the silane coating's performance degrades with solution aging. The condensation of neighboring Si-OH groups lead to the formation of crosslinked Si-O-Si in the solution. Due to fewer number of Si-OH groups in an aged solution, the silane-metal interaction decreases, resulting in fewer Me-O-Si bonds, leading to a poor corrosion resistance. Therefore, silane needs to be hydrolyzed until sufficient Si-OH concentration is obtained but complete hydrolysis is not required due to possibility of aging the silane solution.

2.2 Application of Silane Coating

Usually, silanes are applied from dilute water solutions onto the metal surface, also these solutions can be applied onto metal surfaces mostly by dipping or spraying [20]. Silane formulation is a promising technology for surface modification and corrosion resistance of several metallic substrates such as aluminum alloys, steels, galvanized steels, stainless steels [22], copper, zinc and for magnesium alloys [23].

Silane coating allows processing at ambient temperature. Since activation and passivation are not required, corrosion protection is achieved with fewer process steps and shorter treatment times compared to similar coatings. Hereby, less chemical, water and energy consume in comparison with the other coatings. However, it requires some crucial pre-treatment prior to silane coating like hydroxylation, which was described in detail at the next sections.

2.2.1 Process sequence of silane coating

Silane coating mainly consists of five steps. First step is degreasing for removing oil and solid particles from metal surface. Second step is hydroxylation to obtain Me-OH groups on metal surface; this step plays an important role because silane coating occurs only in presence of Me-OH groups on metal surface, and the hydroxyl groups on metal surface acts as an initiator for chemical reactions. Third step is rinsing to prevent chemistry carry over from previous to the next step. Fourth step is immersing into silane solution; when a metal part is immersed into silane solution, silane solution adsorbs on metal surface and wet layer formation occurs. At the final step, metal parts are cured in other words dried and polymerization takes place, by this step coating is completed.

2.2.1.1 Degreasing

Purpose of degreasing is to remove residual grease, oil, wax, dirt etc. to obtain a long lasting bond between silane and metal. During degreasing, all impurities, which include dirt, metal chips, metal dust, cooling oil and corrosion-resisting oil must be removed [24] because presence of these contaminants has a major drawback on quality of final product. A suitable pretreatment for substrates is necessary in order to obtain a satisfactory bond between silane and metal [21].

There are lots of degreasing methods such as halocarbon solvent vapor/immersion degreasing, acidic degreasing and alkaline degreasing [25]. Generally, hot aqueous alkaline cleaners are used for the removal of grease and chips from components to be coated at automotive industries. Influential parameters in an alkaline cleaner are:

- Type of basis metal
- Type and concentration of the cleaner
- Cleaner temperature
- Immersion time
- The conditions of use, i.e. immersion, ultrasonic/immersion, electrolytic (cathodic or anodic), spray.

Increasing the cleaner concentration, temperature, time of immersion, and use of electrolytic, ultrasonic or spray cleaning will all accelerate rate of cleaning. However, the concentration and alkalinity of a cleaner may have an adverse effect on the rate of cleaning. The recommended concentrations given for the various cleaners should not be exceeded. Operation at concentrations and temperatures higher than those recommended may result in loss of solubility of components of the surfactant system. The components will then float to the surface or sink to the bottom and the loss of detergency will be higher [26].

2.2.1.2 Hydroxylation

The composition and structure of the interfacial region of coatings play important roles in corrosion protection. For instance in silane coating; metal surfaces should have an appropriate structure for effective bonding. Modification of the interfacial region in silane process can be achieved by changing the surface structure chemically [27] with suitable hydroxylation process.

Hydroxylation is a chemical process that takes place in basic chemicals (alkalines) by yielding OH^- to the solution. For example, commonly known hydroxylation chemical; sodium hydroxide (NaOH; Figure 2.1) produces OH^- when it dissociates in water [28]. In addition, hydroxylation mechanism can be explained as follows; it is a alkaline process that produce hydrophilic -OH on a surface by *oxidizing* the surface.

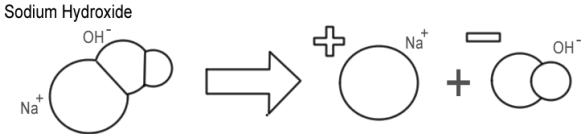


Figure 2.1: Sodium-hydroxide dissociation [28].

By oxidation, one of the main chemical reactions of corrosion occurs on the metal surface. When a metal is placed in aqueous solution, some ions will immediately pass into solution by oxidation [29]. In literature, *oxidation* and *rust* are used interchangeably and frequently. Also rust (corrosion) formation can be explained as the deterioration of a material due to interaction with its surroundings. For example; surface atoms of iron, dissolve in aqueous solution as ions, raising the oxidation state of the iron from 0 to II, leaving electrons as an excess charge in the metal [30].

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad \textbf{(2. 3)}$$

The electrons produced during the oxidation must be consumed in a reduction process such as reduction of dissolved oxygen:

$$\tfrac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \qquad \textbf{(2. 4)}$$

The balance of electrons between equations 2.3 and 2.4 produce Fe^{2+} and OH^{-} ions in the correct ratio for precipitation of soluble $Fe(OH)_2$:

$$Fe^{2+} + 2(OH)^{-} \rightarrow Fe(OH)_2 \qquad \textbf{(2. 5)}$$

Summing of the reactions 2.3 through 2.5 yields the complete process:

$$Fe + \tfrac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2 \qquad \textbf{(2. 6)}$$

In the other perspective; in alkaline solutions, the anodic reaction yields the unprotective soluble ion, Fe^{2+} as the primary anodic product, is not favored and is replaced by an alternative anodic reaction which converts the iron surface directly into a thin, dense, protective layer of magnetite, Fe_3O_4 [30]:

$$Anodic reaction: \quad 3Fe + 8OH^{-} \rightarrow Fe_3O_4 + H_2O + 8e^{-} \qquad \textbf{(2. 7)}$$

$$Cathodic reaction: \quad \tfrac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \qquad \textbf{(2. 8)}$$

According to Beverskog and Puigdomenech in the alkaline solutions; iron dissolves and forms ferrous and ferric anionic complexes; $Fe(OH)_3^-$, $Fe(OH)_4^{2-}$ and $Fe(OH)_4^-$ [40].

Y. Wang et al. [31] also explained that in neutral conditions, not many H^+ and OH^- ions are available for the metal surface reaction, leading to an reaction rate near zero. In mildly alkaline conditions, at pH of 9 to 11, OH^- ions react with Fe to form non-porous Fe_2O_3, which passivates the steel surface. The slight increase in reaction rate may be related to the different availability of oxygen in different pH environments. As the pH of the solution increases further to the strongly alkaline region, the soluble ferrite ion, $FeOOH^-$ is formed according to equation (2.9):

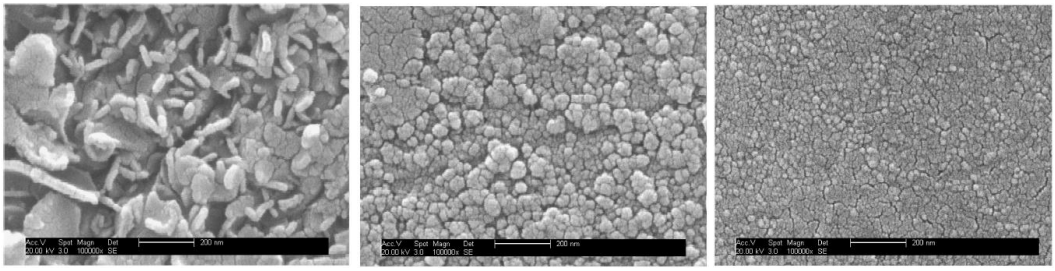
$$Fe + 2H_2O \rightarrow FeOOH^- + 3H^+ + 2e^- \quad \textbf{(2. 9)}$$

Fe_2O_3 and its hydrated product FeOOH are common surface products in aqueous solutions. According to the potential-pH diagram (Pourbaix Diagram) of iron in aqueous solutions, several reaction products are possible for steel over pH 9. Between pH 9-11 the thermodynamically stable species are oxides or hydroxides of iron. At higher pH (12-14) the corrosion product FeOOH dissolves [31].

The hydroxyl groups on metal surface play a vital role in some surface modifications because they are initiation sites for chemical reactions in surface modification process [37]. The adhesion and structure of the silane coating is very sensitive to the surface oxide and indirectly to the surface cleaning procedures for the metal substrate. Silane coating quality depends on the population of hydroxyl groups and their accessibility for bonding. If all hydroxyl groups are capped by silanes [38] and surface is effectively covered, a hydrophobic silane coated surface is achieved.

Y. Wang et al. [31] stated that the amount of hydroxyl groups on the metal surface is directly related to the hydroxylation conditions. In addition, these groups determine the anticorrosion performance of metals. Increasing number of hydroxyl groups lead to fine and dense morphology of surface oxides resulted in the most abundant number of bonds and a thicker silane film. Very different surface oxide morphologies are observed (Figure 2.2) on the steel processed under different pHs.

Loose and coarse surface oxide morphology was observed in strongly acidic conditions (pH 1.0), which may be related to the rapid dissolution of the Fe surface in strongly acidic conditions. A fine, dense and spherical surface oxide morphology was detected on the steel surface processed in alkaline conditions (pH 9.5 and 12.4), which suggests that the alkaline cleaning condition facilitates the formation of a fine and dense surface oxide layer.



a **b** **c**

Figure 2.2: Surface morphology of the CRS surface cleaned at different pH values by SEM. (a) pH 1.0, (b) pH 9.5 and (c) pH 12.4 [31].

Pourbaix diagram is a graphical presentation (Figure 2.3) of the thermodynamic equilibrium states of metal-electrolyte system. The diagrams are plotted in the axes electrode potential of metal versus pH of electrolyte.

However, the diagrams help us to make estimation about corrosion product, has some disadvantages such as;

- It considers only pure metals and aqueous solutions at standard conditions (temperature 25°C, pressure 1 bar, ion concentration 10^{-6} M),
- Thermodynamic conditions of corrosion for alloys and non-standard conditions differ from those described in Pourbaix diagrams [33].

Due to the limitations of Pourbaix diagrams, it is hard to estimate corrosion products of steels after hydroxylation process.

Just according to literature and Pourbaix diagrams it can be assumed that, after hydroxylation process, there could be Fe_2O_3, Fe_3O_4, $FeOOH^-$, $Fe(OH)_3^-$, $Fe(OH)_4^{2-}$, $Fe(OH)_4^-$ species on the steel surface depending on solution pH, temperature etc.

For further preferable precipitations of iron-hydroxides, the characteristics of the processes must be examined in detail at a separate study.

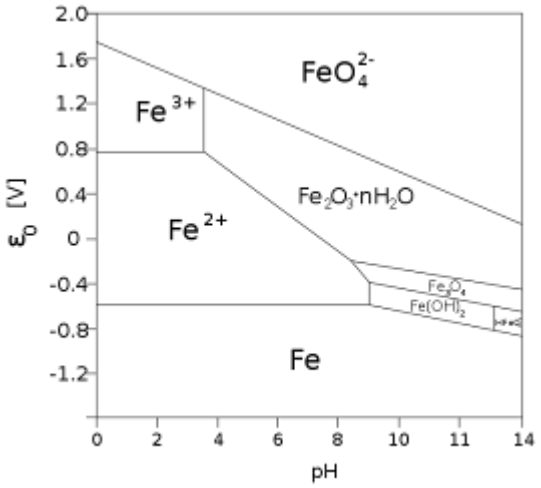


Figure 2.3: Simplified Pourbaix diagram for iron-water system at 25°C [34].

2.2.1.3 Silanization

If a metal part is immersed into silane solution, silane solution adsorbs on metal surface and wet layer formation occurs. The most widely accepted theory assumes that the linkage between the Si-OH and the Me-OH on the metal surface occurs through hydrogen bonding [8, 9, 20, 32].

This simplified schematic bonding mechanism is illustrated in Figure 2.4. Before condensation, silane molecules are adsorbed onto the metal surface through hydrogen bonds formed between Si-OH groups of the silane molecules and Me-OH groups of the metal hydroxides.

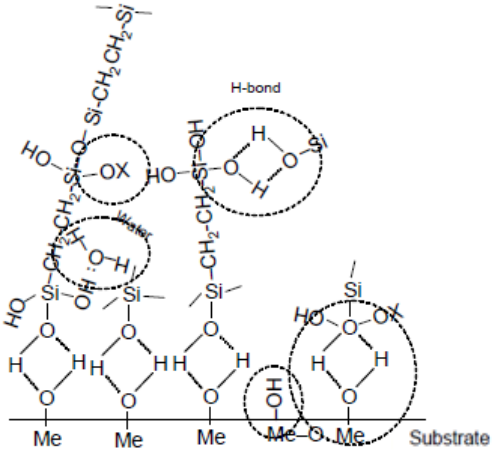


Figure 2.4: Schematic of bonding mechanism between silane molecules and metal surface hydroxide layer: before condensation hydrogen-bonded interface [10].

Concentration, pH, type of the silane, aging of the solution are the most important parameters in silane coating as mentioned previous sections. Franquet et al**.** [35] experimented effect of silane bath concentration and the results showed that an increase of the BTSE (bis-1,2-(triethoxysilyl)ethane) bath concentration induces the formation of a thicker layer (Figure 2.5). Increasing thickness due to increasing concentration improved corrosion resistance properties. It is obvious in Figure 2.6, the film resistance increases almost linearly with the BTSE bath concentration.

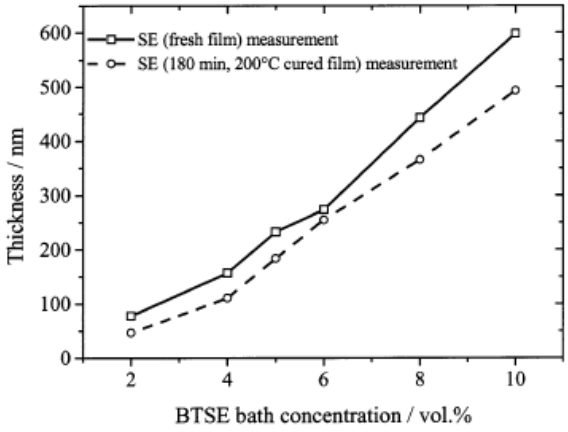


Figure 2.5: Evolution of the thickness determined by SE for silane fresh films and fully cured films as a function of the BTSE bath concentration [35].

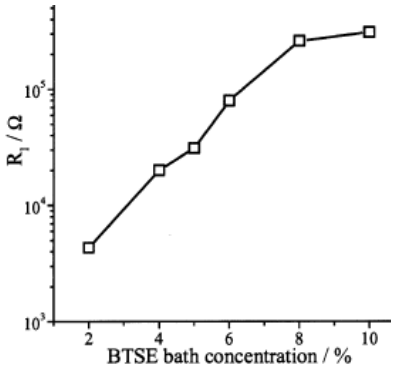


Figure 2.6: Variation of the film parameters for fully cured films (180 min/200°C) as a function of BTSE bath concentration [35].

2.2.1.4 Curing

It is generally assumed that there are two key condensation reactions occurring while curing the silane-treated metals. One is the condensation between Si-OH groups from the silane solution and the Me-OH groups from the metal surface hydroxides, forming covalent metallo-siloxane bonds (Me-O-Si) [36] according to 2.10 reactions also as seen in Figure 2.7. The other is the condensation among the

excess Si-OH groups adsorbed on the metals, forming a siloxane (Si-O-Si) film on the top layer according to 2.11 reactions [20].

$$SiOH_{(solution)} + MeOH_{(Metal\ surface)} \leftrightarrow SiOMe_{(interface)} + H_2O \quad \textbf{(2. 10)}$$

$$SiOH_{(solution)} + SiOH_{solution} \leftrightarrow SiOSi_{(silane\ film)} + H_2O \quad \textbf{(2. 11)}$$

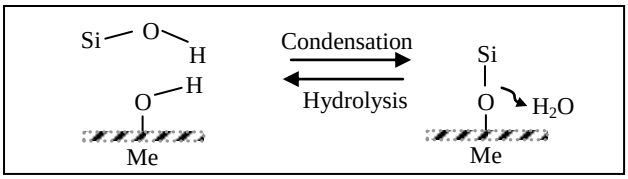


Figure 2.7: Schematic condensation of Si-OH group with Me-OH group on metal surface [39].

After condensation while curing, both Me-O-Si and Si-O-Si covalent bonds are seen at the interface [10] as shown in Figure 2.8, giving an excellent adhesion to the metal substrate, as well as a hydrophobic interface.

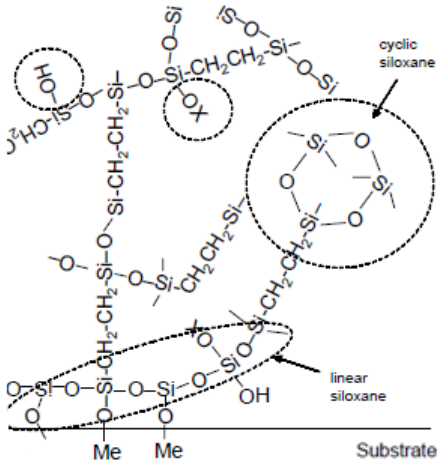


Figure 2.8: Schematic of bonding mechanism between silane molecules and metal surface hydroxide layer: after condensation covalent-bonded interface [10].

Fedel studied [9] on curing temperature effect on film characteristics, also confirmed bonding properties by thickness and contact angle measurements. The film cured at 180°C was thinner and denser compared to the film cured at 120°C. This can be explained by the fact that condensation reactions are promoted by heat.

The contact angle measurements showed that, at higher temperature treated silane film is slightly more hydrophobic compared to the film treated at lower temperature as seen in Table 2.1.

This can attribute to decreasing number of hydrophilic Si-OH groups with higher curing temperature.

Franquet et al. [35] obtained the same effect in their experimental study; decrease of the thickness of the fully cured silane films was noticed compared with fresh silane films containing the same BTSE concentration. However, the decrease of the thickness was around 20-30% for fully cured samples, less porous structure was obtained. Franquet et al. concluded that the curing step creates an important modification for the structure of the thin film. In other words, the condensation reactions lead to the formation of a less porous layer and higher barrier properties against corrosion.

Table 2.1: Silane films' thickness and hydrophobicity according to their curing temperature [7].

Sample	Thickness (Å)	Contact Angle (°)
Cured at 120°C	3000	61
Cured at 180°C	1000	67

2.3 Corrosion Protection by Silane Coatings

This thesis on silane coating is carried with the primary aim to replace phosphate coating process to obtain temporary corrosion protection. The corrosion protection property of silane coating is mainly gained by hydrophobic characteristics of the silanes. The most important criteria that affect hydrophobicity of silane is it's type especially it's hydrolysable groups.

Zucchi et al. [39] investigated the use of γ-aminopropyltriethoxysilane (γ-APS) and 1,2-bis[triethoxysilyl] ethane (BTSE) to form protective coatings on a magnesium–aluminum–zinc alloy that presents good possibility for the application in the automotive industry. They found that BTSE performed much better in terms of corrosion protection as compared with γ-APS in most cases as seen in Table 2.2 and Figure 2.9.

The major difference between these silanes is the number of hydrolysable OR groups. γ-APS has only three OR groups attached to a Si atom where the BTSE molecule has six OR groups in total attached to two Si atoms.

With more OR groups, it is possible to obtain a denser interfacial region through the metallo-siloxane and siloxane reactions. This dense hydrophobic interfacial layer plays a major role in the corrosion protection of metals.

Table 2.2: Salt spray test results of silane coated aluminum alloy 3003 after exposure for 336 h [39].

Treatment	Corroded area (%)
Blank	100±0
γ-APS 5%, pH 10.6	90±5
BTSE 5%, pH 6	15±5

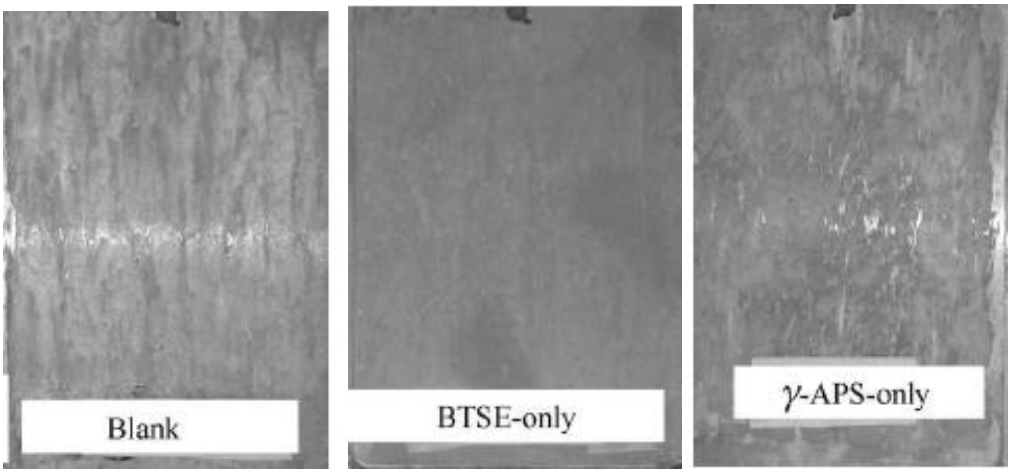


Figure 2.9: Panels of aluminum 3003 after 336 days in salt spray test [39].

One major drawback to the widespread use of silane films is that reversible characteristics of the hydrolysis reaction that allowed the formation of Si-O-Me bonds. The hydrolyzed bonds can re-form. This mechanism may weaken the coating's performance because of coating delamination [12].

Another drawback of silanes pointed out by Zhu [36] that, as compared with chromates, lack of self-healing effect that is very important in service. In reality, mechanical damage such as scratches and small spots on metal surfaces is common.

In the case of chromating, chromate ions can diffuse to the damaged area in an aqueous medium and restore protective compounds with the metal in-situ. Unfortunately, metallo-siloxane bonds are not reproducible in silane coating.

J. van Ooij et al. [12] suggested that the performance of silanes might be enhanced by having higher concentration of Si-O-Me bonds that are formed during condensation and film formation. As the result of this, denser film layer is obtained and reversible characteristics of the hydrolysis reactions may diminish.

The other disadvantages of silane coatings;

- Silanes are sensitive to the surface state of metals, and each silane treatment needs to be optimized individually for each metal applied.
- It is colorless; especially in industries, the coated and uncoated parts could be mixed with each other.
- Silane solutions have a limited lifetime because of reversible reactions [19].

Although silane coating has so many disadvantages, it is promising for temporary corrosion protection by means of its environmentally friendly and easy processing properties. Of course, most of these disadvantages can be overcome by optimizing the silane coating process.

3. EXPERIMENTAL STUDY

This chapter describes the materials, silanes and characterization methods used in this work. It also describes substrate preparation procedure, characterization techniques and performance testing methods. The main objective of the experimental study is to understand silane process mechanism and defining effect of hydroxylation step on coating quality. Experimental procedure of this study was schematized in Figure 3.1.

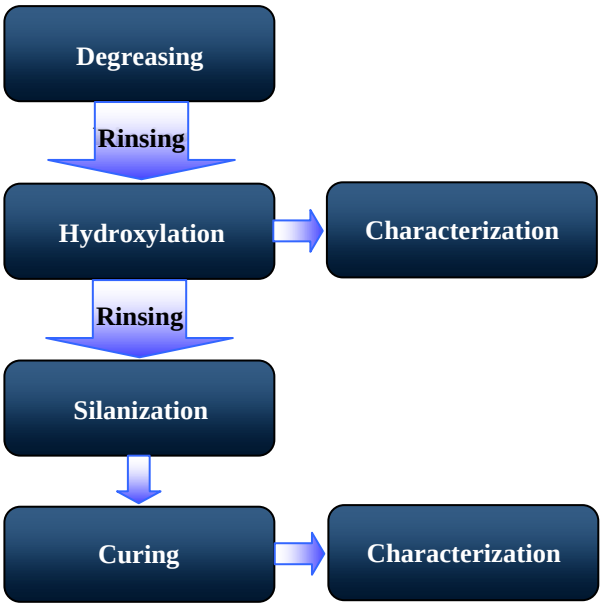


Figure 3.1: Flow chart of experimental procedure

3.1 Materials and Experimental Details

In this study DIN/EN 50CrMo4 (AISI 4150) steel sheets, (chemical composition is as given in Table 3.1) were used as substrate material.

Table 3.1: Nominal chemical composition of 50CrMo4 steel [43]

Chemical Composition (Typical analysis in %)	**C**	**Cr**	**Mo**	**Mn**	**Si**
	0,46-0,54	0,9-1,2	0,15-0,30	0,5-0,8	max. 0,4

50CrMo4 steel is an outstanding material for high-pressure application in diesel injection system. It is mostly used in components for vehicles, engines and machines where both static and dynamic stresses present [42].

3.1.1 Surface pre-treatment

In order to prepare samples for silane coating, all of the substrates were ultrasonically degreased in an alkaline cleaning solution to remove protective oil, grease which come from production process, also handling grease and fingerprints [21], dirt and chips from the surface.

For modification of the interfacial region, as Y. Wang et al. [31] suggested that the alkaline cleaning condition facilitates the formation of a fine and dense surface oxide layer, substrates were hydroxylated in alkaline solutions (Gardoclean®, provided by Chemetall or sodium hydroxide pellets, provided by Merck). As Y. Wang et al. [31] obtained best performance in NaOH solution at pH≈10-11, NaOH pellets were used to make comparison with commercial chemical. Substrates were immersed in the hydroxylation solutions using different concentrations, times and temperatures as given in detail in Table 3.2. After that, samples were immersed in DI water to eliminate chemical carry over to the next step (silanization).

As for design of experiment (DOE) minimum 1%, maximum 8% concentration values and min. 30 sec., max. 480 sec. were selected (Samples from 1 to 5). To see deviations from center point of DOE (4.5% concentration and 255 seconds), different temperature value (45°C) and chemicals (NaOH) were tested. Additionally untreated, uncoated, only hydroxylated only silane coated parts were analyzed.

Table 3.2: Experimental parameters

Substrate code	Concentration (v/v %)	Time (Second)	Temperature (Celsius)	Chemical	Silane
0	0	0	0	-	Uncoated
1	1	30	75	Gardoclean	Coated
2	8	30	75	Gardoclean	Coated
3	4.5	255	75	Gardoclean	Coated
4	1	480	75	Gardoclean	Coated
5	8	480	75	Gardoclean	Coated
6	4.5	255	45	Gardoclean	Coated
7	0.8	255	75	NaOH-pellet	Coated
8	0	0	0	-	Coated
9	4.5	255	75	Gardoclean	Uncoated

3.1.2 Silane solution preparation and silanization

Silane solution was prepared by adding 15 % silane (Oxsilan®, Chemetall) to a mixture of DI water and hydrophobic additive (OSA 9970/1®, Chemetall). Before application on substrates, silane solution was hydrolyzed at least 1 hour to obtain sufficient Si-OH groups for interacting with the metal substrate. The pH value of the solution was continuously controlled and regulated accordingly by high alkaline chemical (Oxsilan-Additive 9934®, Chemetall) or acetic acid. Also the solution was stirred continuously to prevent polymerization in the solution. The duration of silanization was kept constant (2 minutes) in all the experiments.

3.1.3 Curing of the samples

Before optimizing the hydroxylation parameters, it was important to fix the curing parameters (time and temperature). After preliminary tests, the curing temperature and the curing duration was fixed as 160° C and 45 minutes respectively. During silanization Si-OH groups adsorbed weakly onto metal hydroxides via hydrogen bonds. Upon curing at 160°C for 45 minutes, Si-OH groups and Me-OH groups condense to form Me-O-Si or Si-O-Si covalent bonds on the metal surface. At the final step curing, cross-linked silane film was produced on metal substrates.

3.2 Characterization Methods

3.2.1 Salt spray test (SST)

SST is cheap, easily applicable and quick test method that I widely used for the determination of corrosion properties of both metals and coatings. In spite of its advantages, it has some bottlenecks in evaluation of the results such as weak correlation between duration of SST and the expected life of surface treated parts [42], results are not quantitative and they can be subjective. Nevertheless, this method is preferred indispensably in automotive industry.

In the ASTM standards (ASTM B117) it is clearly written that, the standard does not describe the type of samples, the exposure time for a given product or the procedure for interpreting the results. Therefore, it is necessary to define sample preparation, test duration and validation criteria in agreement with requests from customer.

The test was performed by Erichsen Corrosion Testing Apparatus for Salt Spray Tests Model 606/400 (see Figure 3.3). The metal substrates were exposed to salt vapor containing 50±5g/l salt for 5 hours at 35°C in the chamber at an angle of 20 degree and after the test the surface of the substrates were photographed and evaluated according to inspection method sheet of Bosch. In the frame of this thesis, evaluating and calculating the rust level (Ri) of the parts was performed in accordance with Bosch Standard N42 AP 013 (Figure 3.4), where permissible rust level is Ri $\leq$ 3.

Figure 3.2: Erichsen Corrosion Testing Apparatus for Salt Spray Tests

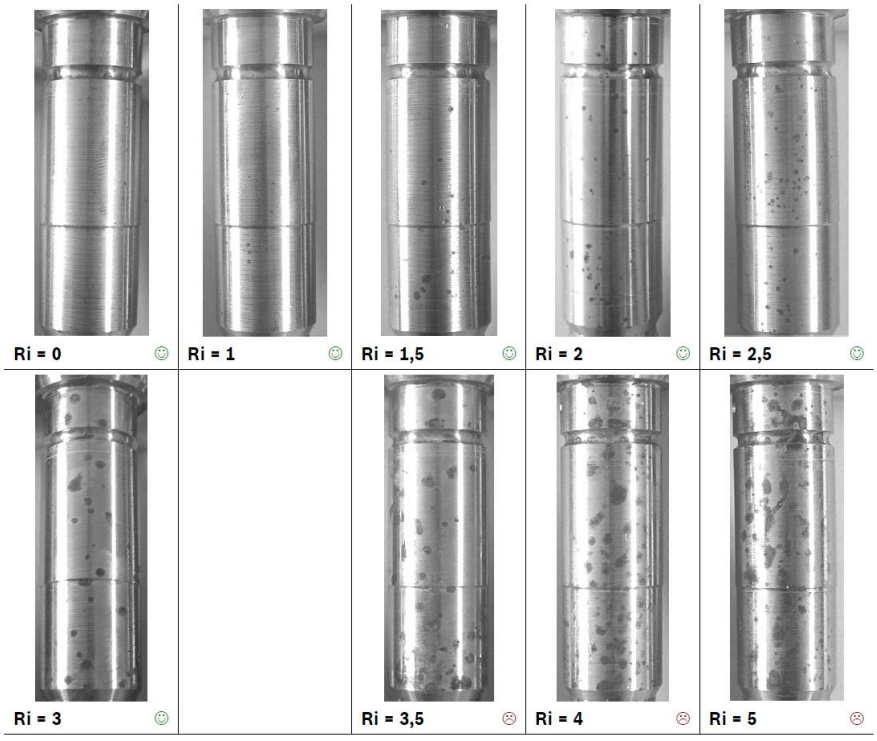


Figure 3.3: Image catalog of Bosch standard N42 AP 013 used for evaluating the rust level in injector bodies after the salt spray test [44]

3.2.2 Contact angle

In this study, wettability of silane coated steel parts was determined by contact angle measurements. The wettability of the metal surfaces is an important factor for determination of corrosion tendency. When the test liquid wet the surface easily, the angle between the liquid and the surface will be low and the substrate will show low corrosion protection performance. It is known that under identical conditions, the difference in corrosion performance is related closely to surface wettability [41]. Considering the correlation between contact angle measurement and corrosion performance, the contact angle measurements were done in order to support and verify salt spray test result.

The measurements were performed by KSV CAM 200 Contact Angle and Surface Tension Meter (Figure 3.5). In all measurements; as light phase air and as heavy phase distilled water were used. The distilled water drop's volume was 5µl and the angle measurements calculated after 10 seconds, 2 minutes and also 10 minutes residence time of droplets on the substrate's surface. Behavior of the droplets was followed according to three different residence time and hydrophobicity/wettability of the surfaces was evaluated.

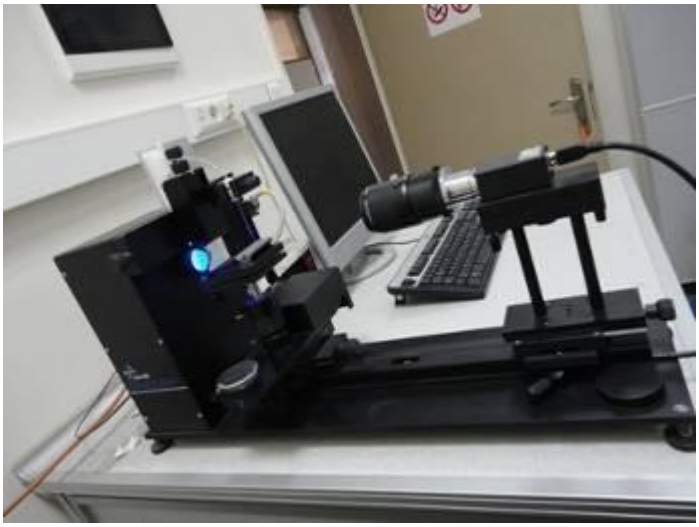


Figure 3.4: KSV CAM 200 Contact Angle and Surface Tension Meter

3.2.3 Copper decoration

Porosity determination of the silane coated substrates was performed by copper decoration method. The coated substrates were immersed into 1% copper sulphate solution for 60 seconds duration. In this decoration technique [45], copper ions get

reduced and cement on pores that are extending through the surface layer by consuming the electrons produced through the corrosion of the substrate (in our case steel).

After the decoration, the samples dipped into DI water then dried. Firstly, samples' surfaces were inspected visually against any discoloration. Lastly, they were examined using LEICA DM4000M optical microscope.

4. RESULTS AND DISCUSSION

4.1 Salt Spray Test Results

The metal substrates were exposed to salt spray for 5 hours at 35°C, after the test surface of the substrates were evaluated according to the inspection method of Bosch.

SST results showed that the part hydroxylated in commercial hydroxylation chemical (sample 3) exhibited better corrosion resistance compared to part hydroxylated in NaOH solution (sample 7) (see Figure 4.1). When they were evaluated according to Ri scale; sample 7 is Ri level 3 and sample 3 is Ri level 1. It is believed that the difference between NaOH and commercial chemical occurred due to the presence of wetting and oxidizing agents in commercial chemical.

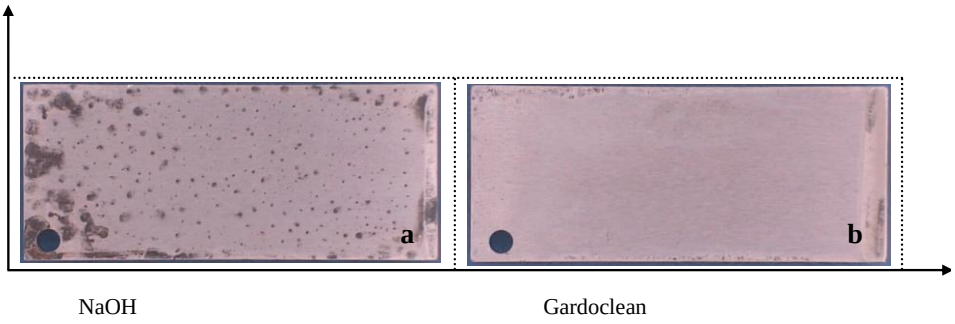


Figure 4.1: Salt spray result of silane coated samples hydroxylated in different chemicals; (a) Sample 7 (hydroxylated in NaOH solution for 255 seconds, pH 11±0,5), (b) Sample 3 (hydroxylated in Gardoclean solution for 255 seconds, pH 11±0,5).

To understand the importance of hydroxylation step, uncoated sample and coated sample without hydroxylation were compared (Figure 4.2). As Wang Y. et.al stated the steel surface is very sensitive to pretreatment process [8] and it is clear that without hydroxylation, silane does not bond to the substrate effectively.

The coated sample without hydroxylation acted like uncoated sample with Ri level>5.

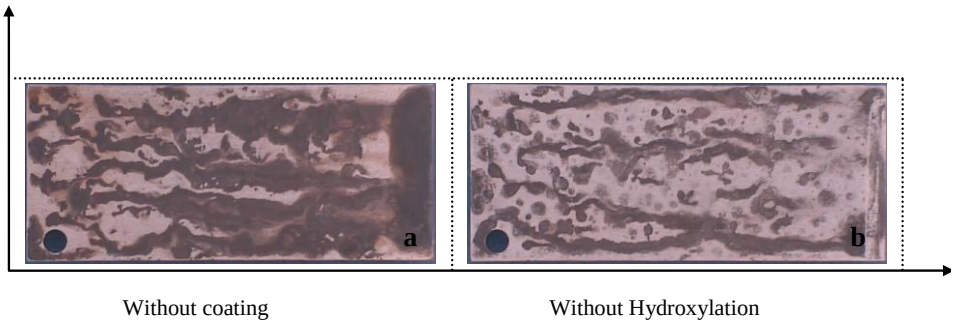


Figure 4.2: Salt spray result of samples; (a) Sample 0 (uncoated), (b) Sample 8 (silane coated without hydroxylation).

Contrary to expectations the 30ºC temperature difference in hydroxylation, did not cause a big difference in corrosion performance. However, the sample hydroxylated at 45ºC was evaluated as Ri level 2,5 and the sample hydroxylated at 75ºC as Ri level 1 (Figure 4.3).

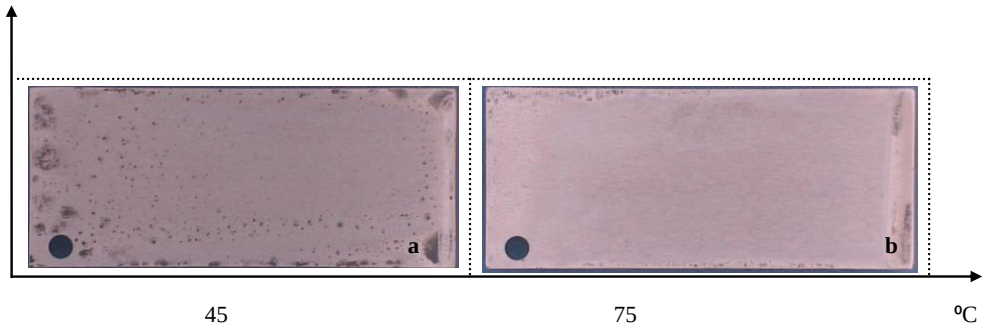


Figure 4.3: Salt spray result of samples; (a) Sample 6 (4.5% and 255 second hydroxylated at 45°C), (b) Sample 3 (4.5% and 255 second hydroxylated at 75°C).

Finally, considering the hydroxylation concentration and time; it is observed that increasing duration is more effective than concentration increase on the corrosion resistance.

In a set of experiments conducted by varying concentration of the solution and the duration it is observed that duration of the process should be min 255 sec. for a solution with 4.5 vol% (Figure 4.4).

Even though we can achieve good corrosion resistance for solutions above 4.5 vol%, concentration, we selected minimum concentration that gave good resistance for economical reasons.

Considering industrial importance of cycle time and costs, it is sufficient to work at optimized parameters when demanded corrosion resistance is obtained.

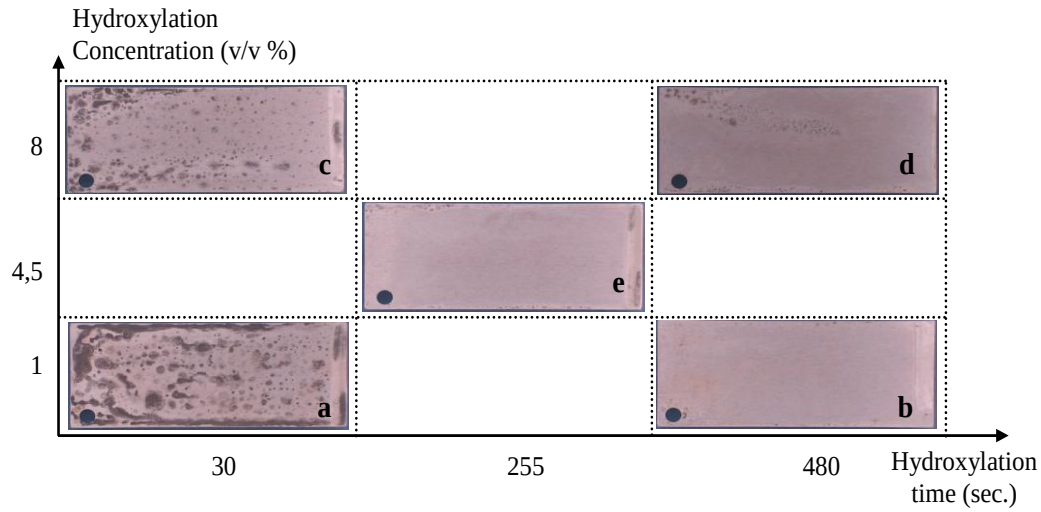


Figure 4.4: Salt spray result of silane coated samples; (a) Sample 1 (1% and 30 seconds hydroxylated), (b) Sample 4 (1% and 480 seconds hydroxylated), (c) Sample 2 (8% and 30 seconds hydroxylated) , (d) Sample 5 (8% and 480 seconds hydroxylated), (e) Sample 3 (4,5% and 255 seconds hydroxylated).

4.2 Contact Angle Results

The contact angles of both hydroxylated and silane coated samples were measured to evaluate hydrophobicity and also porosity of the substrates depending on 10 seconds, 120 seconds and 600 seconds residence time of the drop.

The experimental results highlight that all the silane coated parts are hydrophobic with angle 105^{o} more or less (see Appendix A).

There were only small differences between silane parts that are hydroxylated at different parameters. For example the part hydroxylated in 4,5% Gardoclean for 255 seconds is a little more hydrophobic (average angle 107^{o}), than the part hydroxylated in 1% Gardoclean for 30 seconds (average angle 104^{o}).

With increasing concentration of hydroxylation solution from 1% to 8% the hydrophobicity, hence the corrosion property was not affected at a great extent as seen in Figure 4.5.

Duration of hydroxylation is more influential parameter on corrosion resistance than hydroxylation concentration (Figure 4.6) as observed in SST results.

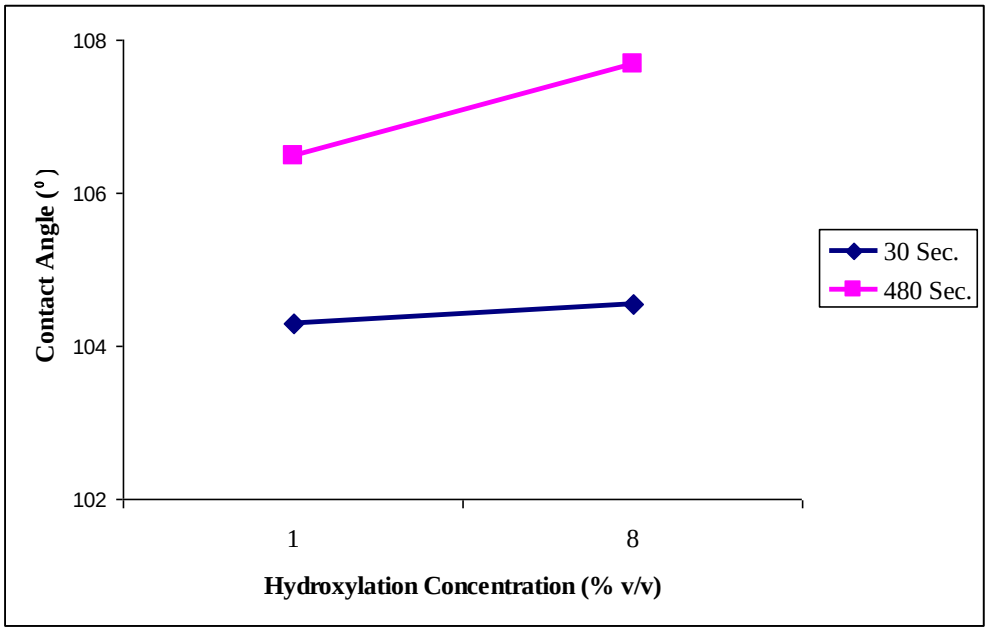


Figure 4.5: Contact angle results of silane coated samples depending on hydroxylation concentration (samples hydroxylated for 30 or 480 seconds).

According to residence time of droplets on silane coated samples, the contact angles decreased as expected (Figure 4.7, Figure 4.8 and Figure 4.9). These results proved that again silane coating is a porous structure, and only provides short-term corrosion resistance.

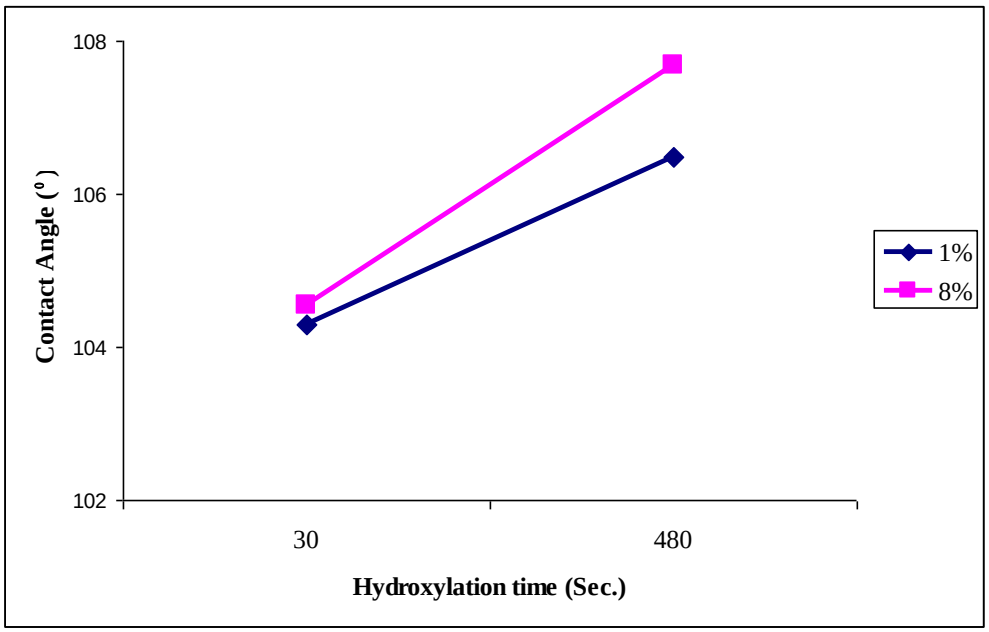


Figure 4.6: Contact angle results depending on hydroxylation time (samples hydroxylated in 1% and 8% concentration).

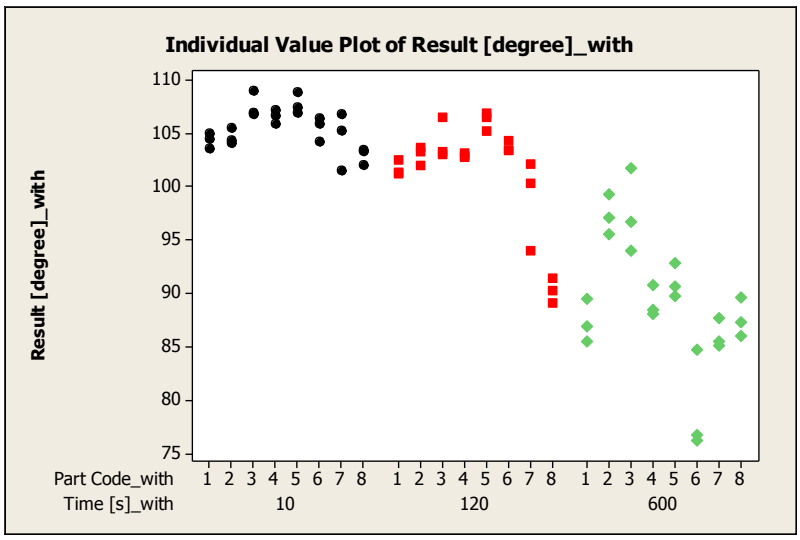


Figure 4.7: Contact angle –residence time results of all silane coated samples

Even though the corrosion resistance as determined with SST is low the contact angle result at 10 seconds measurement of sample 8 (silane coated without hydroxylation) is as high as silane coated samples with hydroxylation step. Even without hydroxylation step, the sample had a weakly bonded hydrophobic silane as a result of immersing into silane solution. Only superficially and weakly bonded silane film occurred due to absence of active hydroxyl groups, which provide effective silane bonding. That is why 10 seconds contact angle measurement show good result, unlike SST (Ri level>5). In addition, contact angle decrease with increasing residence time from 10 seconds to 120 seconds at sample 8 is higher than others, which support this result (see Figure 4.9).

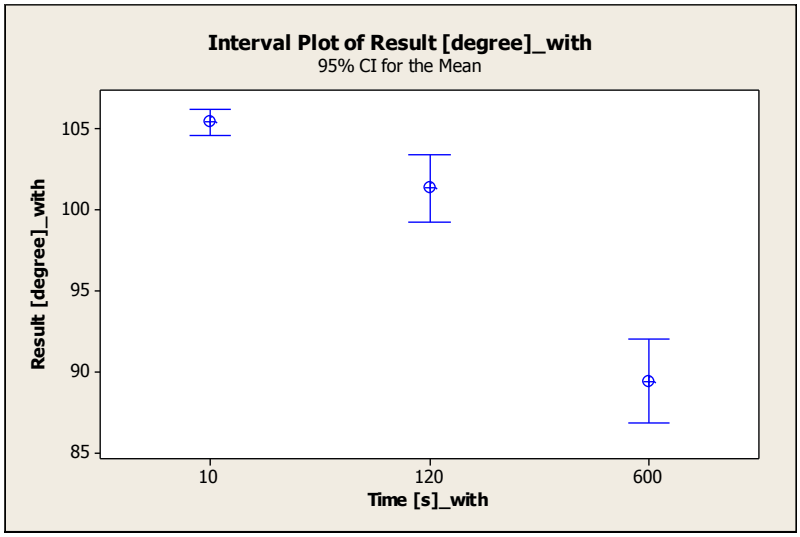


Figure 4.8: Average contact angle results of all silane coated samples according to residence time.

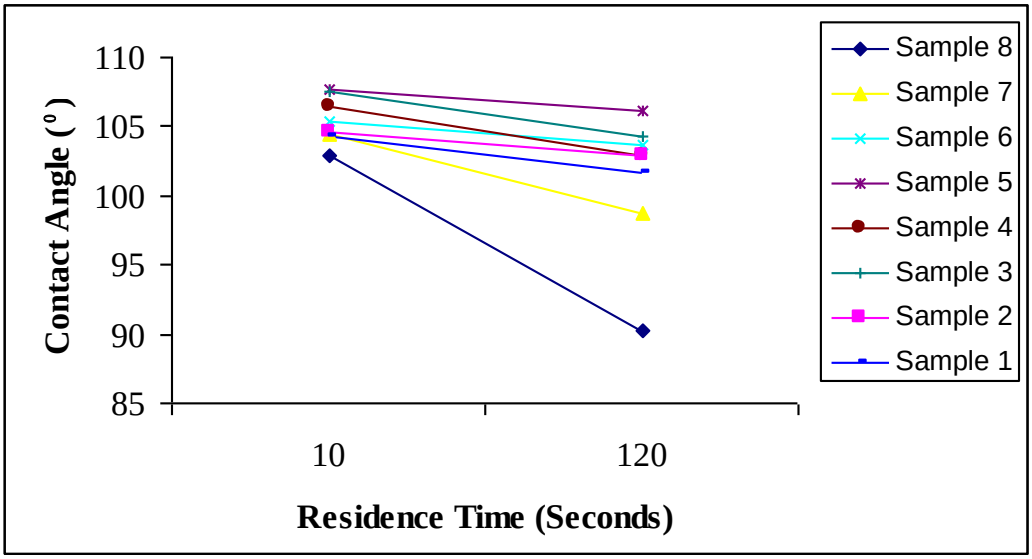


Figure 4.9: Contact angle results of hydroxylated and/or silane coated parts depending on residence time of droplets.

When silane coated parts and only hydroxylated parts were compared; hydrophilic hydroxylated surface could be clearly noticed as seen in Figure 4.10 and Figure 4.11. By means of hydrophilic Me-OH groups, the hydroxylated surfaces have averagely 30° contact angle value.

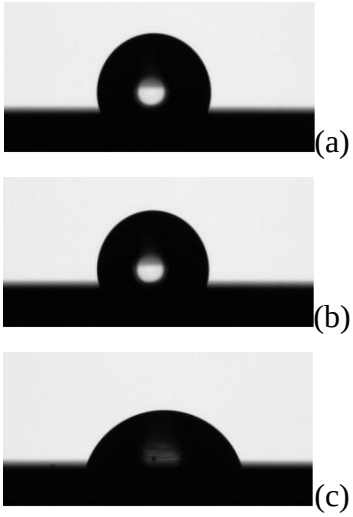


Figure 4.10: Contact angle photo of silane coated part (4.5% and 255 seconds hydroxylated and silane coated) (a) after 10 seconds, (b) after 120 seconds and (c) after 600 seconds.

Figure 4.11: Contact angle photo of hydroxylated part (4.5% and 255 seconds).

In comparison of the samples hydroxylated in different chemicals; it was obvious that hydroxylation in commercial chemical yields higher contact angle (Figure 4.12).

As explained in SST results, it was considered that the difference between NaOH and commercial chemical occurred due to content of rich wetting and oxidizing agents in commercial chemical.

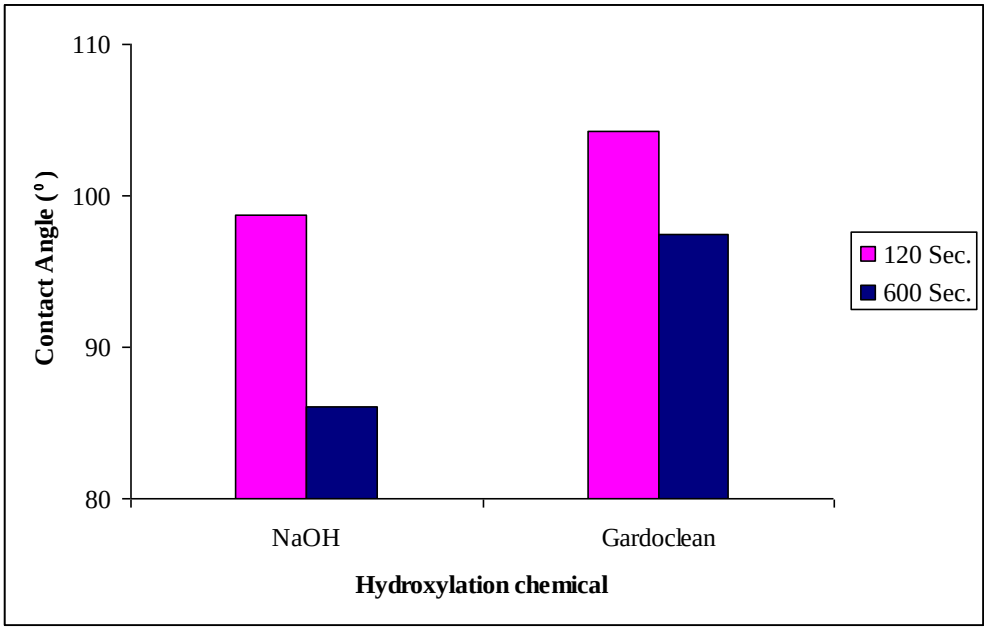


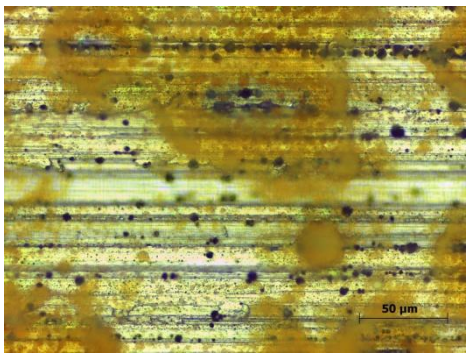
Figure 4.12: Contact angle results depending on hydroxylation chemical (120 and 600 seconds droplet residence time).

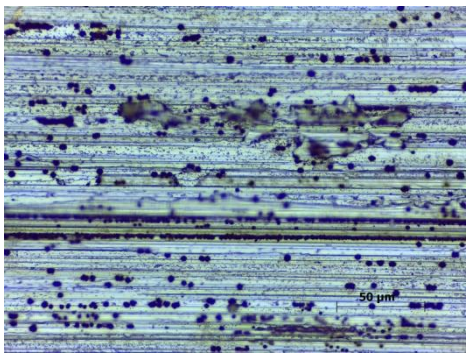
4.3 Copper Decoration Results

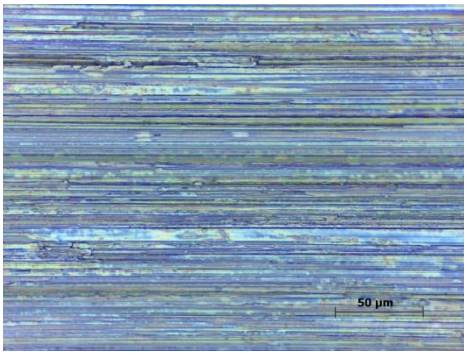
The copper decoration method was performed in order to evaluate homogeneity and porosity of the samples. After the decoration test, all of the silane coated parts (Part no: 1-7 hydroxylated in commercial solution) showed no obvious discoloration, However the importance of hydroxylation step could be clearly seen in Figure 4.13.

Intensive copper-precipitates and discoloration were observed on the uncoated sample and coated sample without hydroxylation step. These results are in accordance with the SST results.

It confirmed again that sample without hydroxylation step behaved like uncoated part and did not have enough corrosion resistance, even it was silane coated.



(a)


(b)


(c)

Figure 4.13: Optical photographs of (a) Sample 0 (untreated), (b) Sample 8 (silane coated without hydroxylation) and (c) Sample 3 (4.5% and 255 seconds hydroxylated and silane coated) after copper decoration.

5. CONCLUSIONS AND FUTURE WORK

The present study focused on the effects of concentration, duration and chemical type of the hydroxylation step on the corrosion performance of silane coated 50CrMo4 steels. The following conclusions can be drawn from the results obtained in the study.

5.1 Conclusions

1) SST study showed that the most effective parameter of hydroxylation step is duration to obtain a satisfactory corrosion protection. Samples hydroxylated in commercial chemical exhibited better corrosion resistance compared to the samples hydroxylated in NaOH solutions. It is believed that presence of wetting and oxidizing agents in commercial chemical is the reason for the observed difference.

2) It is clearly shown that, silane does not bond to the substrate effectively without hydroxylation step. The coated sample without hydroxylation acted like untreated sample in SST.

3) The contact angle results highlighted that all the silane coated parts are hydrophobic with angle $105^{o} \pm 3$. With the increasing concentration of hydroxylation solution the hydrophobicity, hence the corrosion property was not affected to a great extent. Contact angle measurement confirmed that duration of hydroxylation is a more critical parameter on corrosion resistance than hydroxylation concentration. According to the residence time of droplets on silane coated samples, the contact angles decreased as expected: this proved that again silane coating is a porous structure, and only provides short-term corrosion resistance.

4) The copper decoration test gave no comparable results for the silane coated samples. However, the importance of hydroxylation step could be easily seen on the optical photographs: intensive copper-precipitates and

discoloration were observed on the untreated sample and coated sample without hydroxylation step.

5.2 Future work

Investigation of the barrier properties of silane coatings should be done via potentiodynamic techniques to obtain detailed information about corrosion performance.

The silane-metal interface mechanism could be determined with the help of spectroscopic methods and improved according to hydroxylation and silanization parameters.

Accurate techniques should be found to measure thickness of silane coatings especially to understand the correlation between thickness and corrosion properties.

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APPENDICES

APPENDIX A: Tables

APPENDIX A

Table A.1: Contact angle results after 10 seconds

Substrate Code	First Measurement	Second Measurement	Third Measurement	Average
0	67,9	72,77	68,12	70,335
1	104,96	104,45	103,48	104,297
2	103,99	104,23	105,44	104,553
3	106,8	106,84	108,9	107,513
4	105,81	106,55	107,08	106,48
5	106,85	107,43	108,76	107,68
6	105,84	106,37	104,11	105,44
7	101,47	105,17	106,75	104,463
8	103,2	101,99	103,37	102,853
9	33,39	30,42	34,6	31,905

Table A.2: Contact angle results after 120 seconds

Substrate Code	First Measurement	Second Measurement	Third Measurement	Average
1	102,51	101,2	101,29	101,667
2	103,29	103,62	101,95	102,953
3	103,25	103,04	106,46	104,25
4	103,19	102,69	102,93	102,937
5	105,23	106,92	106,47	106,207
6	104,26	103,42	103,36	103,68
7	100,26	102,09	93,93	98,76
8	91,4	90,2	89,13	90,2433

Table A.3: Contact angle results after 600 seconds

Substrate Code	First Measurement	Second Measurement	Third Measurement	Average
1	85,47	89,41	86,89	87,2567
2	97,12	99,29	95,52	97,31
3	101,76	93,96	96,73	97,4833
4	88,03	90,7	88,43	89,0533
5	89,7	90,62	92,86	91,06
6	76,21	76,69	84,72	79,2067
7	85,02	85,44	87,61	86,0233
8	87,32	86,02	89,63	87,6567

CURRICULUM VITAE

Name Surname: Duygu Şadıllıoğlu

Place and Date of Birth: Zonguldak 02.09.1987

Address: 100. Yıl Mah. Prof. Dr. Erdal İnönü Cad. Eylül Sitesi C Blok Daire 9
Nilüfer/Bursa

E-Mail: duygu.sadillioglu@tr.bosch.com

B.Sc.: Dokuz Eylül University - Metallurgical and Material Science Engineer

Professional Experience: Bosch Tic. ve San. 2010-

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- Lippman, N., Martin, A., Şadıllıoğlu, D., 2011: *1st Surface Treatment Symposium- Silanization Process as Temporary Corrosion Protection for High Pressure Resistant Components in Diesel Injection Systems*, June 15-18, 2011 İstanbul, Turkey.