

Surface Science of the adhesion of an alkyd paint to a low carbon aluminium killed steel

by

Pheladi J. Mohlala

Submitted in partial fulfillment of the requirements for the degree

**Philosophiae Doctor
Chemistry**

in the Faculty of Natural Sciences
North-West University
Potchefstroom Campus

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LIST OF ABBREVIATIONS

LCAK :	Low carbon aluminum killed
XPS:	X-ray photoelectron Spectroscopy
FTIR:	Fourier Transform Infrared
ATR:	Attenuated Total Reflectance
SEM:	Scanning Electron Microscopy
EDS:	Energy Dispersive Spectrometer
BATE:	Boric Acid Trymethyl Ester
DN:	Donor Number
AN:	Acceptor Number
VCG:	Van Oss, Chaudhury and Good
IEP:	Iso-electric Point
BE:	Binding Energy
DFT:	Density Functional Theory
PMMA:	Poly(Methyl Methacrylate)

ABSTRACT

An important factor in achieving maximum adhesion of a particular coating system to the substrate lies in the proper pre-treatment of the substrate prior to the application of the coating. The Lewis acid-base properties of the outer metal surface play a determining role in many of these applications, and the chemical reactions involved therein. In this work, the Lewis nature of the low-carbon aluminium-killed (LCAK) substrate has been significantly modified by a chemically activated surface pre-treatment. The wetting properties of the LCAK substrate was determined by contact angle measurements; the coordination of the chemical species on the surface was studied with XPS; FTIR together with the probe molecule $\text{B}(\text{OCH}_3)_3$ was used to explain the chemical bonding on the surface. The novel combination of contact angle, XPS, FTIR and probe molecule enabled the determination of the Lewis acid-base properties of the LCAK surface before coating. The XPS spectra of the LCAK surface rinsed in warm water show that the surface species differ from that rinsed in tap water. With change in pH the wettability properties also drastically changed. The probe molecule $\text{B}(\text{OCH}_3)_3$ did not bond to the warm water rinsed samples but bonded strongly to tap water rinsed samples as the pH decreased. In this study, the adsorption strength of oxygen and water to Fe (110) surfaces was investigated using Cambridge Sequential Total Energy Package (CASTEP) as applied in the Material Studio Software Package. This study gave theoretical information of the adsorption strength of water and oxygen to Fe surfaces and may be the first step in examining the adhesiveness of these compounds on Fe surfaces.

This research has shown that Lewis acid-base properties can be significantly changed with water temperature and pH, which has important implications for industrial pre-treatment.

SAMEVATTING

'n Belangrike faktor wat die hegting van 'n bedekkingsisteem op die substraat bepaal, is die behoorlike voorafbehandeling van die substraat voor aanwending van die deklaag. Die Lewis suur-basiseienskappe van die buitenste metaaloppervlak speel 'n bepalende rol in baie van hierdie toepassings en die chemiese reaksies betrokke daarby. In hierdie projek is die Lewis-aard van die lae-koolstof aluminium-gedempde (LKAG) substraat beduidend gemodifiseer deur dit vooraf chemies te behandel. Die benattingseienskappe van die LKAG-substraat is bepaal met kontakhoekmetings; die koördinasie van die chemiese spesies op die oppervlak is gemeet met XFS; FTIR is saam met die tastermolekuul ($B(OCH_3)_3$) gebruik om chemiese binding te bestudeer. Die unieke kombinasie van die XFS, FTIR en tastermolekuul het dit moontlik gemaak om die Lewis suur-basiseienskappe van die LKAG-substraat te bestudeer voor dit bedek is. Die XFS-spektra van die LKAG-substraat wat met warm water afgespoel is, toon dat dit verskil van dié wat in kraanwater gewas is. Verandering in pH het ook die benatbaarheid van die oppervlak drasties verander. Die tastermolekuul ($B(OCH_3)_3$) het nie met die monsters wat met warm water afgewas is, gebind nie, maar het wel sterk gebind met monsters wat in kraanwater afgespoel is namate die pH verlaag het. In hierdie studie is die adsorpsiesterkte van water en suurstof op Fe(110)- oppervlakke bestudeer met die "Material Design, MedeA-VASP"-sagteware. Die studie toon teoretiese inligting oor die adsorpsiesterkte van water en suurstof op Fe-oppervlakke en kan die eerste stap wees in die evaluering van die klewerigheid van hierdie komponente op Fe-oppervlakke.

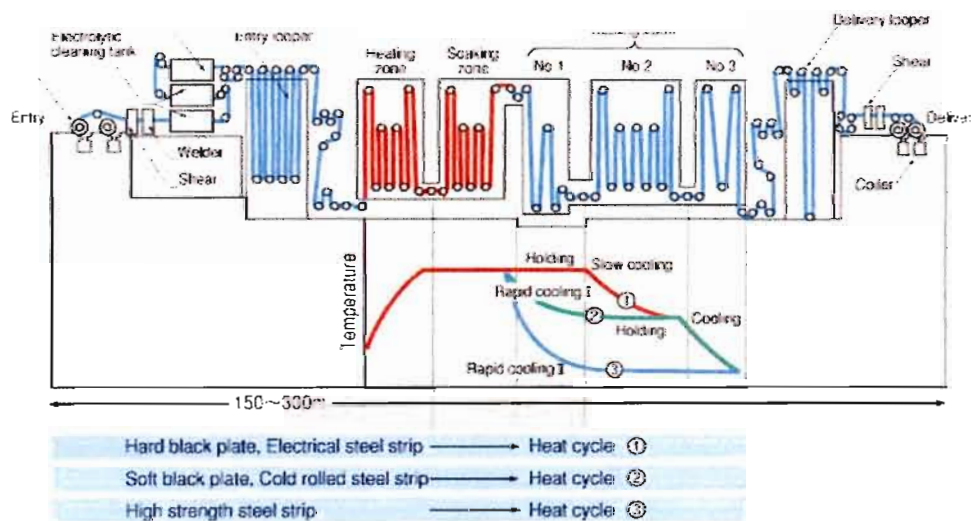
Hierdie navorsing het getoon dat die Lewis suur-basiseienskappe beduidend kan verander word deur watertemperatuur en pH te verander, wat belangrike implikasies inhou vir industriële voorafbehandeling.

CHAPTER 1: INTRODUCTION

1.1 Problem statement and substantiation

The application of formic acid on the delivery looper, causes complications (e.g. corrosion, contaminating other steel products, health and safety issues) during the continuous annealing of steel as experienced by ArcelorMittal SA in their annealing lines (Figure 1-1), [Kawasaki steel, 2003]. The elimination of the formic acid from the final cooling stage could result in the formation of a Lewis base steel surface, which will need a Lewis-acid paint for good adhesion. An in depth study to clarify the Lewis acid-base properties with respect to paint adhesion will be of great value to the steel industry as well as the coating industry.

3C(5) Continuous Annealing Line and Example of Heat Cycles



Ref: "Fusion of the Steel Industry" (Kawasaki Steel) (2003)

Figure 1-1: Schematic representation of a continuous annealing line at Kawasaki steel [Kawasaki steel, 2003].

Steel material hardens after cold rolling due to the dislocation tangling generated by plastic deformation. Annealing is therefore carried out to soften the material. The annealing process comprises heating, holding of the material at an elevated temperature (soaking), and cooling of the material. Heating facilitates the movement of iron atoms, resulting in the disappearance of tangled dislocations and the formation and growth of new grains of various sizes, which depend on the heating and soaking conditions.

The annealing of cold rolled coils has conventionally been conducted by grouping and annealing the coils in batches stacked in a bell-type furnace. This process is called batch annealing. However, continuous annealing is now more commonly used. This type of annealing involves uncoiling, and welding strips together, passing the welded strips continuously through a heating furnace, and then dividing and recoiling the strips. Figure 1-1 shows a continuous annealing line [Kawasaki steel, 2003], which is composed of the entry-side equipment, furnace section, and delivery-side equipment. The delivery equipment comprises a delivery looper, shears, and coilers, and may be linked to a temper rolling mill and plating equipment as part of a larger continuous line.

In this PhD project, various aspects of steel substrate pre-treatment after continuous annealing, the surface chemistry thereof and adhesion mechanisms will be investigated by means of XPS, contact angle measurements, FTIR and molecular modelling. In particular, a Lewis acid-base theory approach will be used to simulate compatibility of organic coatings to different pre-treated steel samples. Emphasis will also be given to the formation mechanism of Lewis acid-base interactions between the steel substrate and the organic coatings.

It has been demonstrated that XPS and contact angle measurements can be used to characterise industrially produced steel surfaces [Mohlala and Strydom, 2007].

The results above will be combined with the study of the organic coatings and probe molecules so that adhesion properties could be evaluated. Molecular modelling techniques will also be used to determine the orientation of species on oxygenated and deoxygenated steel surfaces.

This project's main purpose is to use the adhesion or no adhesion of alkyd paint to a treated low-carbon aluminium-killed (LCAK) surface (steel deoxidised with aluminium in order to reduce the oxygen content to a minimum so that no reaction occurs between carbon and oxygen during solidification) to test whether the Lewis acid-base model of adhesion is applicable to such an interaction.

1.2 Scientific relevance of the project

The adhesion of paint to steel substrates is of crucial industrial importance. It is affected by the nature and composition of the substrate as well as the nature and composition of the paint. Therefore, it is not surprising that there already exists a vast quantity of literature in this field. Previous studies reported on the adhesion in terms of acid-base or electron donor-acceptor interactions [Fowkes, 1964; Fowkes, 1968]. Attention has also been dedicated to Lewis acid-base applications on steel surface characterization and adhesion [Bengu and Boerio, 2006]. However, in many papers information is available on the nature of the types of steels, but more knowledge is required in order to select a specific steel for a particular use. Polar molecules have been characterised by their donor (DN) and acceptor (AN) number as to determine their specific interaction with the solid substrate [Gutmann, 1978]. The characterization and quantitative description of forces at the interface constitute an important study area in interface science [Adamson, 1990, Isaelachvili, 1992]. The understanding thereof would allow the analytical prediction and explanation of material behaviour at interfaces through the quantification of the interactions and, as an immediate outcome, the capability to design polymeric coatings for a specific purpose. Although it is widely accepted that Lewis acid-base interactions of the type advocated by Fowkes [1964; 1968] play an imported part in adhesion phenomenon, there is no universal accepted manner in which the magnitude of such forces can be estimated.

The packaging industry relies on the coating specification from the coating industry. Sometimes additives are changed (for cost effective purposes) without any apparent significant change to the physical properties of the coating. However, by the time problems arise, the product is already on the market and both the quality control and problem tracing, as well as the reclaiming of products becomes very expensive. It is thus always desirable to have a model in place for quality analysis of the incoming stock with regard to chemical properties.

While several studies on the modification of the steel surface to improve adhesion have been done and will be revisited [Fox, 1979; Kern and Manfred, 1979; Elliott and Tupholme, 1981], little has been done to understand the modification of the polymer to improve adhesion with reference to Lewis acid-base theory and mechanism. Thus the aim of this research is to contribute to the existing literature by applying the Lewis acid-base theory to optimize adhesion of alkyd paint to mild steel.

1.3 Research questions

During the first part of the research project a full surface characterization of the LCAK steel with change in pH will be done. According to literature, the LCAK steel surfaces could be modified to be compatible with the chemical characteristics of the paint. Using these findings the following question could be answered:

What is the impact of a Lewis acid-base approach to the interaction between a substrate and its coating?

When situations are identified where new coatings should be considered to stabilise price and ensure no interruption in supply of the product, adhesion performance of that product on steel should be done. It is important to investigate the properties of both the substrate and the

coating and propose models which take into account the chemical and physical effects occurring during adhesion. The main question that this study will be investigating is:

Can the description of the properties of the substrate and the coating in terms of a Lewis acid-base model aid in the choice of both to obtain improved adhesion of organic coatings on steel substrates?

1.4 Methods and techniques of research

The research project addresses the surface chemistry of low-carbon aluminium-killed (LCAK) substrates and adhesion properties of an alkyd organic coating. Due to the complexity of surface chemistry, techniques which were used include XPS, contact angle measurements and FTIR techniques. In order to evaluate the orientation of chemical species on the surface or determination of surface structures, which is the initial stage in understanding surface properties, instruments used to characterize the chemical composition of the surface were used. Probe molecules together with FTIR spectroscopy was used to evaluate the adhesion properties of the coating on different pre-treated LCAK steel surfaces. Molecular modelling of the surface was done to obtain knowledge regarding the orientation of the coating species on the outer layer of the substrate.

CHAPTER 2: STEEL SUBSTRATE

2.1 Introduction

A particular steel is often chosen as a substrate for a specific coating because it has given satisfactory performance in similar applications elsewhere, but as the limits of its properties are approached, other grades have to be considered. A comprehensive knowledge of the range and varieties of steels, together with their uses, is required in order to select the type of steel, to give satisfactory performance.

Much information is available on steels but more knowledge and information is still required in order to select steel for a particular use [Fox, 1979; Kern and Manfred, 1979; Elliott and Tuphime, 1979]. The more critical the application, the greater the care that must be taken during material selection. For this research a carbon and low-alloy steel is considered. The focus of this chapter is on the surface science of the involved steel. Although it is of importance to the steel making industry, the metallurgy of Fe and its related compounds will not be addressed.

Steel is an alloy whose major component is iron, with a carbon content between 0.02% and 1.7% by mass. Carbon is the most cost effective alloying material for iron, but many other alloying elements are also used [Ashby and Jones, 1992]. Carbon and other elements act as hardening agents, preventing dislocations in the iron crystal lattice from sliding past one another. Varying the amounts of alloying elements and their distribution in the steel controls qualities such as the hardness, elasticity, ductility and tensile strength of the steel. Currently there are several classes of steels in which carbon is replaced with other alloying materials.

2.2 Production of steel

2.2.1 Iron and steel

Iron, like most metals, is not usually found in the earth's crust in an elemental state. Iron is found in the crust in combination with oxygen and sulfur: typically as Fe_2O_3 (the form of iron oxide (rust) found as the mineral hematite) and FeS_2 (pyrite).

Iron is extracted from ore by removing the oxygen and combining it with a preferred chemical such as carbon. The ore is heated to melt the minerals and to start to separate it into its components. The smelting process is first applied to metals with lower melting points. Copper melts at just over 1000°C , while tin melts around 250°C . Both temperatures could be reached with ancient methods that have been used for at least 600 years [Kern and Manfred, 1979]. Since the oxidation rate itself increases rapidly beyond 800°C , it is important that smelting take place in a low-oxygen environment. Unlike copper and tin, liquid iron dissolves carbon quite readily, so that smelting results in an alloy containing high carbon (pig iron), to obtain steel. Steel melts at around 1370°C .

2.2.2 Steel manufacturing

China is currently the largest producer of steel in the world (Figure 2-1). Steel is currently the most recycled material in the world, the industry estimates that of new metal produced each year, 42.3% is recycled [World steel, 2005]. Currently all setup steel that is available is recycled, the long service life of steel in applications such as construction means that there is a vast 'store' of steel in use that could be recycled as it becomes available. But new metal derived from raw materials is also necessary to make up demand.

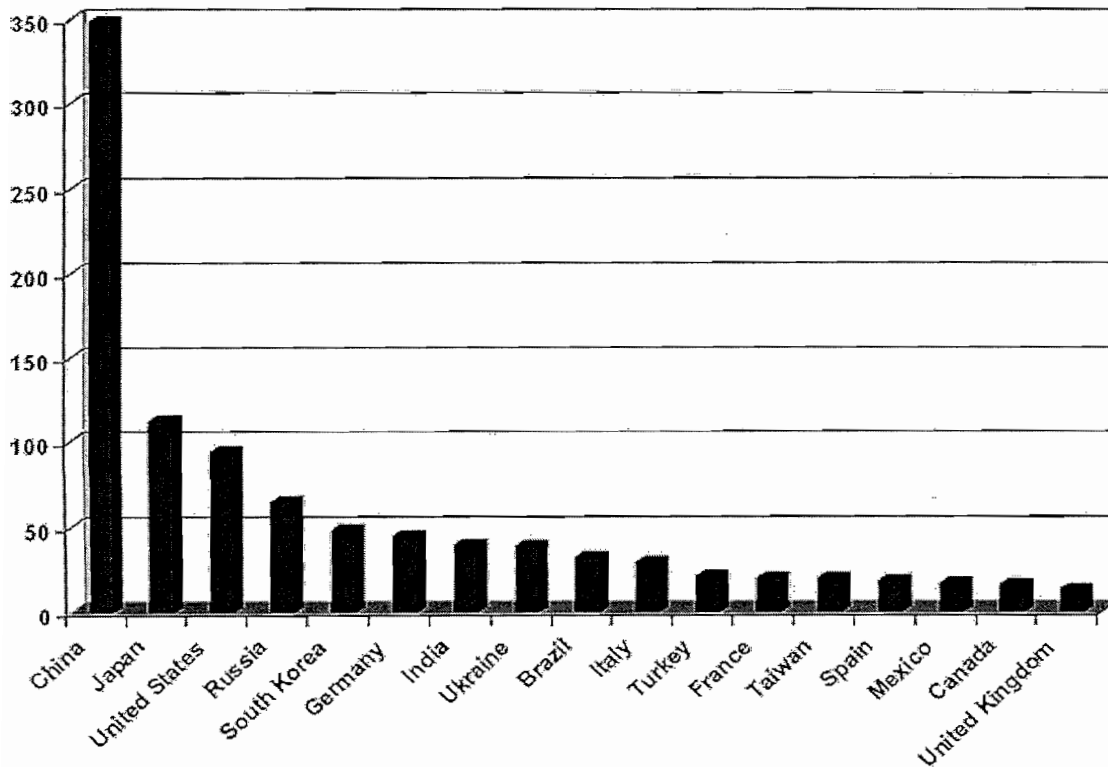


Figure 2-1: Steel production around the world, (2005), in Million Metric Tons (MMT) [World steel, 2005].

2.2.3 Steel production methods

Industry manufactures steel by melting iron ore, scrap metal, and other additives in furnaces. Establishments that use this method of producing steel are called electric arc furnaces (EAF). The molten metal output is then solidified into semi finished shapes before it is rolled, drawn, cast, and extruded to make sheet, rod, bar, tubing, and wire. Other mills produce finished steel products directly from purchased steel.

The schematic representative of the main processes for steel making is shown in figure 2-2.

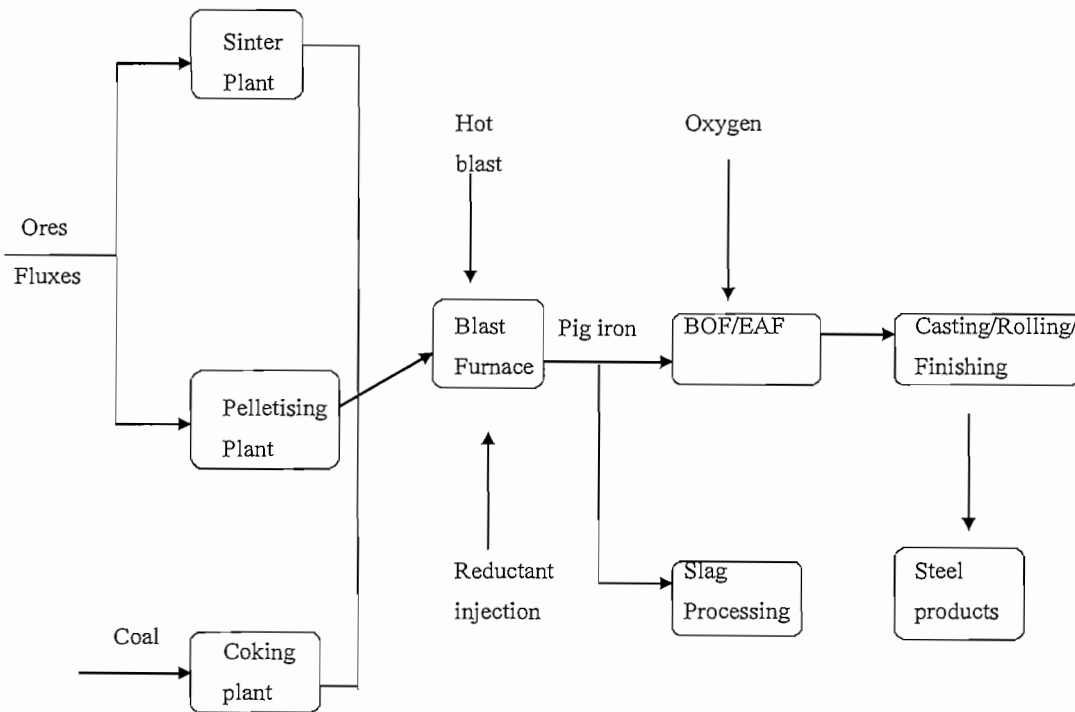


Figure 2-2: Schematic representative of the main processes for steelmaking.

2.2.3.1 Electric arc furnace

The first electric arc furnaces were developed by Paul Héroult from France, with a commercial plant established in the United State in 1907 [Fox, 1979]. An electric arc furnace is a system that heats charged material by means of an electric arc. Arc furnaces range in size from small units of approximately one ton capacity used in producing cast iron products, up to about 400 ton units used for secondary steelmaking. Temperatures inside an electric arc furnace can rise to approximately 1800°C.

2.2.3.2 Blast furnace

A blast furnace is a type of metallurgical furnace used for smelting (Figure 2-3). Fuel and ore are continuously supplied through the top of the furnace, while air is blown into the bottom of the chamber, so that the chemical and physical changes take place throughout the furnace as the material moves downward. The end products are usually molten metal and slag phases tapped from the bottom, and gases exiting from the top of the furnace.

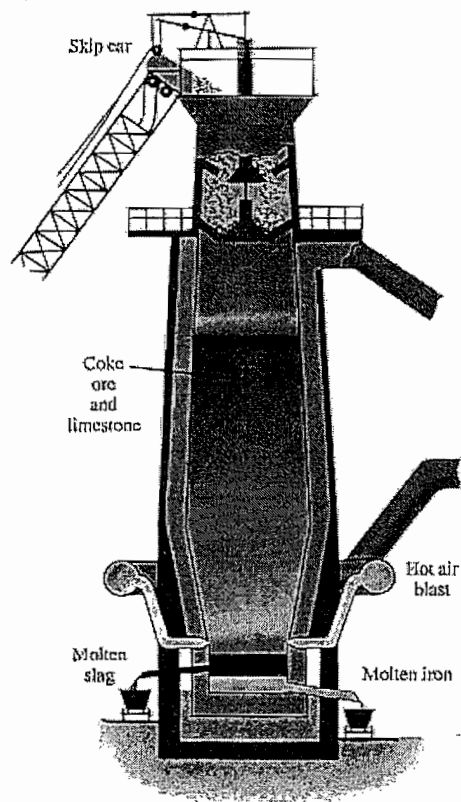


Figure 2-3: A typical blast furnace [Britannica Concises Encyclopedia, 2007].

This type of furnace is used for smelting iron ore to produce raw iron, an intermediate material used in the production of commercial iron and steel. Blast furnaces are also used for non-ferrous smelting processes.

2.3 Uses of steel

During the 1800's steel was expensive and was only used where nothing else would do, particularly for the cutting edge of knives, razors, swords, and other tools where a hard sharp edged were needed. Since 1850, steel has been easier to obtain and much cheaper to manufacture.

Steel is used widely in the construction of roads, railways, infrastructure, and buildings. Most large modern structures, such as stadiums, bridges, and airports, are supported by a steel skeleton. Even those with a concrete structure will employ steel for reinforcing. Steel is used in a variety of other construction-related applications, such as bolts, nails, and screws [Ochshorn, 2002]. Other common applications include shipbuilding, pipeline transport, mining, aerospace, white goods (e.g. washing machines), office furniture, steel wool and tools.

2.4 Steel types

2.4.1 Introduction

Steel is a metal composed of iron plus varying amounts of carbon and/or other alloy elements such as chromium, nickel, tungsten, manganese, etc. Adjusting the chemical composition and adapting the different stages of the steel making process, such as rolling, finishing and heat treatment, produce different types of steel, that is, steel with different properties and characteristics. As each of these factors can be modified, there is potentially no limit to the number of different steel types that can be created. Currently there are over 3000 catalogued grades or chemical compositions of available steel [Johnson, 1979].

Carbon steel (the most common type) depends on carbon and manganese in conjunction with proper processing to improve mechanical properties. A wide variety of alloying elements and

heat treatments can be developed to produce the most desirable combination of properties for a particular steel application.

Steels can be classified by a variety of different systems depending on:

- The composition, such as carbon, low-alloy or stainless steel.
- The manufacturing methods, such as open hearth, basic oxygen process, or electric furnace methods.
- The finishing method, such as hot rolling or cold rolling
- The product form, such as bar plate, sheet, strip, tubing or structural shape
- The de-oxidation practice, such as killed, semi-killed, capped or rimmed steel
- The microstructure, such as ferritic, pearlitic and martensitic
- The required strength level, as specified in ASTM standards
thermo-mechanical processing
- Quality descriptors, such as forging quality and commercial quality.

2.4.2 Carbon steel

Steel is considered to be carbon steel when

- no **minimum** content is specified or required for chromium, cobalt, columbium [niobium], molybdenum, nickel, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect;
- the specified **minimum for copper** does not exceed 0.40 %; and
- the **maximum** content specified for any of the following elements does not exceed the percentages noted: manganese 1.65 %, silicon 0.60 %, copper 0.60 %.

Carbon steels are generally categorized according to their carbon content [Fox, 1979]. Generally speaking, carbon steels contain up to 2% total alloying elements and can be

subdivided into low-carbon steels, medium-carbon steels, high-carbon steels and ultrahigh-carbon steels. A description of a LCAK steel follows.

2.4.2.1 Low-carbon steel

Low-carbon steels contain up to a maximum of 0.30% C. The largest category of this class of steel is flat-rolled products (sheet or strip), usually in the cold-rolled and annealed condition. The carbon content for these high-formability steels is very low, less than 0.10% C, with up to 0.4% Mn. Typical uses are in automobile body panels, tin plate, and wire products. For rolled steel structural plates and sections, the carbon content may be increased to approximately 0.30%, with higher manganese content up to 1.5%. These materials may be used for stampings, forgings, seamless tubes, and boilerplate.

2.4.3 Low-alloy steel

Low-alloy steels constitute a category of ferrous materials that exhibit mechanical properties superior to plain carbon steels as the result of additions of alloying elements such as nickel, chromium, and molybdenum. Total alloy content can range from 2.07% up to levels just below that of stainless steels, which contain a minimum of 10% Cr. For many low-alloy steels, the primary function of the alloying elements is to increase hardenability in order to optimize mechanical properties and toughness after heat treatment. In some cases, however, alloy additions are used to reduce environmental degradation under certain specified service conditions.

As with steels in general, low-alloy steels can be classified according to:

- *Chemical composition*, such as nickel steels, nickel-chromium steels, molybdenum steels, chromium-molybdenum steels
- *Heat treatment*, such as quenched and tempered, normalized and tempered, annealed.

Because of the wide variety of chemical compositions possible and the fact that some steels are used in more than one heat-treated, condition, some overlap exists among the alloy steel classifications. e.g. (1) low-carbon quenched and tempered (QT) steels, (2) medium-carbon ultrahigh-strength steels, (3) bearing steels, and (4) heat-resistant chromium-molybdenum steels.

2.4.4 Cold rolled steel (carbon 0.25%)

Cold-rolled carbon sheet steel is manufactured from hot-rolled, pickled coiled steel by cold reducing to the ordered thickness, followed by annealing to recrystallize the grain structure. The annealed product can be used as-annealed (dead soft) for unexposed applications. For exposed applications, the annealed sheet product is given a skin or temper pass to minimize the phenomenon known as stretcher strains or fluting and to impart suitable surface texture. Cold-rolled sheet steel can be furnished in the full hard (unannealed) condition. Where cold-rolled sheet steel is used for fabrication by welding, chemical composition and mechanical properties should be considered to assure compatibility with the welding process and its effect on altering the properties. Cold-rolled sheet steel is produced in four principal qualities:

- Commercial Quality
- Drawing Quality
- Drawing Quality, special Killed
- Structural Quality

Only Cold-Rolled Commercial Quality steels (CRCQ) will be discussed as it is the type of steel chosen for this study. Cold-Rolled Commercial Quality steel (CRCQ) is ordinarily produced in a ***low-carbon grade of continuous cast aluminium killed steel***. This quality of steel is normally produced with a matte finish for the application of various organic finishes, such as paints, enamels or lacquers. CRCQ may be used when moderate deformation is required, but does not have a high level of ductility or a high degree of uniformity of chemical composition and

mechanical properties. A commercial quality steel is normally manufactured to contain a maximum amount of carbon of 0.15%, a phosphorus content up to 0.030% and a sulphur content of less than 0.035% (by heat analysis).

2.4.4.1 Surface finish of cold rolled sheet steel

“Finish” refers to the degree of smoothness or luster of the surface as distinct from surface imperfections. The degree of surface roughness is altered in the mechanical drawing or stamping of steel, but the roughness will vary over the part, so that the completed stamped part will not have the same surface appearance as the sheet from which it was made. The production of specific finishes requires special preparation and control of the roll surfaces employed. The surface finish of a cold-rolled sheet of steel may be described as follows:

- **Matte Finish** is a dull finish, without luster, produced by rolling on rolls, which have been roughened by mechanical, chemical or electrical means to various degrees of surface texture, depending upon the application. With some surface preparation, matte finish is suitable for decorative painting. It is not generally recommended for bright plating.
- **Commercial Bright** finish is a relatively bright finish having a surface texture intermediate between that of matte and luster finish. With some surface preparation, commercial bright finish is suitable for decorative painting or certain plating applications. If the sheets are deformed in fabrication, the surface may roughen to some degree and areas so affected will require surface preparation to restore surface texture to that of the underformed areas.
- **Luster Finish** is a smooth bright finish produced by rolling on ground rolls and is suitable for decorative painting or plating with additional special surface preparation by the

consumer. The luster may not be retained after fabrication; therefore, the formed parts will require surface preparation to make them suitable for bright plating [Yu, 1985].

Some cold rolled products, usually flat steel, are then coated with other metals or paint to protect the steel surface or to give it special characteristics. The process involves cleaning, annealing and coating of the strip.

A steel surface pre-treatment process is summarized in section 3.6.

CHAPTER 3: COATINGS AND ADHESION

3.1 Introduction

Coatings to steel surfaces are used in a wide range of applications for a variety of purposes (decorative or protective), and irrespective of their intended function they must adhere satisfactorily to the underlying substrate. The importance of adhesion during the use of organic surface coatings is well recognized. It is reflected in the many literature references to methods of measuring this property [Holloway and Walker, 1964], achieving good adhesion by surface preparation and its importance in obtaining good surface protection [Bullett and Prosser, 1972 and 1966; Timmins, 1979].

The adhesion of the paint to the substrate is affected by the nature and conditions of the substrate, at least as much as by the nature or composition of the paint. The primer coating is considered the critical element in most paint coating systems because it is responsible for preserving the metallic state of the substrate, and it must also anchor the paint coating to the steel.

Most coatings adhere to metals by means of hydrogen bonds that develop when two surfaces are brought closely together [Hare, 1978; Allen, 1965]. Paint coatings with polar groups (-OH, -COOH, etc.) have good wetting properties and show excellent physical adhesion characteristics (e.g. epoxies, alkyds, oil paints, etc.). Much stronger chemically bond adhesion is possible when the primer can "react" with the reactive functional group on the metal, as formed during pre-treatment processes [Bullett and Rudram, 1959; Santagata et al., 1998]. A primer coating is not used for this study as the aim is to obtain a better understanding of the direct interaction between the paint coating and the metal surface.

Adhesion takes place when the coating and the substrate separation is not more than approximately 0.5 nm [Guzman et.al., 2000]. Any contaminant on the steel surface will increase

the separation and, as a result, decrease the paint film adhesion. Furthermore, reactive sites on the steel at which adhesion can occur are masked not only by contamination, but also by chemical bonded species, which may themselves occupy sites on the steel that would otherwise be available for reaction with the paint coating.

The study of acid-base properties of coatings and substrates surfaces is of fundamental significance in adhesion. Many methods are proposed in the literature to understand and quantify the acid-base interactions at the interfaces [Yoon et.al., 1979]. It was Fowkes who proposed in the study of adhesion to describe non-dispersive or specific interaction in terms of acid-base or electron donor-acceptor interactions [Fowkes, 1964 and 1968]. Fowkes then considered these non-dispersive interactions to be identical to electron donor-acceptor or acid-base interactions. Polar molecules used to determine the specific interactions with the solid substrate may be characterized by their donor (DN) and acceptor (AN) numbers [Gutmann, 1978]. The concept of donor-acceptor interactions is an extension of Lewis acid-base reactions, dealing with coordinate bonds, which are formed by sharing a pair of electrons between donor and acceptor species.

The characterization and quantitative description of forces at the interface constitute an important study area in interface science [Adamson, 1990; Israelachvili, 1992]. It would allow the analytical prediction and explanation of material behaviour at interfaces through the quantification of the interactions and, as an immediate outcome, the capability to design polymeric coatings for a specific purpose.

3.2 Characteristics of coatings

Coatings are divided into four different types: metallic coatings, polymeric coatings, conversion coatings, and cementitious coatings. Only the polymeric coating will be discussed as the other types are outside the scope of this study.

Coatings are applied to the surface (usually referred to as the substrate) to improve surface properties such as corrosion resistance, adhesion and appearance, while adhesives are compounds that bond the substrate and a coating together. Only adhesion of coatings is of interest for this study.

3.2.1 Polymeric coatings

Protective polymeric coatings fall broadly into three different classes: lacquers, varnishes, and paints. Varnish is a term applied to coatings which are solutions of either a resin alone in a solvent or combinations of an oil or a resin in a solvent (oleo-resinous varnishes). The term lacquer is generally limited to a composition whose basic film former is nitrocellulose, cellulose acetate butyrate, ethyl cellulose, acrylic resin, or other resin that dries by solvent evaporation.

The term paint is applied to more complex formulations of a liquid mixture that dry or harden to form a protective coating. Typical formulation constituents include a liquid vehicle, which may be **water** or an **organic solvent** to effect the application of the coating. It thins the paint, allowing it to be brushed or sprayed. Once on the substrate, the solvent will evaporate, leaving the film dry. **Pigments** are finely dispersed solid particles which give the coating color. In some cases they can be used to impart certain protective properties, such as rust prevention and to control gloss levels. **Filler** materials maintain coating thickness at low cost, **wetting** agents promote penetration of the paint into scratches and pores in the substrate. Other constituents are anti-

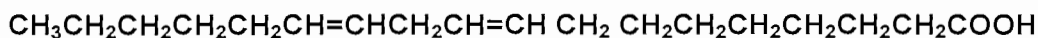
foaming agents, anti-mildew agent, catalysts, which cause polymerization of some coatings, corrosion inhibitors, and constituents which control the rheological properties.

A polymeric coating protects a metal substrate from corroding by two mechanisms: (a) by serving as a barrier from the reactants, water, oxygen, and ions, and (b) by serving as a reservoir for corrosion inhibitors that assist the surface in resisting attack.

The barrier properties of the coating are improved by increasing the thickness, by the presence of pigments and fillers that increase the diffusion path for water and oxygen, and by the ability to resist degradation [Leidheiser, 1981].

3.2.1.1 Alkyd paint

Alkyd paints are the most well known type of oil paint available. The word “alkyd” actually refers to the synthetic resin used as a binder in the paint. This would be the oil in the paint, most commonly vegetable oil. The oils used in preparing modified alkyd resins are important and may be deciding components. For example, if an alkyd with moderate drying speed but good colour retention is desired, the standards of the industry today are soybean oil modified types, although other oils such as sunflower and walnut seed may be used practically interchangeably [Earhart, 1949]. The chemical composition of a typical drying oil is given in the following scheme:



To understand the oil modified alkyds, it is necessary to understand the oils and the reactions of drying or, if they do not dry, what polar properties in the oil can be used in a particular coating

composition. The reason for this phenomenon is that when oxidation of an oil modified alkyds starts, the fatty acids attach themselves to one another by a mechanism of polymerization. During polymerization a small amount of cross-linking by way of oxidation of the fatty acid groups cause a film to set to a gel like structure and makes it appear dry long before the final oxidation reactions have been completed.

Alkyd resins include all those complexes initially resulting from the inter-reaction of a polyhydric alcohol and a polybasic acid. The monoglyceride, ester interchange, and solvent processes are also employed [Kienle, 1949]. Alkyd resins have been largely responsible for the commercial availability of such polybasic acids as fumaric, tricarballic, aconitic, sebacic, adipic, terephthalic and itaconic and maleic and chlorophthalic anhydrides. The formation of alkyd resin has long been known, Van Bemmelen [1856] did the first systematic work where he prepared resins from succinic acid, from citric acid, from a mixture of benzoic and succinic acid, by heating with glycerol. Smith [1901] was the first to prepare a resin from glycerol and phthalic anhydride.

Alkyd resins as film forming materials were first described at the fifth annual meeting of the American Chemical Society [Kienle and Ferguson, 1929]. The search for improved alkyd resins has played a major role in the commercial availability of many new chemicals. With successful use of alkyd resins as decorative finishes, the entire coating composition industry became synthetic resin minded.

Alkyd resin, that is **polyester polymers**, has not been confined entirely to the coating industry. The plastic industry is using large amount of contact or low pressure laminating resins, largely based on polyester polymers [Kienle, 1949]. At the time the electrical industry was entering the household appliance field, durability, tough, flexible, white decorative finishes rapidly became a major requirement. Drying oil modified alkyd resins with low temperature short time baking cycle

and their good colour retention offered a solution. The search for improved alkyd resins has played a major role in the commercial availability of many new chemicals.

3.3 Adhesion: interaction between polymer coating and surfaces

Adhesion is a complex phenomenon related to physical effects and chemical reactions in the interface. Adhesive forces are set up as the coating is applied to the substrate and during curing or drying. The magnitude of these forces depends on the nature of the surface and the binder used in the coating. These forces may be broadly categorized as one of the two types:

- Primary valency forces, and
- Secondary valency forces.

Secondary valency bonding is based on much weaker physical forces. These forces are more likely to be found in material having polar groups such as carboxylic acid functionalities than on non-polar groups such as polyethylene. The actual forces bonding the paint to the substrate may be mechanical interlocking by way of paint diffusion, electrostatic attraction or true chemical bonding between coating and the substrate. Depending on the chemistry and physics of both the substrate surface and the coating used, one or a combination of these postulated mechanisms might be involved.

3.3.1 The mechanical mechanism

Figure 3-1 illustrates the mechanism of bonding by mechanical interlocking.

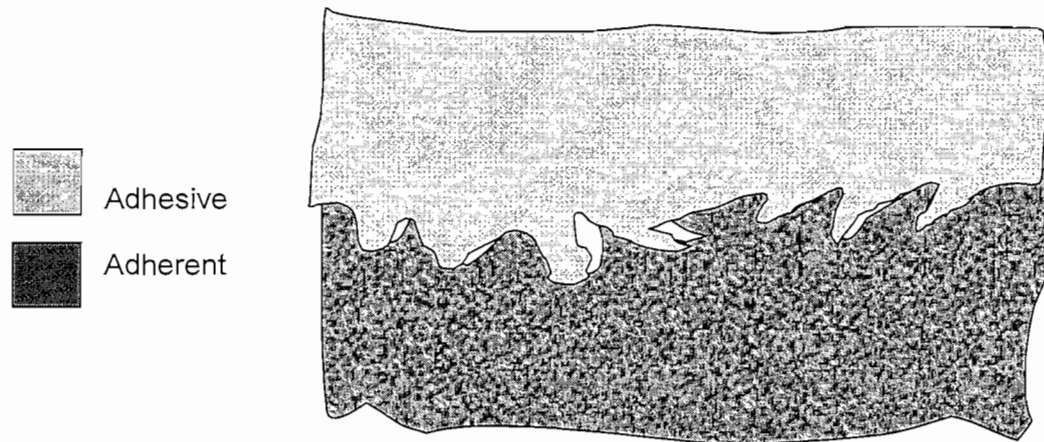


Figure 3-1: Mechanical interlocking mechanism.

This mechanism of coating occurs when the substrate surface upon which the coating is spread contains pores, holes, crevices, and voids into which the coating solidifies [Vakula and Pritykin, 1991]. This mechanistic approach describes the adhesion to a porous substrate. The resulting interlocking combines the cohesive strength of both individual solids to form an interface that acts as a composite material with properties intermediate to those of each material surface. The overall strength of the bond in this mechanism is dependent upon the quality of this interlocking interface. Such a lock and key mechanism of bonding can explain the good resistance of some bonds to water damage.

3.3.2 The Chemical Bond mechanism

According to this mechanism a chemical reaction between two materials coming into contact is responsible for adhesion. This type of bonding is expected to be the strongest and most durable. It does however, require that there be mutually reactive chemical groups that tightly bound the substrate surface and in the coating. Figure 3-2 illustrates the mechanism of chemical bonding, where AA atom or molecules chemically bonds to BB atom or molecules.

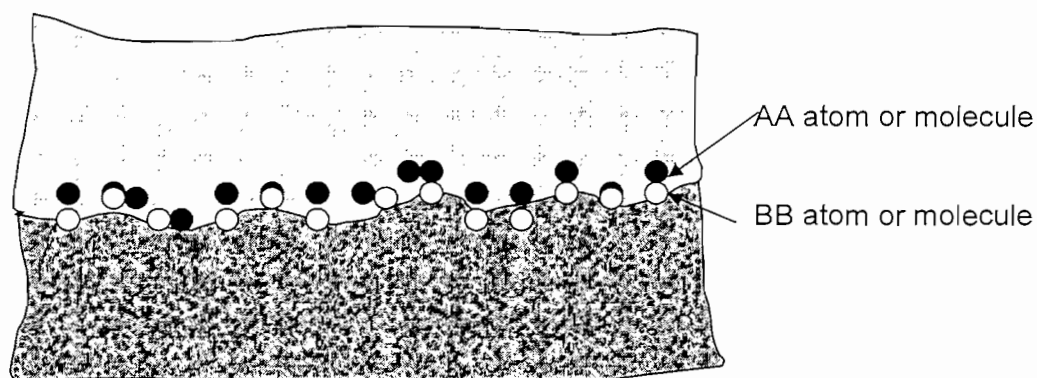


Figure 3-2: Chemical bonding mechanism.

3.3.3 The Electrostatic mechanism

This mechanism postulate that adhesion arises from the interaction of point charges, positive and negative, on either side of an interface, where on the one side there is a solid, and on the other an electric double layer composed of solvated ions and counter-ions. Interaction between these charges account for some adhesion. This model is used mostly in colloid science [Borrorff and Wake, 1949]. Figure 3-3 illustrates the mechanism of electrostatic bonding.

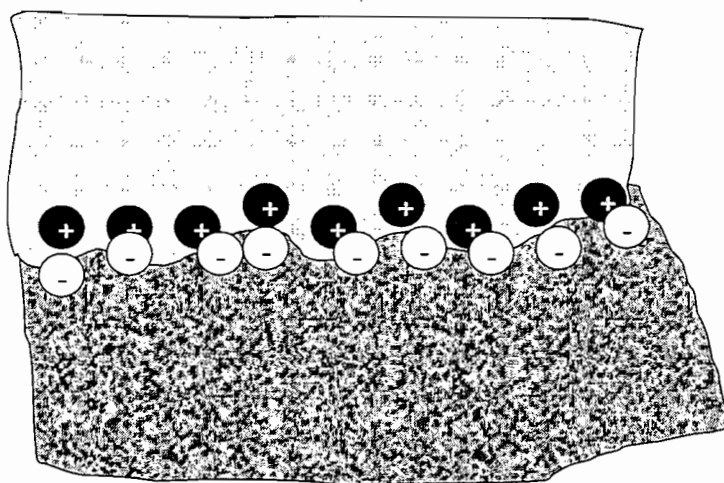


Figure 3-3: Electrostatic bonding mechanism.

3.3.4 The diffusion mechanism

The diffusion mechanism of adhesion occurs where an interfacial area forms between two substrates. Segments of the macromolecules will diffuse across the interface to various extents, depending on material properties and curing conditions. The phenomenon is a two-stage process. Firstly it is wetting, which is followed by inter-diffusion of chain segments across the interface to establish an entangled network. Figure 3-4 illustrates the mechanism of diffusion bonding.

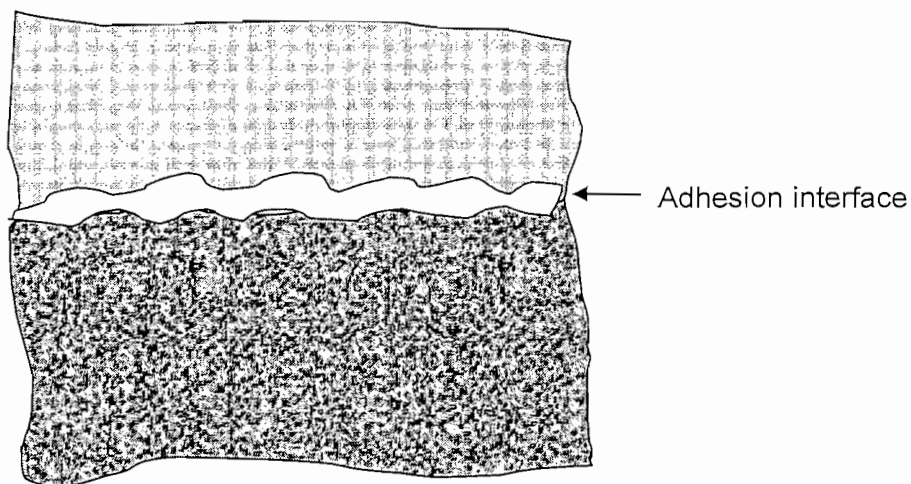


Figure 3-4: Diffusion bonding mechanism.

3.3.5 Lewis acid-base theory

According to this theory, adhesion may result from the polar attraction and reaction of molecules having Lewis acid and base properties [Haines, 1967], thus that electron poor and electron rich components interact at the interface. Among the different definitions of acid and bases, the Lewis theory is most satisfactorily applied to polymers, and it is to this theory that experimental approaches refer to in order to calculate the acid-base components of polymer surfaces [Della Volpe and Siboni, 2000]. The calculation of acid-base properties by wetting measurements involves estimating the fundamental acid-base properties of solid surfaces by their ability to

interact with liquids. The most appropriate experimental procedure developed for this is contact angle measurements.

3.4 Coating selection

Coatings can be classified into a number of different categories, but the most convenient system is categorization by chemical composition. Figure 3-5 shows a summary of major structural coatings categorized by the Society of Mechanical Engineers. Figure 3.6 shows the appropriate coatings to use for particular adherents [Messler, 1993].

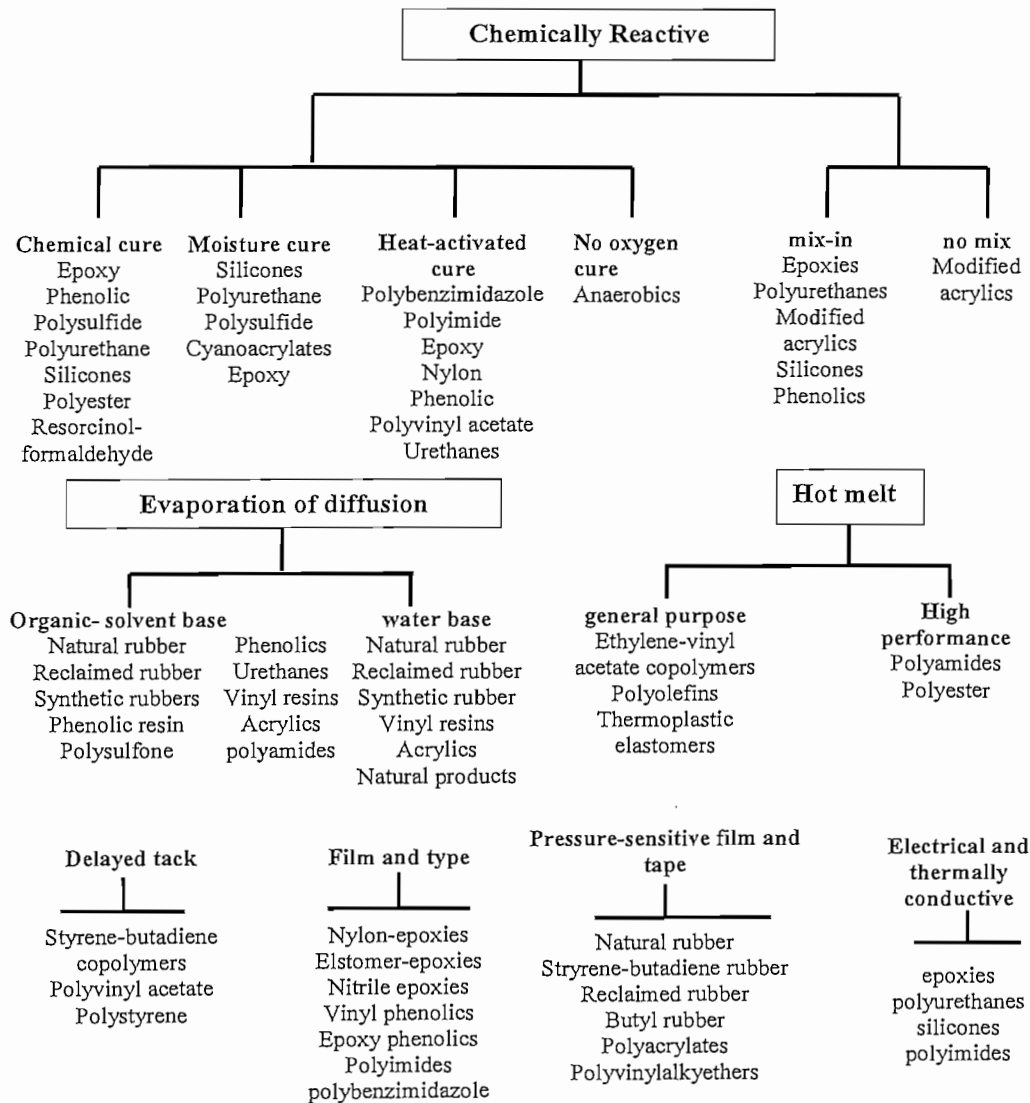


Figure 3-5: Categorization of structural coatings [Messler, 1993].

	Metals																
Coatings	Al	Ag	Au	Be	Bronze	Cd	Cu	Mg	Ni	Pb	Sn	Steel	Stainless steel	Ti	U	W	Zn
Acrylics					•		•					•	•				
2nd generation acrylic	•																
Anaerobics			•		•	•	•										
Cyanoacrylates	•						•	•		•							
Epoxies		•	•	•	•		•	•	•	•	•	•	•	•	•	•	•
Epoxy-phenolic	•		•	•				•		•		•	•	•			
Modified epoxies	•																
Modified phenolics	•																
Neoprene phenolics	•				•		•	•									
Nitrile-epoxies	•		•											•			•
Nitrile-phenolics			•			•	•	•	•		•	•	•				
Nitrile-rubbers																•	
Nylon-epoxy				•	•		•	•	•								
Polyacrylates									•								
Polyamides									•								
Polybenzimidazoles				•					•			•	•				
Polyester				•					•			•	•	•			
Polyurethanes				•	•		•	•		•							
Polyvinyl acetate								•									
Polyvinyl alkyl ether		•	•							•	•						•
Silicones	•				•		•	•		•							
Styrene-butadiene											•						
Vinyl-plastisols	•																
Vinyl-phenolics								•	•								

Figure 3-6: Metal-coating compatibility chart [Messler, 1993].

3.5 Chemical modifications of coatings to improve adhesion.

An important factor in achieving maximum adhesion of a particular coating system to the substrate lies in the proper preparation of the substrate (pre-treatment) prior to the application of paint, or a product added to the coating formulations. This product or additive improves adhesion by creating stronger interfacial interaction between the coating and the substrate. The chemical compounds added in small amounts to coating formulations are known as adhesion promoters.

Kam and Hon [1981] used dibenzoyl methane to promote the physical adhesion of an acrylic paint to metallic surfaces by the formation of an iron-complex on the metallic surfaces. A complex of phosphated emulsifiers, incorporated in the latex paints before applying to a metal surface, was claimed by Standard Oil Company [1981] as an adhesion promoter for acrylonitrile copolymer latex coating. The addition of substituted phenol and dimethylolurea [Mazina, 1980] improves the adhesion of water borne coatings based on latex of fluoropolymer. Doinig and Fenselan [1980] improved the adhesion of polyurethane primers to foamed polyurethane moldings by incorporating a polyether or polyester alcohol and a polymethylene polyphenyl isocyanate, together with a halogenated chloride. A Japanese patent [Dai-Nipol Ink & Chemical INC., 1983] claim that the adhesion of vinyl coatings to plastics is improved by the use of chelates of titanium or aluminium, while a Russian patent [Airapetyan, 1983] claims bis(dialkyl-trioxo hexa hydro triazinyl) ether, structurally derived from dialkyl hydroxyl ethyl isocyanurate, as a good adhesion promoter for epoxy resin adhesives.

The incorporation of an adhesion promoter to improve adhesion to some of the coating formulations has been reported [Sathyanarayana and Yaseen, 1996]. No correlation between the adhesion promoters and the Lewis acid-base theory or mechanism was made, let alone the quantification of the adhesion promoters with reference to Lewis acid-base theory in improving adhesion.

3.6 Steel surface promoters and pre-treatment

The objective of all surface preparation is to present as clean a substrate as possible to the coating system. Once this substrate is cleaned, the coating that is applied to the surface, and, given that it has been developed to be compatible with the material, it will provide optimum performance. Regardless of the type of surface coating involved, the surface preparation will generally determine whether it performs as expected or not. The surface preparation element of

a coating system is essentially an 'invisible' part of the application process. In the case of steel surfaces, debris such as oxides, dirt, dust, grease, oil, old paint, corrosion products, rust, moisture and/or mill scale, and other foreign matter (chlorides, sulphates, ect.) play an important role in the adhesion of paints [Sabata et al., 1993]. When any of these materials is painted over, they interfere with the mechanical and chemical adhesion of the paint film to the substrate and compromise the adhesion.

The type of surface preparation required will depend on the condition of the surface and the performance of the coating in its particular environment. Metal pre-treatments are essential to ensure long-term performance of painted steel. The pre-treatment must act as an adhesion promoter and also provide corrosion protection. During the last decades, the most widely used pre-treatments utilize hexavalent chromium (Cr^{6+}) compounds [Ogarev and Selector, 1992]. However, due to increased environmental concerns and legislation limiting the use of Cr^{6+} -based chemicals, new alternatives must be sought. Recent efforts have been focused on the use of rare-earth (RE) salts as adhesion promoters and corrosion inhibitors [Sabata and Van Ooij, 1994]. Currently, they are used in a wide range of applications, in areas such as metallurgy, glasses and ceramics [Subramanian and Van Ooij, 1998]. These new systems should be able to improve the protection against corrosion and also to provide good adhesion characteristics. In this respect, organosilane technology seems to be promising for the pre-treatment of metal surfaces prior to organic coatings application [Walker, 1982].

Various pre-treatments based on the use of organosilanes have been studied [Montemor et al., 2000; Vold, 1981]. Since the structure and strength of coating-solid interfaces are closely related to each other, the fundamental understanding of the behaviour of coatings or polymer chains near the solid surface is crucial in optimizing the interfacial strength in such systems [Huheey, 1978; Steel structure painting manual, 1997; Wool, 1995].

Generally polymers or coatings can be functionalized or modified to enhance the adhesion of the coating to the solid surfaces [Polymer/inorganic interface II, 1995; Nakayama and Matsuda, 1996]. The surface of the solid substrate can also be modified to enhance the polymer adhesion. The addition of functional groups to polymer or coating chains can results in strong interaction with the solid surface by the formation of hydrogen bonds, covalent, or ionic bonds. This strategy is an efficiently and widely used technique to modify the adhesion strength. For this modification, many industrial techniques are used. Plasma, laser treatment, corona, UV, ozone, and chemical modification treatments were developed for such purposes [Ueta and Matsuda, 1995]. However, most research has been limited to determining the effect of the extent of modification on the improvement in material properties rather than studying their Lewis acid-base nature or mechanisms of adhesion.

3.7 Conclusions

The protection of the substrate is sought against various detrimental agents such as moisture, oxygen, salts and corrosive gases such as HCl, SO₂, SO₃, ect,. However, the nature of each substrate will determine the kind of protection it needs from a particular environment. As part of a program aimed at defining lifetime prediction models for steel sheets coated with organic films, adhesion technology and surface treatment investigations are ongoing research topics.

CHAPTER 4: INTERFACE CHEMISTRY

4.1 Introductions

An interface is a surface forming a common boundary between two different phases, such as an insoluble solid and a liquid, two immiscible liquids or a liquid and an insoluble gas. The importance of the interface depends on which type of system is being treated. Some of the most important chemical and physical processes in our environments occur at a surface or interface. The surface of a medium whether it be a liquid or a solid has very special properties which are often quite distinct from the bulk substance.

Lewis first published his ideas about acids and bases in 1923 [Lewis, 1923], the same year in which the Brønsted-Lowry theory appeared. Lewis agreed with Brønsted that hydroxide ion is the sole manifester of basic properties, but saw no reason to limit acids to hydrogen-containing compounds [Lewis, 1961]. Lewis also objected to the definition of acid and bases on the basis of solvent cations and anions, respectively, according to the solvent systems theory because acids and bases are thereby restricted to species characteristic of ionisable solvents, although acid-base phenomena are observed in nonionizing solvents as well [Luder and Zuffanti, 1961]. Lewis believed, as did Brønsted, that ions were overemphasized as the carriers of acid-base properties, to the neglect of neutral molecules, despite the fact that many ions possess negligible acid-base properties. Although fairly accurate calculations of heat of neutralization based on electrostatic attraction are possible, Lewis maintained that the consideration of acid-base processes as phenomena depended on coulombic forces only is incorrect because the forces are predominantly only at large inter-ionic separation and are in part supplanted by other factors in a close-contact process like neutralization [Lewis, 1961]

Lewis proposed a generalized acid-base definition founded upon a mechanistic approach to chemical behaviour instead of structure or constitution [Luder and Zuffanti, 1961]. He defined a Lewis base as a substance with a lone electron pair available to complete the stable electronic

configuration of another atom, thereby increasing the stability of the latter. A Lewis acid employs a lone electron pair from another molecule to complete the stable electronic configuration of one of its own atom. In other words, a base is an electron pair donor and an acid is an electron pair acceptor.

Although Lewis' original formulation of acid-base definitions still remain quite useful, a growing need was felt from the late 1940s onward for their applications into adhesion phenomena. Such applications were initiated by Fowkes in a series of papers beginning in 1960. He was originally attracted to the subject of adhesion in terms of acid-base or electron donor-acceptor interactions [Fowkes, 1978]. Fowkes's work substantially broadens the scope of the original Lewis concepts. In this chapter the generalized Lewis definitions given by Fowkes for bonding concepts will be explored.

Interactions occur between the molecules of a liquid and those of any liquid or gaseous substance which is not soluble in the liquid; these result in the formation of an interface. Energy is required to change the form of this interface or surface. The work required to change the shape of a given surface is known as the interfacial or surface tension.

4.2 Surface tension components (STC)

Surface tension is a measure of cohesive energy present at the interface. Fowkes [1964] originally proposed the surface tension of a system to consist of the following components:

$$\gamma = \gamma^d + \gamma^i + \gamma^p + \gamma^h \quad (4.1)$$

Where superscripts d, i, p and h represent dispersion, induction, polarization, and hydrogen bonding. Later Fowkes [1987] proposed that the acid-base component γ^{AB} be defined and represents by the three terms in equation (4.2) as follows:

$$\gamma^{AB} = \gamma^i + \gamma^p + \gamma^h \quad (4.2)$$

However, according to Van Oss, Chaudhury, and Good [1988] (VCG), both the induction (i) and polarization (p) components are of secondary importance in comparison with the dispersion (d) and hydrogen bonding (h) components, so they suggested that the first three components in equation (4.1) should be combined into the Lifshitz-van der Waals components, γ^{LW} , instead:

$$\gamma^{LW} = \gamma^d + \gamma^i + \gamma^p \quad (4.3)$$

Then, the acid-base component of surface tension represents only the contributions of the hydrogen bonds.

$$\gamma^{AB} = \gamma^h \quad (4.4)$$

The total surface tension for a "polar" system becomes:

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (4.5)$$

VCG [1988] further divided the asymmetric hydrogen-bond part of the dipolar system into two separate factors: a hydrogen-bonding acidic parameter γ^+ , which is identical to the contribution

of the proton donor, whereas hydrogen-bonding basic parameter γ^- is the contribution of the proton acceptor.

4.3 Contact angle components

In the case of contact angle measurements surface energy is determined by wetting the surface of solids with different liquids. Young based the method on the first description of the wetting state in 1805 [Young, 1805]. Young's equation allows a calculation of the stationary wetting angle under certain conditions. It describes the equilibrium of forces between the surface tension at a three-phase boundary system [Adamson, 1990]. It is used for investigation of the surface characterization of various materials. It is estimated as solid surface energy. When a liquid droplet is placed on a homogeneous smooth solid surface, the contact angle, θ , can be obtained using Young's equation:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (4.6)$$

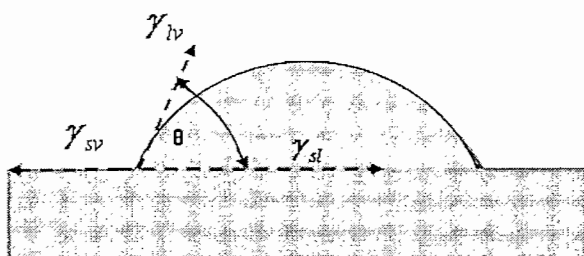


Figure 4-1: Contact angle and gas–liquid–solid related tensions.

γ_{sv} , γ_{sl} and γ_{lv} are the surface-interfacial tensions of the solid-vapor, solid-liquid and liquid-vapor phases, respectively.

The total surface tension is the sum of polar and non-polar components

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (4.7)$$

The total acid-base free energy of interaction between two polar materials (i and j) may be expressed as [Bellon-Fontaine et al., 1990; Van Oss, 1995]:

$$\Delta G_{ij}^{AB} = -2(\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+}) \quad (4.8)$$

Therefore

$$\Delta G_{ij}^{AB} = -2\gamma_{ij}^{AB} \quad (4.9)$$

Because [Van Oss, 1995]

$$\gamma_{ij}^{AB} = 2\sqrt{\gamma_i^+ \gamma_j^-} \quad (4.10)$$

Using Young-Dupre' equation [De Gennes, 1985]:

$$(1 + \cos \theta)\gamma_i = -\Delta G_{ij} \quad (4.11)$$

Equation (4.7) can be re-expressed as [Van Oss et al., 1988]:

$$\Delta G_{ij}^{TOT} = \Delta G_{ij}^{LW} + \Delta G_{ij}^{AB} \quad (4.12)$$

The Lifshitz-van der Waals (LW) interaction is a non covalent interaction that involves permanent dipoles within the molecules (non-polar). The Lewis acid-base interaction (LW) is hydrogen bonding, interaction between electron-donor and acceptor (polar).

But

$$\Delta G_{ij}^{LW} = -2\sqrt{\gamma_i^{LW} \gamma_j^{LW}} \quad (4.13)$$

and

$$\Delta G_{ij}^{AB} = -2(\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+}) \quad (4.14)$$

Therefore Young-Dupre' equation (4.11) can be re-expressed as:

$$(1 + \cos \theta) \gamma_i = 2 \left[\sqrt{\gamma_i^{LW} \gamma_j^{LW}} + \sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+} \right] \quad (4.15)$$

In all the above expressions of the Young equation, i stand for liquids and j for solids. The Young-Dupre' equation correlates the contact angle to the surface and interfacial tensions.

Parameters, which affect contact angle include [Stasyuk and Pyatetskii, 1993]:

- Temperature
- Contaminants
- Absorbed materials
- Polar and non-polar interactions

- Drop dimensions
- Molecular weight
- Surface crystallinity

The wetting of solid surfaces by liquids has important implications for detergency, lubrication, oil recovery, wastewater treatment, and adhesion. In each of these cases, one fluid competes with another fluid for a surface area. Therefore, the contact angle at the interface can be used to determine the relative wetting capabilities of different fluids. Fowkes [1963] pioneered the consistent practice of distinguishing between the non-polar and polar contributions to surface and interfacial tension. He was also among the first to recognize that the polar contributions are essentially congruent with Lewis acid-base interactions. He identified these with van der Waals-London, or dispersion forces.

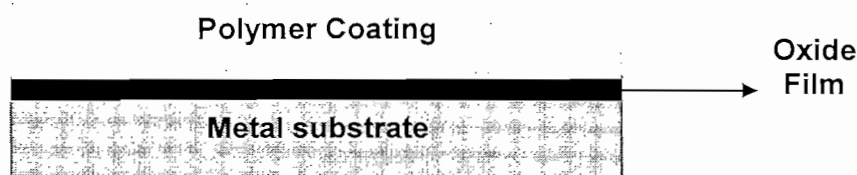
Starkweather and his co-workers [2000] have done experimental studies of the change in the contact angle of oil on a solid surface. They found that the interfacial-surface tension experiments between oil and surfactant solution can be misleading in predicting how the surfactant concentration changes with pH and how that will effect the change in the normalized contact angle of an oil on both stainless steel and glass surfaces. Mohammadi and his co-workers [2004] also investigated the effect of surfactant on the wetting behaviour of super-hydrophobic surfaces. Their advancing and receding contact angle results show that when the concentration of surfactants in water increases, the contact angle and surface tension decreases. Nicolaiewsky et al. [1999] also used contact angles on liquid flow over textured surfaces. They compared the wetting behaviour of liquids with similar surface tension and different viscosities. Their findings showed that different viscosities do not strongly influence the contact angle and also system with low surface tension tend to produce low contact angle, thus

favoring complete wetting of the surfaces. They also concluded that the metal used for samples could influence contact angle.

So far several theories on solid surface free energy determination and approaches have been proposed, but formulation of surface and interfacial free energy is still a very debatable issue. Chibowski and Perea-Carpio [2002] addressed the problems of contact angle and solid surface free energy determination. In their study they showed that direct calculation of the contact angle from Washburn's equation, which are then applied in Young' equation, lead to erroneous results of determined solid surface free energy values. However, Costanzo, Giese and van Oss [1991] determined the acid-base characterization of clay mineral surfaces by contact angles. They have shown that contact angle determination can be done for swelling clay mineral as well as with non-swelling clay minerals.

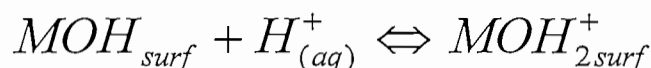
4.4 Oxide films on metals

Most metals exposed to ambient atmosphere are readily oxidized and in the presence of moisture the outer surface of the metal oxide is hydrated. The oxide film on a metal substrate usually terminates in an outermost layer as hydroxyl groups. These hydroxyl groups can be acidic or basic in nature, depending on the identity of the metal cation present in the oxide film [Simmons and Beard, 1987].

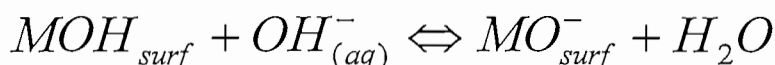


In the aqueous solution, surface hydroxyl groups may remain undissociated, in which case the pH of the solution equals the Iso-electric Point (IEP: the concentration of the potential determining ion that makes the surface potentially zero) of the oxide [McCafferty, 2002].

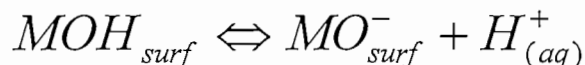
If pH is less than IEP, the surfaces will acquire a positive charge:



If pH is more than IEP, the surface will acquire a negative charge



Or



At the IEP of the oxide film, the oxide surface consists of hydroxyl groups, which can interact with water molecules by hydrogen bonding. Above the IEP, water molecules interact with a negatively charged surface and below the IEP water molecules interact with a positively charged surface.

4.5 Lewis acid-base interactions

Many authors after Fowkes used a **variety of instruments** in trying to understand the Lewis acid-base phenomena in relation to adhesion of organic coatings to substrates. Around 1986 Watts and his co-workers [1986] worked on orientation of molecules at the locus failure positions of polymer coatings on steel. They used angular photoelectron spectroscopy to determine near surface concentration gradients. They also investigated in further work the adsorption of components of an epoxy primer to a galvanized steel surface using TOF-SIMS [Lowe et al., 2003]. They suggested that adsorption of organic molecular species to an oxidized

metal surface does not fully describe how adhesion is achieved. They proposed that there is indirect evidence for the formation of chemical bonds.

Even though Watts and his co-worker found that there is indirect evidence for the formation of true chemical bonds, Rattana and his co-workers [2000] investigated whether the improved durability observed with the combination of hydration and a silane pre-treatment was as a result of a chemical or physical effect and observed that the porous nature of the hydrated surface provides a large surface area over which bonds may be formed. Leadley and Watts [1997] evaluated acid-base properties of PMMA polymer on a silicon treated substrate with XPS and indicated that interaction occurred between the carbonyl group and the treated substrate. Watts and Taylor [1995] studied the interphase chemistry with emphasis on surface adsorption and adhesion and widely documented the phenomena of preferential adsorption as a cause of adhesion failure in certain systems.

Leadley and Watts [1997] showed that monochromated XPS can be used to evaluate acid-base interactions at the Poly(Methyl Methacrylate)-oxidized metal interface. Their data indicated that the acid-base nature of the substrate's surface affects PMMA-substrate interaction. The acid-base interaction between the oxidized metal substrate and PMMA indicated that the orientations of PMMA at the interface are different from that in the bulk PMMA. Although it is widely accepted that Lewis acid-base interactions of the type advocated by Fowkes play an important part in adhesion phenomenon, there is no universal accepted manner in which the magnitude of such forces can be readily estimated. Watts and Gibson [1991] addressed this issue by using XPS spectroscopy. Watts [1995] expanded investigations on the estimation of acid-base interaction by XPS to forces between polymers and inorganic surface.

Li and co-workers [1994] used infrared spectroscopy to study the Lewis base properties of metal oxides. They proposed a new method to characterize surface Lewis base sites and strength by using boric acid trimethyl ester (BATE). Van der Brant and his co-workers [2004] showed that despite different surface preparations procedures, oxides do not show different chemistry on the surface as compared to the inner phase. However, the oxides differ in the amount of hydroxyls that are present on the surface.

Flexibility is the watchword in industry today and the chemical industry is no exception. "If you understand the basics of colloid and surface science, you can be very flexible because you can apply the science to a wide range of areas," says Ward [1998].

CHAPTER 5: SURFACE ANALYSES TECHNIQUES AND INSTRUMENTATION

5.1 Introduction

This chapter introduces the background of the surface analyses techniques and instruments that will be used for this study. Methods used to analyze surfaces have the potential to alter the surface. Because of potential artifacts and the need for more information to construct a picture of the surface, more than one method should be used if possible. The data derived from two or more methods should always be corroborative. When the data are contradictory, a third or fourth method may be necessary to allow confident conclusions to be drawn about the nature of a surface.

5.2 Surface analysis techniques

Surface analysis involves the determination of the chemical distribution and structural composition of the outermost layers of solid surfaces. In particular, surface analysis is a sensitive method of performing chemical analysis on very small quantities of material in the first atomic layers of the solid surface [Grant and Briggs, 2003]. Some surface analytical techniques are also capable of measuring variations in composition with depth.

Each technique probes a unique depth into the surface. Table 5-1 summarizes surface analysis techniques.

Table 5-1: Common methods to characterise surfaces [Ratner et al., 2004].

Method	Principle	Depth of analysis	Spatial resolution	Analytical sensitivity
Contact angle	Liquid wetting of surface is used to estimate the energy of surfaces	3-20 Å	1 mm	low to high depending on the chemistry
XPS	X-ray induce the emission of electron of characteristic energy	10-250 Å	10-150 µm	0.1 at%
Auger electron spectroscopy	A focused electron beam stimulates the emission of Auger electrons	50-100 Å	100 Å	0.1 atom %
SIMS	Ion bombardment sputters secondary ion from the surface	10 Å -1 µm	100 Å	Very high
FTIR-ATR	IR radiation is adsorbed and excites molecular vibrations	1-5 µm	10 µm	1 mol%
STM	Measurements of the quantum tunneling current between a metal tip and a conductive surface	5 Å	1 Å	single atom
SEM	Secondary electron emission induced by a focused electron beam is spatially imaged	5 Å	40 Å, typically	high, but not quantitative

5.2.1 Contact angle

The contact angle (θ) is the angle that a small drop of liquid makes as it meets the surface or interface of another phase, usually a solid. The procedure used to measure the contact angle is based on the ASTM D724 standard. The instrument used for measurements was a Ramé-Hart Goniometer (Figure 5.1). The image of each single drop was acquired by a video-camera connected to a computer (Figure 5-2). The contact angle's (θ) value was calculated by measuring the base (b) and height (h) of the drop profile and using the relationship [Carrino et al., 2002]:

$$\theta = \arcsin\left(\frac{4bh}{4h^2 + b^2}\right) \quad (5.1)$$

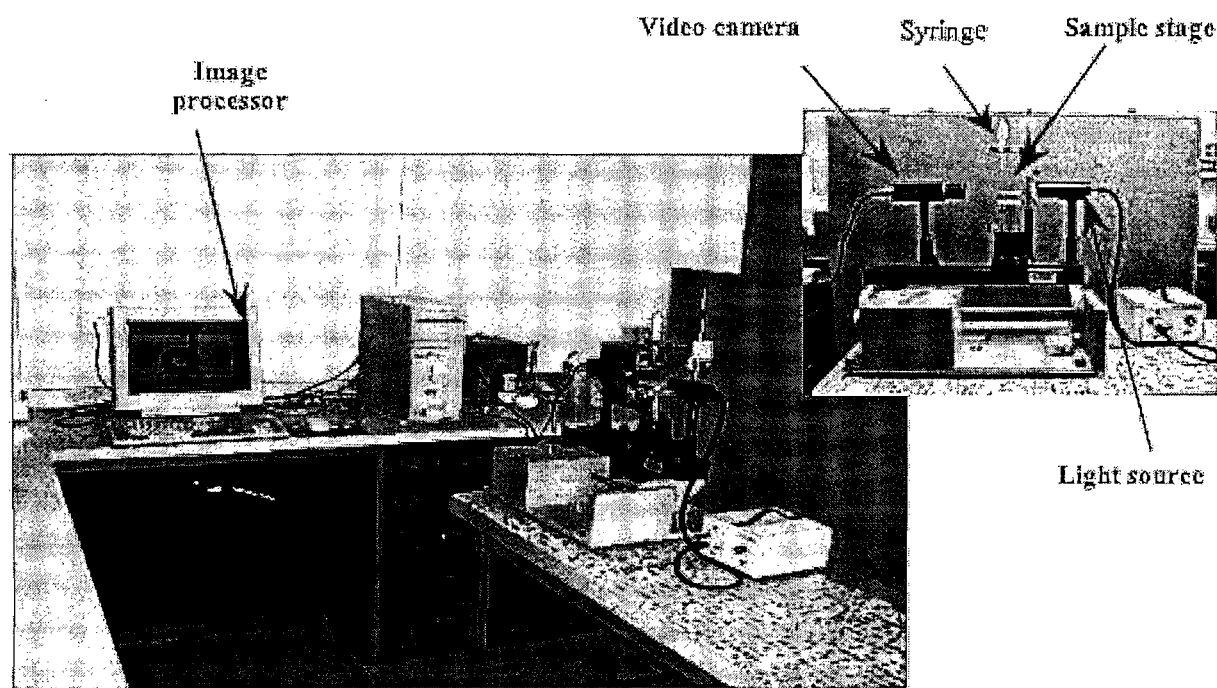


Figure 5-1: Ramé-hart Goniometer.

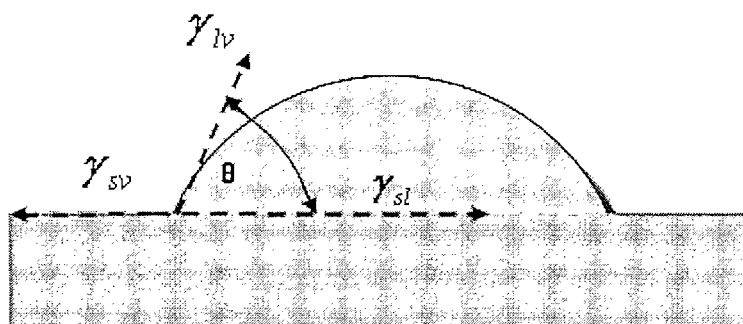


Figure 5-2: Contact angle measurements, where γ_{sv} , γ_{sl} and γ_{lv} are the surface-interfacial tensions of the solid-vapor, solid-liquid and liquid-vapor phases, respectively.

The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the Young-Laplace equation [Young, 1992]. Its value for a spherical surface was deduced in 1805 independently by Thomas Young (1773-1829) and by Pierre Simon de Laplace (1749-1827), and is given by

$$p_{\alpha} - p_{\beta} = \frac{2\gamma}{r} \quad (5.2)$$

where p_{α} and p_{β} are the internal and external pressures of the spherical surface and r is its radius. The Young-Laplace equation shows that the pressure inside a spherical surface is always greater than the pressure outside, but the difference decreases to zero as the radius becomes infinite (when the surface is flat). The contact angle is not limited to a liquid/vapor interface; it is equally applicable to the interface of two liquids or two vapors.

5.2.1.1 Measuring methods

The sessile drop method

The sessile drop method is an optical contact angle method. This method is used to estimate wetting properties of a localized region on a solid surface. The angle between the baseline of the drop and the tangent at the drop boundary is measured.

5.2.1.2 Typical contact angles

On extremely hydrophilic surfaces, a water droplet will completely spread (an effective contact angle of 0°). This occurs for surfaces that have a large affinity for water (including materials that absorb water). On many hydrophilic surfaces, water droplets will exhibit contact angles of 10° to 30° . On highly hydrophobic surfaces, which are incompatible with water, one observes a large contact angle (70° to 90°). Some surfaces have water contact angles as high as 150° or even close to 180° [Zhang et al., 2005].

In this work, the wetting properties of a LCAK steel substrate have been largely modified by surface treatment.

5.2.2 X-ray Photoelectron Spectrometer

XPS provides quantitative compositional information for the top 10 nm of a sample surface. Furthermore, information regarding the chemical states of elements present can also be obtained. The sample is irradiated with a beam of monochromatic soft X-rays. Photoelectron emission results from the atoms in the specimen. The kinetic energies of these electrons relate to the atom and orbital from which they originated. The distribution of kinetic energies from a sample is then measured directly by the electron spectrometer [Crist, 2005].

Atomic orbitals from atoms of the same element in different chemical environments are found to possess slightly different (but measurable) binding energies. These "chemical shifts" arise because of the variations in electrostatic screening experienced by core electrons as the valence and conduction electrons are drawn towards or away from the specific atom. Differences in oxidation state, molecular environment and co-ordination number cause different chemical shifts. Photoelectron binding energy shifts are, therefore, a source of chemical information. It should be noted that these shifts can be very small and can only be detected using a high performance instrument with suitable software [Crist, 2004]. The basic components of a monochromatic XPS system are shown below.

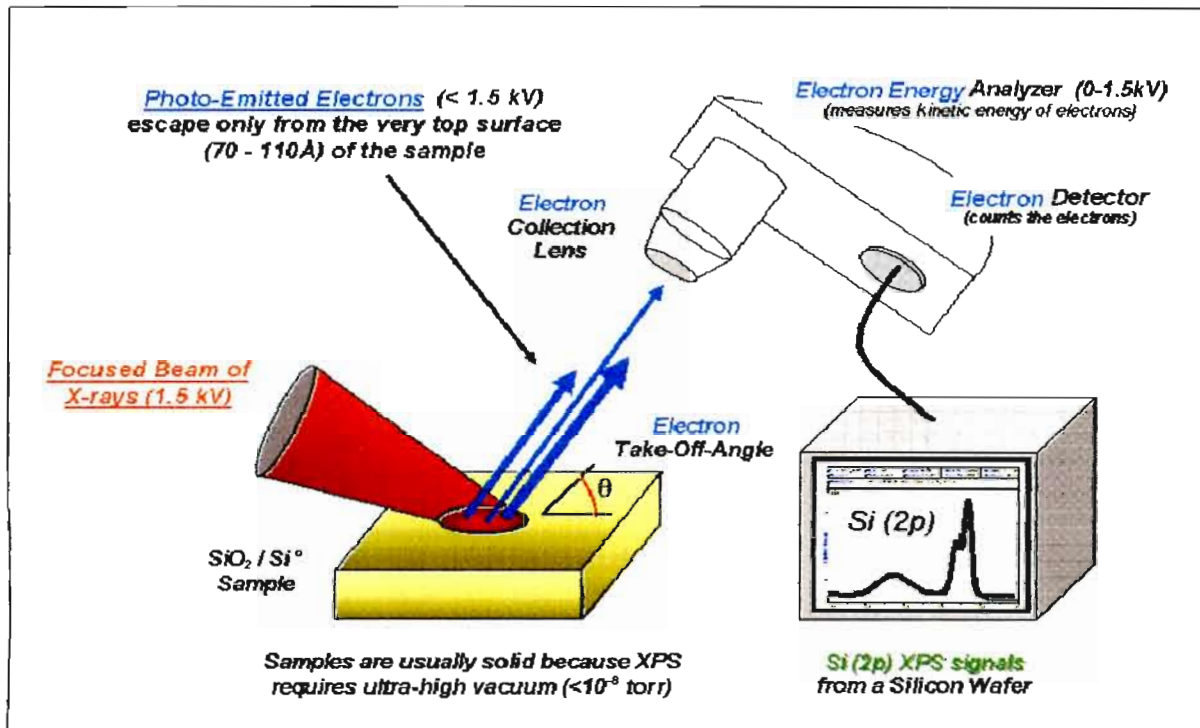


Figure 5-3: Basic components of a monochromatic XPS system [www.wikipedia.org].

5.2.2.1 Components of an XPS system

The main components of an XPS system are [Grant and Briggs, 2003]:

- A source of X-rays
- An ultra-high vacuum (UHV) stainless steel chamber with UHV pumps
- An electron collection lens
- An electron energy analyzer
- An electron detector system
- A moderate vacuum sample introduction chamber
- Sample mounts
- A sample stage
- A set of stage manipulators.

5.2.2.2 Uses and capabilities

XPS is routinely used to determine:

- the elements and quantities thereof in the first 10 nm of the sample surface;
- whether contamination, exists in the surface or the bulk of the sample;
- the empirical formula of a material that is free of excessive surface contamination;
- the chemical state identification of one or more of the elements in the sample;
- the binding energy (BE) of one or more electronic states;
- the thickness of one or more thin layers (1–8 nm) of different materials within the top 10 nm of the surface and the density of electronic states.

5.2.2.3 Routine limits of XPS

Analysis times required may be summarized as follows:

- 1–10 minutes for a survey scan that measures the amount of all elements, 1–10 minutes for high energy resolution scans that reveal chemical state differences, 1–4 hours for a depth profile that measures 4–5 elements as a function of etched depth (usual final depth is 1,000 nm) [Seah and Briggs, 1992].

The instrument's detection limit may be summarized as follows:

- 0.1–1.0 atom % (0.1 atom% = 1 part per thousand (PPT_h) = 1000 PPM). The ultimate detection limit for most elements is approximately 100 ppm, which requires 8–16 hours of analysis time.

Analysis area limits may be summarized as follows:

- Analysis area depends on instrument design. The minimum analysis area ranges from 10 to 200 μm . The largest size for a monochromatic beam of X-rays is 1–5 mm. Non-monochromatic beams are 10–50 mm in diameter.

Sample size limits may be summarized as follows:

- Older instruments accept samples: 1x1 to 3x3 cm. Very recent systems can accept full 300 mm wafers and samples that are 30x30 cm.

Degradation of the sample during analysis may be summarized as follows:

- Depending on the sensitivity of the material to the wavelength of X-rays used, the total dose of the X-rays, the temperature of the surface and the level of the vacuum, can contribute to the degradation of the sample during analysis. Metals, alloys, ceramics and most glasses are not measurably degraded by either non-monochromatic or monochromatic X-rays. Some, but not all, polymers, catalysts, certain highly oxygenated compounds, various inorganic compounds and fine organics are degraded by either monochromatic or non-monochromatic X-ray sources [Seah and Briggs, 1983].
- Because the vacuum removes various gases (eg. O_2 , CO) and liquids (eg. water, alcohol, solvents) that were initially trapped within or on the surface of the sample, the chemistry and morphology of the surface will continue to change until the surface achieves a steady state. This type of degradation is sometimes difficult to detect.

5.2.2.4 Analysis Details

Charge Compensation Techniques [International Standard Organization, 2001; Moulder et al., 1992; Wagner et al., 1979]

Charge compensation methods involve putting low energy electrons back to the surface of the sample. This can be achieved by using a source and generating other low energy electrons to the sample, e.g.:

- Low Voltage Electron Beam (1-20 eV)
- UV light
- Low Voltage Argon Ion Beam with Low Voltage Electron Beam (1-10 eV)
- Aperture mask
- Mesh screen with Low Voltage Electron Beam

Sample Preparation

- XPS applications sample preparation and mounting is critical. Typically the sample is mechanically mounted to a specimen holder, and analysis is begun with the sample in the as received condition. Sample preparation might modify the surface composition.
- Surface cleanliness depends on the technique used. In XPS the surface is clean if the contamination is below the detection limit at about 0.1 atomic %. The samples can be cleaned as follows:
 - Heating
 - Washing
 - Ion etching or
 - By keeping a good vacuum in the analysis chamber.

Charge referencing insulators

Surface charging brings difficulties in obtaining correct information about sample, various ways are provided to eliminate these effects. When the conductivity of the sample is large enough, the charge resulting from the process is immediately neutralized by an electron flux. With

insulators, neutralization is only partial and a significant net positive charge accumulated at the surface.

Software

The software used in this study is CasaXPS processing software, which offers powerful analysis techniques for both spectral and imaging data.

Peak-fitting

Small and sometimes not so small differences between the initial and final state of an atom when a core level electron is excited by an X-ray is fundamental to XPS as an analytical technique. In terms of an XPS spectrum, the increase in counts as a function of kinetic energy associated with the excitation of a core level electron appears as an ensemble of peaks rather than a single peak. These chemically shifted peaks offer information about the chemistry of the surface. Consider the XPS spectrum (Figure 5-4) of the carbon 1s electrons measured from a nylon sample; the chemical formula for nylon [Beamson and Briggs, 1992] indicates four chemical environments for a carbon atom. The C 1s spectrum clearly contains two chemically shifted C 1s peaks; however the more subtle shifts associated with the peaks labeled CH₂ are the reason peak fitting is an important tool in XPS.

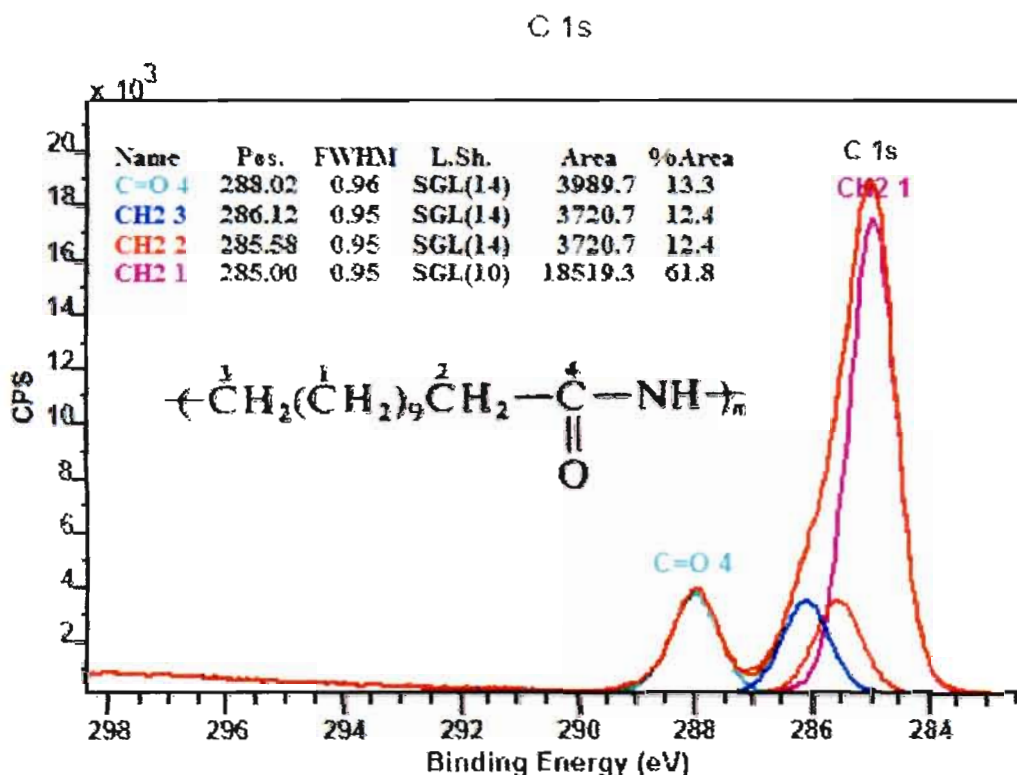


Figure 5-4: C 1s region measured from a nylon sample [Beamson and Briggs, 1992].

5.2.2.5 Applications of XPS to surface chemistry

X-ray photoelectron spectroscopy (XPS or ESCA) has long been recognized as a primary tool for the detection of chemical changes on the surfaces of solids [Barr, 1991]. Dickie and his co-workers [1981] determined the composition of the interfacial surfaces generated as a result of corrosion induced adhesion loss from steel substrate. They suggested that the coating near the substrate may be more oxidised than the bulk of the coating film. These results, and the results of a subsequent study of the interfacial chemistry of humidity-induced adhesion loss by Holubka and his co-workers [1984] suggested that the nature of the substrate may influence the composition and properties of the organic coating in the interfacial region, and in particular that the normal oxide surface of the cold rolled steel may promote the oxidation of coatings in the interfacial region. Von Moltke and Sandenbergh also used XPS to characterize the organic coatings on steel surfaces [Von Moltke and Sandenbergh, 2003]. They indicated that the

availability of surface analysis techniques to characterize industrially produced steel surfaces can contribute significantly to the development of production route control measures to ensure consistent functional properties of steel products.

5.2.3 FTIR Spectroscopy

Fourier Infrared spectroscopy (FTIR Spectroscopy) deals with the infrared region of the electromagnetic spectrum. As with all spectroscopic techniques, it can be used to identify a compound and to investigate the composition of a sample [Haaland, 1990].

5.2.3.1 Background

The infrared portion of the electromagnetic spectrum is divided into three regions; the near-, mid- and far- infrared regions, named for their relation to the visible spectrum. The far-infrared region, (approx. $400\text{--}10\text{ cm}^{-1}$) lies adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid- infrared region (approx. $4000\text{--}400\text{ cm}^{-1}$) may be used to study the fundamental vibrations and associated rotational-vibrational structure, whilst the higher energy near-IR region ($14000\text{--}4000\text{ cm}^{-1}$) can excite overtone or harmonic vibrations [Haaland, 1990].

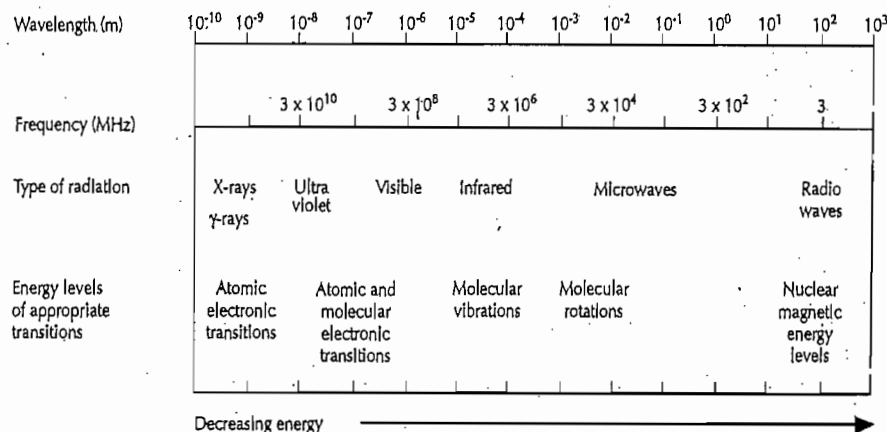


Figure 5-5: Electromagnetic spectrum [www.wikipedia , 2009].

Infrared spectroscopy uses the fact that chemical bonds have specific frequencies at which they vibrate corresponding to energy levels. The vibrational frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, eventually by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole.

Simple diatomic molecules have only one bond, which may stretch. More complex molecules may have many bonds, and vibrations can be conjugated, leading to infrared absorptions at characteristic frequencies that may be related to chemical groups. The atoms in a CH_2 group, commonly found in organic compounds can vibrate in six different ways, symmetrical and asymmetrical stretching, scissoring, rocking, wagging and twisting movements (Figure 5-6).

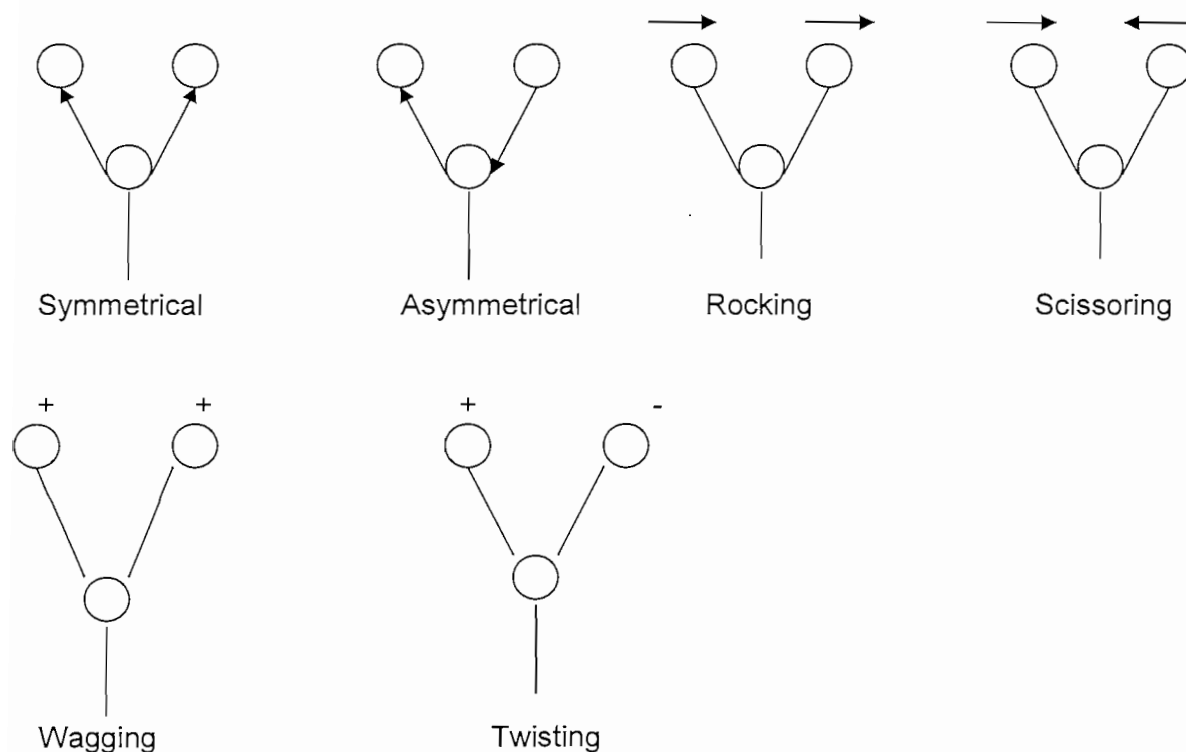


Figure 5-6: Possible vibrational modes.

5.2.3.2 Energy of a molecule

The internal energy of a molecule consists of translational, rotational, vibrational and electronic energy [Van der Pol, 2008]

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}}$$

The translational energy of a molecule is associated with movements of the molecule as a whole, for example in a gas. Rotational energy is related to the rotation of the molecule, whereas vibrational energy is associated with the vibration of atoms within the molecule. Electronic energy is related to the energy of the molecule's electrons.

The energy of a molecule is quantized and a molecule can exist only in certain energy levels. Within an electronic energy level a molecule has many possible vibrational energy levels. A

simplified representation of the quantized electronic energy levels of a molecule are shown in figure 5-7

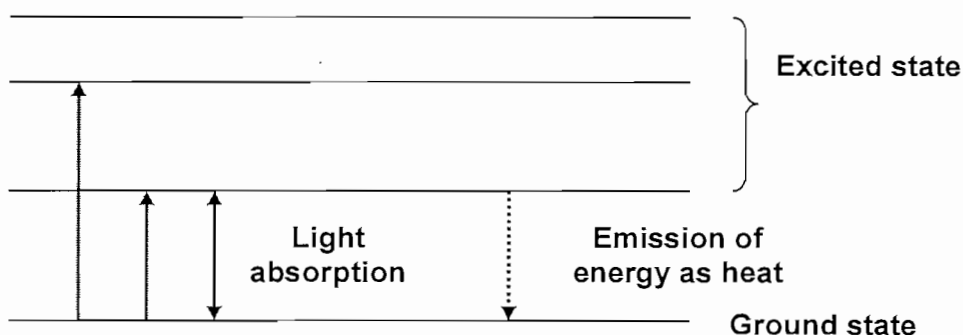


Figure 5-7: A schematic representation of the quantized electronic energy levels of a molecule.

5.2.3.3 Measurements of an IR spectrum

In order to measure the vibrational energies of a sample, a beam of infrared light is passed through the sample, and the amount of energy absorbed at each wavelength is recorded. This may be done by scanning through the spectrum with a monochromatic beam, which changes the wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum may be plotted, which shows the wavelengths where the sample absorbs the energy, and allows an interpretation of which bonds are present.

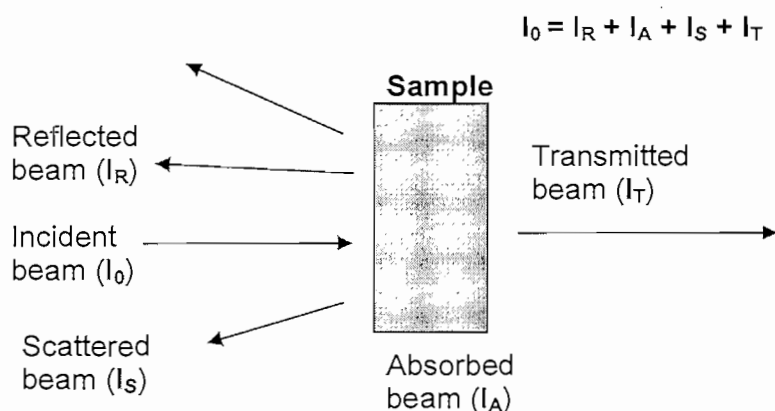


Figure 5-8: Schematic representation of the infrared light beam.

The intensity of each beam depends on the:

- Intensity and wavelength of incident radiation;
- Optical properties of the specimen;
- Concentration of the species; and
- Geometry of experimental setup.

5.2.3.4 Principles of FTIR Spectrometers

5.2.3.4.1 Obtaining the spectrum

An interferometer utilizes a beamsplitter to split the incoming infrared beam into two optical beams. One beam reflects off a flat mirror which is stationary. Another beam reflects off a flat mirror which is moving a very short distance (typically a few millimetres) away from the beamsplitter. The two beams reflect off their respective mirrors and are recombined when they meet at the beamsplitter. The re-combined signal results from the “interfering” with each other. Consequently, the resulting signal is called interferogram, which has every infrared frequency “encoded” into it. When the interferogram signal is transmitted through or reflected off the sample surface, the specific frequencies of energy are adsorbed by the sample due to the

excited vibration of function groups in molecules. The infrared signal after interaction with the sample is uniquely characteristic of the sample. The beam finally arrives at the detector and is measured by the detector. The detected interferogram can not be directly interpreted. It has to be “decoded” with a well-known mathematical technique in term of Fourier Transformation. The computer can perform the Fourier transformation calculation and present an infrared spectrum, which plots absorbance (or transmittance) versus wavenumber.

The good performance of FTIR spectrometers is largely due to a number of specially designed components which have been incorporated into the instrument.

The source

The source is a wire wound source which is located within a ceramic cavity. This becomes stabilized at its operating temperature (around 1400°C). It is thermally insulated from the rest of the optical bench to reduce the temperature gradient to a minimum, and to minimize heat transfer to the base plate of the interferometer, thereby minimizing alignment difficulties.

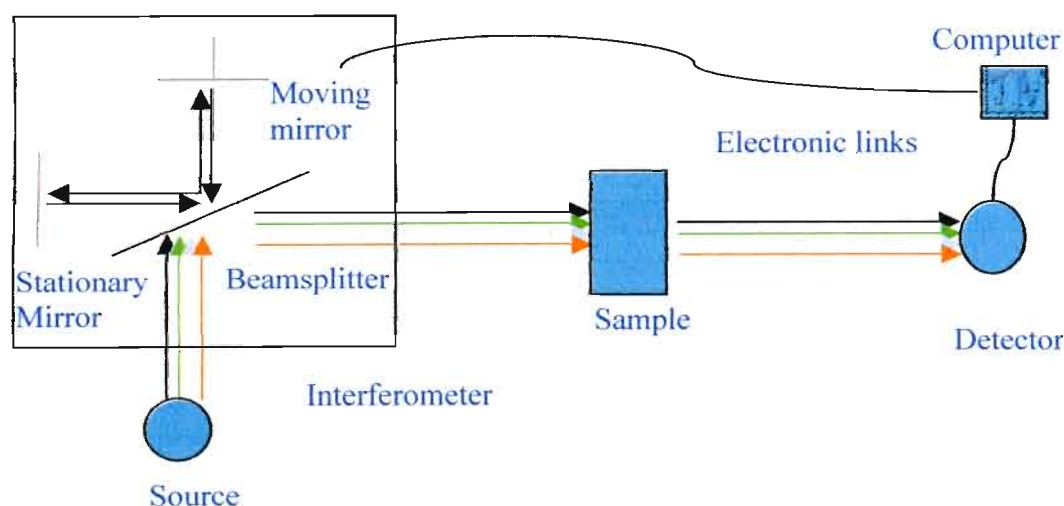


Figure 5-9: Schematic representation of a typical Fourier Transform Spectrometer.

The interferometer

The basic components of the Michelson interferometer are a beamsplitter, fixed mirror and movable mirror (Figure 5-9). The interferometer utilizes a series of moving mirrors rather than just a single moving mirror. This is to avoid problems caused by shearing and tilting.

The beamsplitter

The traditional material for the beamsplitter is germanium, but in most modern interferometers the beamsplitter is comprised of a series of optical layers (including germanium) which are sandwiched between two KBr plates. A variety of alternative beamsplitters is available, depending on the spectral range required. Some instruments allow the beamsplitter to be changed by the operator.

5.2.3.5 FTIR measurement techniques

A given sample may be examined in many ways. It is important to select the technique or accessory which will give a spectrum from which the required analytical results can be obtained. Having selected the most suitable technique, care should always be taken to obtain a good quality spectrum, especially when quantitative results are required.

5.2.3.5.1 KBr pellets

This is more properly referred to as the "alkali-halide" disc technique since, in principle, other alkali halides may also be used (e.g. KCl, NaCl, KI, CsI). However, 'KBr disc' is the commonly used term. It is a sample preparation technique that is very useful for solids which may be in the powdered form. It is especially useful when there is only a small amount of the sample available. Dry KBr is mixed with the sample in a prescribed manner. A press and a standard die are required for making KBr pellets (Figure 5-10).

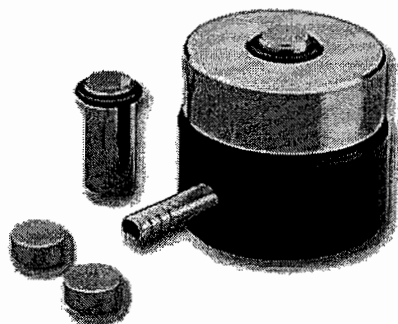


Figure 5-10: A press and a standard die for making KBr pellets.

One of the main advantages of this method is that the matrix (KBr) has no absorption bands which interfere with the spectrum of the sample. The sample may also be recovered (with care) after the spectrum has been measured, or the disc itself may be retained for further use at a later date.

5.2.3.5.2 Reflection measurements

5.2.3.5.2.1 *Specular reflectance*

When a ray of light is reflected at a surface the angle of reflectance is equal to the angle of incidence. This is referred to as specular reflectance. The amount of light specularly reflected will depend on the nature of the surface and the refractive index of the material under consideration. Highly polished metal surfaces reflect infrared radiation to a large extent. Materials such as carbon filled polymers reflect very little infrared radiation, most of the radiation being absorbed by the sample [Stevenson and Garton, 1987]. Most reflectance spectra are made with reference to a plain mirror.

Consider the situation where a reflecting surface is coated with a thin layer of organic coating (Figure 5-11). Incident radiation will pass through the layer, be reflected at the reflection surface

(metal) at the rear of the layer, and pass through the layer a second time. This is often referred to as Reflection/Absorption measurement, or a double transmission measurement.

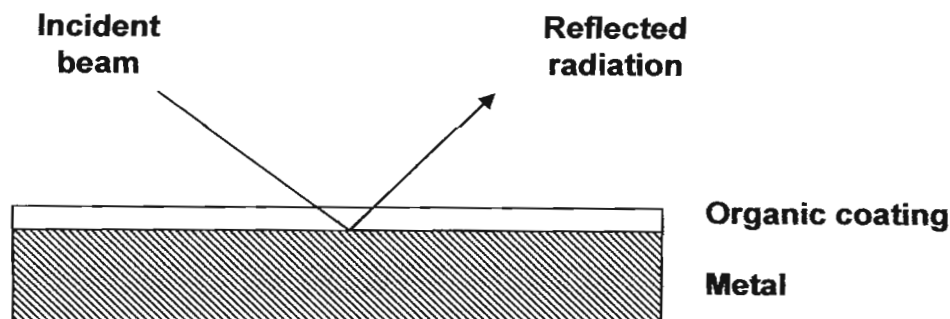


Figure 5-11: Reflection – absorption measurement.

5.2.3.5.2 Diffuse reflectance

Diffuse reflectance (DR) is a relatively modern method of measurement. The DR technique is used for the analysis of solid samples which have an irregular (rough) surface, or which can be finely ground. During DR, infrared radiation undergoes either

- i) reflection from the front surface of the sample and /or
- ii) penetration into the surface layer and maybe beyond by transmission through or absorption by the sample particles.

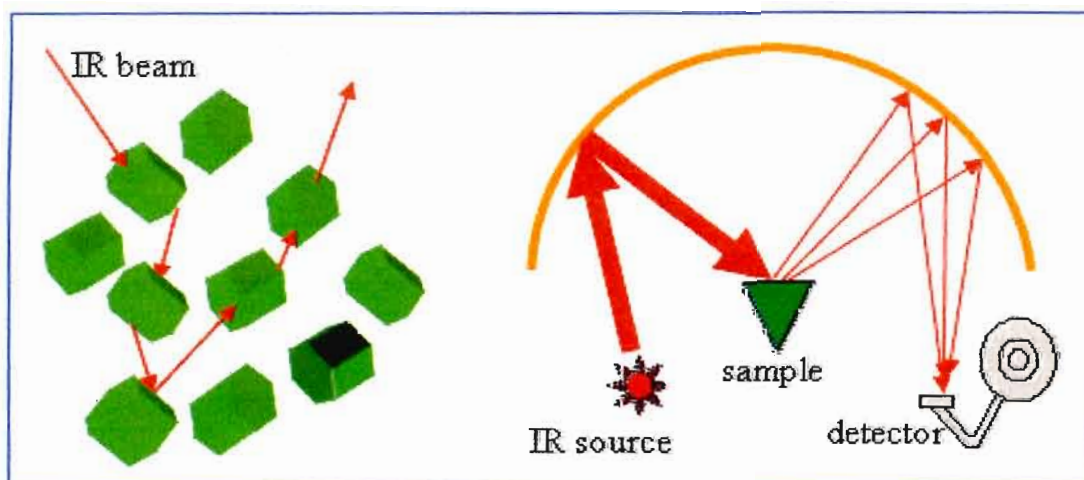


Figure 5-12: Diffuse reflectance measurement.

The resulting spectra may dramatically vary in appearance, depending on a number of factors. Two of these important factors over which the operator usually has some control are particle size and sample concentration.

Some samples cannot be ground to a suitable fine powder. It may be possible to abrade the sample with an abrasive rod or paper, or silicon carbide, carborundum or diamond paper pads. These are readily available from the accessory manufacturers. A small area of the sample is abraded to give a light dusting of the sample on the rod or pad. This is then inserted into the spectrometer and the spectrum measured in the usual way.

5.2.3.5.3 Attenuated Total Reflectance (ATR)

In recent years the technique of ATR has become a standard sampling method for Infrared Spectroscopy. It is a surface analytical technique, used mainly when the sample will not transmit infrared radiation, or where it cannot be put into a suitable form for analysis by standard transmission methods. The principle of this technique lies in the use of a crystal of high refractive index. The crystal is often trapezoidal in shape (figure 5-13).

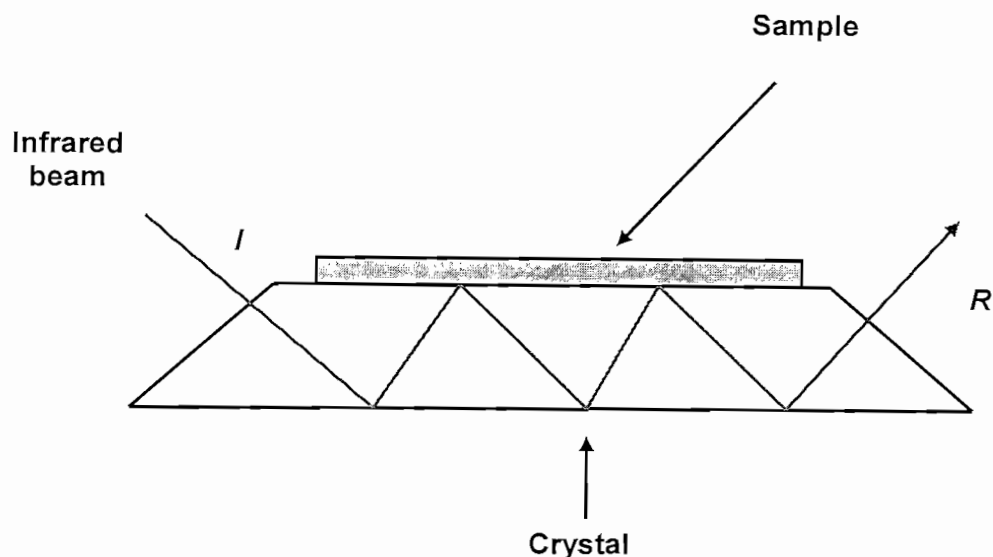


Figure 5-13: Total internal reflection at the crystal/surface interface.

The infrared beam enters the crystal normally at one of the short sides. It is transmitted through the crystal to the adjacent surface. Since the critical angle is exceeded at the crystal/air interface total internal reflection occurs, thus forcing the beam to travel along the length of the crystal being successively internally reflected until it reaches the exit face of the crystal and passes through. At each point of reflection the radiation will interact with any sample which is placed in contact with the crystal face, and thus a spectrum can be obtained which is similar to a normal transmission spectrum.

5.2.3.5.3.1 Factors which affect ATR spectra

- Number of reflections – the greater the number of reflections the stronger will be the spectrum.
- Sample size – the larger the surface area of the sample which is in contact with the crystal, the more intense the spectrum will be.
- Angle of incidence – as the angle of incidence increases, the depth of penetration into the sample is reduced. By using different angles the penetration depth can be varied.

- Refractive index – the refractive index of the crystal should exceed that of the sample.
- Thickness of the sample – the depth of penetration of the radiation into the sample varies with wavelength, but it is of the order of 0.5-5 microns.

5.2.3.5.3.2 Disadvantages of ATR technique

- Only the surface layer is analyzed, the homogeneity of the sample must be considered.
- The crystal is easily scratched, leading to loss in throughput of energy
- Generally it cannot be used for quantitative analysis.

5.3 Scanning Electron Microscope

The **scanning electron microscope (SEM)** is a type of electron microscope that creates various images by focusing a high energy beam of electrons to the surface of a sample and detecting signals from the interaction of the incident electrons with the sample's surface. The type of signals gathered in a SEM varies and can include secondary electrons, characteristic x-rays, and back scattered electrons. The SEM is capable of producing high-resolution images of a sample surface in its primary use mode and secondary electron imaging [Goldstein, 1992]. Due to the manner in which this image is created, SEM images have great depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This great depth of field and the wide range of magnifications are the most familiar imaging mode for specimens in the SEM. Characteristic X-rays are emitted when the primary beam causes the ejection of inner shell electrons from the sample and are used to tell the elemental composition of the sample [Verhoeven, 1986].

5.3.1 Components of the SEM

5.3.1.1 The vacuum system

A vacuum of $\sim 1.3 \times 10^{-4}$ Pa must be maintained in the column and specimen chamber. A high quality vacuum is needed mainly for the following reasons:

- It enables thermionic emission of electrons providing a stable electron beam.
- It allows "free" electron movement through the optical lenses without scattering.
- It allows detection of electron signals with minimal noise.

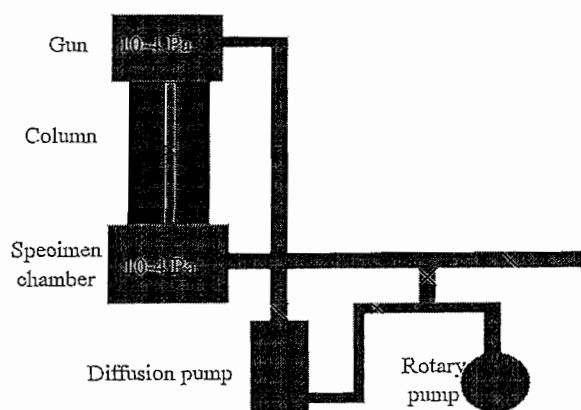


Figure 5-14: The SEM vacuum system [Chapman, 1998].

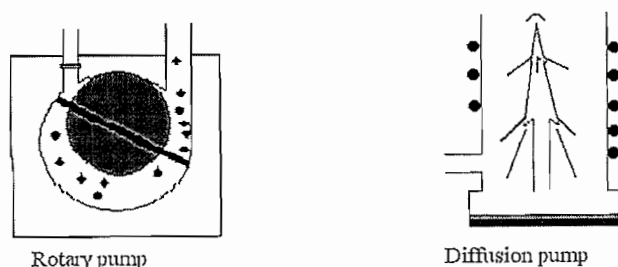


Figure 5-15: Vacuum pumps [Chapman, 1998].

5.3.1.2 Electron sources

Two modes of electron emission may be used as sources:

1. Thermionic emission (Tungsten hairpin electron gun and the Lanthanum Hexaboride (LaB_6) electron gun)
2. Field emission (Cold field, thermal field and Schottky emitters)

5.3.1.3 Electron lenses

Electromagnetic lenses reduce the diameter of the crossover in the electron gun, d_0 ($\sim 10 - 50\mu\text{m}$) to the final spot size on the sample surface ($1\text{nm} - 1\mu\text{m}$). For high-resolution images a small spot size is essential, as is the case for light optics (Figure 5-16).

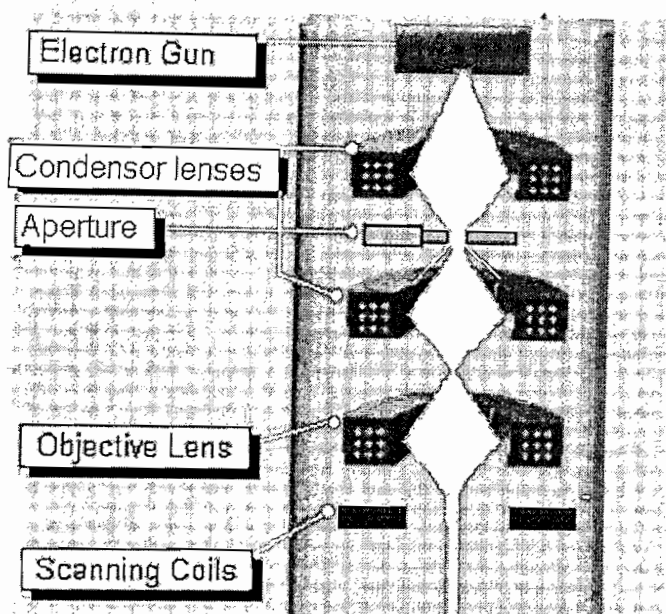


Figure 5-16: The electron optical system [Jeol, A Guide to Scanning Microscope Observation].

5.3.1.4 Electron detectors [Jeol, A Guide to Scanning Microscope Observation, 2006]

Depending on the type of instrument used, different detectors can be used. The SEM instrument used in this study has the following detectors:

Everhard-Thornley detector

This detector can be used to detect both secondary and backscattered electrons.

Scintillator backscatter detectors

Secondary electrons do not have enough energy to excite the scintillator, so that only backscattered signal information is collected.

Solid state detectors

The detector is a thin wafer, usually placed just below the lens pole piece so that specimen can be brought close to the detector, giving a very large acceptance angle and area.

Channel Plate Detector

This detector was developed for producing BSE images when working at low electron accelerating voltages (0.5 – 1keV).

5.3.2 Image formation and interpretation

An image is constructed by moving the beam (scanning) point by point over the sample surface, and simultaneously dumping the signal information point by point on the viewing screen (CRT).

5.3.3 Magnification

The magnification is the ratio of the length of the scan (L) on the CRT to the length of the scan (l) on the specimen. For a CRT screen that is 10 cm square:

$$\text{Magnification} = L/l = 10\text{cm}/l$$

5.3.3.1 Picture element (pixel size)

The unaided human cannot resolve features smaller than about 0.1 mm (100 μm), and so the diameter of the beam in the CRT need not be made smaller than this. Thus, the diameter of an image point on the CRT is $D = 100 \mu\text{m}$ [Murr, 1970]. The conjugate point on the specimen from

which the image signal is produced, which is called the 'pixel' P, will have a smaller diameter, depending on the magnification, of:

$$P = D / \text{Mag} = 100 \mu\text{m} / \text{Mag}$$

5.3.3.2 Image contrast

Contrast is defined as $C = \frac{(S_2 - S_1)}{S_2}$

where S_1 and S_2 represent the signals detected at any two arbitrarily chosen points in the scan raster that defines the image field. S_1 and S_2 represent the signal before any amplification in the signal processing chain. Contrast is a measure of the real information in the signal related to the properties of the sample.

5.3.3.3 Image quality.

The SEM image is constructed from the signal (either secondary or backscattered electrons) arriving at the detector within a dwell time in the scanning cycle. Repeated counts on the same spot will vary around the average $\bar{n}$, with a standard deviation of $\bar{n}^{1/2}$. Signal quality is described as the signal to noise ratio

$$\frac{S}{N} = \frac{\bar{n}}{\sqrt{\bar{n}}}$$

5.3.4 Sample preparations

The most important part of SEM is adequate sample preparations. The sample preparations vary from a simple preparation of inert geological or metallurgical samples to complex methods used for many biological specimens. Specimen preparation is often the limiting factor of the quality of a micrograph.

- Metal specimens require no special preparation for SEM, except for trimming to appropriate size to fit in a specimen chamber, and make appropriate sectioning if necessary.
- Nonconductive solid specimens are coated with a layer of conductive material. An ultrathin coating of electrically-conducting material is deposited either by high vacuum evaporation or by low vacuum sputter coating of the sample. This is done to prevent the accumulation of static electric fields at the specimen due to the electron irradiation during imaging. Such coatings include gold, gold/palladium, platinum, tungsten, graphite etc. Another reason for coating, even when there is more than enough conductivity, is to improve contrast [Lee, 2002].
- A biological specimen requires fixation to preserve its structure, which is usually performed by incubation of specimen in solution of fixative, such as gluteraldehyde or formalin.

5.3.5 Energy dispersive spectrometer (EDS)

One of the instruments most commonly used in conjunction with the SEM is the Energy Dispersive X-ray Spectrometer (EDS). The X-ray spectrometer converts a X-ray photon into an electrical pulse with specific characteristics of amplitude and width. This spectrometer utilizes a solid-state detector. Most often this is a lithium drifted silicon detector, but intrinsic germanium is also used.

The display is a histogram of the X-ray energy received by the detector, with individual "peaks," the heights of which are proportional to the amount of a particular element in the specimen being analyzed [QEMScan].

The locations of the peaks are directly related to the particular X-ray "fingerprint" of the elements present. Consequently, the presence of a peak, its height, and several other factors, allows the analyst to identify elements within a sample, and with the use of appropriate standards and software, a quantitative analysis can be made of elements with atomic number of 4 (carbon) or greater.

Combining the EDS system with the SEM allows the identification, at microstructural level, of compositional gradients at grain boundaries, second phases, impurities, inclusions, and small amounts of material. In the scanning mode, the SEM/EDS unit can be used to produce maps of element location, concentration, and distribution [FEI].

CHAPTER 6: SURFACE CHEMISTRY OF LOW CARBON STEEL

6.1 Introduction

Iron is the fourth most abundant element in the earth's crust. It is found in the sun and many types of stars in considerable quantity. It occurs in many forms including foil, chips, sheet, wire, granules, nanosized activated powders, powders and rod. It has a very important role in the geochemistry of the lithosphere and natural water [Cepria, 2003].

The pure metal is not often encountered commercially, but is usually alloyed with carbon and other metals. The pure metal is very reactive with water and air, and rapidly corrodes, especially at elevated temperatures [Townsend, 1970]. The formation of a surface oxide/hydroxide film on iron in air or in aqueous solution is of interest for many fundamental applications on such topics as corrosion, catalysis, water treatment, and environmental protection [Mielczarski, 2005].

Nearly all iron produced commercially is used in the steel industry and manufactured using a blast furnace. Most chemistry text books cover the blast furnace process (see chapter 1-1.2.3 *Steel production methods*). Although iron has been one of the most used materials for centuries and its oxidation has been studied extensively, there is still a considerable controversy concerning the composition and structure of the iron surface layer produced in air or aqueous solutions. Iron corrosion depends on its open circuit potential and aqueous solution composition [Jones, 2005].

The knowledge of the surface chemistry of iron and its interfaces is fundamental for understanding iron oxidation.

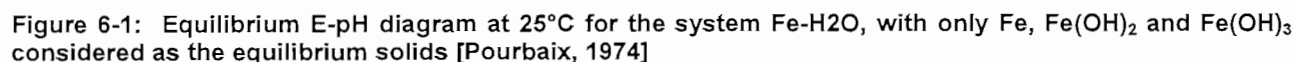
6.2 Solid and aqueous species of iron

The electron configuration of iron is $[\text{Ar}]3d^64s^2$. The most common oxidation numbers for iron in a water solution are 2+ and 3+. Strongly alkaline solutions may contain iron (IV) and iron (VI).

Acidic solution of iron(II) contains the Fe^{2+} ion, which hydrolyses to $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})_2$ (aq) in neutral solution it may precipitate as $\text{Fe}(\text{OH})_2$ (s). In alkaline solutions anionic complexes, such as $\text{Fe}(\text{OH})_3^-$ and $\text{Fe}(\text{OH})_4^{2-}$ are formed [Beverskog, 1996].

For iron(III) the aqueous ion Fe^{3+} is formed in very acidic solutions, and it hydrolyses easily as pH increases to $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_3$ (aq). $\text{Fe}(\text{OH})_3$ precipitates in neutral solutions, but the solubility increases again in very alkaline solution through formation of $\text{Fe}(\text{OH})_4^-$ [Cotton and Wilkinson, 1976].

The hydrolysed anionic ferrous complexes in alkaline solutions are denoted as $\text{Fe}(\text{OH})_3^-$ and $\text{Fe}(\text{OH})_4^{2-}$ and not with the traditional notation of HFeO_2^- and FeO_4^{2-} generally used in Pourbaix diagrams (Figure 6-1) [Pourbaix, 1974].



Although iron has been one of the most used materials for centuries and its oxidation has been studied extensively, there is still a considerable controversy concerning the composition and structure of iron surface layer produced in air or aqueous solutions.

Condition	oxidation number	Iron species
Crystalline	0	Fe
Crystalline	II	Fe(OH) ₂
Crystalline	II	Fe _{1-x} O
Crystalline	II	FeO
Crystalline	II/III	α-Fe ₃ O ₄
Crystalline	II/III	Fe ₃ O ₄ · H ₂ O
Crystalline	II/III	γ-Fe ₃ O ₄
Crystalline	III	Fe(OH) ₃
Crystalline	III	β-FeOOH
Crystalline	III	γ-FeOOH
Crystalline	III	α-FeOOH
Crystalline	III	δ-FeOOH
Crystalline	III	δ'-FeOOH
Crystalline	III	Fe ₅ HO ₈ · H ₂ O
Crystalline	III	α-Fe ₂ O ₃
Crystalline	III	γ-Fe ₂ O ₃
Dissolved	II	Fe ²⁺
Dissolved	II	FeOH ⁺
Dissolved	II	Fe(OH) ₂ (aq)
Dissolved	II	Fe(OH) ₃ ⁻
Dissolved	II	Fe(OH) ₄ ²⁻
Dissolved	III	Fe ³⁺
Dissolved	III	FeOH ²⁺
Dissolved	III	Fe(OH) ₂ ⁺
Dissolved	III	Fe(OH) ₃ (aq)
Dissolved	III	Fe(OH) ₄ ⁻
Dissolved	III	Fe(OH) ₄ ²⁺
Dissolved	III	Fe(OH) ₅ ⁴⁺
Dissolved	IV	FeO ²⁺
Dissolved	IV	FeO ₃ ²⁻
Dissolved	V	FeO ₂ ⁺
Dissolved	VI	Fe(OH) ₄ ²⁻

Table 6-1: Considered Iron species in the iron-water system [Beverkov and Puigdomenech, 1996]

Iron species	Possible reaction at 25°C	Reference
Fe^{2+}	$\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ $1/2\text{Fe}_2\text{O}_3(\text{s}) + 11/2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 3\text{OH}^-$ $\text{Fe}(\text{OH})_{2(\text{s})} + 2\text{H}^+_{\text{aq}} \rightarrow \text{Fe}^{2+}_{\text{aq}} + 2\text{H}_2\text{O}_{\text{aq}}$	[Antena et al., 2005]
Fe^{3+}	$\text{Fe}(\text{OH})_{(\text{s})} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$ $\text{FeOOH}_{(\text{s})} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 3\text{OH}^-$ $2\text{Fe}(\text{OOH})_{(\text{s})} + 3\text{H}^+_{\text{aq}} \rightarrow \text{Fe}^{3+}_{\text{aq}} + 2\text{H}_2\text{O}_{\text{aq}}$	[Stefánsson, 2007; Parker and Khodakovskii, 1995]
FeOH^{2+}	$\text{Fe}(\text{OH})_2^+ + \text{H}^+ \rightarrow \text{FeOH}^{2+} + \text{H}_2\text{O}$ $\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^{2+} + \text{H}^+$	[Stefánsson, 2007]
FeOH^+	$\text{Fe}(\text{OH})_{\text{ad}} \rightarrow \text{FeOH}^+ + \text{e}^-$	[Antena et al., 2005]
$\text{Fe}(\text{OH})_2^+$	$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	[Stefánsson, 2007; Byrne et al., 2000; Majzlan et al., 2004]
$\text{Fe}(\text{OH})_2$	$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$ $\text{FeOH}^+ + \text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$	[Antena et al., 2005]
$\text{Fe}(\text{OH})_3^-$	$\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3^- + \text{H}^+$ $\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3^- + 3\text{H}^+ + 2\text{e}^-$ $\text{Fe}(\text{OH})_{2(\text{s})} + \text{OH}^-_{\text{aq}} \rightarrow \text{Fe}(\text{OH})_{3\text{aq}}^-$	[Stefánsson, 2007; Parker and Khodakovskii, 1995]
$\text{Fe}(\text{OH})_3$	$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 3\text{H}^+$ $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_3$ $\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$	[Stefánsson, 2007; Byrne et al., 2000]
FeOOH	$\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{FeOOH}$ $\text{Fe}(\text{OH})_2 + 1/4\text{O}_2 \rightarrow \text{FeOOH} + 1/2\text{H}_2\text{O}$ $\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{FeOOH} + \text{H}_2\text{O}$	[Stefánsson, 2007; Majzlan et al., 2004]
$\text{Fe}(\text{OH})_4^-$	$\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_4^- + 4\text{H}^+$ $\text{Fe}(\text{OOH})_{(\text{s})} + \text{OH}^-_{\text{aq}} + \text{H}_2\text{O}_{\text{aq}} \rightarrow \text{Fe}(\text{OH})_{4\text{aq}}^-$	[Stefánsson, 2007]

Table 6-2: Summarised Iron species and possible reactions at 25°C

6.3 Iron oxides

Iron oxides are common compounds that are widespread in nature. Iron oxide can be used as model systems in studying the fundamental colloid and surface properties of metal oxides [Kaneka and Uekawa, 2004]. They are important chemical materials in industry that can be applied extensively in many fields.

According to the available literature data, great attention is devoted to the preparation and characterization of iron oxide [Liao et al., 2001; Raming et al., 2002], while less attention has been devoted to the explanation of their formation mechanism. In this field there are still many uncertainties about the mechanism of the formation of iron oxides and the relationship between the method of preparation and physical properties.

There are as many as 15 phases formed by Fe and O, as iron oxide [Cornell and Schwertmann, 2003]. They can be synthesized in pure, mixed oxides as well as doped structures. Iron oxide is used as an electrode in non-aqueous and alkaline batteries and as a cathode in brine electrolysis [Kenichi et al., 1986; Sanehiro et al., 1981; Keiji and Itsuaki, 1979]. Fe_2O_3 is found to have large third-order non-linear optical susceptibility and faster response time showing potential applications in optical computing [Ando et al., 2002]. It appears to have catalytic properties useful for N_2 fixation [Khader et al., 1987]. These oxides have been widely used in several industrial processes, such as dehydration, oxidation and Fischer–Tropsch synthesis [Daza et al., 2000; Kung, 1989; Rofer-Depoorter, 1981].

6.4 Electrochemical behaviour of iron in acidic and alkaline media

Various mechanisms have been proposed to describe the electrochemical behaviour of iron in acid and in alkaline media. The subject has been frequently reviewed [Lorenz and Heusler, 1987; Dražić et al., 1989; Brockis and Khan, 1993]. According to the mechanism proposed by

Dražić and his co-workers an adsorbed intermediate $[\text{Fe}(\text{OH})]_{\text{ads}}$ results from more than one reaction. Thus, in an alkaline medium, this step is represented by [Dražić et al., 1989]



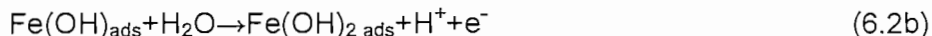
whereas, in acid medium, it is represented by [Brockis and Khan, 1993]



The rate-determining step varies according to the pH of the medium. Thus in a strong acidic medium, the rate-determining step is represented by



while, in alkaline media, it is represented by



As the reaction proceeds, the adsorbed $\text{Fe}(\text{OH})_2$ changes into bulk $\text{Fe}(\text{OH})_2$ on the metal surface, i.e.



All the above reactions involve one electron transfer in what is described as a consecutive mechanism.

At low pH the two most accepted mechanisms were proposed by Bockris and his co-workers [1961] and Heusler [1958]. Both mechanisms consider the already mentioned reaction (6.1a) and (6.2a), but they differ just by the type of rate-determining step, which is reaction (6.1a) for Bockris's mechanism and reaction (6.2a) for Heusler's mechanism in both acidic and alkaline media.

Iron corrosion depends on its open circuit potential and the aqueous solution composition. Iron can be dissolved, or a surface passive layer can be formed. Passivation is the process of making a material "passive" in relation to another material prior to using the materials together.

Revie and his co-workers [1975] used Auger spectroscopy and concluded that the passive film on iron is ferrous hydroxide in a polymeric layered structure. O'Grady and Bockris [1973] used in situ Mössbauer spectroscopy to describe the surface layer as a polymeric gel-like film on hydrated oxides. Mitchell and Grahan [1986] did not observed hydroxyl ions in the passive layer when using SIMS, suggesting the presence of iron oxides. In recent Raman spectroscopy studies of iron surface composition the major surface products detected was magnetite or hydrated magnetite: $\text{Fe}(\text{OH})_2$ and $2 \text{Fe}(\text{OOH})$ [Bonin et al., 1998]. The results were reported for iron in contact with aqueous solution for approximately 70 hours in the pH range 7 to 10. After a shorter reaction time, approximately 15 minutes, the surface layer produced was too thin to be detected [Bonin et al., 2000; Adziemkowski et al., 1998].

The ability of an oxide surface (silica, alumina, magnesia and phosphate) for electron donor-acceptor interaction with other species was described using the Lewis acid-base approach [Mullins and Averbach, 1988], while the ability of H^+ and OH^- exchange was considered using the Brønsted approach [Simmons and Beard, 1987]. X-ray Spectroscopy is a powerful method for the study of the acid-base properties using both the Lewis and Brønsted definitions [Delamar, 1990; Watts and Gibson, 1991]. The close correlation of these two definitions was demonstrated by Casamassima and his co-workers [1991], where acid-base behaviour of aluminium and silicon oxide studied by XPS and rest potential methods was demonstrated. Kurbavo and Darque-Ceretti [1993] attempted to determine the chemical composition and structure of the hydroxylated iron oxide film, which is crucial for the determination of acid-base

properties. They proposed a model of hydroxylated oxide multilayer structure formation of hydroxylated iron oxide.

Daniell and his co-workers [2000] showed that the surface layer of alumina-silica oxide can be observed as a chain of co-ordinately unsaturated oxygen ions and metal cations. They showed that a collection of repeating molecules with Lewis acid and bases character can be formed. The net charge on each surface site depends on the stoichiometry, ionicity and local surface structure.

CHAPTER 7: SURFACE CHARACTERISTIC OF LCAK STEEL PREPARED UNDER WET CONDITIONS

7.1 Introduction

The characteristics of a low-carbon aluminium-killed (LCAK) steel was investigated in order to obtain insight into the chemical surface groups or species found on this steel under wet conditions. This type of steel is frequently used by the packaging industry. Organic coatings are not only used for decorative purposes but also to label the content of the steel containers. The surface condition of this steel used for low-cost, mass-produced items is critical, because expensive surface preparation is not financially viable prior to the application of organic coatings.

The LCAK steel surface was investigated by using contact angle and X-ray photoelectron spectroscopy (XPS).

7.2 Experimental

7.2.1 Surface treatments of LCAK steel

Low-carbon aluminium-killed steel (LCAK) was used. The chemical analysis of the steel was determined by spark emission. Results are summarized in table 7-1. All samples were mounted and polished to a 5 μm finish.

7.2.1.1 Preparation of the standard surface

The standard sample was etched in HIBITEX (inhibited hydrochloric acid with organic additives that tend to coat the cleaned steel to inhibit the attack on the steel) to remove all oxides from the surface, then rinsed in tap water at room temperature to remove all chlorides contamination from the surface, which could influence the wettability, and then rinsed in RADCHEM ethanol 99.9% absolute (A.R) to remove the water film, followed by a hot air drying step to remove the ethanol and water and to prevent flash rusting.

Steel	C	Mn	S	Si	Cu	Ni	Cr	Al
LCAK	0.047	0.2	0.003	0.018	0.008	0.006	0.025	0.059

Table 7-1: Trace element composition of low-carbon aluminium-killed steel in micrograms per gram

In all instances a standard procedure, (section 7.2.1.1), was followed before various experimental conditions were employed to achieve specific results.

7.2.1.2 Warm water treatment

This treatment simulated the surface composition obtained on the production line. In this case the polished sample was rinsed with warm water at ca. 40°C, which was previously boiled for four hours to remove oxygen. The surface was then rinsed with ethanol to remove the water film, followed by a hot air drying step to remove the ethanol and water and to prevent flash rusting [Raffass et al., 2005].

7.2.1.3 Formic acid treatment

The sample was rinsed with a 1:1 v/v Saarchem chemically-pure formic acid 85% (A.R): distilled water solution and then rinsed in ethanol to remove the water film, followed by a hot air drying step. This procedure simulated a temporary production line step.

7.2.1.4 Untreated steel surface

After polishing the sample was rinsed with ethanol, followed by a hot air drying step.

Surface treatment was performed for 10 min. Exposure of the LCAK surface to the laboratory ambient was minimized by performing the contact angle measurements of water and α -bromonaphthalene immediately after surface treatment. This reduces the effects of slow buildup of an adsorbed organic layer on the treated surfaces.

7.2.2 Surface tension measurements

The test liquids used for the surface tension and contact angle measurements were chosen to cover a range of densities and viscosities (Table 7-2), which characterize some of the solvents used in organic coatings. Surface tension measurements were performed on a Ramé-Hart imaging system. The liquids were injected with a syringe to form a drop on the tip of the needle. The drop was observed optically and the surface tension was calculated from the shape of the drop using the Young-Laplace equation,

$$P_{\alpha} - P_{\beta} = \frac{2\gamma}{r} \quad (7.1)$$

where P_{α} and P_{β} are the internal and external pressures of the spherical surface and r is its radius. In this experiment, the surface tension of the liquid solution was determined against air using the pendant drop shape method.

Liquids	Density/ g cm ⁻³	Viscosity at 25°C /cp
Hexane	0.66	0.51
Xylene	0.86	0.62
Water	0.99	0.89
α-bromonaphthalene	1.48	1.65

Table 7-2: Test liquid and their properties at 25°C

7.2.3 Contact angle measurements

The procedure used to measure the contact angle or wettability is based on the ASTM D724 standard method [Carrino et al., 2004]. The instrument used for measurements was a Ramé-Hart Goniometer (*see 5.2.1 in chapter 5*). The contact angles of all treated and untreated (LCAK) surfaces were measured in the laboratory ambient. A drop of ($\sim 2\mu\text{L}$) was formed on the end of a syringe needle and lowered into contact with the surface. As the needle was raised, the drop detached from the tip and adhered to the surface. The sessile drop was observed optically and the contact angle was calculated from the shape of the drop using Young's equation. Contact angle measurements were performed with deionised water and Fluka 95.0% α -bromonaphthalene (GC) at room temperature. The contact angles were measured within 30 s of detachment.

7.2.3.1 Influence of acidic and basic solution on wettability

The term 'wetting', in general, is connected with the area covered by a liquid drop placed on a solid surface. It depends on the liquid and surface properties and it is characterized by the contact angle, defined as the angle between the drop and the surface, as shown in Fig. 7-1. Low contact angles (value near zero) indicate good wetting properties while high values indicate poor wettability [Garbassi et al., 1998]. The procedure used to measure the contact angle or wettability is based on the ASTM D724 standard method [Carrino et al., 2004].

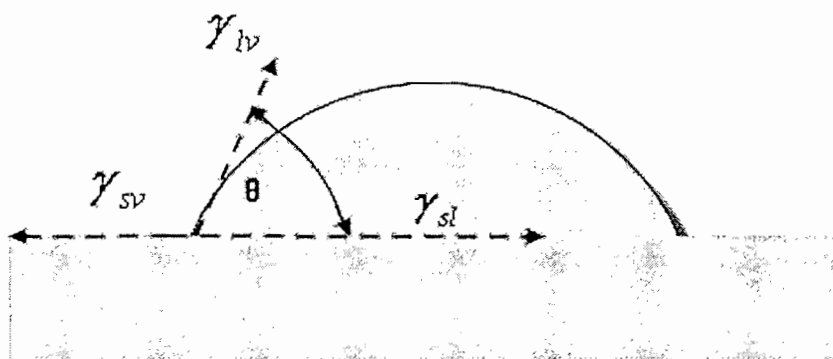


Figure 7-1: Contact angle and gas-liquid-solid related tensions.

Hydrochloric acid 32% (A.R) and sodium hydroxide pellets (A.R) from Promark Chemicals were used. Unbuffered aqueous solutions, representing both acidic and basic conditions, were prepared. The concentrations of the acidic solutions were approximately 1.0 mol dm^{-3} , $2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $4.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $3.0 \times 10^{-6} \text{ mol dm}^{-3}$, while the concentrations of the basic solutions were approximately 1.0 mol dm^{-3} , $1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ and $4.0 \times 10^{-6} \text{ mol dm}^{-3}$. The pH was measured using a Labotec Orion 410A+ pH-meter with an Orion 91-65 Ag/AgCl electrode in the temperature range 0 to 100°C , calibrated with solutions of pH 4 and 10. The pH values of the acidic and basic solutions are shown in table 6-3. The influence of pH on the wettability (contact angle) of a standard polished sample of LCAK and warm water treated sample of LCAK was determined. The wettability measurements on the samples were performed making use of the liquids prepared as in table 7-3. The effect investigated here is the acid-base interaction of the solutions and the surface. Other factors such as ionic strength influenced were neglected.

	Approximate concentration (mol dm ⁻³)	pH
Acidic solutions	1	0.8
	2.0×10^{-2}	2.5
	4.0×10^{-4}	3.6
	3.0×10^{-6}	4.1
Basic solutions	4.0×10^{-6}	9.1
	2.0×10^{-5}	10.5
	1.0×10^{-2}	12.1
	1	13.1

Table 7-3: The pH values of the acidic and basic solutions

7.2.4 XPS analysis

XPS measurements were performed to assess surface composition of LCAK steel surface, as well as to investigate the chemistry of the surface pre-treatment. The aim is to understand the surface chemistry of the interface to provide specific properties during adhesion of coatings. To obtain chemical information as a function of depth of the surface layers, angle resolved X-ray photoelectron spectroscopy (XPS) analysis, described in paragraph 5.2.2 chapter 5, was carried out on the standard sample (sample without surface modification), formic acid treated samples, untreated samples and samples treated with warm water.

The XPS spectra were obtained on a PHI (model 5400) XPS analyser equipped with a Mg/Al dual mode source and a small area analyzer with PSD detector. An achromatic Mg K_α X-Ray (1253.6 eV) source was operated at 300 W. The vacuum pressure was $>10^{-8}$ Torr during spectra acquisition. The O1s, C1s, and Fe2p peaks were obtained in multiplex mode.

7.3 Results and discussions

Most metal surfaces are covered with metal oxide. In the laboratory ambient, the oxides at the surface hydrate to form a high density [Bolger, 1983; Boehm, 1966] of hydroxyl groups (1 to 5 hydroxyl groups per 10^{-8} m^2 of surface area). Practically, such a surface can be represented as $\text{MO}_m(\text{OH})_n$, where M is a metal.

7.3.1 Correlation between contact angle and surface tension

As demonstrated in figure 7-2, low surface tension systems were found to yield low contact angles. The liquids used in this investigation had diverse properties (Table 7-4) to cover most common solvents used in organic coatings. The contact angle increases with increasing surface tension, indicating that, for a given surface, better wetting is obtained for the lower surface tension liquids.

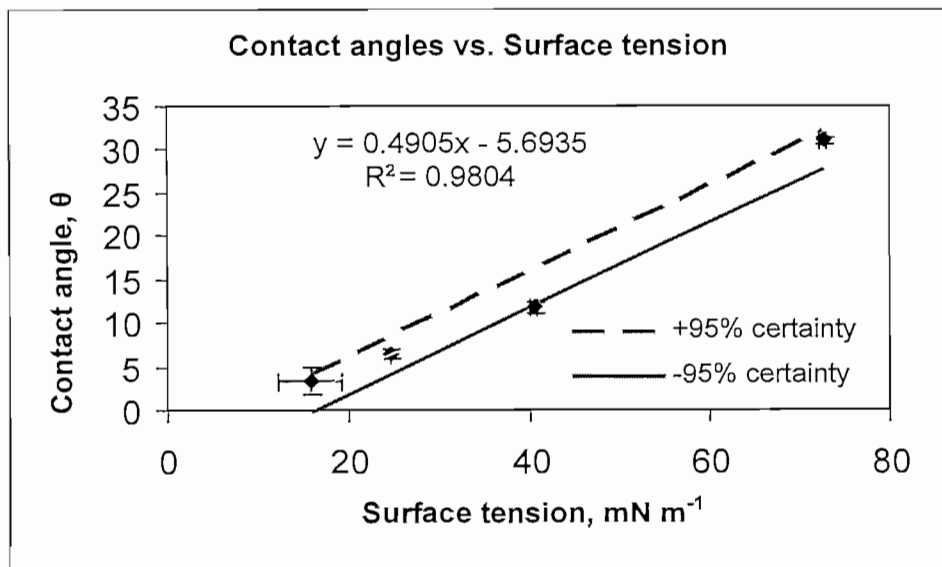


Figure 7-2: The relationship between contact angle and surface tension

Liquids	Density/ g cm ⁻³	Viscosity at 25°C /cp	Surface tension/ mN m ⁻¹	Contact angle on the standard sample (°)
Water	0.99	0.89	72.20	31.20
α-bromonaphthalene	1.48	1.66	40.50	11.10
Xylene	0.86	0.62	24.40	6.30
Hexane	0.65	0.51	18.50	3.50

Table 7-4: Test liquids and their surface tension and contact angle properties at 25°C

Contact angle measurements using deionised water were performed to establish the surface conditions of the polished LCAK substrates prior to chemical treatment. It was found that a drop of water produced an average contact angle of 31.2° on this surface. For hexane, xylene and α-bromonaphthalene, contact angles of 3.5°, 6.3° and 11.1° were measured respectively.

7.3.2 Contact angle measurements of treated and untreated surfaces

Contact angle measurements with different liquid probes with known surface tension form the basis for the surface wettability of solids. However, the solid surface wettability, or parameters related to the surface free energy, can be different depending on the model chosen. Surface wettability for the LCAK steel surfaces were assessed using polar (water) and apolar (α-bromonaphthalene) surface tension components.

The contact angle results for the treated and untreated surfaces are summarized in table 7-5. LCAK surfaces activated chemically with warm water strongly enhance wettability behaviour when compared to other surface pre-treatments. This is suggested by the spreading of the water and of α-bromonaphthalene on the warm water treated surface, where contact angles of 28.8° and 4.9°, respectively are observed in comparison to the values of 45.2° and 13.4° for the untreated LCAK steel surface and 42.5° and 9.5° for formic acid treated LCAK steel surface.

Sample	Surface pre-treatment	Liquid	Contact angle (θ) ($^{\circ}$)
1	Untreated	Water	45.20
2	Untreated	α -bromonaphthalene	13.40
3	Formic acid	Water	42.50
4	Formic acid	α -bromonaphthalene	9.50
5	Warm water	Water	28.80
6	Warm water	α -bromonaphthalene	4.90

Table 7-5: Contact angle of water and α -bromonaphthalene on pre-treated LCAK surfaces

The contact angle (θ) is a characteristic constant for each individual system. A small contact angle value (less than 45°) is an indication of good wetting properties, but only for that particular system. Another liquid on the same surface can give completely different results.

7.3.3 Surface chemical analysis with XPS

All spectra were first analyzed using the Casa-XPS software [Fairley and Carrick, 2005]. Peak shifts due to charging were normalised with the C1s peak set to 285.2 eV. High resolution O 1s spectra were also analyzed to determine the presence of oxide/hydroxide species [Castle and Watts, 1981]. In figure 7-3 the XPS survey spectrum obtained for the standard low-carbon aluminium-killed (LCAK) sheet is shown. The clean surface shows the presence of carbonaceous species (Figure 7-4), which could be due to hydrocarbon contamination from the pre-treatment process (paragraph 7.2.1.1). The main carbon peak (I) at 285.2 eV is attributed to hydrocarbon C (C-H) and peak (II) at 289.1 eV to carbonates (C=O) [Pinzari et al., 2000]. On deconvolution of the O 1s peak (Figure 7-5), three chemical species were identified and attributed to adsorbed water (H_2O , ~ 534 eV), hydroxyl ($Fe(OH)_2$, ~ 532 eV) and hydroxy-oxides ($Fe(OOH)$ ~ 531 eV) [Von Moltke and Sandenbergh, 2003, Roberts and Wood, 1977; Castle and

Watts, 1981; Grosvenor et al., 2004; Reffass et al., 2005; NIST XPS database version 3.5, 2000]. The binding energy values for these three species are shown in table 7-6. O 1s binding energies are among the most difficult to assign because of the proximity in binding energies values of many bulk and surface species with different chemical states [Grosvenor et al., 2004]. An estimated correlation (Table 7-7) is determined between $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OOH})$ using the resolved peak areas. Peak heights or areas are directly related to the concentrations of the species on the surface. Previous research indicated that good paint adhesion of Lewis-base alkyd paint is associated with a 1:1 ratio of $\text{Fe}(\text{OH})_2$ to $\text{Fe}(\text{OOH})$ species on the surface of a steel [Von Moltke and Sandenbergh, 2003].

The Lewis acid-base properties of a hydroxyl group depend on the electronegativity values of the species to which it is bonded [Pinzari et al., 2000]. For $\text{Fe}(\text{OH})_2$, the hydroxyl groups are bonded to Fe^{2+} , which make them Lewis-base species, and for $\text{Fe}(\text{OOH})$ the hydroxyl groups are bonded to 'oxides' and are thus Lewis-acid species [Von Moltke and Sandenbergh, 2003].

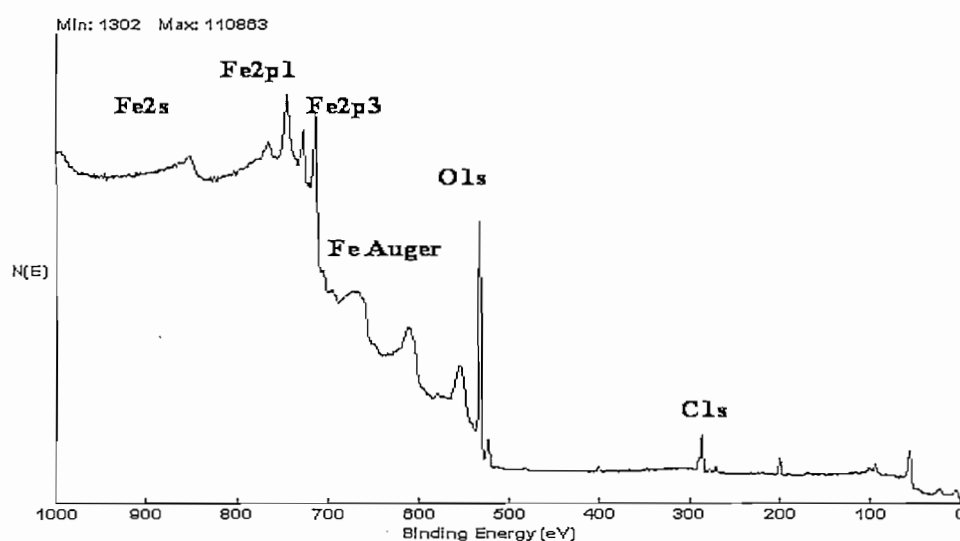


Figure 7-3: XPS survey spectrum obtained for the standard low-carbon aluminium-killed (LCAK) steel

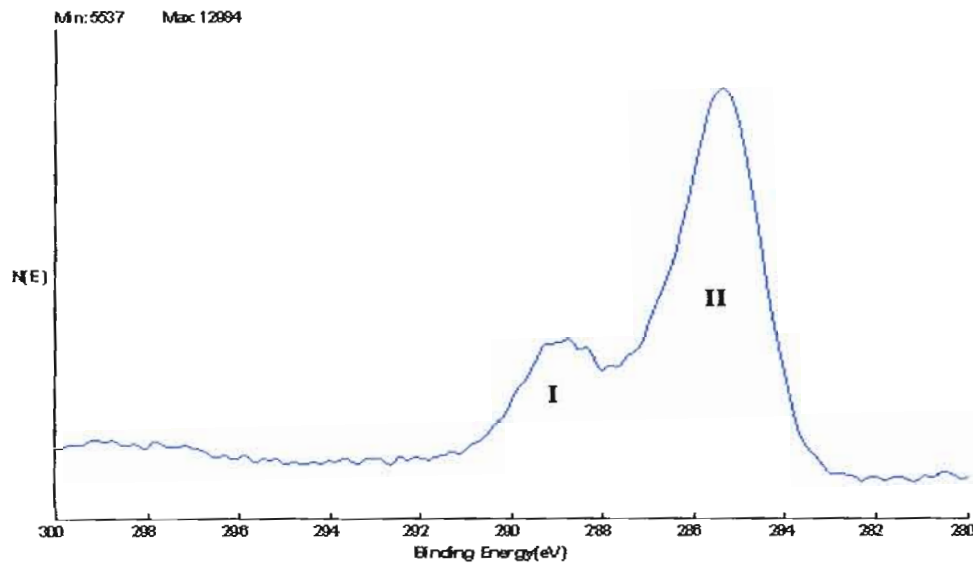


Figure 7-4: High-resolution XPS spectrum of the C 1s region obtained on the standard steel surface

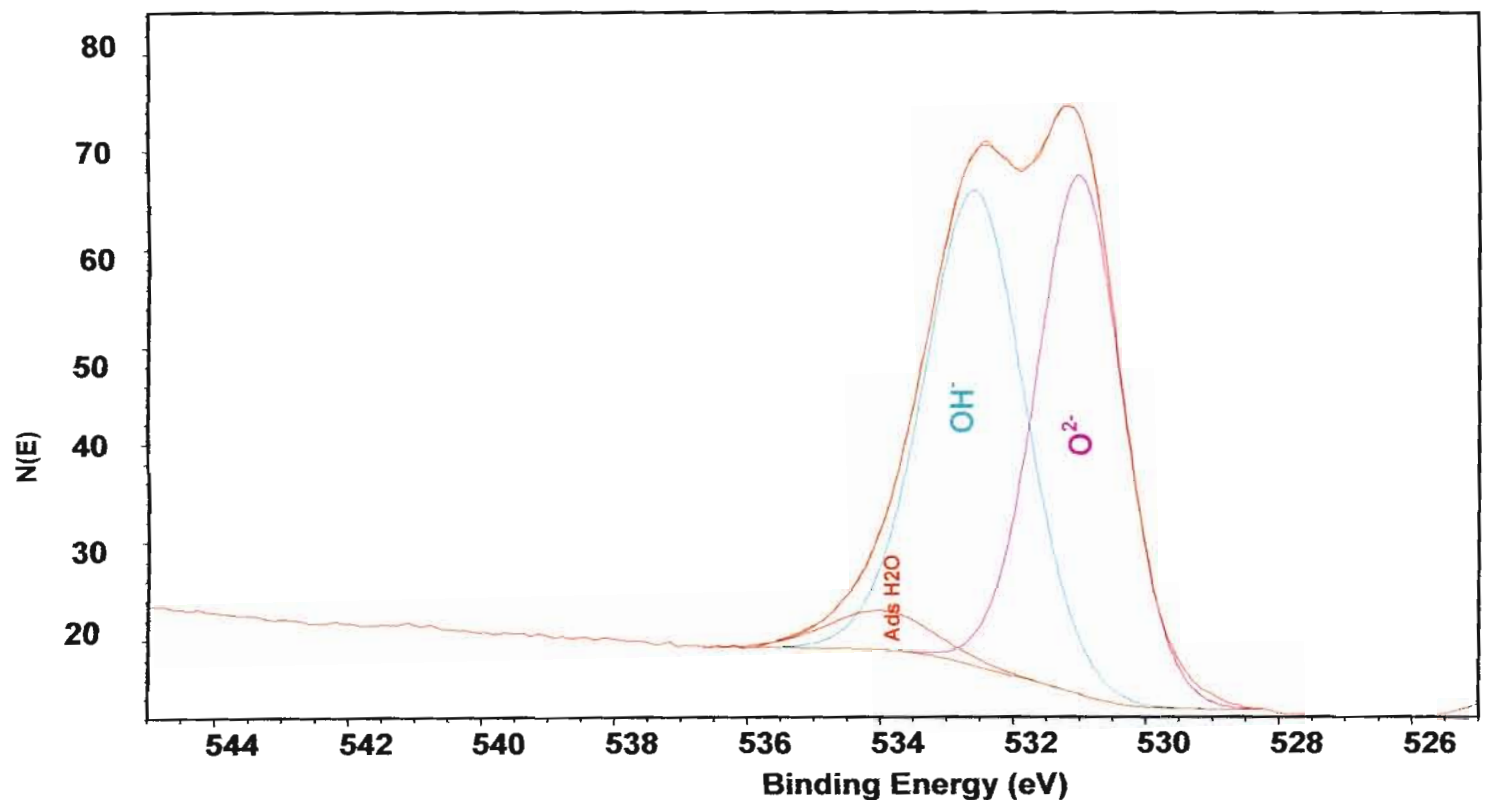


Figure 7-5: High-resolution XPS spectrum of the O 1s region obtained on the standard steel surface with indication of the 'oxides' and hydroxide species

Chemical surface species (eV)			
	Adsorbed water (H ₂ O)	Hydroxide [OH ⁻]	Hydroxy-Oxide [O ²⁻]
Standard	534.00	532.58	531.01
Warm water	534.08	532.40	531.01
Formic acid	534.76	532.99	531.06
Untreated	---	532.54	530.97

Table 7-6: The assignments of the O 1s binding energy (eV) to the surface species for the standard, treated and untreated steel surfaces. [Von Moltke and Sandenbergh, 2003; Roberts and Wood, 1977; Castle and Watts, 1981; Grosvenor et al., 2004; Reffass et al., 2005; NIST XPS database version 3.5, 2000].

Name	Binding energy (eV)	Chemical Surface species	Standard % Area	Warm water % Area	Formic acid % Area	Untreated % Area
O 1s	534	H ₂ O	4.24	3.55	17.15	---
O 1s	532	OH ⁻	49.18	78.06	36.65	52.24
O 1s	531	O ²⁻	46.59	18.38	43.19	47.24
Ratio		OH ⁻ /O ²⁻	1.05	4.20	0.84	1.10

Table 7-7: Estimated area percentages between Fe (OH)₂ and Fe(OOH) peaks

O²⁻ and OH⁻ were characterized and distinguished using XPS (figure 7-5 to 7-8). The difference between the two compounds was observed in the O 1s peak, where the OH⁻ and O²⁻ maximum peak heights differed. The peak heights and peak area ratios are summarized in table 7-7. Standard and untreated LCAK steel surfaces seem to have *ca.* a 1.1 ratio of OH⁻/O²⁻ which could give better adhesion properties with Lewis-base alkyd paint than the warm water and the formic acid treated LCAK steel surfaces, as previously observed by Von Moltke and Sandenbergh [Von Moltke and Sandenbergh, 2003].

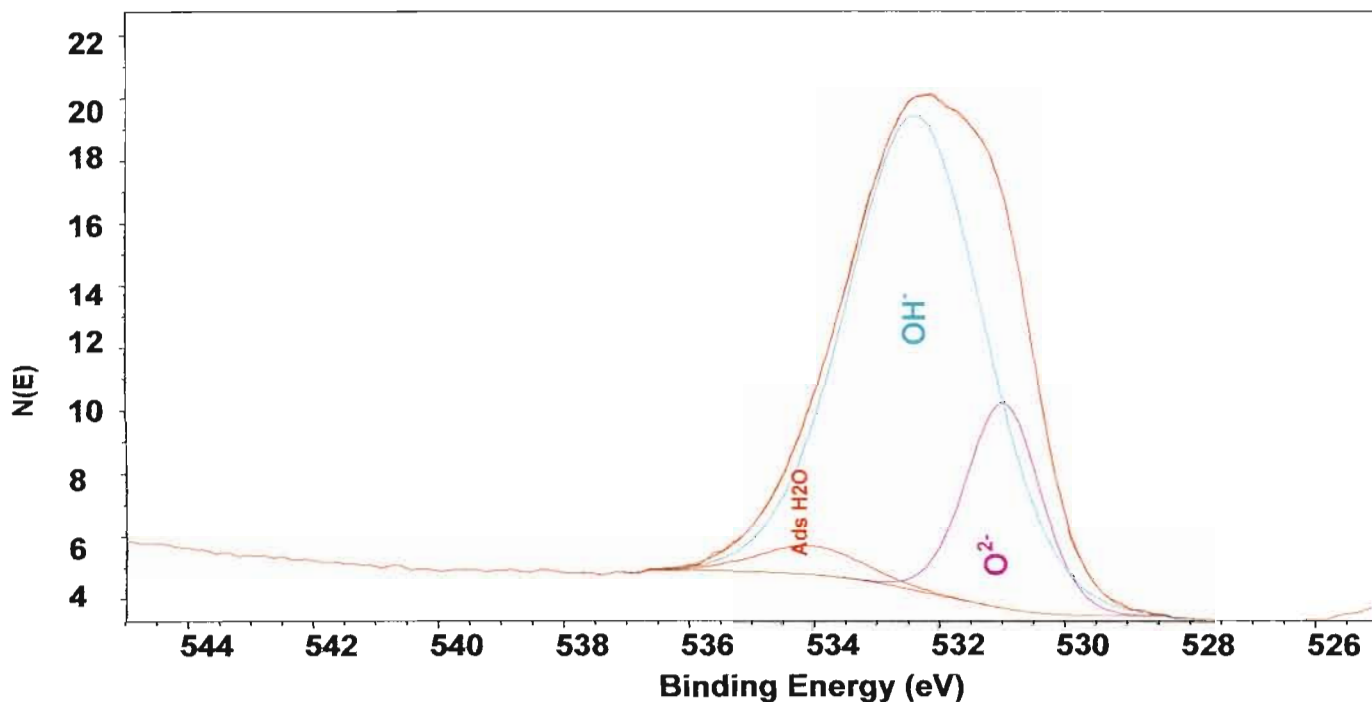


Figure 7-6: High-resolution XPS spectrum of the O 1s region obtained on a surface treated with warm water

O 1s

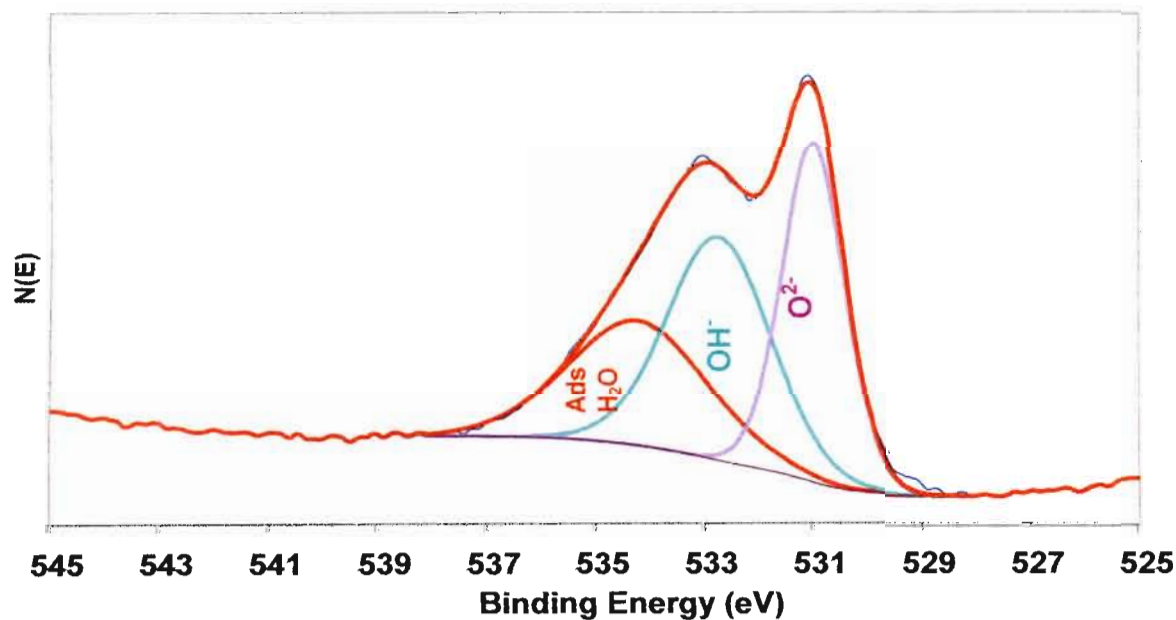


Figure 7-7: High-resolution XPS spectrum of the O 1s region obtained on a surface treated with formic acid.

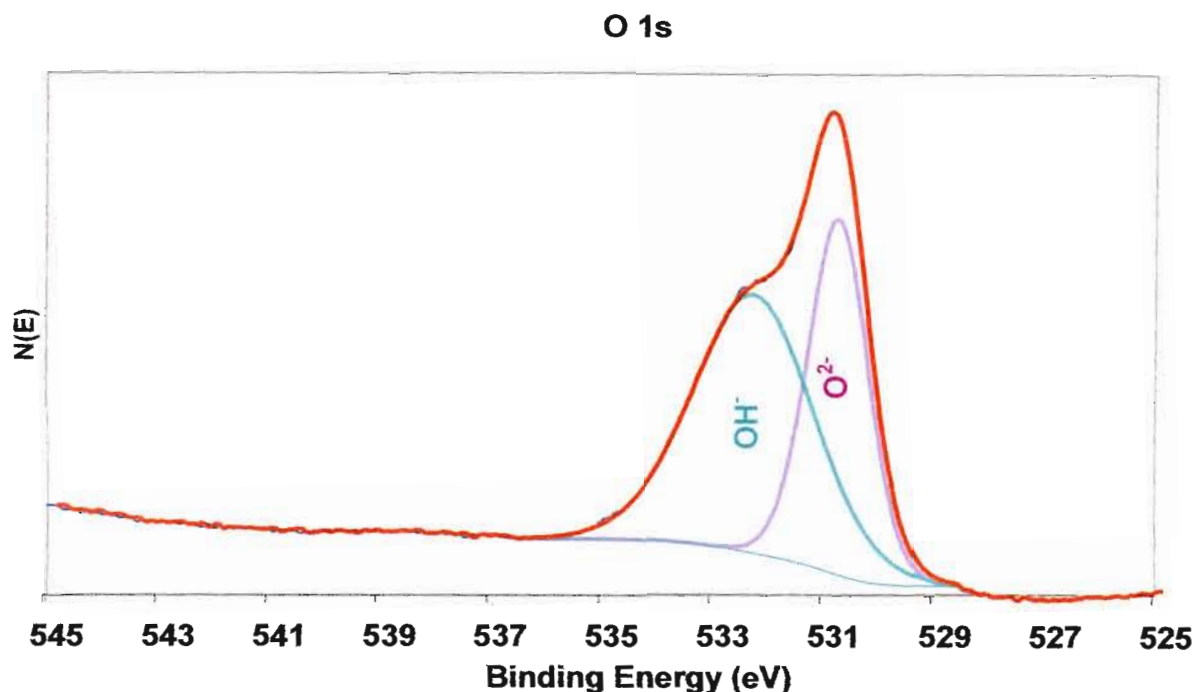


Figure 7-8: High-resolution XPS spectrum of the O 1s region obtained on the untreated surface.

The XPS surface chemical analysis of the LCAK steel surface indicated that the standard and untreated LCAK steel surface would give **better adhesion properties** with Lewis-base alkyd paint [Von Moltke and Sandenbergh, 2003], while the contact angle measurements (7.3.2) showed that warm water pre-treated LCAK steel surface exhibited **better wetting properties** compared to the standard and untreated LCAK steel surfaces. The surface could wet better but this does not indicate that it could adhere better.

7.3.4 Wetting properties of aqueous solutions on treated and untreated LCAK steel surface

The standard and warm water treated LCAK steel surfaces were considered in this assessment as they showed different adhesion properties as shown in 7.3.3. Considering water as the

wetting liquid, a high surface energy substrate will wet fairly readily, while a low surface energy substrate will not wet so readily [Watt, 1998].

In figure 7-9 and 7-10, the contact angles obtained for the different concentrations of the acid and base solutions (and thus pH values) onto the standard and warm water treated LCAK surfaces are shown respectively. Each point was measured ten times and the average thereof was plotted. The statistical variance of each data point was very small (approximately 0.0002), thus no error bars were included. The samples show changes in the contact angle as a function of the pH with opposite behaviour.

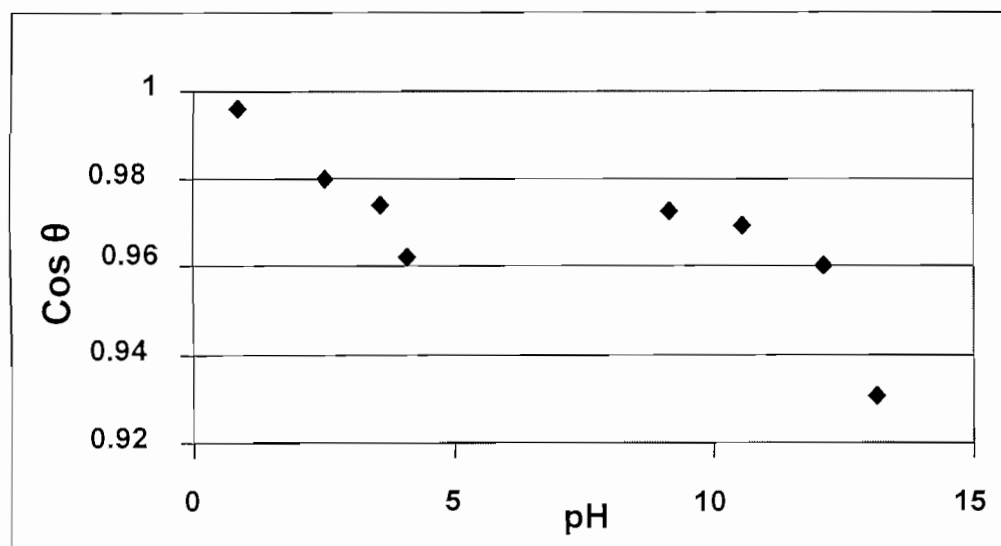


Figure 7-9: The acid-base contact angle versus pH behaviour of the standard LCAK surface

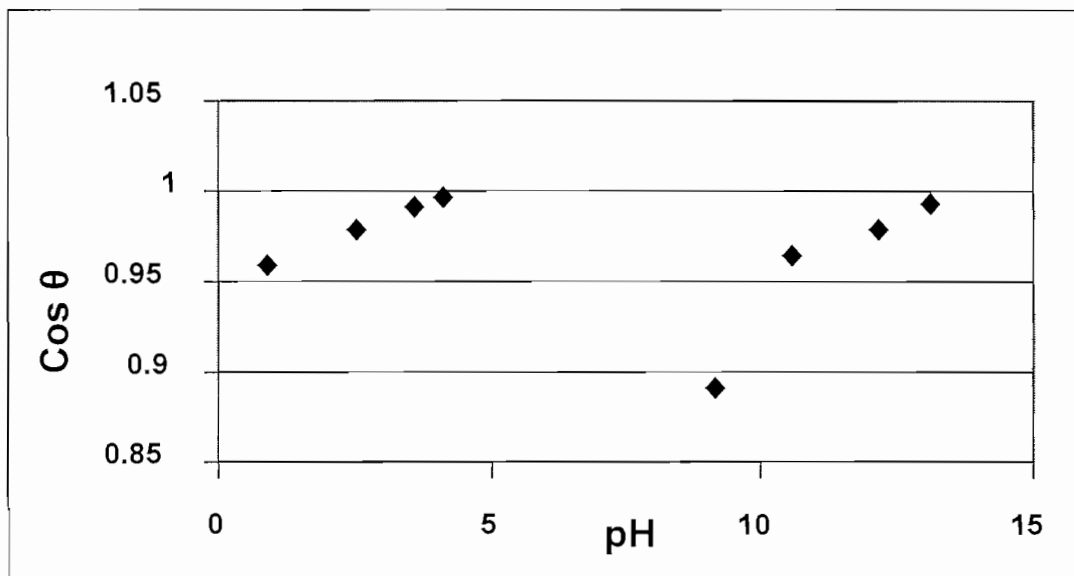


Figure 7-10: The acid-base contact angle versus pH behaviour of the warm water treated LCAK surface

The observed characteristics of a small drop of acidic and basic aqueous solutions of on the standard and warm water treated LCAK substrate indicated difference in the free energy and wettability of the solid surfaces.

Figure 7-10 shows that pre-treatment with warm water improve wetting properties of the LCAK steel surface with acidic and basic solutions. However, the case is not the same for the standard LCAK steel surface (Figure 7-9), where an increase in contact angle was observed with a decrease in pH.

7.4 Conclusions

There is a wide variety of reasons that leads one to asses the properties of a substrate for adhesion purposes. This range from simply ensuring it is clean, through to the need to assess the quality of a pre-treatment. The variety of possible methods that can be used is equally as broad, ranging from simple to sophisticated methods.

To obtain a clear, concise, and accurate picture of a LCAK surface it was essential to use more than one method and the best combination was to use contact angle measurements and XPS to provide surface chemical analysis. This enabled the qualitative comparison of the important characteristics of the standard LCAK surface and enabled understanding of the changes brought about by treated and untreated LCAK surfaces to be related to adhesion.

As expected from theory, liquids with low surface tension produce low contact angles, thus favouring complete wetting of the surface.

An oxide with Fe(III) dominating on the outer surface formed on LCAK steel in contact with water containing higher/saturated oxygen content, while an oxide with Fe(II) dominating on the outer surface formed in water containing a lower oxygen content. It was also found that the 'oxide films' produced during different treatments behave oppositely during wetting with water solutions containing acidic and basic characters.

The XPS (adsorption) studies indicated Lewis-acid properties for the standard LCAK steel surface and Lewis-base properties for the steel surface treated with warm water.

The contact angle (wettability) measurements with acidic and basic aqueous solutions showed improved wetting properties for the warm water treated LCAK steel surface as compared with the standard LCAK steel surface.

CHAPTER 8: DETERMINATION OF LEWIS ACID-BASE PROPERTIES OF LCAK STEEL SURFACE USING A PROBE MOLECULE

8.1 Introduction

The aim of this chapter is to report on the study of the treated low-carbon aluminium-killed (LCAK) steel surface properties with regard to Lewis acid-base theory using probe molecules. The studies on surface acid-base properties have received much attention in surface science. There have been several successful approaches to characterize surface acid sites and acid strength [Basila and Kantner, 1967]. For instance, pyridine (C_5H_5N) and ammonia (NH_3) have been frequently used to distinguish surface acid sites [Parry, 1963]. However, the surface base properties, particularly Lewis-base properties of solids, are poorly understood.

In this chapter we apply a method [Li et al., 1994] to characterize surface Lewis acid-base sites by using a novel probe molecule, boric acid trimethyl ester (BATE). The boron atom of BATE has one empty p_z -orbital which is horizontal to the plane of the molecule. Since the empty orbital of the boron atom has a tendency to accept an electron pair, BATE is a Lewis-acid molecule.

X-ray photoelectron spectroscopy (XPS) was used to determine the relative surface position of the surface species on the treated LCAK steel, while Fourier transform infrared spectroscopy (FT-IR) was used to determine if steel surface treatment influence bonding of BATE molecule to the Lewis-base sites on the surface.

8.2 Experimental procedures

8.2.1 LCAK surface treatment with acidic and basic solutions

The steel surfaces prepared as in paragraph 7.2.1.1 and 7.2.1.2 of chapter 7 was used for these experiments. The steel surfaces were treated with the acidic and basic solutions prepared as in paragraph 7.2.3.1.

8.2.2 XPS study of the LCAK-water interaction

To determine the surface chemical composition of the standard and warm water treated samples after exposure to acidic and basic solutions, XPS spectroscopy was used as described in chapter 7, paragraph 7.2.4. Survey spectra were obtained at take-off angles of 15°C; 45°C and 80°C. The O 1s regions have been recorded.

8.2.3 BATE adsorption

The surface treated samples (standard and warm water treated with acidic and basic solutions) were immersed in boric acid trimethyl ester (BATE) (A.R) from MERCK Chemicals for 30 seconds and were allowed to dry at room temperature for 10 minutes in an inert atmosphere.

8.2.4 FTIR spectroscopy and microscopy analyses

A Perkin-Elmer GX 2000 FTIR Spectrometer was used, with a Perkin-Elmer Auto Image Microscope System equipped with a liquid nitrogen cooled MCT detector attached to it. The samples were analysed under the Auto Image FTIR microscope using the internal reflectance method. With this technique, the absorption of IR-radiation in a thin surface layer with a diameter 10 µm and a thickness of about 10 µm were studied. All spectra were recorded at room temperature using standard instrument settings.

8.2.5 Contact angle measurements

Contact angle measurements on the LCAK steel surface was obtained using the procedure described in paragraph 7.2.3 with acidic and basic aqueous solutions as prepared in paragraph 7.2.3.1.

8.3 Results and discussions

8.3.1 XPS study of the LCAK-water interaction

After polishing, the LCAK samples were immersed in an aqueous solution with pH adjustment using HCl or NaOH. After treating the LCAK samples in the solutions at pH 3 and pH 8 the spectroscopic results obtained are shown in figure 8-1 and 8-2. Because in spin orbit (j-j) coupling $\text{Fe}2p_{3/2}$ has a degeneracy of four states, while $\text{Fe}2p_{1/2}$ has only two, $\text{Fe}2p_{3/2}$ peak is greater than that of $\text{Fe}2p_{1/2}$. The value of 710.6 and 711.2 eV for the peak position of $\text{Fe}2p_{3/2}$ has been reported by many researchers [Roosendaal et al., 1999; Hawn and DeKoven, 1987; and Muhler et al., 1992]. The binding energies of Fe(III) component and the Fe(III) shake-up satellite obtained from this study are 712.4 and 725.2 eV, respectively. The Fe 2p peaks indicate the metallic iron (708.2 eV) from the substrate beneath the passivating layer. This is evident from the larger $\text{Fe}2p_{1/2}$ (oxide) and $\text{Fe}2p_{3/2}$ (oxide) peaks at 45 degree take-off angle. The observed metallic peak indicate that the analysed 'oxide' on LCAK steel is in the range of 2 to 3 nm and the inorganic phase is in the Fe(III) state. Yamashita and Hayes [2008] showed that the Fe 2p spectra obtained with XPS showed good agreement with previous studies, that the peak of $\text{Fe}2p_{3/2}$ for Fe^{2+} is a 'shoulder' peak, whereas that for Fe^{3+} is a distinct peak.

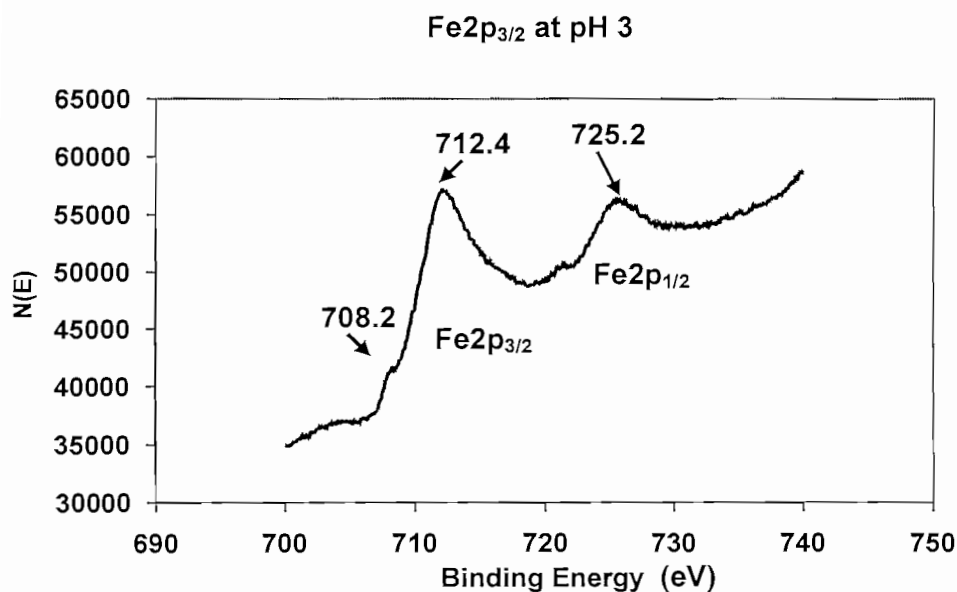


Figure 8-1: XPS survey spectrum of the iron surface layer produced in an aqueous solution at pH 3 .

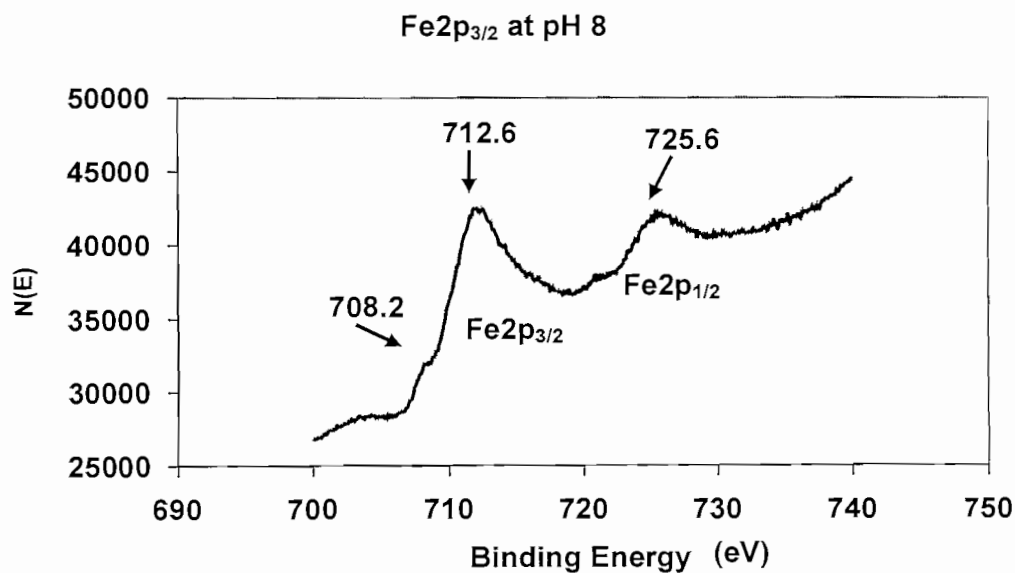


Figure 8-2: XPS survey spectrum of the iron surface layer produced in an aqueous solution at pH 8.

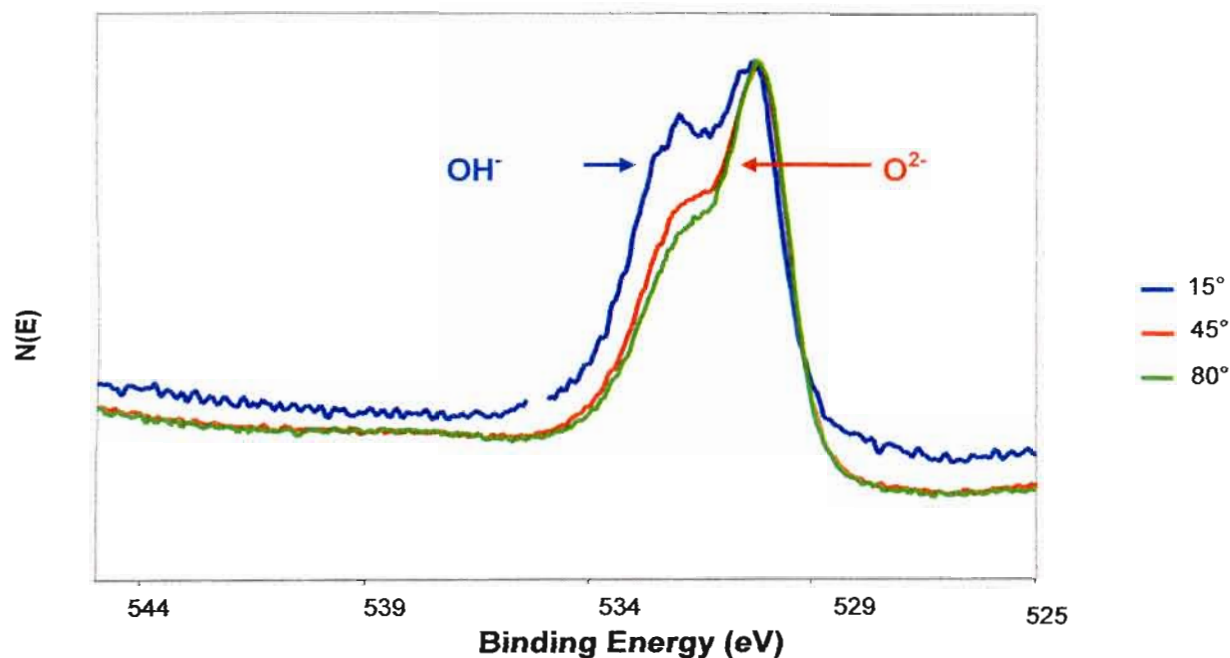


Figure 8-3: High-resolution XPS spectrum of the O 1s region obtained for a standard steel surface at pH 4 at take-off angles of 15°, 45° and 80°.

The possible iron species formed during the surface treatment of the LCAK steel surface with acidic and basic aqueous solution are shown in table 8-1 [Pourbaix, 1974; Atenas and Mielczarski, 2005 and Stefánsson, 2007].

pH	Iron species	References
0.8	Fe^{2+} , Fe^{3+}	[Pourbaix, 1974]
2.5	Fe^{2+} , Fe^{3+}	[Pourbaix, 1974]
3.6	Fe^{2+} , $\text{Fe}(\text{OH})^{2+}$	[Pourbaix, 1974; Atenas and Mielczarski, 2005]
4.1	Fe^{2+} , $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$	[Pourbaix, 1974; Atenas and Mielczarski, 2005,36]
9.1	Fe^{2+} , $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3^-$	[Pourbaix, 1974; Atenas and Mielczarski, 2005,6]
10.5	$\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_4^-$, FeOOH	[Pourbaix, 1974; Atenas and Mielczarski, 2005; Stefánsson, 2007]
12.1	$\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_4^-$	[Pourbaix, 1974; Atenas and Mielczarski, 2005; Stefánsson, 2007]
13.1	$\text{Fe}(\text{OH})_3^-$	[Stefánsson, 2007]

Table 8-1: Summarized iron species at different pH values

According to the reports of Lui and his co-workers [2005], in the pH range from 5 to 9, Fe(II) ions exist in the form of Fe^{2+} , FeOH^+ , $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3^-$. At pH 5, the species of Fe(II) ions in the system comprise both Fe^{2+} and FeOH^+ , but the concentration of Fe^{2+} ions predominates. At pH 7, the species of Fe(II) are Fe^{2+} , FeOH^+ and $\text{Fe}(\text{OH})_2$ but the concentration of FeOH^+ ions is the largest (about 60%). And at pH 9, the amount of $\text{Fe}(\text{OH})_2$ instead of FeOH^+ and $\text{Fe}(\text{OH})_3^-$ predominates [Pourbaix, 1974; Atenas and Mielczarski, 2005; and Stefánsson, 2007]. $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are thermodynamically stable at $\text{pH} > 7$ [Ma and Zaera, 2006].

The angle-resolved XPS results on the treated standard LCAK steel surface at pH 4 and pH 13 are shown in figure 8-3 and 8-4 respectively. The graphs show that, despite different surface treatments with acidic and basic solutions, the oxygen containing species remain OH^- and O^{2-} . The XPS angle-resolve technique indicates that the OH^- surface species concentrate towards

the outer surface layer, while O^{2-} surface species do not change in concentration with the change in take-off angles and thus surface depth.

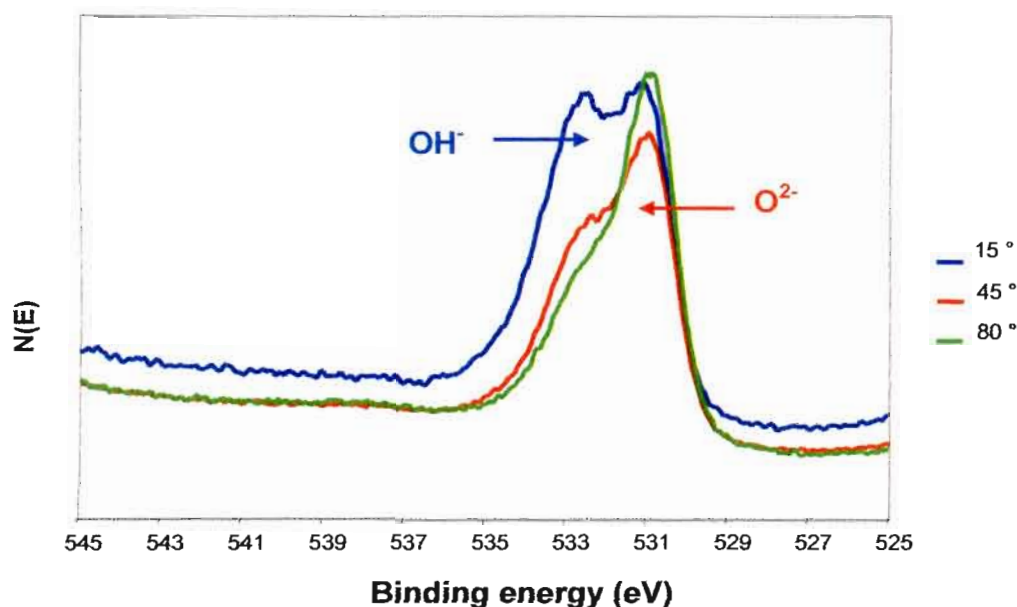


Figure 8-4: XPS 1s oxygen peaks obtained for a standard steel surface at pH 13 at take off angles of 15°, 45° and 80°.

8.3.2 Adsorption of BATE to the untreated steel substrate

The molecular formula of BATE is $B(OCH_3)_3$. The boron atom in the BATE molecule has one empty p-orbital which is trigonally orientated to the methoxy groups [Liu, Wei and Sun, 2005]. Since the empty orbital of the boron atom has a tendency to accept an electron pair, BATE acts as a Lewis acid molecule. A surface Lewis basic site thus may coordinate with a boron atom of the BATE, affecting the B-O bond energy.

The infrared spectra of BATE molecule adsorbed to the untreated standard and warm water treated steel substrate (as prepared previously in paragraph 7.2.1.1 and 7.2.1.2 of chapter 7) are shown below in figure 8-5. From the spectra it can be seen that the adsorption of BATE was

more on the warm water treated steel substrate than on the standard steel substrate. This is shown by the higher intensity of (B-O, 1195 cm^{-1}) and (C-O, 1042 cm^{-1}) stretching vibration peak of BATE molecule [Lui, Wei and Sun, 2005]. Because BATE molecule is characterized as a Lewis-acid molecule, therefore the warm water treated surface exhibit stronger Lewis-base properties before treated with acidic and basic solutions.

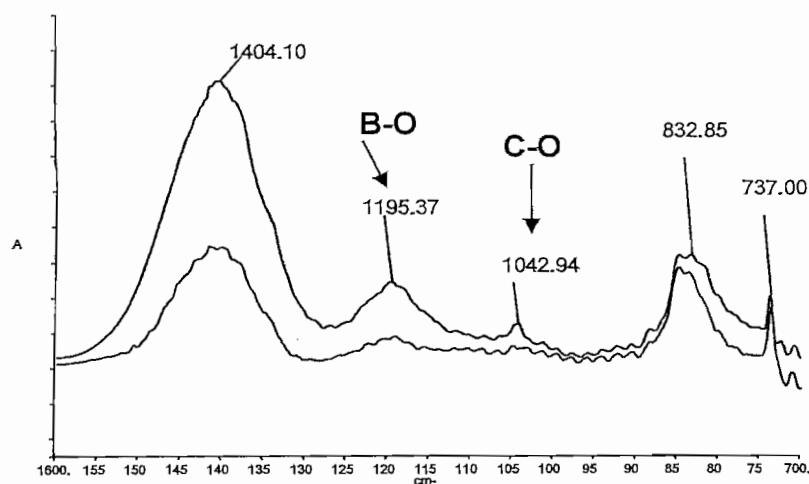


Figure 8-5: FTIR spectra of adsorbed BATE on standard LCAK surface (red spectrum) and warm water treated steel substrate (green spectrum)

The pictures showing the adsorption of BATE molecule to the standard and warm water treated surface are shown in figure 8-6 and 8-7 below. The surface morphology of the adsorption of BATE on both surfaces differs significantly. A rougher surface was observed on the standard steel surface and a smoother surface was observed on the warm water treated steel substrate. This could also indicates that the BATE molecule has chemically bonded to the warm water treated steel substrate and not on the standard steel substrate.

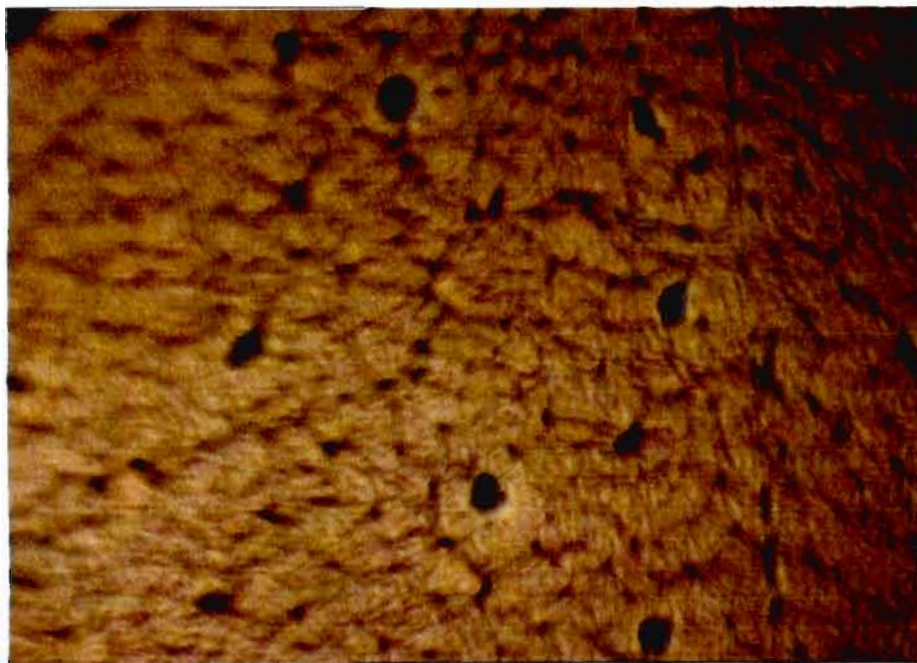


Figure 8-6: FTIR microscope image of adsorbed BATE on standard LCAK surface



Figure 8-7: FTIR microscope image of adsorbed BATE on warm water treated LCAK surface

8.3.3 Adsorption of BATE to the treated steel substrates

As no influence on the B-O binding energy and BATE molecule was observed for the acidic and basic treated warm water LCAK steel surface, it was concluded that the warm water treated LCAK surface exhibits Lewis acid properties [Mohlala and Strydom, 2007].

The FTIR – microscopy (external reflectance) spectra of adsorbed BATE on the pH treated surfaces (Figure 8-8) are shown in figure 8-9 and 8-10. These FTIR spectra in the vibrational regions of B-O ($1420-1250\text{ cm}^{-1}$) and C-O ($1100-1000\text{ cm}^{-1}$) bonds were used to measure interaction of BATE with the surfaces [Lui, Wei and Sun, 2005]. With an increase in pH an increase and shifts in B-O and C-O peak intensities were observed as shown by the shifts in the B-O (1194 cm^{-1}) and C-O (1042 cm^{-1}) stretching vibrations for the adsorbed BATE (Figure 8-9 and 8-10). This implied that the BATE molecule interacts with the surface Lewis-base sites so that the vibration involving the B-O bond splits (1109 cm^{-1}) and shifts significantly (1199 cm^{-1}).

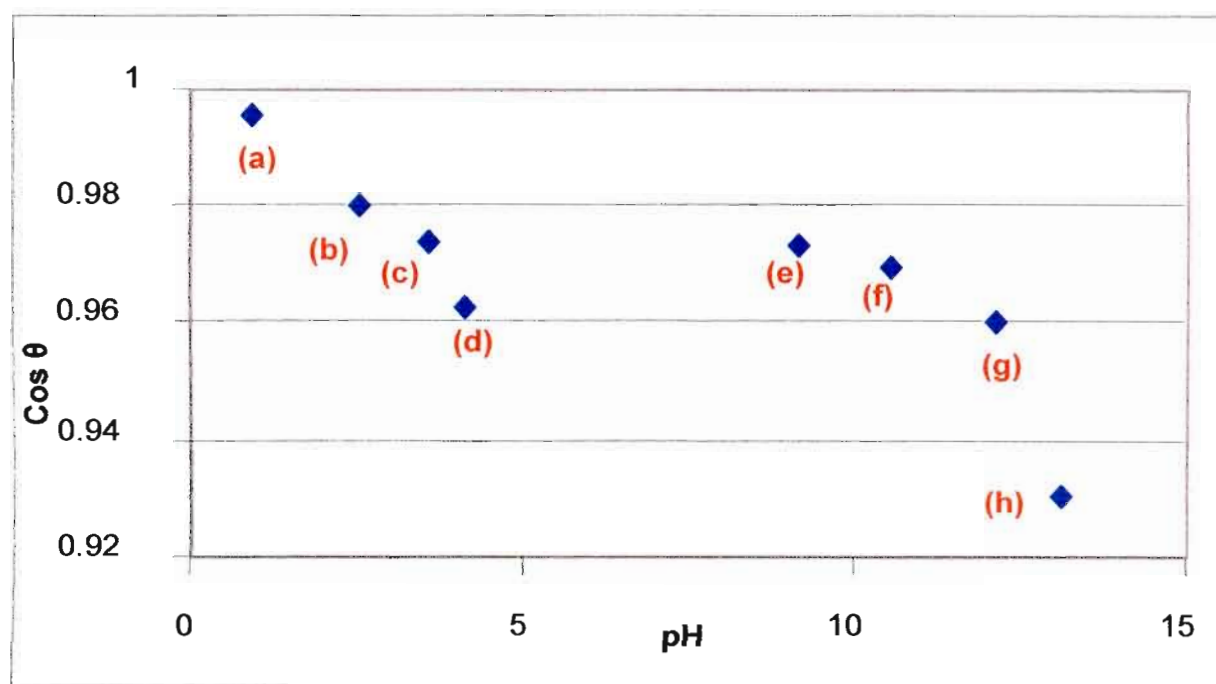


Figure 8-8: The acid-base contact angle curve of the reference LCAK steel

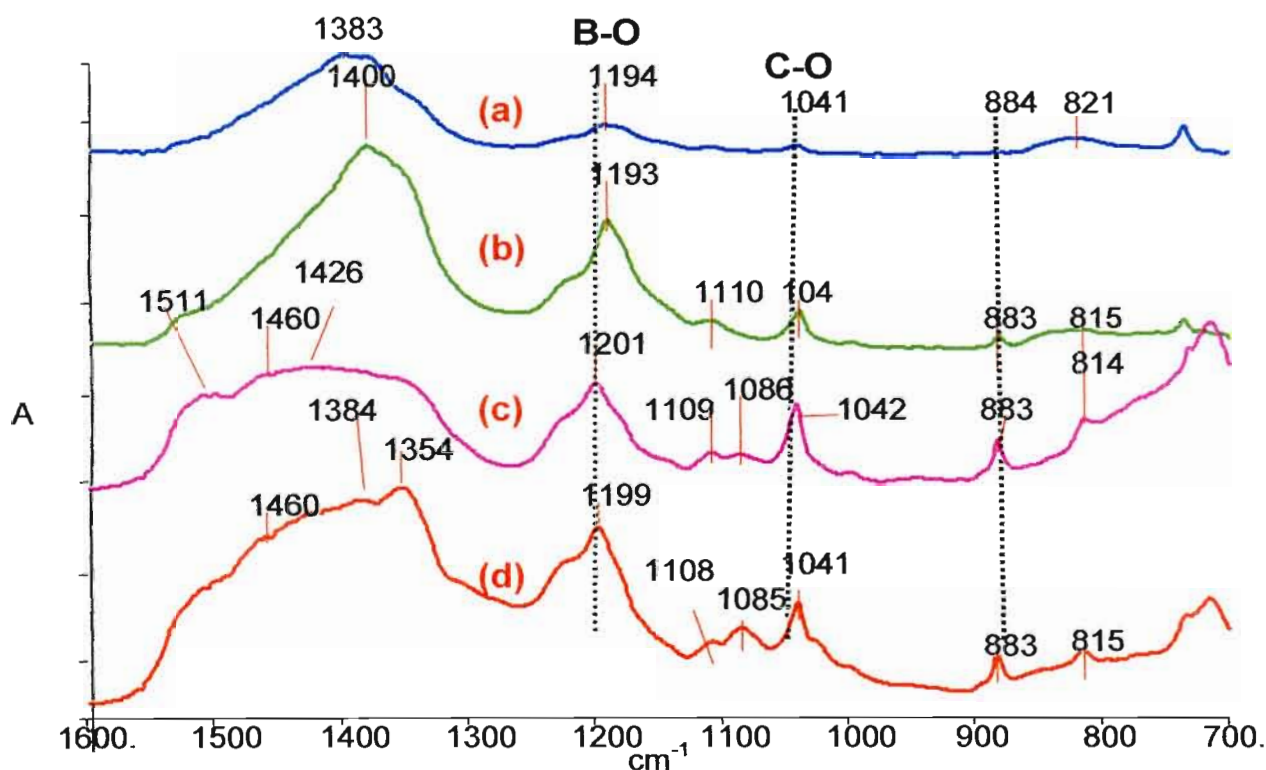


Figure 8-9: FTIR spectra of adsorbed BATE on standard LCAK surface at pH(a), 0.8, (b) 2.5, (c) 3.6 and (d) 4.1

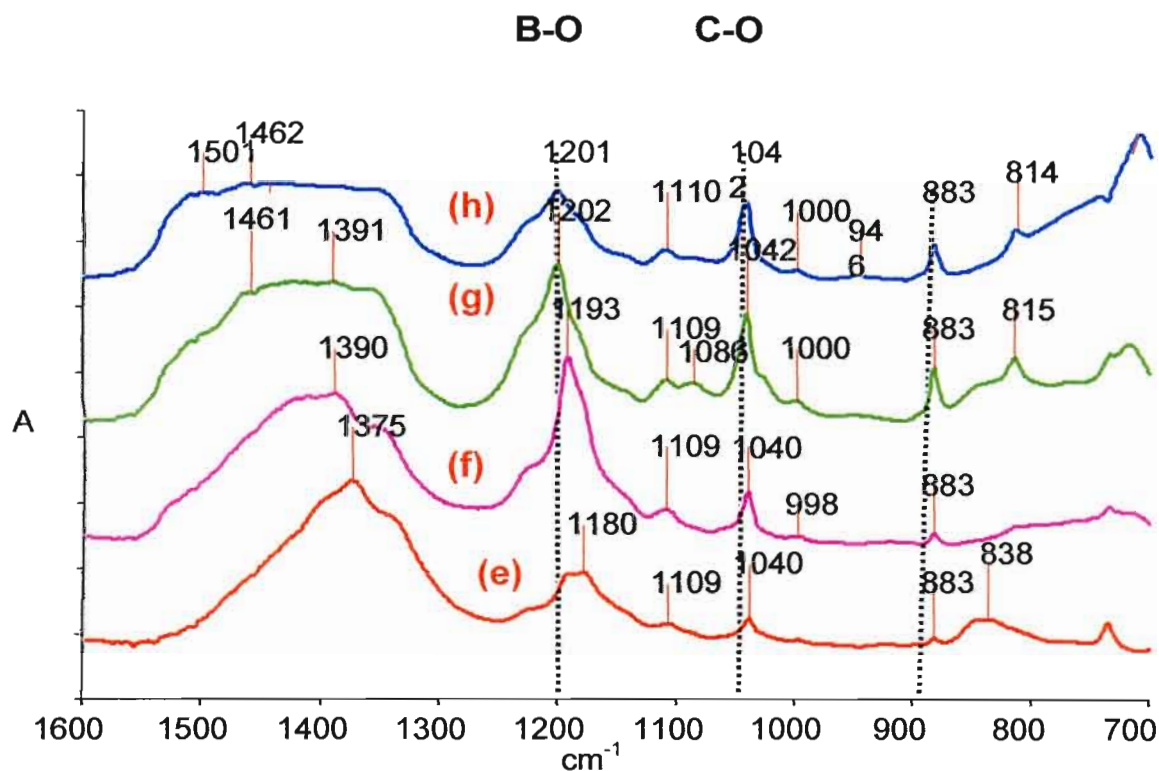


Figure 8-10: FTIR spectra of adsorbed BATE on standard LCAK surface at pH (e) 9.1, (f) 10.5, (g) 12.1 and (h), 13.1

The relationship between the C-O peak area intensities against pH is shown in figure 8-11. An increase in C-O peak area intensities with a decrease in pH was observed, again with a definite break in the relationship at a pH of 7. The increase in contact angle measurements on the acidic and basic treated standard LCAK steel surfaces (Figure 8-8) showed a similar but opposite relationship. From the above it can be concluded that the treated standard LCAK steel surface has Lewis base properties.

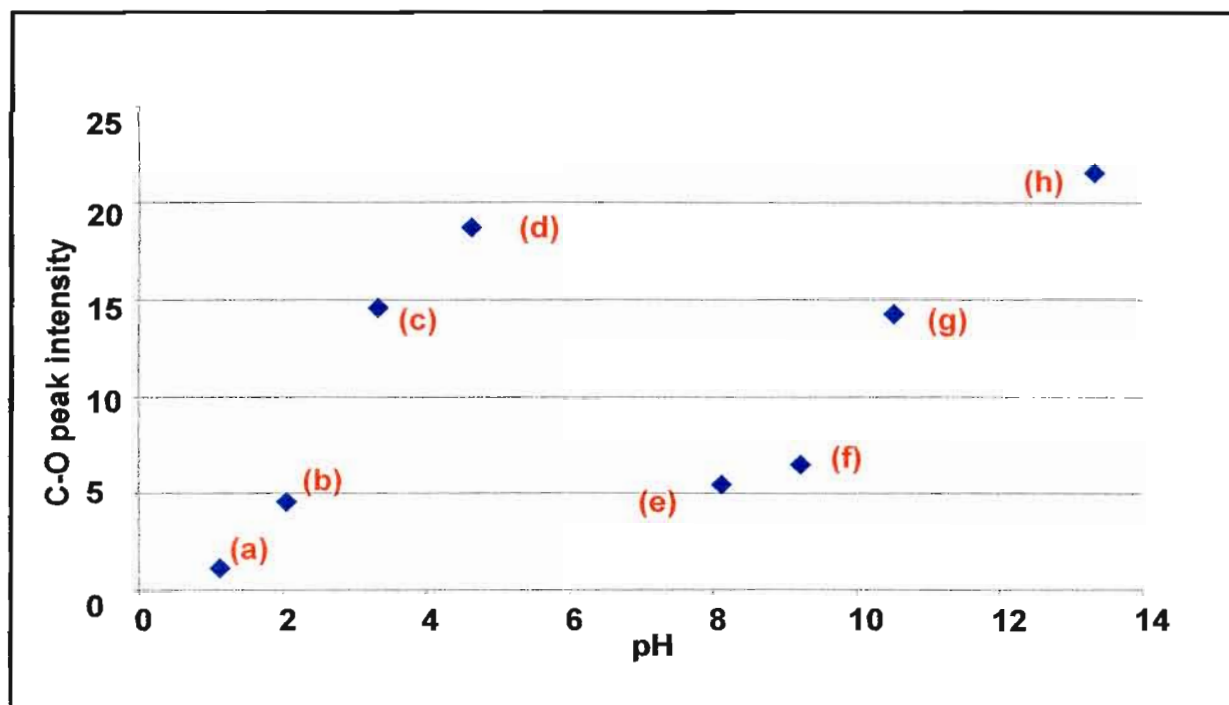
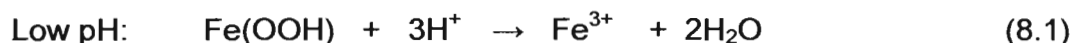


Figure 8-11: The C-O peak intensities on the standard LCAK surface versus pH (a), 0.8, (b) 2.5, (c) 3.6, (d) 4.1, (e) 9.1, (f), 10.5 (g) 12.1 and (h) 13.1

8.4 Conclusions

The XPS study of the O 1s peak indicated the Lewis base properties of LCAK steel are attributed to OH⁻ groups being available on the outside surface.

It seems that, in contact with acidic and basic solutions, oxide and hydroxide surfaces may acquire an ionic charge through the following reactions:



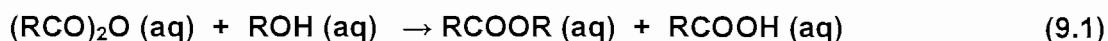
where reaction (8.1) and (8.2) are representative of the basic and acidic reactivities of the oxide respectively, and reaction (8.3) and (8.4) are representative of the basic and acidic reactivities of the hydroxide respectively. For the standard LCAK steel sample, it is postulated that hydrogen ions adsorb on the O^{2-} surface, and contribute to a Fe(II)/Fe(III) oxidation/reduction process (reaction (8.1)). The number of O^{2-} species on the surface decreases with increasing pH (reaction (8.2)), forming $Fe(OH)_4^-$ species in a basic medium. It is known that $Fe(OOH)$ species were characterized as having a Lewis-acid character [Von Moltke and Sandenbergh, 2003] and therefore $Fe(OH)_4^-$ species seem to contribute to a Lewis base character. The $Fe(OH)_3^-$ species seem to increase on the surface with an increase in pH, lowering the contact angle which gives good wetting properties. $Fe(OH)_3^-$ species seem to have Lewis acid character and $Fe(OH)_2$ species have Lewis base character.

It was also observed that BATE is a sensitive probe molecule to detect and distinguish the surface Lewis-base sites of the treated and untreated LCAK steel substrates. BATE interacts selectively with surface Lewis-base sites and its IR spectrum shows the direct interaction with Lewis-base sites of the metal oxides.

CHAPTER 9: CHARACTERIZATION AND ADHESION OF ALKYD PAINT ON LCAK STEEL SUBSTRATE

9.1 Introduction

Alkyd coatings are a class of polyester coating derived from the reaction of an alcohol and an acid or acid anhydride. The reaction can be presented by the following scheme:



The products are an ester compound and an acid compound. They may be modified with unsaturated fatty acid (from vegetable and plant oils) to give them air drying properties (oils which hardens to a solid film after a period of exposure to air) [Wikipedia, n.d.].

For alkyd containing non-drying oils (e.g. coconut oil, palm oil) various amino resins such as urea-formaldehyde, melamine-formaldehyde or glycouril-formaldehyde, are used as cross-linking agents [Prane, 1986]. Cross-linking is the formation of chemical links or reactions between molecular chains to form networks of connected molecules and is a process that occurs during the curing of paint.

9.2 Experimental

9.2.1 Raw materials and equipment

Alkyd paint (traffic green colour) obtained supplied by Greiff packaging company.

Ethyl formate obtained from MERCK chemicals

Methyl ethyl ketone (MEK) obtained from MERCK chemicals

9.2.2 Separation techniques

9.2.2.1 Ultra-centrifugation technique

This procedure has proved effective in the removal of fine solids ($<0.5\ \mu\text{m}$) from both aqueous and organic media [Kotlyar, 1993]. Firstly the alkyd paint from Van Leer (local coating supplier) was homogenized by mixing. Homogenization in coating is done to obtain the uniformity of chemical components and texture as some additives and pigments could settle at the bottom. This solution was transferred into high speed centrifuge tubes and spun for 10 min at 250 000 gravities using a Hettich E RA 12R centrifuge. This treatment produces a relatively dense layer of sedimented solids and a clean liquid. After carefully decanting the liquid, the sediments were rinsed with ethyl formate. The sediments were stirred on an ultra sonic bath for 15 min. After removing the supernatant layer by pipette, fresh ethyl formate is added and re-stirred. The procedure is repeated until the ethyl formate layer is colourless which indicates that all the organic particles are washed out. The sediments ($<0.5\ \mu\text{m}$) are collected with a pipette and carefully transferred to a dry glass vial. After evaporating residual ethyl formate, the solids were analysed using SEM.

9.2.2.2 Simple distillation technique

The clean polymeric liquid decanted from the centrifuge tubes was transferred into a 50 ml round bottom flask with glass beads. The apparatus was set up as illustrated in figure 9-1. A 10 ml graduated cylinder was used as the receiving flask. When the mixture began to boil, the heating mantle was adjusted so that the distillate collect at a rate of 1 to 2 drops per second until all the distillate was collected. The volatiles (distillates) and the polymeric residues in the round bottom flask were analysed using FTIR.

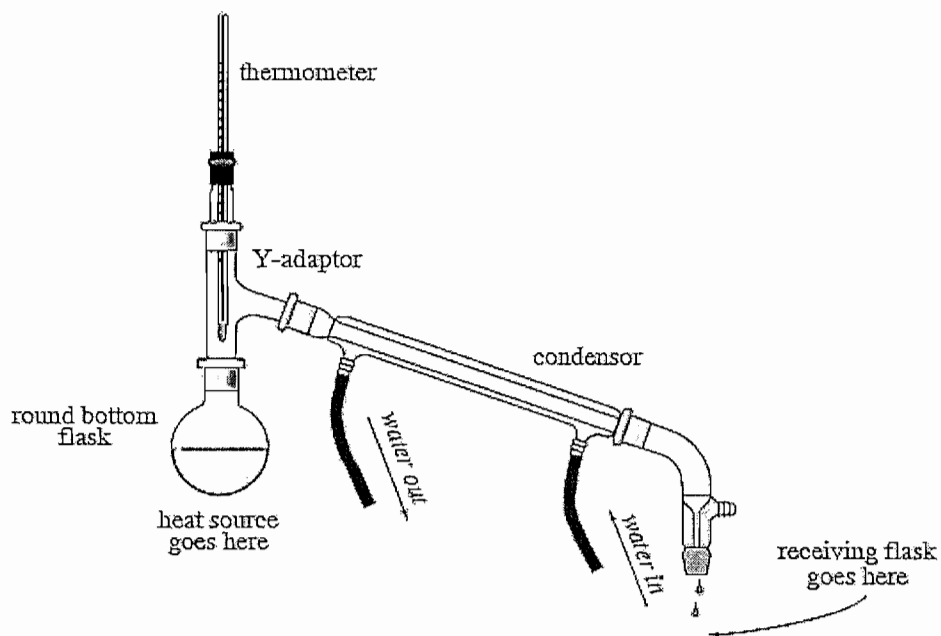


Figure 9-1: Experimental set-up for simple distillation

9.2.3 Characterization techniques

9.2.3.1 FTIR (Fourier Transform Infrared) spectroscopy

The instrumentation used is described in chapter 5, paragraph 5.2.3. Infrared spectra of the mixed solvent (distillates) were recorded with a ZnSe horizontal ATR accessory and the polymer residues were applied on a KBr disc and analyzed in the transmission mode.

9.2.4 SEM (Scanning Electron Microscope)

The inorganic components of the coating were analyzed using a Scanning Electron Microscope [JEOL (JSM 6300)] equipped with an energy dispersive X-ray (EDS) system. The sample was sputter coated with gold to make it conductive. The electron beam energy of 15keV and the working distance of 25mm were used. The X-rays were collected for 100 sec live time.

9.2.5 Adhesion of alkyd paint on LCAK steel substrates

9.2.5.1 LCAK steel samples

The LCAK steel samples used in this study were prepared as described in paragraphs 7.2.1.1 and 7.2.1.2 for standard and warm water-treated LCAK steel substrate respectively.

9.2.5.2 Adhesion of alkyd paint on LCAK steel substrate

Paint adhesion tests were performed to determine the adhesion properties of the LCAK steel substrates. The adhesion test used conforms to the ASTM testing procedure (ASTM Test Number 3359-78) [ASTM D 3359-78]. Although this test method has been revised to (ASTM D 3359-08 or ASTM D 3359-09), the previous method was used for comparison purposes with previous work done by the coating industry (Greiff packaging company). The adhesion test entails the following procedure:

The LCAK steel samples were dip-painted and cured at 120°C for 10 minutes. The adhesion test entails putting the cross-hatched samples in a temperature-controlled water bath at 40°C to a depth of ≈ 160 mm with a spacing of ≈ 25 mm between the samples for a period of 24 hours. The adhesion test (ASTM D1654) consists of a tape pull-off test on a crosshatched pattern cut through the paint layer with a carpet knife. The degree of adhesion was evaluated on an eight-point scale by the area of the paint removed from the surface of the LCAK steel. On the eight point scale zero indicated perfect adhesion and seven no adhesion (Figure 9-2).

9.2.5.3 Adhesion of alkyd paint on pH treated substrate LCAK steel substrates

LCAK steel substrate treated with acidic and basic solutions as prepared in paragraph 7.2.3.1 were coated with alkyd paint as described in paragraph 9.2.5.2.

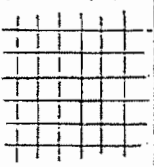
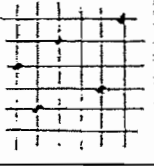
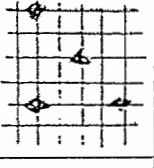
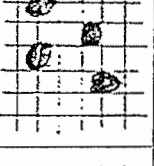
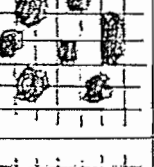
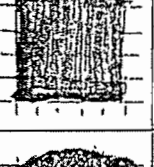
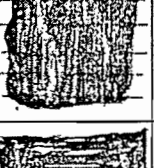
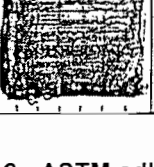
Grade	Tape Test Result	Description
0		No visible adhesion loss, not even on points where lines intersect.
1		Adhesion loss only at points of intersections. Very small flakes can be removed. Adhesion loss < 5 % of total area.
2		Small parts can be removed at intersections. Adhesion loss < 15 % of total area.
3		Strips of paint are partly or totally removed along cuts. Some small areas can be partly or totally removed. Adhesion loss < 35 % of total area.
4		Wide strips of paint are removed along cuts. Large areas are partly or totally removed. Adhesion loss < 65 % of total area.
5		Nearly all paint removed from cross hatched area. Adhesion loss between 90 - 100 % of total area.
6		All paint removed from cross hatched area. Some paint removed from surrounding area.
7		Paint removed without cross hatching. Paint can be pulled from surface.

Figure 9-2: ASTM adhesion grading scale [ASTM D 3359-78]

9.3 Results and discussions

9.3.1 Composition of the paint

9.3.1.1 FTIR analysis

9.3.1.1.1 Volatile matter

The infrared spectrum of the solvent (distillate) matter is shown below (Figure 9-3). To identify the chemical composition of the solvent matter, a comparison function was run against the library databases in the FTIR software (Spectrum Search Plus version 3.0). The solvent matter compared well with 2-ethyl-1-hexanol and m-xylene. It was therefore concluded that the solvents used with this paint (alkyd) contains 2-ethyl-1-hexanol and m-xylene. The infrared spectra of the pure 2-ethyl-1-hexanol and m-xylene are shown in figures 9-4 and 9-5 respectively for comparison purposes.

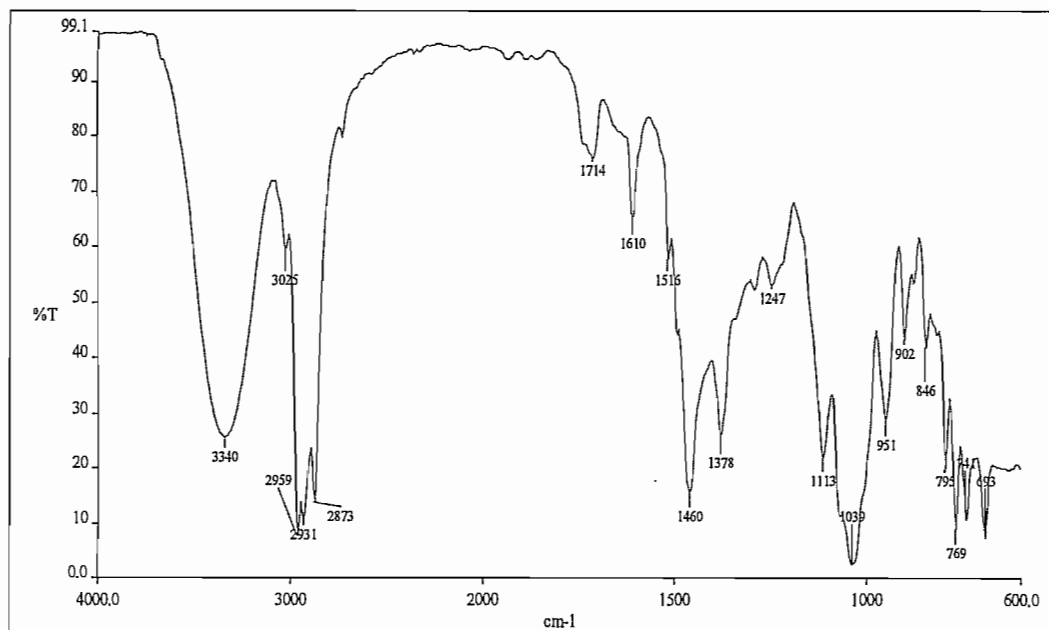


Figure 9-3: Infrared spectrum of the volatile mixture

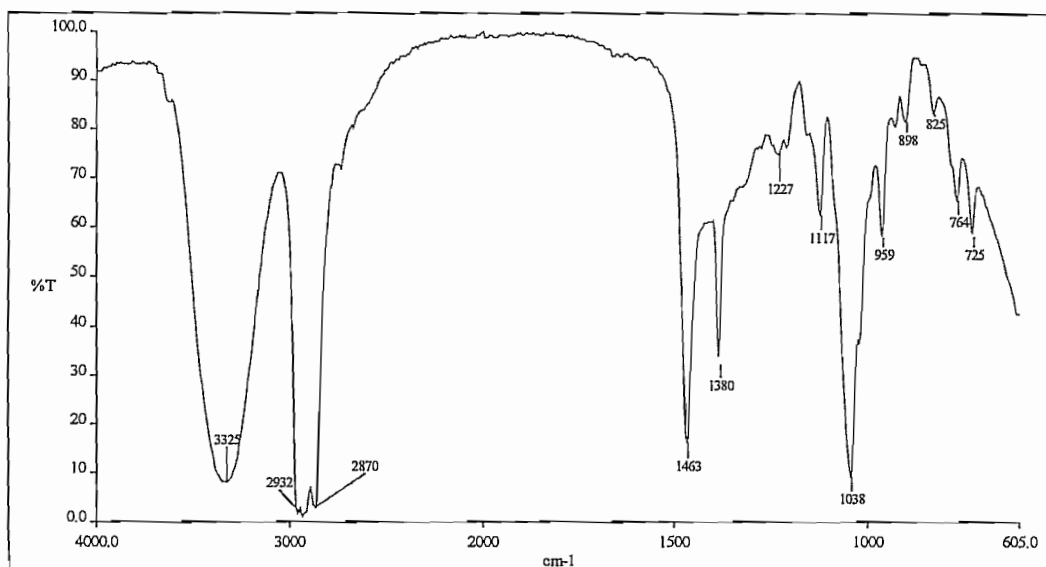


Figure 9-4: Infrared spectrum of pure 2-ethyl-1-hexanol [Spectrum Search Plus database]

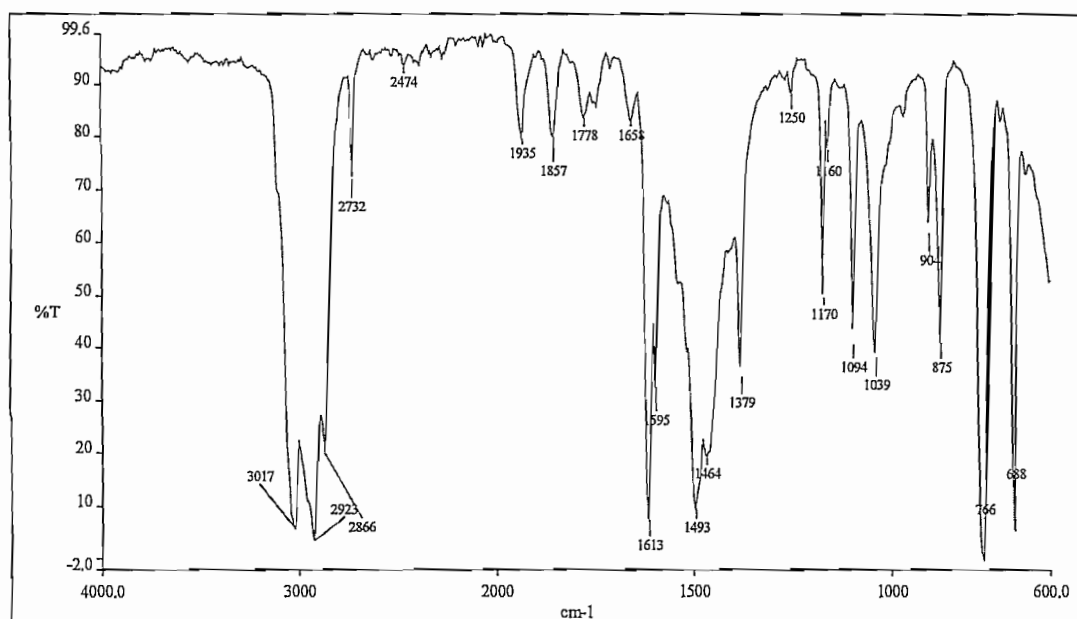


Figure 9-5: Infrared spectrum of pure m-xylene [Spectrum Search Plus database]

9.3.1.1.2 Polymer system

The infrared spectrum of the polymer system is shown below in figure 9-6. The polymer system was identified as an ortho-phthalate polyester paint. The Spectrum Search Plus version 3.0 database was also used to identify this paint system. The spectrum of the isolated alkyd resin is shown in figure 9-7 below.

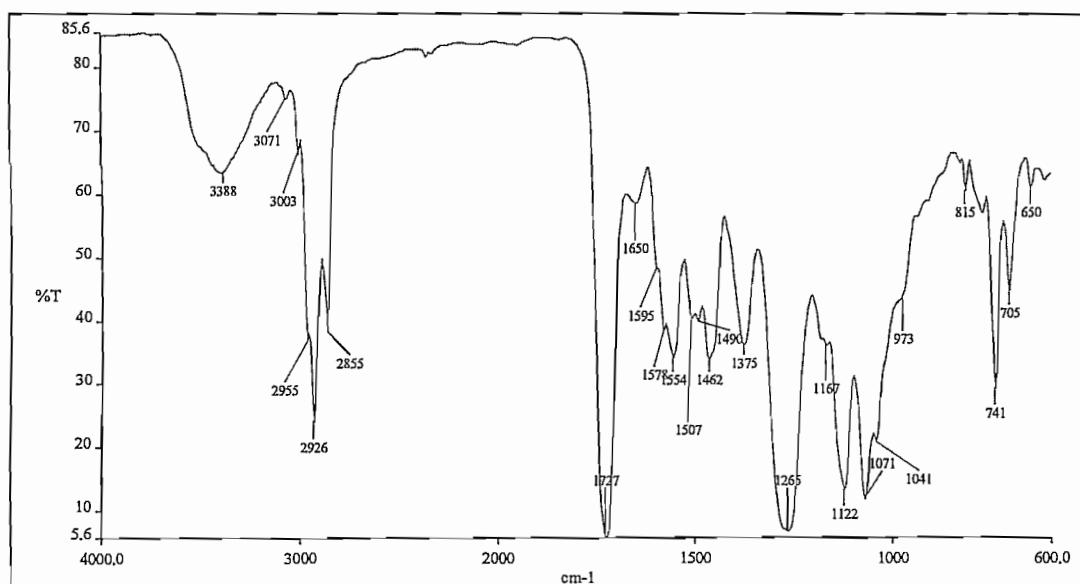


Figure 9-6: Infrared spectrum of the polymer system

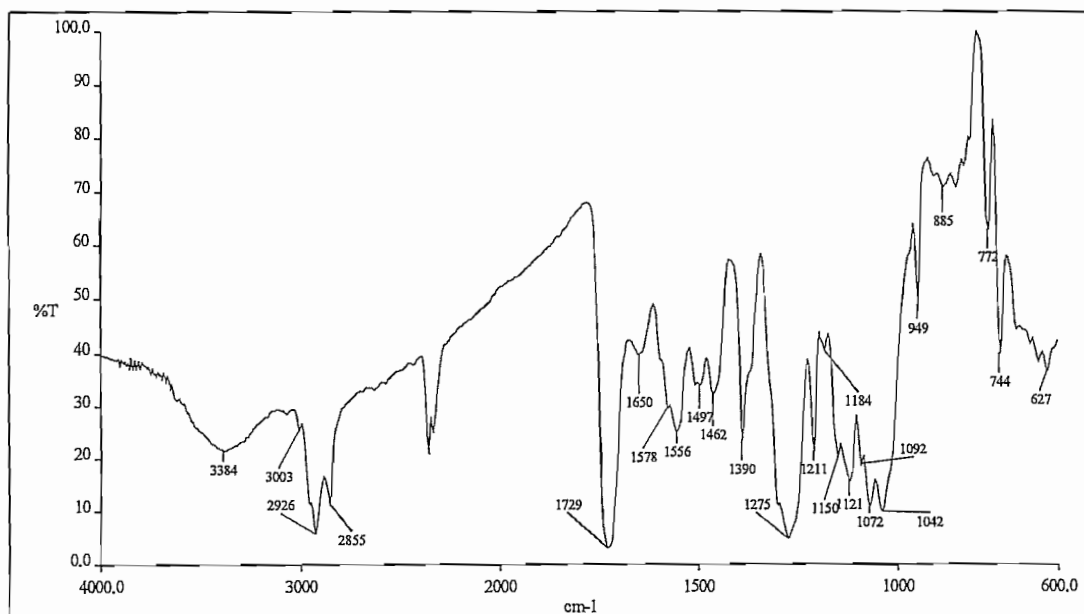
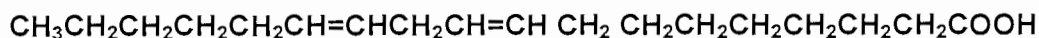
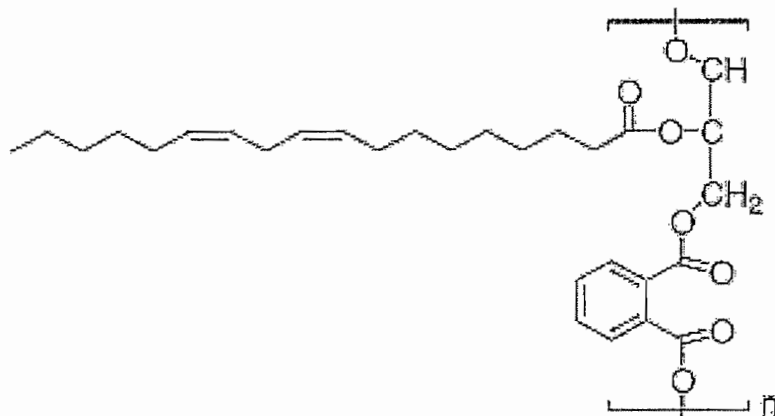


Figure 9-7: Infrared spectrum of the isolated alkyd resin

Characteristic bands assignments [Anderson, 1980] of the polymer system and the alkyd resin are shown in table 9-1. The presence of 1042 cm^{-1} and 744 cm^{-1} band in figure 9-7 shows that the investigated alkyd could be a phthalate ester (see table 9-1 for vibrations and assigned of bands). The presence of the band at 3003 cm^{-1} is characteristic for unsaturated C=C-H groups. This indicates the presence of a drying oil. The chemical composition of a typical drying oil is given in the following scheme:



Natural oil with a high content of poly-unsaturated fatty acids, such as linoleic or linolenic acid, can be categorized as drying oils. Thus the idealized structure of an alkyd resin used can be presented as follows [Van Gorkum and Bouwman, 2005]:



Polymer System	Alkyd resin	Assignment
3388	3384	O-H stretching
3071		overtone C-H stretching of phthalate
		C=C-H stretching of unsaturated groups
3003	3003	
2955	2955	CH ₃ asymmetric stretching
2926	2926	CH ₂ asymmetric stretching
2855	2855	CH ₂ symmetric stretching
1727	1729	C=O stretching of an ester
1650	1650	C=O stretching of an amide I band
1595		Aromatic C=C stretching
1578	1578	Aromatic C=C stretching
1554	1556	Aromatic C=C stretching
1504	1497	Aromatic C=C stretching
1490		Aromatic C=C stretching
1462	1462	CH ₂ and CH ₃ bending
	1390	Methyl stretching
1375		CH ₃ bending
		C-N stretching mixed with N-H
	1275	bending III amide
1265		C=C-O- stretching
	1211	C=C-O-C stretching
	1184	Methyl rocking
1167		C-O stretching of phthalate
	1150	C-O stretching of phthalate
1122	1121	C-O stretching of phthalate
	1092	Stretching of tertiary hydroxyl group
		C-O-C stretching of etherified methylol group
1071	1072	C-O-C stretching of etherified methylol group
1041	1042	group
973		out-of-plane CH of trans double bond
	949	in-plane bending
		out-of-plane bending of terminal methylene
	885	
815		out-of-plane CH bending
	772	mono-substituted phenyl
741	744	phthalate ring bending
705		mono-substituted phenyl
650		NH ₃ , NH, OH out of plane bending

Table 9-1: Characteristic bands assignments for polymer systems and alkyd resins [Anderson, 1980]

9.3.1.2 SEM analysis

9.3.1.2.1 Inorganic compounds

The inorganic part of the paint was analyzed using SEM (Scanning Electron Microscope). The EDS spectrum is given in figure 9-8. According to the given spectrum only the following elements are indicated – C, Ti, Cr, O, Fe, Al, Si, Pb and Cl. It is known [Leidheiser, 1981] that the inorganic part of the paint contains rutile, TiO_2 , as a filler and a mixture of lead chromate, PbCrO_4 , and $\text{Fe}(\text{NH}_4)\text{Fe}(\text{CN})_6$ as a light green pigment. Pigments produce the paint colour and are derived from natural or synthetic materials that have been ground into fine powders [Paintideas, n.d.].

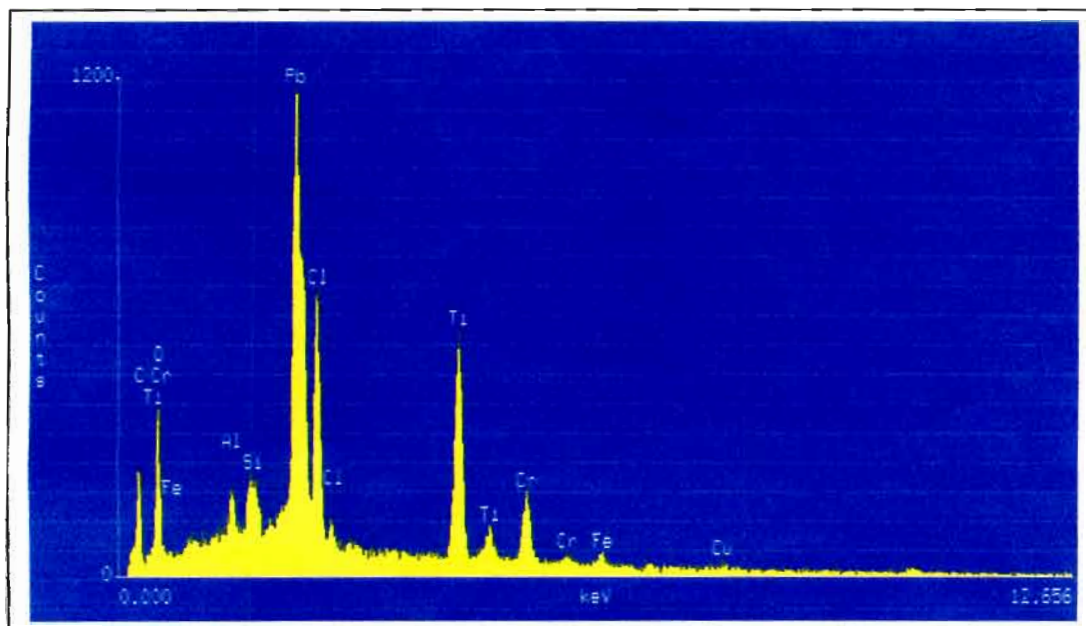


Figure 9-8: EDS spectrum of the inorganic part of the paint

9.3.2 Adhesion of alkyd paint to the LCAK steel substrate

9.3.2.1 Adhesion of alkyd paint to the LCAK steel substrates

Standard LCAK steel samples and warm water treated samples were coated with alkyd paint, conditioned and tested according to the procedures mentioned previously. In figures 9-9 and 9-10 the results of the paint adhesion test done on these samples are shown. The eight point ASTM test yielded good results to indicate poor and good adhesion for standard substrate and warm water treated substrate respectively. The standard sample showed an adhesion failure with a grading scale of 4 (figure 9-2). These results correlate with the BATE adsorption results shown in figures 8-5, 8-6 and 8-7.

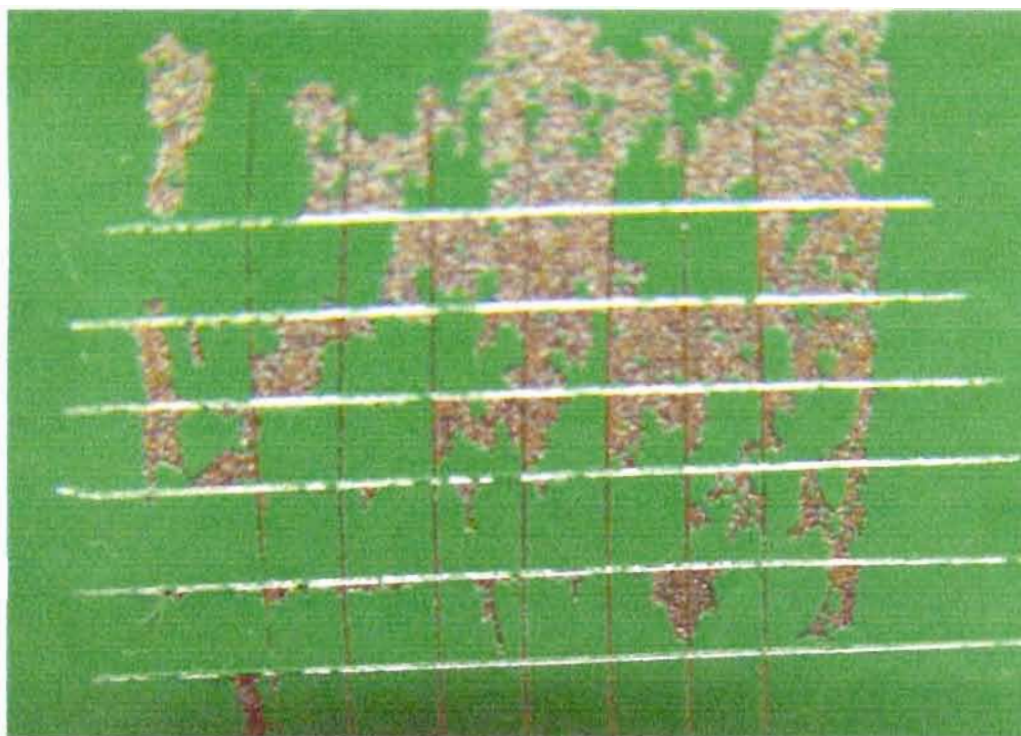


Figure 9-9: Painted adhesion results obtained on standard LCAK steel sample

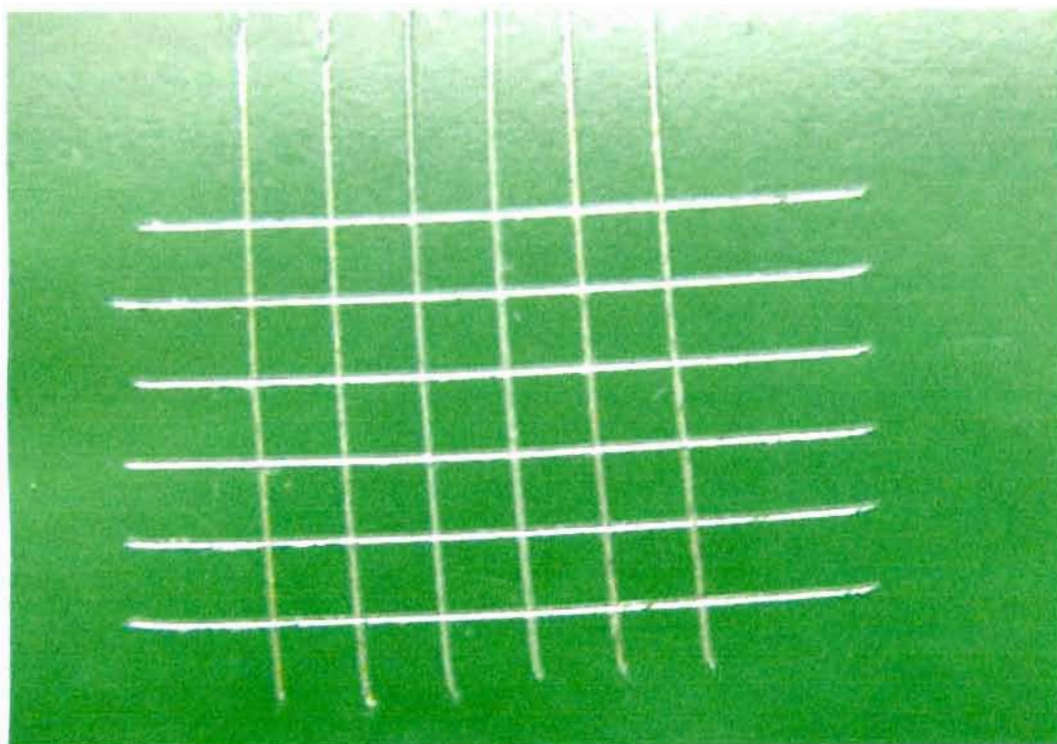


Figure 9-10: Paint adhesion results obtained on warm water treated painted LCAK steel sample

9.3.2.2 Adhesion of alkyd paint to LCAK steel substrates treated with acidic and basic solutions

The pictures of standard LCAK steel substrate treated with acidic and basic solutions are shown below. No difference in terms of adhesion was observed between pH 1 to 13. All samples showed blistering and adhesion failure with a grading scale of 4 (figure 9-2). This could be due to the presence of Na and Cl containing salts on the surface, which favours osmotic blistering [Gay, 1949]. This was also showed in the work done by Von Moltke and Sandenbergh [2003] where XPS was used to show the presence of Na and Cl on the steel surface after adhesion failure. When a salt residue on steel is over-coated with an organic polymer and is then exposed to an aqueous environment, the movement of water through the semi-permeable polymer membrane generates an osmotic pressure underneath the coating, which invariably results in the separation of the coating from the substrate [Von Moltke and Sandenbergh, 2003].

Figures 9-11 and 9-12 show the blistering of the LCAK steel substrates treated with the acidic and basic solutions respectively. The pictures showing the adhesion failure of the standard LCAK steel substrates treated with acidic and basic solutions are shown on figures 9-13 and 9-14 respectively.

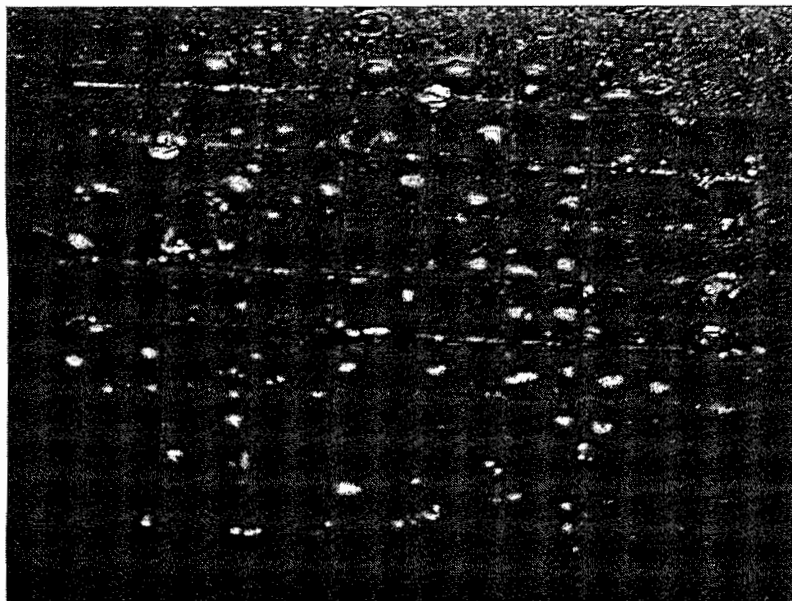


Figure 9-11: Painted standard LCAK steel sample treated with acidic solution with $\text{pH} \approx 3$

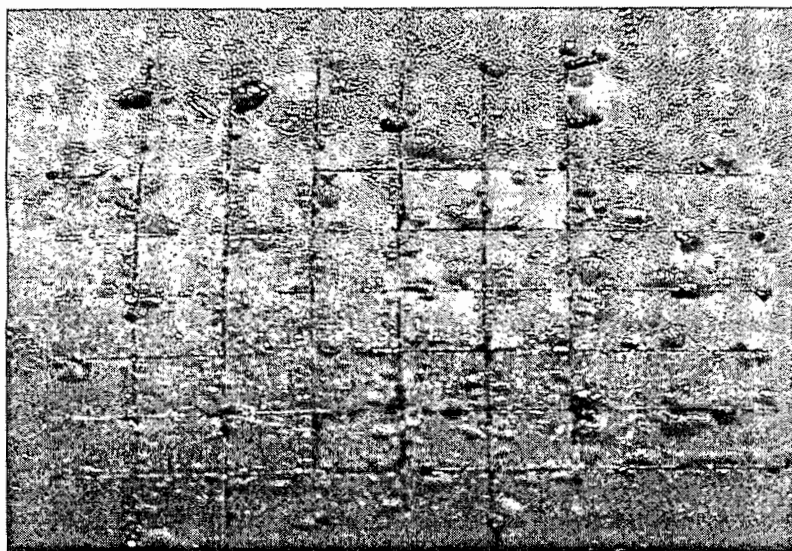


Figure 9-12: Painted standard LCAK steel sample treated with basic solution

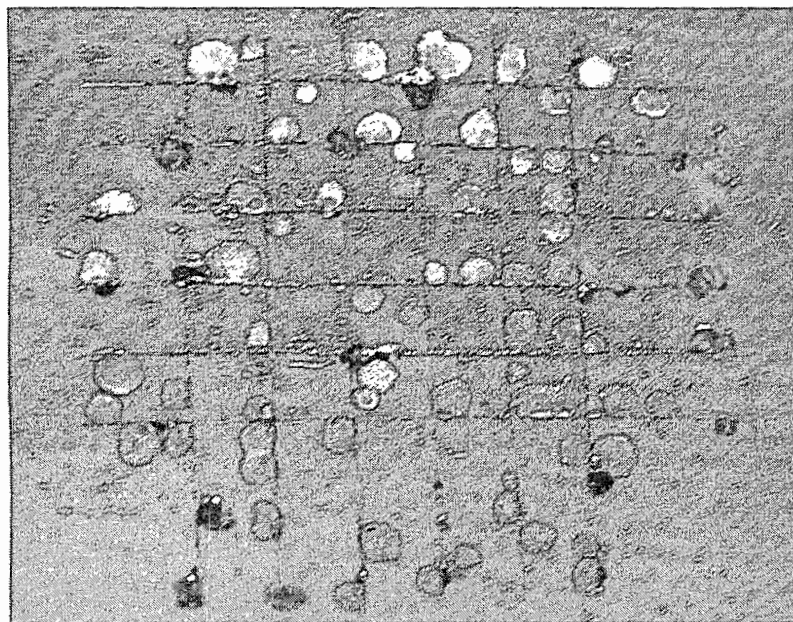


Figure 9-13: Painted standard LCAK steel sample treated with acidic solution ($\text{pH} \approx 3$) after adhesion test

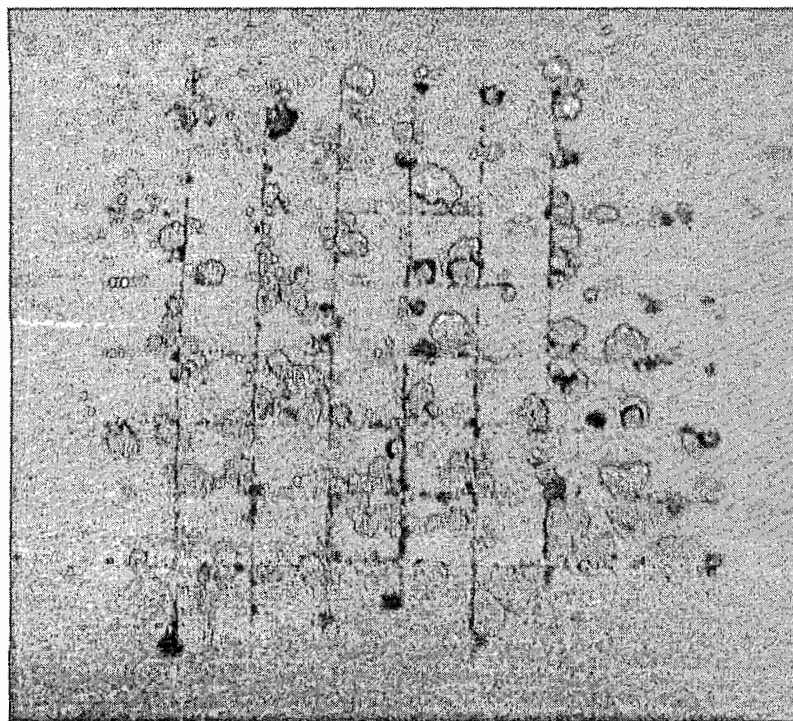


Figure 9-14: Painted standard LCAK steel sample treated with basic solution ($\text{pH} \approx 12$) after adhesion test

9.4 Conclusions

It has been shown that the availability of sophisticated analytical techniques, such as FTIR and SEM, can be used to characterize organic coatings. The coating was identified as a fatty acid modified alkyd resin containing the following elements – C, Ti, Cr, O, Fe, Al, Si, Pb and Cl.

With respect to alkyd paint adhesion, LCAK surfaces followed a behaviour reflecting its Lewis acid-base nature. A Lewis base surface will engage in sufficiently strong chemical bonds with some acidic groups of the alkyd coating. As a result, strong durable alkyd coatings on LCAK are obtained. The untreated standard LCAK steel surface exhibited a Lewis acid surface while the warm water treated surface exhibited Lewis base properties.

CHAPTER 10: MOLECULAR MODELLING OF SURFACES

10.1 Introduction

The use of molecular modelling and simulation to investigate research problems concerning surfaces and understanding the composition of the surface interface layer constitutes one of the major objectives in surface chemistry. Molecular modelling plays a big role in theoretical surface chemistry since an accurate knowledge of the outer surface layer is needed in an attempt to describe other surface chemical phenomena such as adhesion mechanisms.

The technology grew from the combination of computer graphics and computational methods initially used to investigate the interactions of drug candidates with protein structure [Matsukawa et al., 2000]. As software and hardware improved and more general computational algorithms were developed, the application of these techniques diversified [Materials Design, MedeA-VASP], first to address problems in polymer science [Liau and Cheng, 1998], and then to deal with more general organic and inorganic materials [Mendes, 2002].

In this study, the adsorption strength of water and oxygen to Fe (110) surfaces was investigated using the Cambridge Sequential Total Energy Package (CASTEP) [Segall et al., 2002] as applied in the Material Studio Software Package [MS Modelling 4, www.accelrys.com]. This study shows theoretical information of the adsorption strength of water and oxygen to Fe surfaces and may be the first step in examining the adhesiveness of these compounds on Fe surfaces.

10.2 Modelling surfaces

Simulation of graphic models of surface structure, constructed from 3D models, can provide valuable insight into surface chemistry. Energy calculations in algorithms, which minimize the energy of the surface – thus studying surface relaxation – can be used. Models of additive or solvent molecules can be placed on the surfaces and computation methods, to study their

binding or their motion, used to provide valuable information about surface diffusion, adsorption, and stability [Pestryaev, 2006].

Energy calculations are usually based either on molecular or quantum mechanics. Molecular mechanics approximates the energy of a system by summing a series of empirical functions representing components of the total energy, such as bond stretching, Van der Waals forces, or electrostatic interactions [Leach, 2001]. Although only semi-quantitative, it has the advantage of being very fast. Quantum mechanical methods use various degrees of approximations to solve the Schrödinger equation [Martin, 2000]. These methods deal with electronic structures and enable researchers to characterize chemical reactions.

Coveney and Humphries [Coveney and Humphries, 1996] published work examining the behaviour of phosphonate retarders on hydrating cements. Their study provided an excellent illustration of molecular modelling applications on surfaces. Cement retarders are used to control the setting of slurries. The rate of setting and the microstructure of the set material can have an effect on the mechanical behaviour of the cement. Coveney and Humphries wanted to obtain information on an improved, semi-quantitative action of retarders. They examined a process which they had identified as a key rate-controlling step in the hydration, the nucleation and growth of the inorganic crystalline phase, ettringite, from its gelatinous precursor. Starting with a model of the known crystal structure of ettringite, they computed a theoretical morphology for the crystal (Figure 10-1).

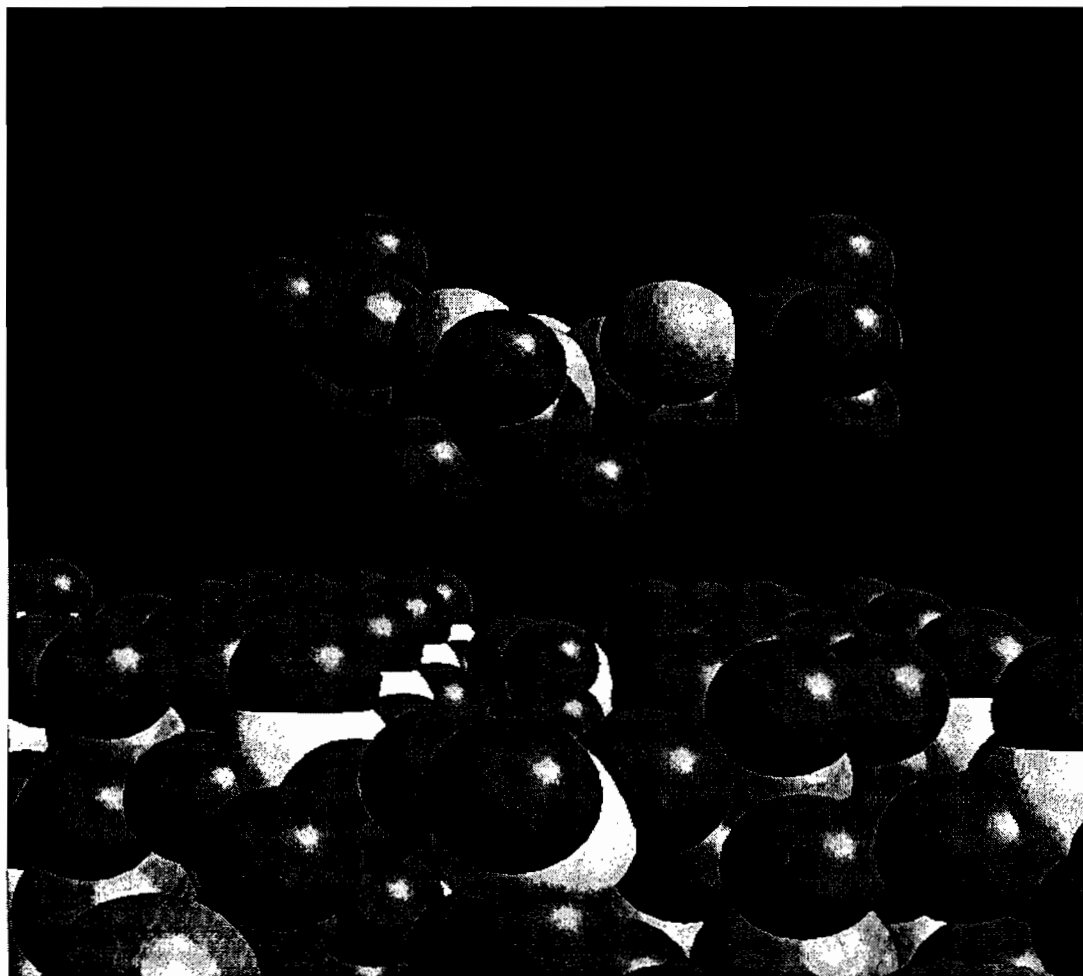


Figure 10-1: Phosphonate additive on a surface of ettringite, a key phase in the hydration of cement. This interaction has been successfully modelled by Coveney and Humphries, [Coveney and Humphries, 1996].

Modelling of the chemisorption of carbon monoxide on the surface of palladium catalyst [Hu et al., 1993] showed that calculated chemisorption energy agrees closely with the experimentally obtained value. Calculations of charge density and electrostatic potential allowed Hu and his co-workers to understand the possible mechanism of attack during any reaction with the chemisorbed molecules (Figure 10-2).

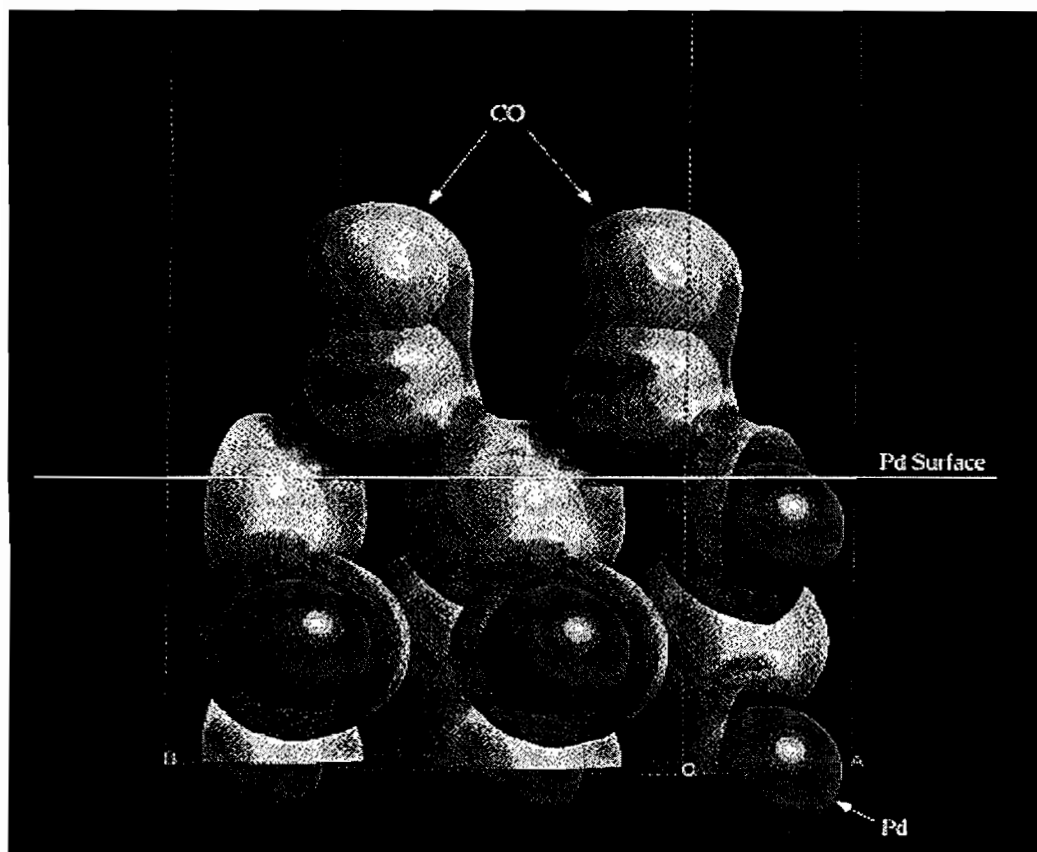


Figure 10-2: Chemisorption of CO molecules on a catalytic surface as simulated by the CASTEP program [Payne, et al., 1992]

The charge density difference is shown mapped to the charge density iso-surface. This shows valence charge redistribution relative to the superposition of free atoms.

The studies shown above represent a minute fraction of current surface modelling research work. Other applications include predicting the adhesion of polymer coatings to metals, understanding the nature of chemical vapor deposition processes, and determining surface structure [Deak and Jackson, 1993].

Molecular modelling can be used to draw together information from theoretical predictions, analytical studies, and structural databases. Combining all of these with graphical visualization

and the user's chemical intuition, offers a uniquely powerful vehicle for understanding some of today's toughest research challenges.

10.2.1 Adsorption of water to metallic surfaces

Adsorption of water to metal surfaces has been the focus of many investigations [Ludwig, 2005; Ogasawara et al., 2002; Henderson, 2002; Thiel and Madey, 1987] due to its importance in electrolysis, fuel cells, catalysis and corrosion. Many different approaches have been applied to the study of this subject, ranging from first principles of molecular dynamics [Lee et al., 1984] to Monte Carlo simulations [Jönsson, 1981]. The intact monolayer of water on different surfaces is thought to form a hydrogen-bonded structure comprised of hexagonal rings of water, arranged in two layers to form an extended honeycomb network. The inner layer of water has the oxygen lone pair directed towards the surface, forming a weak bond to the metal with OH nearly parallel to the surface, while the second layer water completes the hydrogen bonding structure. The nature of this outer layer has been an issue of controversy. Experiments from previous researchers support the assumption that the water molecules arrange in a bilayer of 'flat ice' (Figure 10-3) on the following surfaces: Ru(001), Ag(111), Pt(111) and Cu(110) [Björneholm et al., 1994].

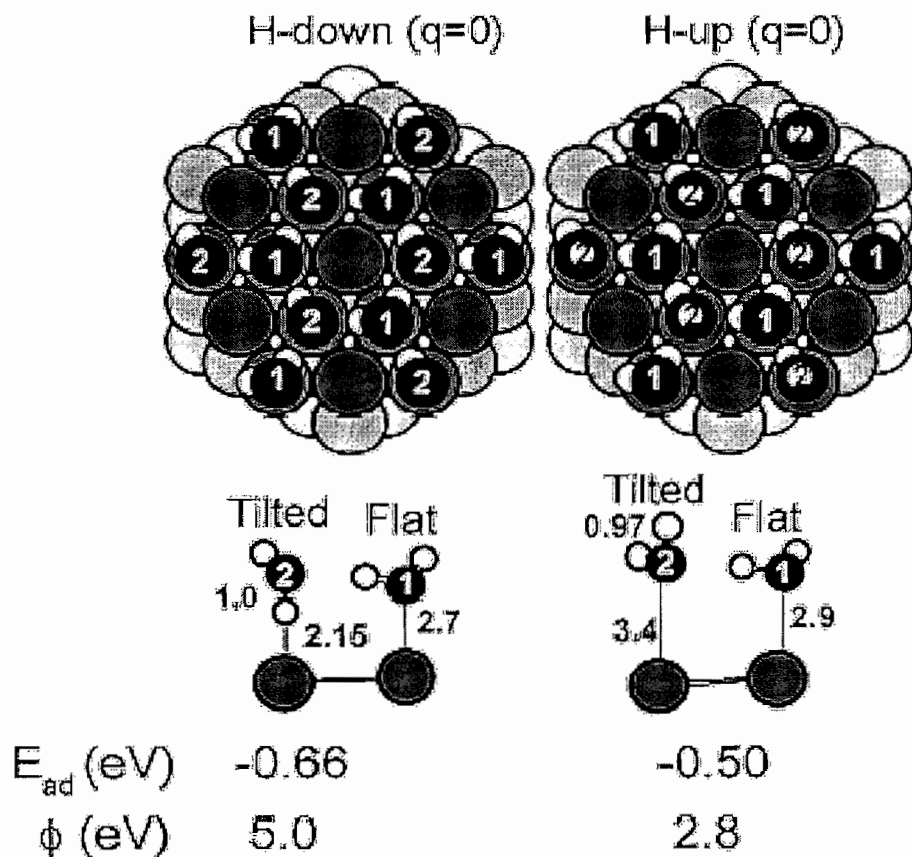


Figure 10-3: Large-scale top and side views of the optimized adsorption geometry for the two conventional models of 'flat ice' bilayers on a neutral ($q = 0$) Pd surface [Björneholm et al., 1994]

Large-scale top and side views of the optimized adsorption geometry for the two conventional models of 'flat ice' bilayers on a neutral ($q = 0$) Pd surface: H-down (left), H-up (middle) labels define the orientation of the free O–H bond not involved in the hydrogen bonding network. Dark blue, light blue, black and spheres correspond to Pd, sublayer Pd, O and H atoms, respectively. [Filhol and Bocquet, 2007].

Density Functional Theory (DFT) calculations in combinations with X-ray spectroscopy methods were used by Ogasawara and his co-workers to study the water bilayer structure on Pt(111) [Ogasawara et al., 2002]. They studied the coordination of water atoms on the surface with X-

ray Photoelectron Spectroscopy (XPS), the orientation of the O-H bond on the surface by X-ray Adsorbed Spectroscopy (XAS) and used DFT calculations together with X-ray Emission Spectroscopy (XES) to explain the bonding mechanism of water to the surface. It has been believed that the non-hydrogen-bonded OH of the second layer water molecules points up towards the vacuum (H-up) but Ogasawara and his co-workers showed that those OH bonds are pointing into the surface (H-down) on Pt(111) [Ogasawara et al., 2002]. The DFT calculations showed reliable results which were compared with measured X-ray spectra (Figures 10-4 and 10-5).

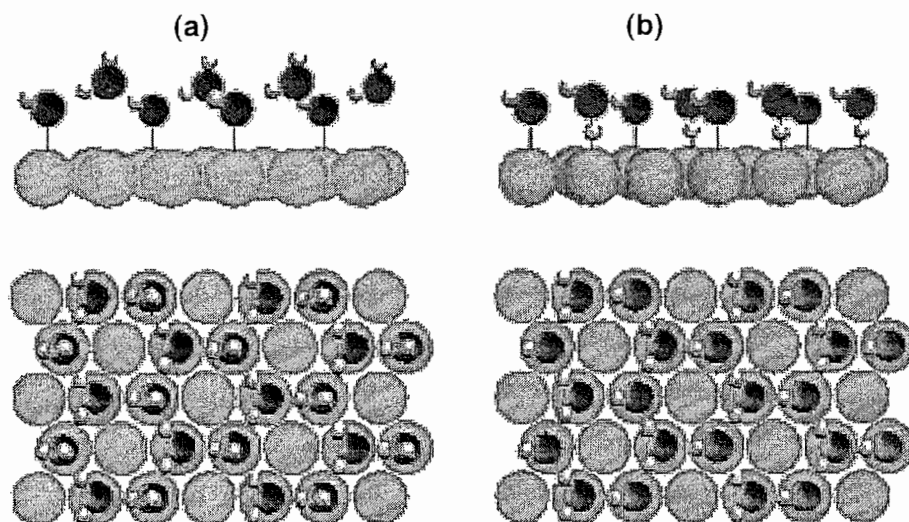


Figure 10-4: (a) The bilayer ice structure on metal surfaces. (b) The flat ice structure on metal surfaces [Ogasawara et al., 2002].

(a) The bilayer ice structure on metal surfaces: Dark spheres represent O atoms. Half of the water molecules bind directly to the surface metal atoms. The other half is displaced toward the vacuum (H-up) configuration. (b) The flat ice structure on metal surfaces: Dark spheres represent O atoms in Pt-O and Pt-HO bonding water molecules respectively. All water molecules bind to the surface metal atoms. The thickness of the layers is $0.96\text{\AA}$ (a) and $0.25\text{\AA}$ (b), respectively [Ogasawara et al., 2002].

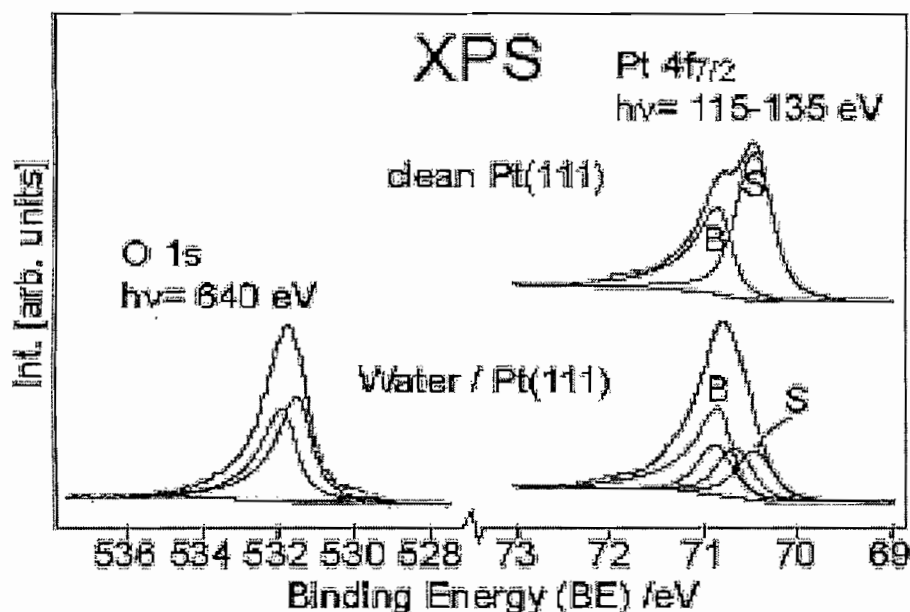


Figure 10-5: XPS spectra for clean and water covered Pt(111) [Ogasawara et al., 2002]

XPS spectra for clean and water covered Pt(111). The components obtained from a curve fitting analysis, according to the structural model (Figure 10-4(b)), are shown with solid lines. (Left) O 1s photoemission spectrum estimated with two separated peaks corresponding to the Pt-O and Pt-HO bonding water molecules. For clean Pt(111), the bulk (B) and surface (S) binding energies are split by 0.4 eV [Ogasawara et al., 2002].

A step-by-step procedure to determine the number of water molecules coordinated to the platinum surface was proposed by Ludwig [Ludwig, 2005] following the Ogasawara [Ogasawara et al., 2002] protocol. It was estimated that 2/3 of the platinum atoms on the surface are coordinated to water molecules. The water molecules are thought to bind to the metal surface through the oxygen lone pair orbital [Doeting and Madey, 1982]. They thus indicated that the steric arrangement of water to the surface is with the oxygen atom orientated towards the platinum surface, with the hydrogen atoms forming the outer layer. The orientation of water in

the first wetting layer will influence the stability of water adsorbed on top of this structure and the subsequent multilayer growth and wetting behaviour of the surface [Kimmel et al., 2005].

A study of the orientation of water adsorbed on the open Cu(110) surface with DFT geometry optimization, total energy calculations, XA spectral and XPS was done as to explore the structure of water on the surface [Schiros et al., 2006]. It was found that open surfaces can provide sites where the energy between H-down and H-up is nearly zero, or favours H-up, and both H-down and H-up structures co-exist. Illustrations of the open and closed packed surfaces are shown below.

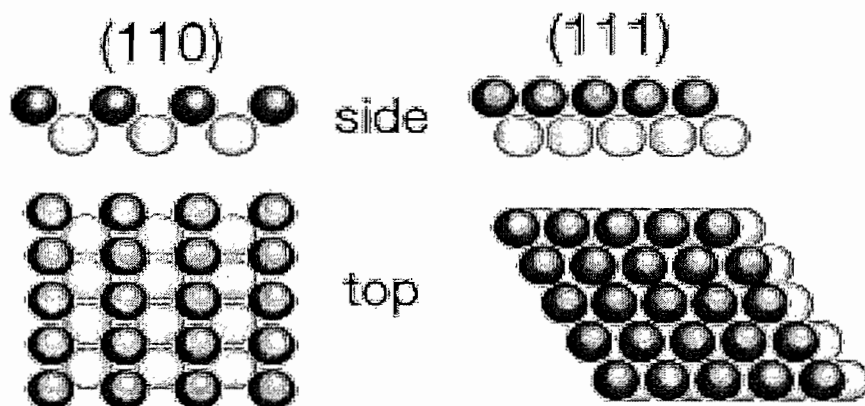


Figure 10-6: Illustration of the open (110), and close-packed (111) [Schiros et al., 2006]

10.2.2 Combined adsorbed OH and H₂O on the metal surfaces

Dissociation of water at metal surfaces is an activated process. A well-ordered OH + H₂O layer was systematically produced by dosing water on an oxygen pre-covered metal surface, such as Pt(111) [Schiros et al., 2007]. The water activates the reduction of atomic oxygen at a Pt(111) surface to generate a mixed OH + H₂O phase which proceeds via the reaction:



Comparison of the OH + H₂O layer with a pure water layer provides an opportunity to probe the competitive behaviour between water-metal bonding and hydrogen bonding in the adsorbed layer. The OH + H₂O phase has a significantly higher adsorption energy which varies significantly between metal surfaces [Michaelides and King, 2004]. The origin of this behaviour is thought to be related to the strong OH-metal ionic bond, stabilized by charged transfer from the metal substrate to partially occupied 1 π (lone pair) orbital of OH [Bagus and Hermann, 1984]. Therefore water is a weaker acceptor and strong donor of H-bonds in the mixed OH + H₂O adsorbed layer. The adsorbed hydroxyl (OH_{ad}) has an influence on the structure and bonding of water at a metal surface, which affects reactivity of the surface, however the exact mechanism is unknown.

Detailed knowledge of adsorbed water molecules at the interfaces of the LCAK steel surface is essential to understand the adhesion mechanism in terms of Lewis acid base theory. In the present work we propose the use of molecular modelling and XPS to study the water-Fe(110) system as to explain whether water orientates on the surface as a Lewis acid or Lewis base in the absence of oxygen.

CHAPTER 11: MOLECULAR MODELLING: METHOD AND MODEL VERIFICATION

11.1 Introduction

Most molecular modelling studies involve three stages. In the first stage a model is selected to describe the intra- and inter- molecular interactions in the system. The two most common modes that are used in molecular modelling are quantum mechanics and molecular mechanics. These models enable the energy of any arrangement of atoms and molecules in the system to be calculated, and allow the modeller to determine how energy of the system varies as the position of the atoms and molecules change [Koch and Holthausen, 2002]. The second stage of the molecular modelling study is the calculation itself, such as an energy minimization, a molecular dynamics [Lee et al., 1984] or Monte Carlo simulation [Jönsson, 1981], or a conformational search. Finally the calculations must be analyzed, not only to calculate properties, but also to check that it has been properly performed.

Computational methods are currently very widely used to compliment and understand experimental observations, as well as in the development of predictive theories [Matsukawa et al., 2000]. These types of computational chemical methods are widely applied in various fields of research including chemistry, physics and engineering [Mendes, 2002]. The theoretical modelling of iron and iron surfaces in particular has received some interest in the past [Ludwig, 2005; Ogasawara et al., 2002; Henderson, 2002; Thiel and Madey, 1987]. The industrial importance of modelling the iron system can be seen in surface science and the steel industry [Mendes, 2002].

11.2 Computational chemistry methods

Computational chemistry is a branch of chemistry that uses computers to assist in solving chemical problems. It uses the results of theoretical chemistry, incorporated into efficient

computer programs to calculate the structures and properties of molecules and solids. The theoretical results normally complement the information obtained by chemical experiments.

The available atomic scale computational methods can be divided into two groups. The first group uses force fields to describe the interatomic interactions. These force fields are usually empirically parameterized. These types of models are useful in describing geometry structures, intermolecular interactions and energy trends, and can be used to calculate systems with many atoms [Pestryaev, 2006]. The force field approach does not attempt to solve the Schrödinger equation and it is therefore usually not used to study chemical bonds [Martin, 2000].

The second group uses quantum mechanics. This principal method is designed to calculate the electron structure of the considered system [Leach, 2001]. By using quantum mechanics, the electronic structure of various chemical systems can be approximated. There are various approaches in the group, including Hatree Fock (HF), an extension of molecular orbital theory, in which the correlation electron-electron repulsion is not significantly taken into account, only its average effect is included in the calculation. Post-HF ab initio methods are corrected for electron-electron repulsion and is also referred to as electronic correlation and Density Functional Theory (DFT) methods [Koch and Holthausen, 2002]. DFT methods are often considered to be ab initio methods for determining the molecular electronic structure, even though many of the most common functionals use parameters derived from empirical data or from more complex calculations. In DFT the total energy is expressed in terms of the total one-electron density rather than the wave function. DFT methods can be very accurate at little computational cost [Koch and Holthausen, 2002]. In this study we mainly aim to describe the chemical bonding and reactivity on an iron surface. The DFT method is therefore a very useful theoretical approach to study this system.

11.2.1 Density Functional Theory

The development of DFT, the contribution for which Walter Kohn shared the 1998 Nobel Prize in Chemistry, has opened imported and previously unexplored aspects of science to surface science researchers [Kohn, 1999]. The main aim in the first principal method is to solve the time-independent Schrödinger equation [Schrödinger, 1926]

$$\hat{H}\Psi = E\Psi \quad (11.1)$$

where E = Energy of the particle or system, Ψ = The wave function of the particle or system and $\hat{H}$ = The Hamiltonian operator.

While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on approximations for the so-called exchange correlation potential.

There are two main approximations which are generally applied to chemical systems. The first is the Born-Oppenheimer approximation [Born and Oppenheimer, 1927] in which it is assumed that the electronic and nuclear wavefunctions are independent due to the large mass mismatch. This decouples the nuclear and electronic movements and, in most chemical systems, the nuclei can be considered as point charges. To calculate the energy of a system in this case, only the solution of the electronic wave function is required. The second approximation concerns the electron-electron interaction. To describe a multi-electron system the electrons are considered as moving within the force field of the other electrons.

DFT, developed by Kohn, Hohenberg and Sham [Hohenberg and Kohn, 1964; Kohn and Sham, 1965] is used to give a quantum chemical description of systems with a high concentration of electrons. In the first Hohenberg-Kohn theorem [Hohenberg and Kohn, 1964] it is stated that the

electron density of any system determines the external potential and, consequently, the Hamiltonian of the system.

In DFT the total energy of a chemical system, $E(\rho)$, can be expanded as:

$$E(\rho) = U(\rho) + T(\rho) + E_{xc}(\rho) \quad (11.2)$$

where:

U = Coulombic interaction energy

T = Kinetic energy

E_{xc} = Exchange-correlation energy contribution [Parr and Yang, 1989].

The first two terms can be expressed, but there is no exact expression for E_{xc} . Therefore different DFT exchange-correlation functionals are used to estimate the E_{xc} term.

The simplest approximation is the local-density approximation (LDA), which is based on exact exchange energy for a uniform electron gas. In the LDA the exchange-correlation contribution for a point with a specific electron density is set to that of a homogeneous free electron gas with the same electron density. When applied, the LDA approach generally leads to stronger than observed binding effects in chemical bonds [Perdew, et al., 1992] and in some cases (as for iron) the prediction of an incorrect magnetic state [Singh et al., 1991 and Bagno et al., 1989]. To improve on this over-simplification, non-local gradient effects have been included. This resulted in what is known as the generalized gradient approximation (GGA). In this approximation the effect of both the electron density and the electron density gradient are included to express the exchange-correlation. Many different exchange-correlation functionals within the GGA have been proposed. Among these are widely used functionals such as:

BP = Becke-Perdew [Becke, 1988]

PW91 = Perdew-Wang 1991 [Perdew and Wang, 1992]

PBE = Perdew-Burke-Emzerhof [Perdew et al., 1996]

BLYP = Becke-Lee-Yang and Parr [Lee et al., 1988]

RPBE = Revised Perdew-Burke-Emzerhof [Hammer et al., 1999].

Despite the improvement in DFT since 1990, whereby it was considered accurate enough for calculations in quantum chemistry, there is still difficulty in using density functional theory to properly describe intermolecular interactions, especially Van der Waals forces, charge transfer excitations, transition states, global potentials energy surfaces and some other strongly correlated systems [Leach, 2001]. The development of new DFT methods designed to overcome some of these challenges are presently under investigation by theoretical chemists.

11.2.2 Molecular modelling of surfaces: The approach

Graphic models of surface structure, often constructed by cleaving surfaces from 3D models of crystalline or amorphous solids, can provide valuable insight into surface chemistry. Different surface molecules modelling approaches exist, which employ one of the DFT methods. The most preferred methods are cluster, embedded cluster and periodic slab calculations [Whitten and Yang, 1996].

11.3 Computational method used

The Density-Functional-Theory (DFT) quantum chemical calculations used in this study were done using the Cambridge Sequential Total Energy Package (CASTEP) [Segall et al., 2002] as applied in the Material Studio Software Package [MS Modelling 4, www.accelrys.com]. The program solves the Kohn-Sham equation within periodic boundary conditions and the pseudopotential approximation using a plane wave basis set.

The generalized gradient approximation (GGA), using the Perdew-Wang 1991 functional (PW91) [Perdew and Wang, 1992] was used to calculate the electron exchange-correlation contribution. The electron interactions were described by ultrasoft pseudopotentials as included in the CASTEP suite [MS Modelling 4, www.accelrys.com]. Geometry optimizations were performed by using the BFGS [Fisher and Almlof, 1992] method as implemented in CASTEP.

11.4 Optimizing bulk Fe

Conflicting demands are faced in applying the DFT approach to model verification of bulk iron. The calculation must be set-up in such a way that it describes the surface and adsorbent's interaction as accurately as possible. Also, it must be considered that computational time is dependent on the number of atoms present and the calculation parameters [Whitten and Yang, 1996]. The optimization of the calculation parameters is very important in establishing a model that can be used to study a broad range of possible systems. Since the structural and electronic properties of the surfaces and the surface reactions depend on the chosen bulk model, it is therefore of utmost importance to obtain a very accurate bulk model, which is fully converged with regard to the modelling parameters.

11.4.1 Bulk Fe verification method

There are a number of optimization parameters that need to be considered when building a bulk and surface DFT model. These are the exchange-correlation functionals, the pseudopotentials used to represent the electron-ion interaction, the special k-points for Brillouin zone interaction, the plane-wave cut-off energy, the applied electron smearing, and the vacuum spacing and slab thickness [Mattsson et al., 2005]. In optimizing these parameters, the accuracy of the bulk iron model can be evaluated by comparing some calculated values to experimental values. In this

study the bulk Fe was optimized for the special k-points and plane-wave cut-off energies; other parameters were out of the scope of this study.

11.4.2 Fe bulk calculations

In this section we describe the verification of various models parameters of the bulk Fe system. The parameters we considered are the cut-off energy and k-points.

11.4.2.1 Cut-off energy and k-points

Two of the most important parameters are the plane wave basis set cut-off energy and k-point set. The wave function components of the system are calculated at each k-point by using a combination of plane waves with kinetic energies lower than the cut-off energy. A change in the number of k-points will therefore be accompanied by a change in the minimum number of plane waves that are needed to describe the wavefunction at a specific k-point. The two parameters are therefore interdependent. Various combinations of the two parameters have to be evaluated to find a converge set of these parameters. The parameter values to be used for further calculations must be optimized to converge within a range of 1 meV to limit their effect on the bulk energy. To analyze this a graph was used, while varying the k-points from 6x6x6 to 10x10x10 using only even number steps. At each k-mesh the cutoff energy was varied from 260 eV to 500 eV. The resulting graph can be seen in figure 11.1. The system energies vary and go down as the k-points are changed to 10x10x10. At 6x6x6 to 10x10x10 the energy starts to converge within 1 meV at a cut-off energy of 380 eV. It can therefore be assumed that working at a 380 eV cut-off energy and an 8x8x8 k-mesh would yield an optimized set of parameters for bulk iron calculations.

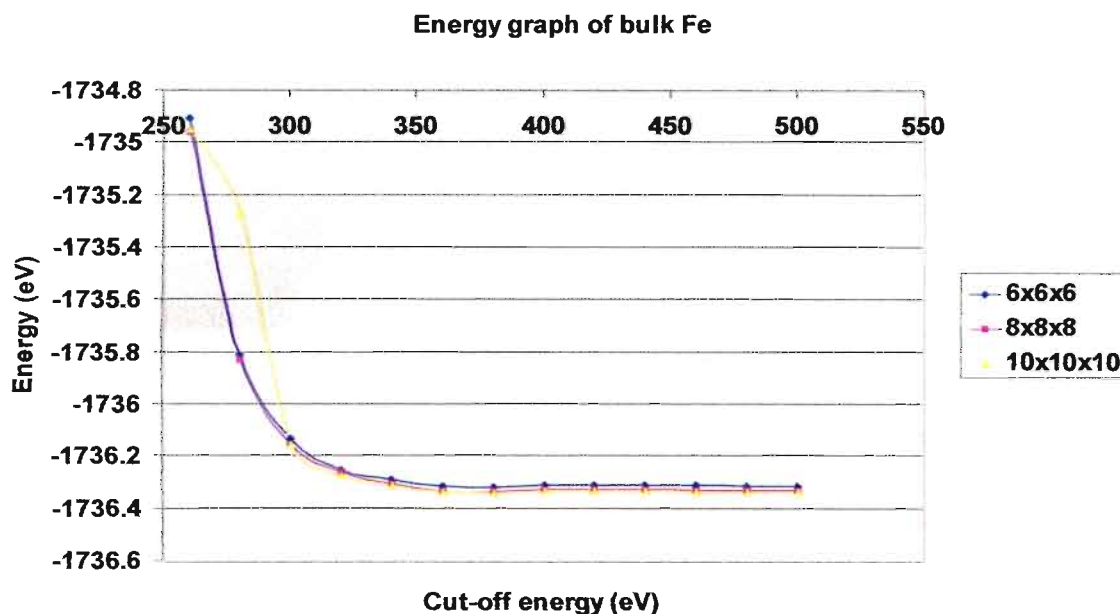


Figure 11-1: The graph indicating the effect of k-point meshes and cut-off energies for bulk Fe

11.4.3 Fe(110) surface calculations

When the iron bulk model has been fully optimized, the next step is to calculate the surfaces. In this section the surface energies of the Fe(110) surface were considered. Parameters that are optimized are unit cell k-mesh and cut-off energy.

11.4.3.1 K-points and cut-off energy

The k-mesh and cutoff energies for Fe(110) surface were optimized as described below. To analyze this, a graph was used, while varying the k-points from 9x9x1 to 13x13x1 using only the odd number steps. At each k-mesh the cut-off energy was varied from 280 eV to 520 eV. The resulting graph can be seen in figure 11-2. The system energies vary and go down as the k-points are changed to 13x13x1. At 9x9x1 to 13x13x1 the energy starts to converge within 1 meV at a cutoff energy 380 eV. It can therefore be assumed that working at a 380 eV cut-off energy and an 9x9x1 k-mesh would yield the most optimized set of parameters for Fe(110) surface calculations.

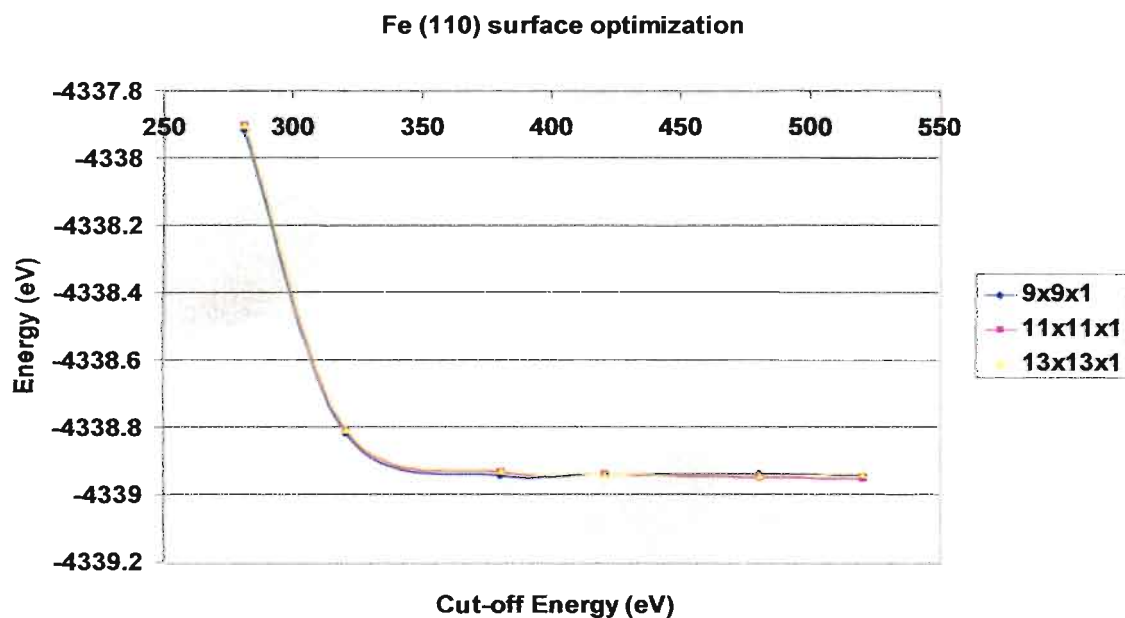


Figure 11-2: The graph indicating the effect of k-point meshes and cut-off energies for Fe(110) surface

11.5 Conclusions

We presented the background of the DFT calculations that was the basis of our theoretical work, as well as the verification of the bulk and surface iron models. The optimization of the k-points and cut-off energies were investigated. In the following chapter we will discuss the adsorption of hydrogen, oxygen, hydroxyl and water with the optimized Fe(110) surface slabs.

CHAPTER 12: ABSORPTION OF OXYGEN AND WATER ON Fe (110) SURFACE

12.1 Introduction

A standard and severe operating condition in the adhesion of organic coatings to metal surfaces is pre-treatment, which may cover the active metal surface resulting in different chemical adsorption on the surface. In the previous chapters, it was shown that the driving force in poor or good adhesion properties was the presence or absence of oxygen in the rinsing step during pre-treatment. This could result in Lewis-acid or Lewis-base properties of the metal surface.

It is important to establish how the adsorbed water molecule on the metal surface would “orientate” to the surface with or without the presence of oxygen. The theoretical study of water and oxygen adsorption at the Fe(110) and also Fe(100) surfaces has been studied previously [Błoński et al., 2005; Yin et al., 2007; Eder and Terakura, 2001]. Some of these studies claim that the molecular adsorption of water shows very small effect on the surface structure due to the weak interaction between water and the substrate [Yin, 2007], while others have predicted the adsorption geometry and transition path for the dissociation process $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ for both Fe(110) and Fe(100) surfaces [Eder, 2001]. There is no agreement on the nature or the strength of adsorption of water and oxygen on the Fe(110) surface.

This chapter explores the nature and strength of the adsorption of water with or without oxygen on the Fe(110) surface. Periodic DFT provides an efficient and accurate model to calculate properties of metal surfaces and is in this study.

12.2 Experimental procedures

12.2.1 DFT calculation setup

Periodic slab calculations were performed for Fe(110) and adsorbed water and oxygen to understand the interactions that exist between water, with or without oxygen, and the surface.

All calculations were performed using CASTEP based on density functional theory (DFT) (see discussion in Chapter 11). The exchange-correlation energy was described using the Perdew and Wang 1991 (PW91) form of the spin-polarized generalized gradient approximation (GGA). Cut-off energy of 380 eV was used for the plane wave-basis set. The k-spacing interactions were performed using a 5 x 5 x 1 Monkhorst-Pack mesh [Monkhorst and Pack, 1976] for the 2 x 2 surface unit cell and their quality was improved by using the first order Methfessel-Paxton [Methfessel and Paxton, 1989] method for Fermi surface smearing with a width 0.1 eV.

The surface was modelled by slabs consisting of five Fe layers separated by a vacuum layer of 10Å, and repeated periodically throughout space. In the previous chapter, this set-up has been shown to be sufficiently thick to avoid interaction between the surface of neighboring slabs and through the slab. Oxygen atoms were adsorbed on one side of the slab. The positions of Fe-atoms in the two topmost layers, and of all oxygen atoms, were allowed to relax until the forces on unconstrained atoms converged.

12.3 Results and discussions

12.3.1 On-surface oxygen

For the Fe(110) surface, slab models of 4-, 5- and 6- metal layers were used with oxygen on one side of the slab. The adsorption energies E_{ads} for different slab thicknesses with oxygen on-surface were checked for convergence using the formula:

$$E_{ads} = E_{slab}^{O/Fe} - E_{slab}^{Fe} - E^O \quad (12.1)$$

where $E_{slab}^{O/Fe}$ is the total energy of the O covered Fe slab, E_{slab}^{Fe} is the total energy of the clean Fe substrate, and E^O is the energy of oxygen molecule.

The different adsorption sites examined for O adsorption on Fe(110) surface are shown in figures 12-1 to 12-4. Coverage factor of 0.25 ML, corresponding to one O atom per 2×2 surface cell, was studied.

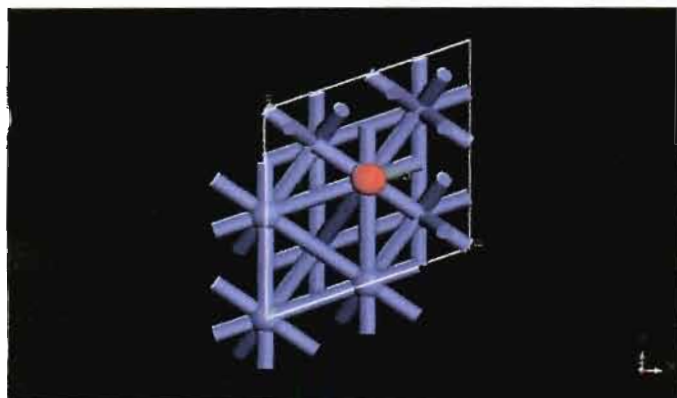


Figure 12-1: Top view of the Fe(110) surface showing the on-surface on-top (ot) oxygen (red atom) adsorption site

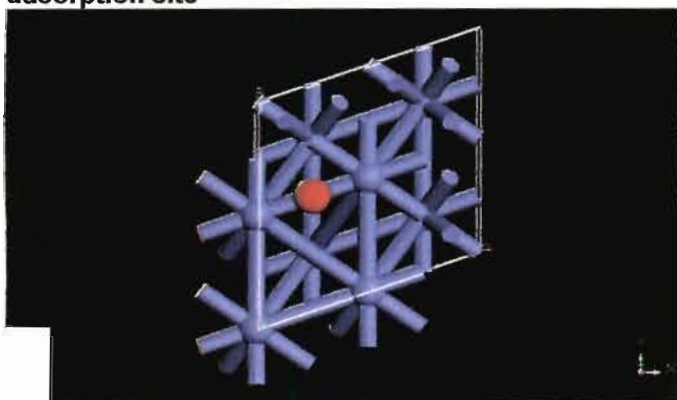


Figure 12-2: Top view of the Fe(110) surface showing the on-surface short bridge (sb) oxygen (red atom) adsorption site

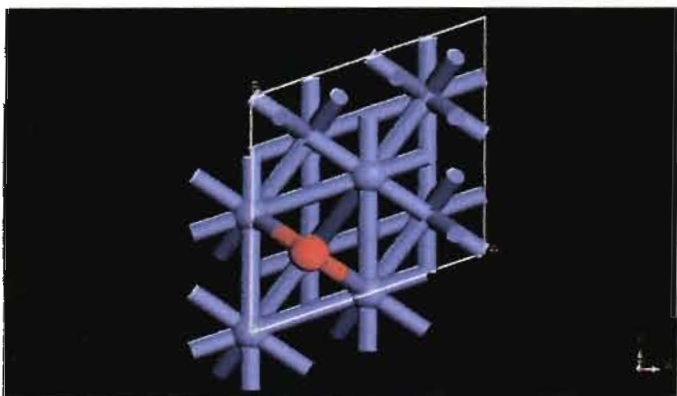


Figure 12-3: Top view of the Fe(110) surface showing the on-surface long bridge (lb) oxygen (red atom) adsorption site

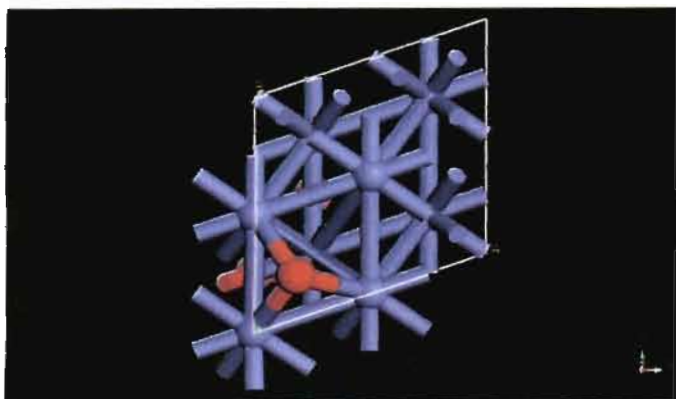


Figure 12-4: Top view of the Fe(110) surface showing the on-surface fourfold-hollow (fh) oxygen (red atom) adsorption site

The fourfold-hollow site on the Fe(110) surface was found to be energetically most stable, as is shown in Table 12-1. The calculated adsorption energies for the O atoms in the most favored site (fourfold-hollow), as a function of slab thickness, are presented in Table 12-2. From the table, five layer thickness slab seems to be converged. All adsorption calculation of water with and without the oxygen will be done on a five layer slab.

O atoms adsorbed on Fe(110)	Energies (eV)
on-top oxygen (ot)	-17794.05
short bridge (sb)	-17795.28
long bidge (lb)	-17795.79
fourfold-hollow (fh)	-17795.80

Table 12-1: The energy for O adsorbed in the on-top, short bridge, long bridge and fourfold-hollow sites on Fe(110) surface

Slab thickness	$E_{slab}^{O/Fe}$ (eV)	E_{slab}^{Fe} (eV)	E^O (eV)	E_{ads} (eV)
Four layers	-14322.86	-13882.77	-433.66	-6.43
Five layers	-17795.81	-17355.79	-433.66	-6.36
Six layers	-21268.19	-20828.12	-433.66	-6.38

Table 12-2: The calculated adsorption energy, Eads, for O atoms adsorbed in the most favored fourfold-hollow site on Fe(110)

12.3.2 Adsorption of H₂O on Fe(110)

Although molecular H₂O has a lot of configurations in which it can orientate on surfaces, only three unique possible molecular configurations were optimized:

- (1) H₂O standing on the surface with O binding to the surface Fe atom.
- (2) H₂O lying on the surface with its oxygen binding to the surface Fe atom.
- (3) H₂O standing with a tilt so that one H comes closer to a near surface O.

The adsorption energy was calculated according to the expression:

$$E_{Ads} = E_{slab}^{water / Fe} - (E_{slab}^{Fe} + E^{water}) \quad (12.2)$$

where $E_{slab}^{water / Fe}$ is the total energy of the adsorbate and surface system, E_{slab}^{Fe} is the total energy of clean surface, and E^{water} is the energy of free water. Negative E_{Ads} corresponds to a stable adsorption system [Yin et al., 2007].

Figure 12-5 to 12-7 shows the optimized structures of these three Fe configurations. Adsorption energies, as well as those of clean surfaces, are summarized in Table 12-3. Adsorption energies of -1.43 eV, -36.12 eV and -1.43 eV in these three structures were calculated, with structure (2) energetically favoured, but not the favourable position for water molecules as it is repulsed from the surface into the air. In the two structures, configuration (1) and (3), adsorption energies were similar. In the present model one water molecule was dissociated and co-adsorb as OH and H on the surface of Fe(110). The water molecule seems to be very mobile on the iron surfaces [Eder and Terakura, 2001]. At the surface the oxygen can act as electron-donating Lewis-base sites [Wielant et al., 2007]. Generally it is believed that molecular H₂O binds to oxide surfaces as a Lewis-base to the ionic charge [Yin et al., 2007]. However, the detailed mechanism of dissociative adsorption is poorly understood because oxide surfaces vary

drastically in geometry and electronic structures. It is widely recognized that the acid-base properties of oxide surfaces alter the adhesion of organic compounds. In chapter 7 of this study, the XPS (adsorption) studies indicated Lewis-acid properties for the standard LCAK steel surface and Lewis-base properties for the steel surface treated with warm water.

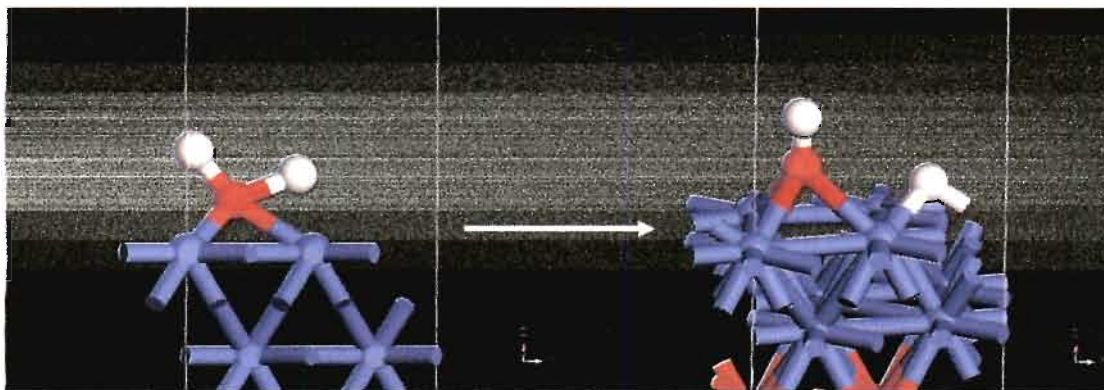


Figure 12-5: Structure of H₂O molecular (O-red, H-white) adsorption on Fe(110) standing on the surface, showing dissociation of water on Fe(110) surface and co-adsorption of OH and H.

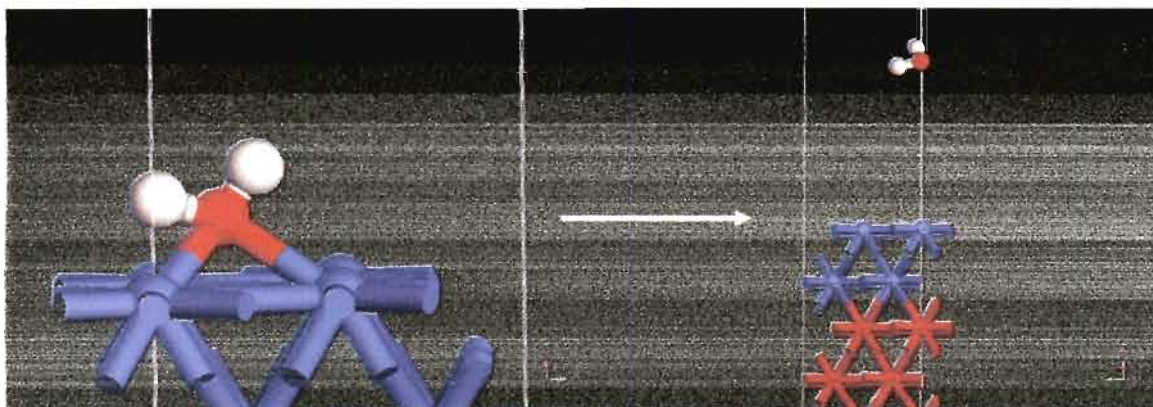


Figure 12-6: Structure of H₂O molecular (O-red, H-white) adsorption on Fe(110) lying on the surface, showing water molecules going into gas phase on Fe(110) surface.



Figure 12-7: Structure of H₂O molecular (O-red, H-white) adsorption on Fe(110) tilted on the surface, showing dissociation of water on Fe(110) surface and co-adsorption of OH and H.

H ₂ O	$E_{slap}^{water/Fe}$ (eV)	E_{slap}^{Fe} (eV)	E^{water} (eV)	E_{ads} (eV)
Standing on surface	-17828.08	-17355.79	-470.86	-1.43
Lying on surface	-17862.76	-17355.79	-470.86	-36.12
Tilted on surface	-17828.08	-17355.79	-470.86	-1.43

Table 12-3: The calculated adsorption energy for H₂O molecules adsorbed on Fe(110) surface

12.4 Conclusions

To describe the adsorption process of water on the Fe(110) surface, the adsorption energies for all the molecules and atoms involved in this process were calculated using the density functional method. It was observed that water dissociates $H_2O \rightarrow OH + H$ and co-adsorbs as OH and H on Fe(110) surface. It is known that adsorbed hydroxyl on a metallic surface gives Lewis-base properties [Wielant et al., 2007]. The theoretical results are in agreement with XPS results which predicted Lewis-acid properties for the standard LCAK steel surface and Lewis-base properties for the steel surface treated with warm water (water with less oxygen), and provides a fundamental understanding of the initial stages of adhesion mechanism.

CHAPTER 13: CONCLUSIONS

The aim of this study was to examine the influence of different pre-treated steel surfaces on the adhesion of alkyd paint with regard to Lewis acid-base theory. There is a wide variety of reasons that leads one to assess the properties of a substrate for adhesive bonding. This ranges from simply ensuring that it is clean, through to the need to assess the quality of a pre-treatment. The variety of possible methods that can be used is equally as broad, ranging from simple to sophisticated methods.

To obtain a clear, concise, and accurate picture of an LCAK surface it was essential to use more than one method and the best combination was to use contact angle measurements and XPS to provide surface chemical analysis. This enabled the qualitative comparison of the important characteristics of the standard LCAK surface and enabled understanding of the changes brought about by treated and untreated LCAK surfaces to be related to adhesion. As expected from theory, liquids with low surface tension produce low contact angles, thus favouring complete wetting of the surface.

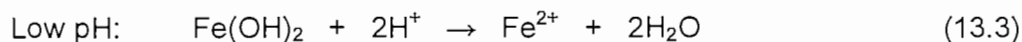
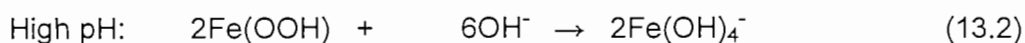
An 'oxide', with Fe(III) dominating on the outer surface, formed on LCAK steel in contact with water containing higher/saturated oxygen content, while an 'oxide' with Fe(II) dominating on the outer surface formed in water containing a lower oxygen content. It was also found that the 'oxide films' produced during different treatments behave oppositely (e.g. as Lewis-acid, then Lewis-base) during wetting with water solutions containing acidic and basic characters.

The XPS (adsorption) studies indicated Lewis-acid properties for the standard LCAK steel surface and Lewis-base properties for the steel surface treated with warm water.

The contact angle (wettability) measurements with acidic and basic aqueous solutions showed improved wetting properties for the warm water treated LCAK steel surface as compared to the standard LCAK steel surface.

The XPS study of the oxygen 1s peak indicated the Lewis base properties of LCAK steel are attributed to $\text{Fe}(\text{OH})_2$ groups being available on the outside surface.

It seems that, in contact with acidic and basic solutions, oxide and hydroxide surfaces may acquire an ionic charge through the following reactions:



where reaction (13.1) and (13.2) are representative of the basic and acidic reactivities of the oxide, respectively, and reaction (13.3) and (13.4) are representative of the basic and acidic reactivities of the hydroxide, respectively. For the standard LCAK steel sample, it is postulated that hydrogen ions adsorb on the $\text{Fe}(\text{OOH})$ surface, and contribute to a $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ oxidation/reduction process (reaction (13.1)). The number of $\text{Fe}(\text{OOH})$ species on the surface decreases with increasing pH (reaction (13.2)), forming $\text{Fe}(\text{OH})_4^-$ species in a basic medium. It is known that $\text{Fe}(\text{OOH})$ species were characterized as having a Lewis-acid character and therefore $\text{Fe}(\text{OH})_4^-$ species seem to contribute to a Lewis base character. The $\text{Fe}(\text{OH})_3^-$ species seem to increase on the surface with an increase in pH, lowering the contact angle, which gives

good wetting properties. $\text{Fe}(\text{OH})_3^-$ species seem to have a Lewis-acid character and $\text{Fe}(\text{OH})_2$ species have Lewis-base character.

It was observed also that BATE is a sensitive probe molecule to detect and distinguish the surface Lewis-base sites of the treated and untreated LCAK steel substrates. BATE interacts selectively with surface Lewis-base sites and its IR spectrum show the direct interaction with Lewis-base sites of the metal oxides.

It has been shown that the availability of sophisticated analytical techniques, such as FTIR and SEM, can be used to characterize organic coatings. The coating was identified as a fatty acid modified alkyd resin containing the following elements – C, Ti, Cr, O, Fe, Al, Si, Pb and Cl.

With respect to alkyd paint adhesion, LCAK surfaces followed a behaviour reflecting its Lewis acid-base nature. A Lewis-base surface will engage in sufficiently strong chemical bonds with some acidic groups of the alkyd coating. As a result, strong durable alkyd coatings on LCAK are obtained. The untreated standard LCAK steel surface exhibited a Lewis-acid surface while the warm water treated surface exhibited Lewis-base properties.

The basis of the theoretical work, using DFT calculations, was presented, as well as the verification of the bulk and surface iron models. The optimization of the k-points and cut-off energies were investigated. The adsorption of oxygen and water with the optimized $\text{Fe}(110)$ surface slabs were also investigated with regard to molecular orientation at the surface.

To describe the adsorption process of water on the Fe(110) surface, the adsorption energies for all the molecules and atoms involved in this process were calculated using the density functional method. It was observed that water dissociates $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ and co-adsorb as OH and H on Fe(110) surface. It is known that adsorbed hydroxyl on a metallic surface gives Lewis-base properties [Wielant et al., 2007]. The theoretical results are in agreement with XPS results which predicted Lewis-acid properties for the standard LCAK steel surface and Lewis-base properties for the steel surface treated with warm water (water with less oxygen), and provide a fundamental understanding of the initial stages of the adhesion mechanism.

From this study the description of the properties of the substrate and the organic coating in terms of the Lewis acid-base theory can help in the choice of both (substrate and organic coating) to obtain improved adhesion of organic coatings on steel substrate.

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APPENDIXES: WORK PUBLISHED FROM THIS STUDY

Lewis Acid-Base Properties of a Low Carbon Aluminium Killed Steel Substrate

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ABSTRACT

An important factor in achieving maximum adhesion of a particular coating system to the substrate lies in the proper preparation of the substrate prior to the application of paint. The Lewis acid-base properties of the outer metal surface play a determinant role in many of these applications, and the chemical reactions involved therein. In this work, the wetting properties of a low carbon aluminium killed (LCAK) substrate have been largely modified by a chemically activated surface treatment. XPS analysis was performed on the surface. Wettability in water, a polar and protic probe liquid, and in α -bromonaphthalene, a non-polar and aprotic probe liquid, of the LCAK surface is strongly modified when the LCAK surface is treated with dilute formic acid and warm water. Formic acid forms formate ions which have a higher reactivity with respect to molecular species and are able to react with the exposed surfaces, changing the relative structure of the hydroxyl layer.

KEYWORDS

XPS, Lewis acid-base, wettability, steel, surface.

1. Introduction

The adhesion of paint to a substrate is affected by the nature and conditions of the substrate and by the nature and composition of the paint. The study of acid-base properties of coatings and substrate surfaces is of fundamental significance in adhesion. Many methods have been proposed in the literature to understand and quantify the acid-base interactions at the interfaces.¹ Fowkes proposed describing adhesion in terms of acid-base or electron donor-acceptor interactions.^{2,3} Fowkes then considered non-dispersive interactions to be identical to electron donor-acceptor or Lewis acid-base interactions. (A Lewis acid is any substance that can act as an electron-pair acceptor and a Lewis base any substance that can act as an electron-pair donor).

Polar molecules used to determine the specific interactions with the solid substrate are characterized by their donor (DN) and acceptor (AN) numbers.⁴ The concept of donor-acceptor interactions is an extension of the Lewis acid-base theory, dealing with coordinate bonds, which are formed by sharing a pair of electrons between donor and acceptor species.

The characterization and quantitative description of forces at the interface constitute an important study area in interface science.^{5,6} Its solution would allow the analytical prediction and explanation of material behaviour at interfaces through the quantification of the interactions and, as an immediate outcome, the capability to design polymeric coatings for a specific purpose.

Often particular steel is chosen as a substrate for coatings because it has given satisfactory performance in similar applications elsewhere, but as the limits of its properties are approached other grades have to be considered. A comprehensive knowledge of the range and variety of steels, together with their uses, is required in order to select steel which will give satisfactory performance. Much written information is available on steels but considerable experience is required in order to select steel for a particular use.^{7–9} Low carbon aluminium killed (LCAK) steel

(steel deoxidized with aluminium in order to reduce the oxygen content to a minimum so that no reaction occurs between carbon and oxygen during solidification) was considered. This type of steel is used mostly by the packaging industry. Organic coatings are used not only for decorative purposes but also for labelling the content of LCAK steel containers. The surface condition of the steel used for low-cost, mass-produced items is more critical, where extensive surface preparation is typically done prior to the application of organic coatings.

1.1. Surface Tension and Contact Angle Theory

1.1.1. Surface Tension Components (STC)

Surface tension is a measure of the cohesive energy present at the interface. Fowkes² originally proposed the surface tension of a system to consist of the components:

$$\gamma = \gamma^d + \gamma^i + \gamma^p + \gamma^h, \quad [1]$$

where the superscripts d, i, p and h represent dispersion, induction, polarization and hydrogen bonding. Later Fowkes¹⁰ defined the acid-base component, γ^{AB} , to include the last three terms on the right hand side of Eq. [1] as follows:

$$\gamma^{AB} = \gamma^i + \gamma^p + \gamma^h. \quad [2]$$

However, according to Fowkes and van Oss, Chaudhury and Good (VCG),¹¹ both the induction (i) and polarization (p) components are of secondary importance in comparison with the dispersion (d) and hydrogen bonding (h) components, so VCG suggested that the first three components on the right hand side of Eq. [1] should be combined into the Lifshitz-van der Waals components, γ^{LW} , instead:

$$\gamma^{LW} = \gamma^d + \gamma^i + \gamma^p. \quad [3]$$

Then, the acid-base component of surface tension represents only hydrogen bonding.

$$\gamma^{AB} = \gamma^h. \quad [4]$$

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The total surface tension for a 'polar' system then becomes:

$$\gamma = \gamma^{LW} + \gamma^{AB}. \quad [5]$$

VCG further divided the asymmetric hydrogen-bond part of the dipolar system into two separate factors: a hydrogen-bonding acidic parameter, γ^+ , which is identical to the contribution of the proton donor, and a hydrogen-bonding basic parameter, γ^- , associated with the proton acceptor.

1.1.2. Contact Angle Components

In the case of contact angle measurements, surface energy is determined by wetting the surfaces of solids with different liquids. Young's equation allows a calculation of the stationary wetting angle under certain conditions. It describes the equilibrium of forces between the surface tension terms at a three-phase boundary. When a liquid droplet is placed on a homogeneous smooth solid surface, the contact angle, θ , can be obtained using Young's equation:¹²

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}, \quad [6]$$

where γ_{sv} , γ_{sl} , and γ_{lv} are the surface/interfacial tensions of the solid-vapour, solid-liquid and liquid-vapour phases, respectively.

Now the total surface tension is the sum of polar and non-polar components:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}. \quad [7]$$

However, whilst γ_i^{LW} suffices for the description of the non-polar part of the surface tension of i , γ_i^{AB} is composed of two different surface tension parameters, namely the parameter representing its electron-acceptivity, designated as γ_i^+ , and the parameter representing its electron-donicity, designated as γ_i^- , such that

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-}. \quad [8]$$

The total acid-base Gibbs energy of interaction between two polar materials (i and j) may be expressed as:¹²

$$\Delta G_{ij}^{AB} = -2\left(\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+}\right). \quad [9]$$

Using the Young-Dupré equation:¹³

$$(1 + \cos \theta) \gamma_i = -\Delta G_{ij}, \quad [10]$$

Equation [7] can be re-expressed as:

$$\Delta G_{ij}^{TOT} = \Delta G_{ij}^{LW} + \Delta G_{ij}^{AB}, \quad [11]$$

where ΔG_{ij}^{LW} , the Lifshitz-van der Waals interaction, is a non-covalent interaction that involves permanent dipoles within the molecules, and ΔG_{ij}^{AB} , the Lewis acid-base interaction is a hydrogen bonding interaction between electron-donor and acceptor.

Therefore the Young-Dupré equation [10] can be re-expressed as:

$$(1 + \cos \theta) \gamma_i = 2\left[\sqrt{\gamma_i^{LW} \gamma_j^{LW}} + \sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+}\right]. \quad [12]$$

In the above expressions of the Young equation, i represents the liquid and j the solid. The Young-Dupré equation relates the contact angle to the surface and interfacial tensions.¹²

So far several theories on solid surface Gibbs energy determination and approaches have been proposed, but formulation of surface and interfacial Gibbs energy is still a very debatable issue. Chibowski and Perea-Carpio¹⁴ addressed the problems of contact angle and solid surface Gibbs energy determination. In their study they clearly showed that direct calculation of the contact angle from Washburn's equation, which was then

Table 1. Composition details of low carbon aluminium killed steel.

Steel	C	Mn	S	Si	Cu	Ni	Cr	Al
LCAK	0.047	0.2	0.003	0.018	0.008	0.006	0.025	0.059

applied in Young's equation, led to erroneous results of the solid surface Gibbs energy components. However, Costanzo, Giese and van Oss¹⁵ determined the acid-base characterization of clay mineral surfaces by contact angle. They showed that contact angle determination can be done for swelling clay minerals as well as for non-swelling clay minerals. Pinzari and his co-workers¹⁶ have studied surface acid-base properties of titanium and an oxidized titanium sheet. Both from their wettability and adsorption studies they found a basic behaviour for the titanium metal and acidic behaviour for the oxidized titanium metal.

In this work, the wetting properties of LCAK substrate have been largely modified by a chemically-activated surface treatment. The surface was investigated through XPS analysis and contact angle measurements. Wettability in water, a polar and protic probe liquid, and α -bromonaphthalene, a non-polar and aprotic probe liquid, of LCAK surfaces may be strongly modified when the LCAK surface is treated with dilute formic acid and warm water. In this way formic acid produces formate ions which have a higher reactivity¹⁷ and are able to react with exposed surfaces, changing the relative structure of the hydroxyl layer.

2. Experimental

2.1. Standard Surface

Low carbon aluminium killed steel (LCAK) was used; the composition of the steel is given in Table 1. All samples were mounted and polished to a 5 μm finish. The standard sample was washed in hebitex (inhibited hydrochloric acid with organic additives that tend to coat the cleaned steel to inhibit the attack on the steel) to remove any existing oxide layer, rinsed in tap water at room temperature to prevent the possibility of organic contamination on the surface, which could influence the wettability, and then cleaned with Radchem 99.9% absolute ethanol (A.R.) to remove the water film, followed by a hot air drying step to prevent the formation of corrosion on the surface.

2.2. Test Liquids

The test liquids were carefully chosen to cover a range of surface tensions and viscosities (Table 2). Surface tension measurements were performed on a Ramé-Hart imaging system. The liquids were injected with a syringe to form a drop on the tip of the needle. The drop was observed optically and the surface tension was calculated from the shape of the drop using the Young-Laplace equation. In this experiment, the surface tension of the liquid solution was determined against air using the pendant drop shape method.

2.3. Contact Angle

The procedure used to measure the contact angle is based on the ASTM D724 standard. The image of each single drop was acquired by a video-camera connected to a computer. The value of the contact angle, θ , was calculated by measuring the base (b) and height (h) of the drop profile and using the relationship:¹⁸

$$\theta = \arcsin\left(\frac{4bh}{4h^2 + b^2}\right). \quad [13]$$

The following surface treatments were performed prior to the contact angle measurements.

Table 2 Test liquids and their properties at 25 °C.

Liquids	Density/ g cm ⁻³	Viscosity at 25 °C/ cp	Surface tension/ mN m ⁻¹	Contact angle of the reference sample ^a
Water	0.997	0.89	72.2	31.2
Hexane	0.659	0.510	18.5	3.5
Xylene	0.860	0.620	24.4	6.3
α -Bromonaphthalene	1.48	1.65853	40.5	11.1

2.3.1. Warm Water Treatment

The polished sample was rinsed in warm water at *ca.* 40 °C which was previously boiled for four hours to remove oxygen, and then cleaned with ethanol to remove the water film, followed by a hot air drying step to prevent the formation of corrosion on the surface.¹⁹

2.3.2. Formic Acid Treatment

The sample was rinsed in 1:1 v/v Saarchem 85% chemically pure formic acid (A.R.) and then cleaned with ethanol to remove the water film, followed by a hot air drying step.

2.3.3. Non-Formic Acid Treatment

After polishing, the sample was rinsed in ethanol, followed by a hot air drying step.

Surface treatment was performed for 10 min. Exposure of the LCAK surface to the laboratory ambient was minimized by performing the contact angle measurements of water and α -bromonaphthalene immediately after surface treatment. This reduces the effects on the measurements of slow buildup of an adsorbed organic layer. The contact angle measurements of all treated (LCAK) surfaces were measured in the laboratory ambient using a Ramé-Hart Inc. goniometer imaging system.²⁰ A drop of a fixed volume ($\sim 2 \mu\text{L}$) was formed on the end of a syringe needle and lowered into contact with the surface. As the needle was raised, the drop detached from the tip and advanced across the surface. The sessile drop was observed optically and the contact angle was calculated from the shape of the drop using Young's equation. Contact angle measurements were performed with deionized water and Fluka 95.0% α -bromonaphthalene (GC) at room temperature. The contact angles were measured within 30 s of detachment.

2.4. XPS Analysis

To obtain chemical information on induced surface modifications and on their influence on wettability behaviour, X-ray photoelectron spectroscopy (XPS) analysis was carried out on the reference sample (sample without surface modification), formic acid treated sample, non-formic acid sample and sample treated with warm water.

The XPS spectra were obtained using a PHI spectrometer (model 5400) equipped with Mg/Al dual mode source and a small area analyser with PSD detector. An achromatic Mg K α X-ray (1253.6 eV) source was operated at 300 W. The vacuum pressure was 10^{-8} Torr during spectra acquisition. Survey spectra were obtained at a take-off angle of 45°. The C 1s and O 1s regions were recorded.

2.5. Wettability

The term 'wetting', in general, is connected with the area covered by a liquid drop placed on a solid surface. It varies on the basis of the liquid and surface and it is measured by the contact angle, defined as the angle between the drop and the surface, as shown in Fig. 1.²¹ When the contact angle has a value near zero,

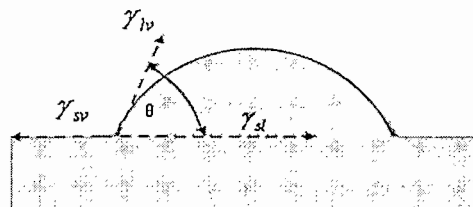


Figure 1 Contact angle and gas-liquid-solid related tensions.

Table 3 The pH values of the acidic and basic solutions.

	Concentration/ mol L ⁻¹	pH
Acidic	1	0.8
	2.0×10^{-2}	2.5
	4.0×10^{-4}	3.6
	3.0×10^{-6}	4.1
Basic	1	13.1
	1.0×10^{-2}	12.1
	2.0×10^{-5}	10.5
	4.0×10^{-6}	9.1

the liquid is said to wet the surface perfectly, otherwise it is said not to wet the surface.²² The procedure to measure the contact angle is described in the ASTM D724 standard.¹⁸

Hydrochloric acid (32%) (A.R.) and sodium hydroxide pellets (A.R.) from Promark Chemicals were used. Un-buffered aqueous solutions representing both acid and basic conditions were prepared. The concentrations of the acidic solutions were approximately 1.0 mol L^{-1} , $2.0 \times 10^{-2} \text{ mol L}^{-1}$, $4.0 \times 10^{-4} \text{ mol L}^{-1}$ and $3.0 \times 10^{-6} \text{ mol L}^{-1}$, while the concentrations of the basic solutions were approximately 1.0 mol L^{-1} , $1.0 \times 10^{-2} \text{ mol L}^{-1}$, $2.0 \times 10^{-5} \text{ mol L}^{-1}$ and $4.0 \times 10^{-6} \text{ mol L}^{-1}$. The pH was measured using a Labotec Orion 410A+ basic pH meter with an Orion 91-65 Ag/AgCl electrode in the temperature range 0 to 100 °C, calibrated with solutions of pH 4 and 10. The pH values of the acidic and basic solutions are shown in Table 3. The influence of pH on the wettability (contact angle) of a standard polished sample of LCAK and a warm water treated sample of LCAK was determined. The wettability measurements on the samples were performed making use of the liquids prepared as in Table 3. The primary effect here is the acid-base interaction of the solutions and the surface. Other factors such as ionic strength influences were neglected.

3. Results and Discussion

Most metal surfaces are composed of metal oxide. In the laboratory ambient, the oxides at the surface hydrate to form a high density^{23,24} of hydroxyl groups (1 to 5 hydroxyl groups per 10^{-8} m^2 of surface area). Practically, such a surface can be represented as $\text{MO}_m(\text{OH})_n$, where M is a metal. The surface hydroxyl groups adsorb water molecules via hydrogen bond interactions,

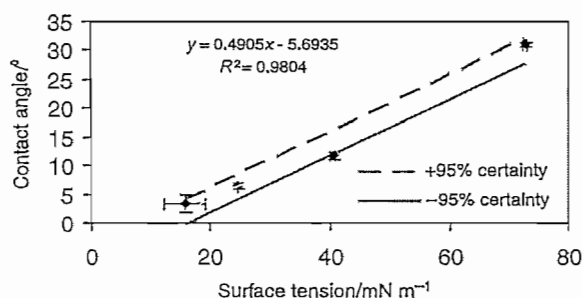


Figure 2 The relationship between contact angle and surface tension.

wherein the surface acts as either the acid or the base. An acidic surface site shows a tendency to donate a proton or a cation or to accept electrons or an anion, whereas a basic surface site shows a tendency to accept a proton or a cation or to donate electrons.²⁵

3.1. Surface Tension and Contact Angle

As demonstrated in Fig. 2, low surface tension systems were found to yield low contact angles. The liquids were not of the same family and thus had diverse properties (Table 2). The contact angle increases with increasing surface tension, indicating that for a given surface, better wetting is obtained for the lower surface tension liquids. Water contact angles were determined to ensure surface cleanliness on the polished LCAK substrates prior to treatment, and it was found that a drop of water produced an average contact angle of approximately 31.2° in this case. For hexane, xylene and α -bromonaphthalene, contact angles of 3.5°, 6.3° and 11.1° were measured, respectively.

3.2. Contact Angle of Treated Surfaces

The contact angle results for the treated surfaces are summarized in Table 4. LCAK surfaces activated chemically with warm water strongly enhance wettability behaviour when compared with other surface treatments. This is suggested by the spreading of the water and of the α -bromonaphthalene on the warm water treated surface, where contact angles of 28.8° and 4.9°, respectively, were observed.

Table 4 Contact angles of liquids on a standard LCAK sheet.

Sample	Surface treatment	Liquid	Contact angle/°
1	formic acid	water	42.5
2	formic acid	α -bromonaphthalene	9.5
3	non-formic acid	water	45.2
4	non-formic acid	α -bromonaphthalene	13.4
5	warm water	water	28.8
6	warm water	α -bromonaphthalene	4.9

3.3. XPS Analysis

In Fig. 3 the XPS survey spectrum obtained for the reference low carbon aluminium killed (LCAK) sheet is shown. Carbon contamination is clear from Fig. 4. The main carbon peak (I) at 285.2 eV is attributed to hydrocarbon C (C-H) and peak (II) at 289.1 eV to carbonates (C=O).¹⁶ The O 1s peak (Fig. 5) shows three components that were attributed to adsorbed water (H₂O), hydroxyl (OH) and oxides (OOH).¹⁹ The XPS peak maxima of the O 1s species for the other samples are shown in Table 5.

An estimated correlation (Table 6) is determined between the Fe(OH)₂ and Fe(OOH) peak heights. Peak heights or areas are directly related to the concentrations of the species on the surface. From previous work, good paint adhesion of Lewis-base alkyd paint was associated with a 1:1 ratio of Fe(OH)₂ and Fe(OOH) species on the surface of the steel.²⁶

The Lewis acid-base properties of a hydroxyl group depend on the electronegativity values of the species to which it is bonded.¹⁶ For Fe(OH)₂, the hydroxyl groups are bonded to Fe²⁺, which make them Lewis base species and for Fe(OOH) the hydroxyl groups are bonded to oxides and are thus Lewis acid species.²⁶

3.4. Wettability

In Figs 6 and 7, the acid-base contact angle curves of the reference and warm water treated LCAK sheet are shown respectively. The samples show changes in the contact angle as a function of the pH with opposite behaviour.

Fe(OOH) and Fe(OH)₂ were characterized and distinguished

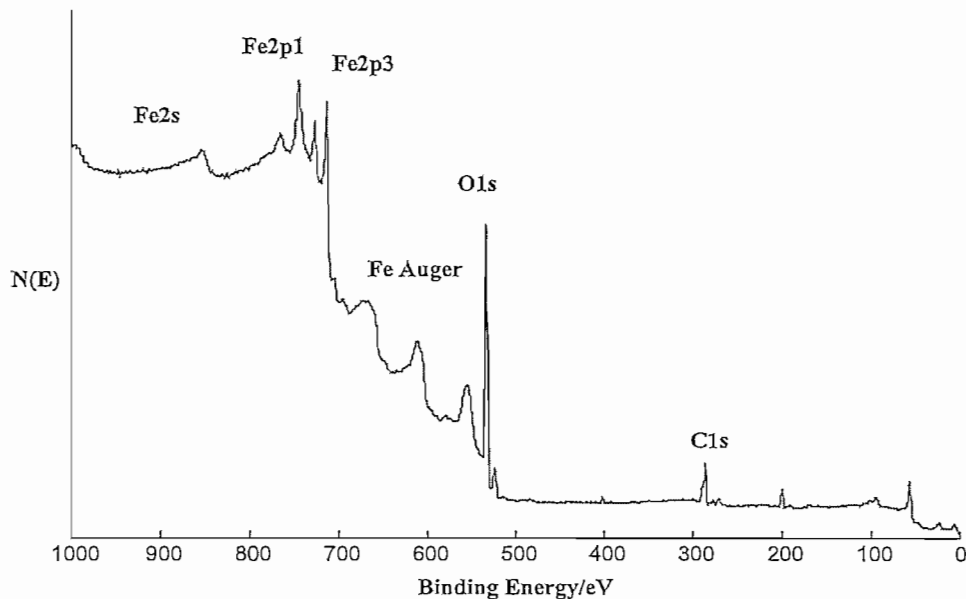


Figure 3 XPS survey spectrum obtained for the reference low carbon aluminium killed (LCAK) steel.

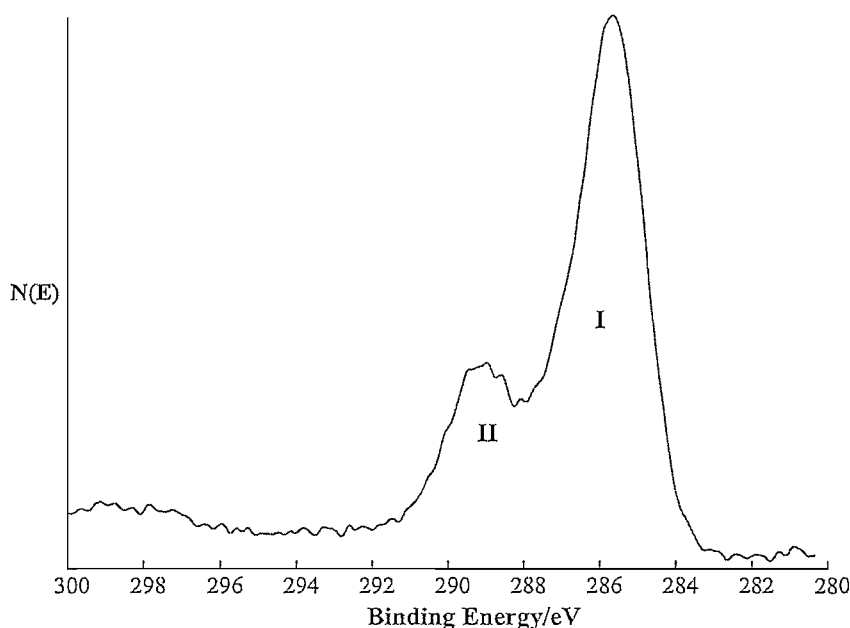
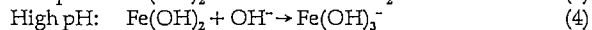
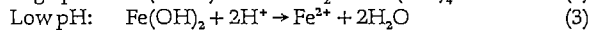
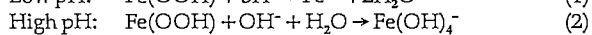
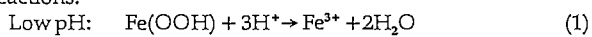


Figure 4 XPS C 1s peak obtained on a reference steel surface.

using XPS (Figs 5 and 8), respectively. The difference between the two iron compounds was observed in the O 1s peak, where the OH and OOH maximum peak height ratios differed. The peak heights and peak height ratios are summarized in Table 6.

Upon contact with acidic and basic solutions, oxide and hydroxide surfaces may acquire an ionic charge by the following reactions:



where Equations (1) and (2) are representative of the basic and acidic reactivities of the oxide, respectively, and Equations (3) and (4) are representative of the basic and acidic reactivities of

the hydroxide, respectively.

It is shown (Figs 6 and 7) that the surface modified steel substrates change their wetting properties with acidic and basic water characters. Decreased wetting (increased contact angle) was observed with increased pH on the reference sample and better wetting (decreased contact angle) was observed with increased pH on the warm water treated sample. For the reference sample, it is postulated that hydrogen ions adsorb on the Fe(OOH) surface, and contribute to a Fe(II)/Fe(III) oxidation/reduction process (reaction (1)). The number of Fe(OOH) species on the surface decreases with increasing pH (reaction (2)), forming Fe(OH)₄[−] species in a basic medium. It is known that Fe(OOH) species were characterized as having a Lewis acid character²⁶ and therefore Fe(OH)₄[−] species seem to contribute to

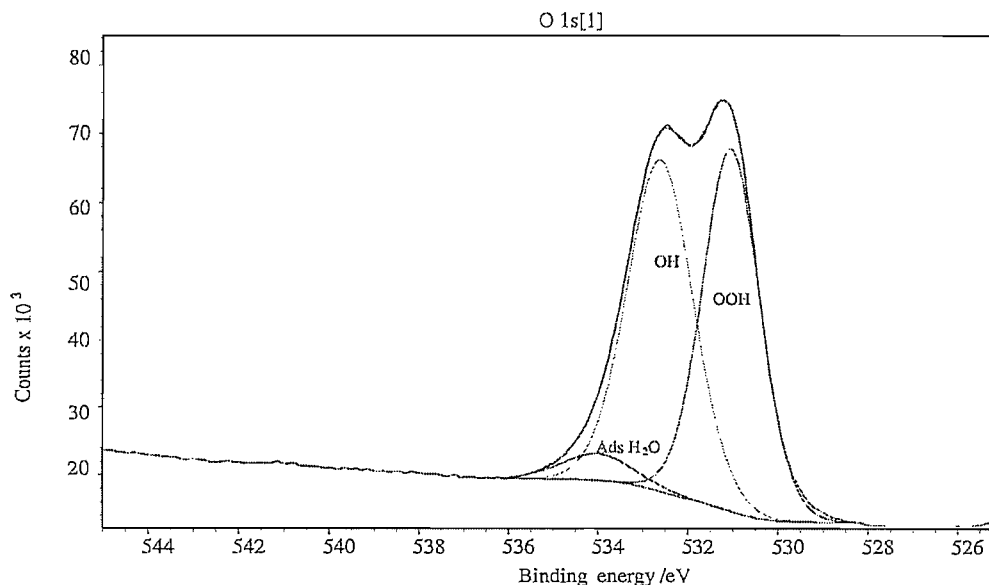


Figure 5 XPS O 1s peak obtained on a reference steel surface.

Table 5 The assignments of the O 1s binding energies (eV) to the surface species for the other samples. All values are in eV.

	Chemical surface species		
	Adsorbed water (H ₂ O)	Hydroxide [Fe(OH) ₂]	Metal oxide [Fe(OOH)]
Reference	534.00	532.58	531.01
Warm water	534.08	532.40	531.01
Formic acid	534.76	532.99	531.06
Non-formic acid	—	532.54	530.97

Table 6 An estimated correlation determined between Fe(OH)₂ and Fe(OOH) peaks.

Name	Binding energy/eV	Chemical surface species	Reference % height	Warm water % height	Formic acid % height	Non-formic acid % height
O 1s	534	H ₂ O	4.238	3.556	17.153	—
O 1s	532	Fe(OH) ₂	49.175	78.064	36.651	52.243
O 1s	531	Fe(OOH)	46.587	18.380	43.195	47.243
Ratio		Fe(OH) ₂ /Fe(OOH)	1.05	4.2	0.84	1.1

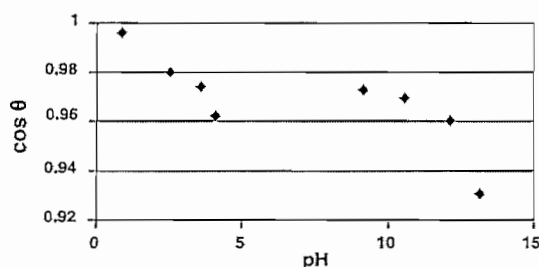


Figure 6 The acid-base contact angle curve of the reference LCAK steel.

a Lewis base character.

The Fe(OH)₂⁻ species seem to increase on the surface with an increase in pH, lowering the contact angle which gives good wetting properties. Fe(OH)₃⁻ species seem to have Lewis acid character and Fe(OH)₂ species have Lewis base character. The

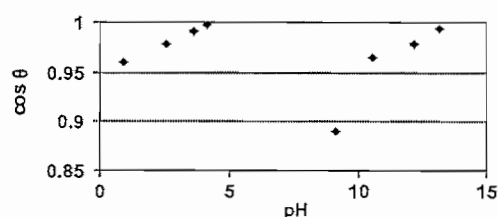


Figure 7 The acid-base contact angle curve of the warm water treated LCAK steel.

increased concentration of observed Fe(OH)₂ species on the surface of the warm water treated sample exhibit Lewis base character, resulting in better wetting (decreasing contact angle) with increasing pH. The results indicate that the wettability measurements predict a basic reactivity for reference LCAK, and an acidic reactivity for warm water treated LCAK.

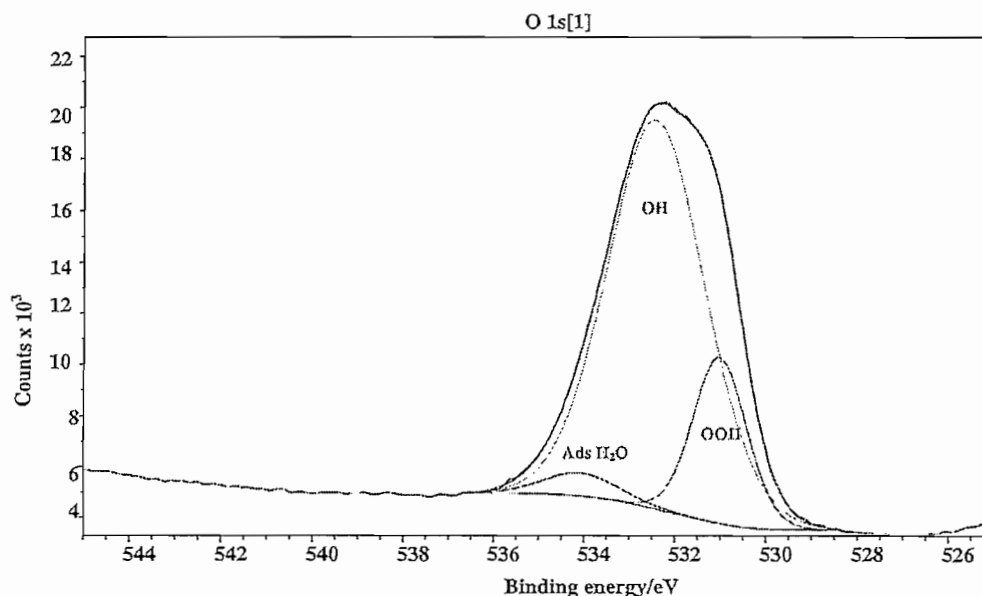


Figure 8 XPS O 1s peak obtained on a surface treated with warm water.

4. Conclusions

As expected from theory, liquids with low surface tension produce low contact angles, thus favouring complete wetting of the surface.

An oxide with Fe(III) dominating on the outer surface formed on LCAK steel in contact with water containing higher/saturated oxygen content, while an oxide with Fe(II) dominating on the outer surface formed in water containing a lower oxygen content. It was also found that the 'oxide films' produced during different treatments behave oppositely during wetting with water solutions containing acidic and basic characters.

The XPS (adsorption) studies showed Lewis-acid properties of standard LCAK steel and Lewis-base properties of the steel surface treated with warm water, while contact angle (wettability) measurements with acidic and basic solutions showed Lewis-base properties for standard LCAK steel and Lewis-acid properties for steel surfaces treated with warm water.

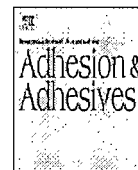
Contact angle and XPS measurements could be used to characterize industrially produced steel surfaces. Low carbon aluminium killed steel surfaces could be modified to be compatible with the chemical characteristics of the paint.

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FTIR and XPS study of the adsorption of probe molecule used to model alkyd resin adhesion to low carbon aluminum killed steel

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ABSTRACT

An important factor in achieving maximum adhesion of a particular coating system to the substrate lies in the proper pre-treatment of the substrate prior to the application of the coating. The Lewis acid–base properties of the outer metal surface play a determining role in many of these applications, and the chemical reactions involved therein. In this work, the Lewis nature of the low carbon aluminum killed (LCAK) substrate has been significantly modified by a chemically activated surface pre-treatment. The wetting properties of the LCAK substrate was determined by contact angle measurements; the coordination of the chemical species on the surface was studied with XPS; FTIR together with the probe molecule $B(OCH_3)_3$ was used to explain the chemical bonding. The novel combination of contact angle, XPS, FTIR and probe molecule enabled the determination of the Lewis acid–base properties of the LCAK surface before coating. The XPS spectra of the LCAK surface rinsed in warm water show that the surface species differ from that rinsed in tap water. With change in pH, the wettability properties also drastically changed. The probe molecule $B(OCH_3)_3$ did not bond on the warm water rinsed samples but bonded strongly on tap water rinsed samples as the pH decreased. This research has shown that Lewis acid–base properties can be significantly changed with water temperature and pH, which has important implications for industrial pre-treatment.

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1. Introduction

The acidic and basic nature of metal surfaces has been documented [1], but remains a matter of controversy. A variety of techniques have been used to measure acidity including the use of acidic indicators [2], titration with bases using indicators [3] and the measurement of chemisorbed compounds at different temperatures [4]. These techniques have given conflicting and widely differing results for the same materials. Surface acid–base properties are important characteristics, in particular for metal oxides that form on the surface. The acid–base interactions have been widely used in various applications in the chemical industry and the acid–base theory forms a large component of the description of current–surface interaction phenomena [5]. In order to achieve a durable structural adhesion, the formation of this type of chemical bond is necessary and is a strong function of the surface treatment of the substrate.

With this approach to surface interaction phenomena or adhesion phenomena, it is important to characterize and evaluate the chemical sites and, then, to determine their reactivity toward a specific molecule. The acid–base properties of coatings and substrates surfaces are of fundamental significance in adhesion.

Lewis' original formulation of acid–base behavior remains useful and from the late 1940s onward a growing need was felt for its application to adhesion phenomena. Such applications were initiated by Fowkes, starting with a paper in 1964 [6]. Fowkes' work substantially broadens the scope of the original Lewis concepts and merits further discussion in this study.

Many methods are proposed in the literature to understand and quantify the acid–base interactions at the interfaces [7]. It was Fowkes who proposed in the study of adhesion to describe non-dispersive or specific interaction in terms of acid–base or electron donor–acceptor interactions [8,9]. Fowkes then considered these non-dispersive interactions to be identical to electron donor–acceptor or acid–base interactions. Polar molecules used to determine the specific interactions with the solid substrate were characterized by their donor (DN) and acceptor (AN) numbers [10]. The concept of donor–acceptor interactions is an extension of the Lewis acid–base reactions, dealing with coordinate bonds,

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which are formed by sharing a pair of electrons between donor and acceptor species.

Other authors [11,12] have studied the Lewis acid–base phenomena by angular photoelectron spectroscopy and TOF–SIMS methods; however, only give indirect evidence of the formation of chemical bonds during adsorption processes. Leadley and Watts [13] showed usefulness of monochromated XPS, but their adhesion system involved a poly(methyl methacrylate)-oxidized metal (PMMA) interface. While in this present study, a more fundamental approach in terms of the coating system was considered. By using XPS spectroscopy, Watts and co-workers [14,15] showed that the magnitude of Lewis acid–base interactions plays an important part in adhesion.

Coatings can be classified into a number of different categories, but the most convenient system is by chemical composition. Alkyd coatings are widely used for structural bonding purposes, and decorative or labeling containers. Adhesives of this family are a class of polyester coatings derived from the reaction of an alcohol and an acid or acid anhydride. The product will be an ester compound and an acid compound. They are modified with unsaturated fatty acids (from vegetable and plant oils) to give air-drying properties. The unsaturated oils react with oxygen from air, which causes the oils to polymerize or crosslink [16]. All these functions are likely to interact strongly with the basic sites that may be present on the surface of the metallic substrate. These sites can be identified by probing the molecular adsorption and analysis by XPS, SIMS, FTIR, etc., as has been used in combination to determine the chemical nature (Lewis or Brönsted character), the density, and the strength of acid sites at the surface of many solid substrates [17].

Mostly, fully formulated coatings are generally a mixture of large complex molecules, additives and filler materials. As such mixtures are difficult to analyze and to handle, the use of probe molecules was considered for fundamental research purposes [18]. These probe molecules must be representative of some active functions of the coating and also possess a well-established chemical behavior, with respect to their acid–base properties.

In this study, firstly the chemical sites on the low carbon aluminum killed (LCAK) steel substrate were characterized and evaluated. Then the adsorption of boric acid trimethyl ester ($B(OCH_3)_3$), an acidic probe molecule, also representative of ester groups present in organic coatings were investigated. The adsorption of the alkyd coating was then studied. The representative structure of the molecule is shown in Fig. 1. Adsorption was carried out on the standard LCAK surface and on this alloy after different surface treatments.

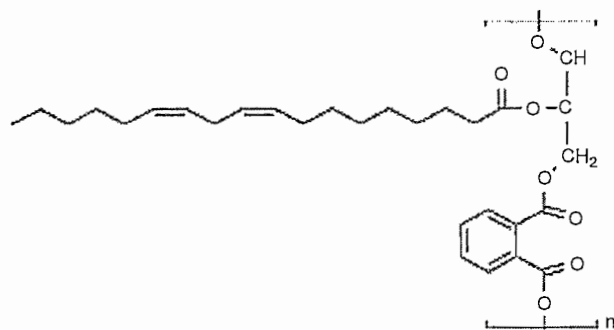


Fig. 1. Schematic alkyd resin used as a binder compound in alkyd coating.

2. Experimental

2.1. Preparation of standard surface

LCAK has been used. The chemical analysis of the steel was determined by spark emission spectrometry. Results are summarized in Table 1. All samples were mounted and polished to a 5 μm finish. The standard sample was washed in HIBITEX (inhibited hydrochloric acid) to remove oxides from the surface layer, rinsed in tap water (aerated) at room temperature to prevent the possibility of organic contamination on the surface, which could influence the wettability and then cleaned with ethanol 99.9% absolute analytical reagent (AR) to remove the water film, followed by a hot-air drying step to prevent corrosion of the surface.

2.2. Warm water treatment of standard surface

The polished sample was rinsed with warm water (de-aerated) at $\pm 40^\circ\text{C}$, which was previously boiled for 4 h to remove the oxygen. The surface was then cleaned with ethanol to remove the water film, followed by a hot-air-drying step to prevent corrosion of the surface [19].

2.3. Treatment with acidic and basic solutions

Hydrochloric acid 32% (AR) and sodium hydroxide pellets (AR) aqueous un-buffered solutions representing acidic and basic solutions, respectively, were prepared. The concentrations of the acidic solutions were approximately 1.0 , 2.0×10^{-2} , 4.0×10^{-4} and $3.0 \times 10^{-6} \text{ mol dm}^{-3}$, while the concentrations of the basic solutions were approximately 1.0 , 1.0×10^{-2} , 2.0×10^{-5} and $4.0 \times 10^{-6} \text{ mol dm}^{-3}$. The pH values for the solutions were measured using a Labotec Orion 410A+ pH-meter with an Orion 91–65 Ag/AgCl electrode that was calibrated with pHs 4 and 10 solutions. pH values of the acidic and basic solutions are summarized in Table 2. Wettability (contact angle) measurements have been performed on the warm water treated LCAK samples as well as the standard LCAK samples, making use of the solutions prepared as in Table 2 as contact liquids for contact measurement. The procedure used to measure the contact angle or wettability is based on the ASTM

Table 1
Trace element composition of low carbon aluminum killed steel in $\mu\text{g g}^{-1}$

Steel	C	Mn	S	Si	Cu	Ni	Cr	Al
LCAK	0.047	0.2	0.003	0.018	0.008	0.006	0.025	0.059

Table 2
The pH values of the acidic and basic solutions

Approximate concentration (mol dm^{-3})	pH
Acidic solutions	
1	0.8
2.0×10^{-2}	2.5
4.0×10^{-4}	3.6
3.0×10^{-6}	4.1
Basic solutions	
1	13.1
1.0×10^{-2}	12.1
2.0×10^{-5}	10.5
4.0×10^{-6}	9.1

D724 standard method [20]. The image of each single drop of the solution was acquired by a video-camera connected to a computer. The contact angle's (θ) value was calculated by measuring the base (b) and height (h) of the drop profile and using the following relationship [20]:

$$\theta = \arcsin\left(\frac{4bh}{4h^2 + b^2}\right).$$

2.4. XPS analysis

To obtain chemical information of surface modifications, angle resolved X-ray photoelectron spectroscopy (XPS) analysis has been carried out on the standard sample and samples treated with warm water.

The XPS spectra have been obtained using a PHI spectrometer (model 5400) equipped with an Mg/Al dual mode source and a small area analyzer with PSD detector. An achromatic Mg K_{α} X-ray (1253.6 eV) source was operated at 300 W. The vacuum pressure was 10^{-8} Torr during spectra acquisition. Survey spectra were obtained at a take-off angle of 15, 45 and 80 °C. The O 1s regions have been recorded.

2.5. $B(OCH_3)_3$ adsorption

The prepared samples (standard and warm water treated) were then rinsed in the solutions prepared as in Table 2 and then immersed in boric acid trimethyl ester ($B(OCH_3)_3$) (AR) solution for 30 s and were allowed to dry at room temperature for 10 min in an inert atmosphere.

2.6. FTIR spectroscopy and microscopy analysis

A Perkin-Elmer GX 2000 FTIR Spectrometer was used, with a Perkin-Elmer Auto Image Microscope System equipped with a liquid nitrogen cooled MCT detector attached to it. The samples were analyzed under the Auto Image FTIR microscope using the internal reflectance method. With this technique, the absorption of IR-radiation in a thin surface layer with a diameter 10 μ m and a thickness of about 10 μ m were studied. All spectra were recorded at room temperature using standard instrument settings. The prepared samples (2 cm²) were identical to those used for the XPS analysis. These samples were also used to study the adsorption of $B(OCH_3)_3$ on the LCAK steel surface.

2.7. Adhesion measurements

The organic coating used in this study was a fatty acid modified alkyd resin, typically used as a low-cost labeling paint on steel substrate. The alkyd resin was commercially obtained from a local coating company. The LCAK steel samples were dipped, painted, cured at 120 °C for 10 min. The paint adhesion tests were performed to determine the adhesion properties of the alkyd resin. The adhesion test used conforms to the ASTM testing procedure (ASTM Test Number 3359-78) [21]. The adhesion test entailed putting the crosshatched samples in a temperature controlled water bath at 40 °C to a depth of $\approx$ 160 mm with a spacing of $\approx$ 25 mm between the samples for a period of 24 h. The adhesion test (ASTM D1654) consists of a tape pull-off test on a crossed hatched pattern, cut through the paint layer with a carpet knife. The degree of adhesion was evaluated on an eight-point scale by the area of the paint removed from the surface of the LCAK steel. On the eight-point scale, zero indicated perfect adhesion and seven indicated no adhesion.

3. Results and discussions

3.1. Contact angle

After preparation of the standard LCAK steel surface and warm water treated LCAK steel surface, the contact angle measurements were done using a series of acidic and basic solutions at different pH (see Section 2 for detail and Table 2). Figs. 2 and 3 show the contact angle graphs of the acidic and basic solutions on the standard and warm water treated LCAK steel surfaces, respectively. It can be seen from Fig. 2 that the standard LCAK steel surface shows a decrease in contact angle with decrease in pH and from Fig. 3 that the warm water treated LCAK steel surface shows an increase in contact angle measurements with decrease in pH. Both of these graphs gave a definitive break in the relationship between contact angle and pH at a pH of 7. This indicates a difference in the dominating surface species for pH values above and below 7 for both these surfaces. A decrease in contact angle shows better surface wettability, while the increase in contact angle shows poor surface wettability. Surface wettability (generally referred to as hydrophobicity and hydrophilicity) is one of the most important parameters affecting adhesion of molecules onto a material [21]. To determine whether the treated standard LCAK steel surface and warm water treated LCAK steel surface have Lewis acid or Lewis base character, adsorption of the $B(OCH_3)_3$ (boric acid trimethyl ester) molecule was used as described earlier.

3.2. Adsorption of $B(OCH_3)_3$ onto the treated steel substrates

The boron atom in the $B(OCH_3)_3$ molecule has one empty p-orbital, which is trigonally orientated to the methoxy groups [22].

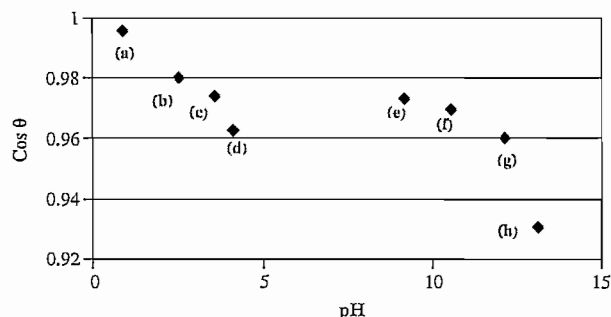


Fig. 2. Contact angles of acidic and basic solutions on standard LCAK surface with pH: (a) 0.8, (b) 2.5, (c) 3.6, (d) 4.1, (e) 9.1, (f) 10.5 (g) 12.1 and (h) 13.1.

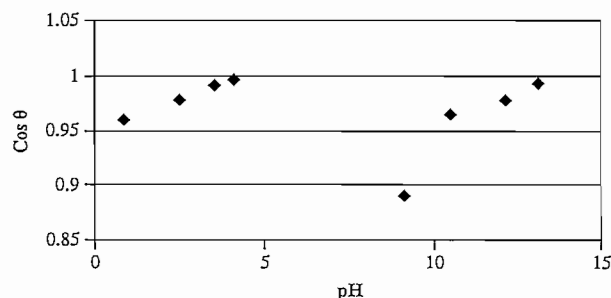


Fig. 3. Contact angles of acidic and basic solutions on warm water treated LCAK surface with aqueous solution of pH between 0.8 and 13.1.

Since the empty orbital of the boron atom has a tendency to accept an electron pair, $B(OCH_3)_3$ acts as a Lewis acid molecule. A surface Lewis basic sites thus may coordinate with a boron atom of the $B(OCH_3)_3$, affecting the B–O bond energy. As no influence on the B–O binding energy and $B(OCH_3)_3$ molecule was observed for the warm water treated LCAK steel surface, it was concluded that the warm water treated LCAK surface exhibits Lewis acid properties [23].

The FTIR microscopy (external reflectance) spectra of adsorbed $B(OCH_3)_3$ on the pH-treated surfaces are shown in Figs. 4 and 5. These FTIR spectra in the vibrational regions of B–O (1420 – 1250 cm^{-1}) and C–O (1100 – 1000 cm^{-1}) bonds were used to measure interaction of $B(OCH_3)_3$ with the surfaces [22]. With a decrease in pH an increase and shifts in B–O and C–O, peak intensities were observed as shown by the shifts in the B–O (1194 cm^{-1}) and C–O (1042 cm^{-1}) stretching vibrations for the adsorbed $B(OCH_3)_3$. This implied that the $B(OCH_3)_3$ molecule interacts with the surface

Lewis base site so that the vibration involving the B–O bond splits (1109 cm^{-1}) and shifts significantly (1199 cm^{-1}).

The relationship between the C–O peak areas and pH is shown in Fig. 6. An increase in C–O peak intensities with a decrease in pH was observed, again with a definite break in the relationship at a pH of 7. The decrease in contact angle measurements on the acidic and basic treated standard LCAK steel surfaces (Fig. 2) showed a similar but opposite relationship. From the above it can be predicted that the standard LCAK steel surface has Lewis base properties.

3.3. XPS study of the LCAK–air interaction

To determine the surface chemical composition of the standard and warm water treated samples before exposure to acidic and basic solutions, XPS spectroscopy was used. The XPS survey

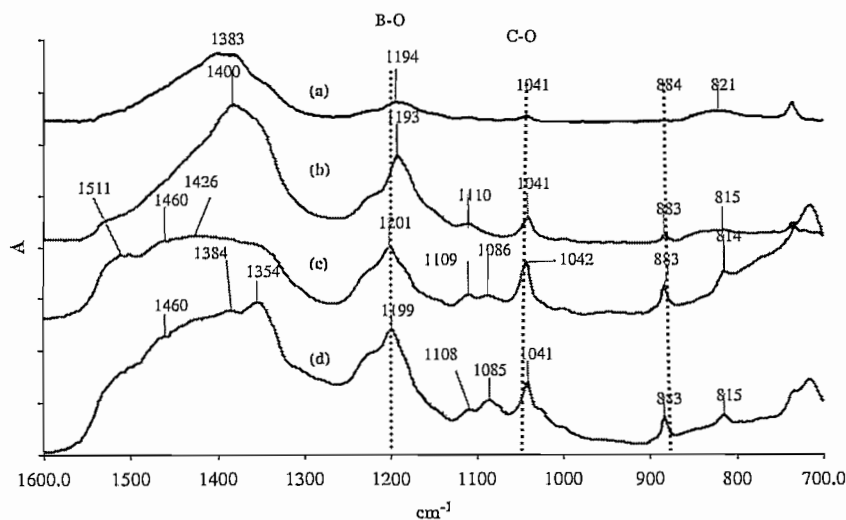


Fig. 4. FTIR spectra of adsorbed BATE on standard LCAK surface at pH: (a) 0.8, (b) 2.5, (c) 3.6 and (d) 4.1

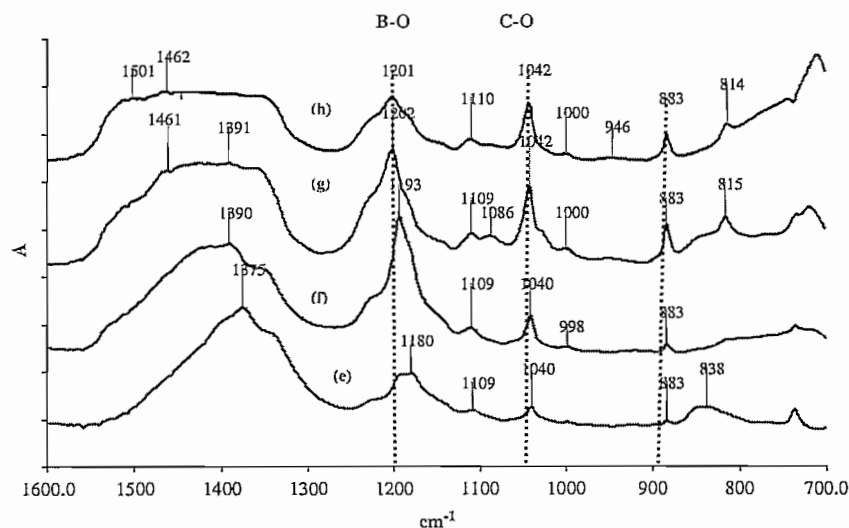


Fig. 5. FTIR spectra of adsorbed BATE on standard LCAK surface at pH: (e) 9.1, (f) 10.5, (g) 12.1 and (h) 13.1.

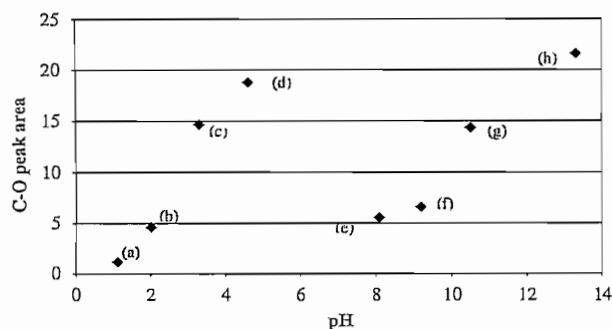


Fig. 6. The C-O peak intensities on the standard LCAK surface versus pH: (a) 0.8, (b) 2.5, (c) 3.6, (d) 4.1, (e) 9.1, (f) 10.5, (g) 12.1 and (h) 13.1.

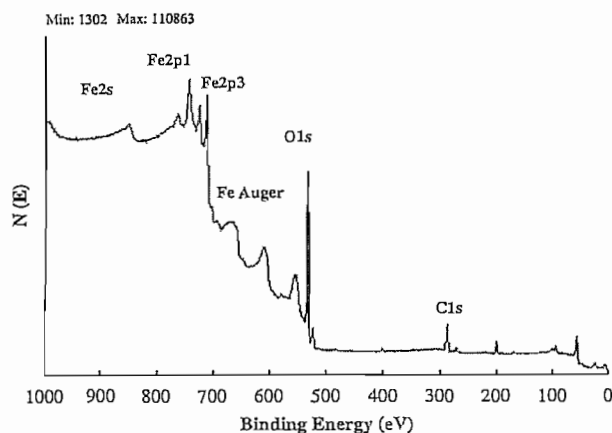


Fig. 7. XPS survey spectrum of standard LCAK steel surface.

spectrum of the LCAK steel surface is shown in Fig. 7. No significant difference in elemental composition between the standard LCAK steel surface and the warm water treated LCAK steel surface was observed with regard to XPS survey spectrum. The XPS survey spectra of both samples show the presence of three elements: carbon, oxygen and iron.

The detailed oxygen peak was used to differentiate between the surface species on the standard LCAK steel surface and warm water treated LCAK steel surface. The different components constituting the O 1s peak correspond to $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OOH})$ and adsorbed H_2O were determined by curve fitting [24]. The O 1s peak of the standard LCAK steel surface and warm water treated LCAK steel surface are given in Figs. 8 and 9, respectively. The values of the binding energies of these components, their peak heights and peak height ratios are summarized in Table 3. The peak height ratio of $\text{Fe}(\text{OH})_2$ to $\text{Fe}(\text{OOH})$ was 1.05 for the standard LCAK steel surface and 4.2 for warm water treated LCAK steel surface. A previous report indicated that a surface with an $\text{Fe}(\text{OH})_2/\text{Fe}(\text{OOH})$ ratio of 1:1 gives good adhesion properties [25]. Using contact angle measurement results, $\text{B}(\text{OCH}_3)_3$ molecule adsorption and FTIR spectroscopy, the standard and warm water treated LCAK were predicted as having Lewis base and Lewis acid properties, respectively.

3.4. XPS study of the LCAK–water interaction

After polishing, the LCAK samples were immersed in an aqueous solution with pH adjustment using HCl or NaOH. After

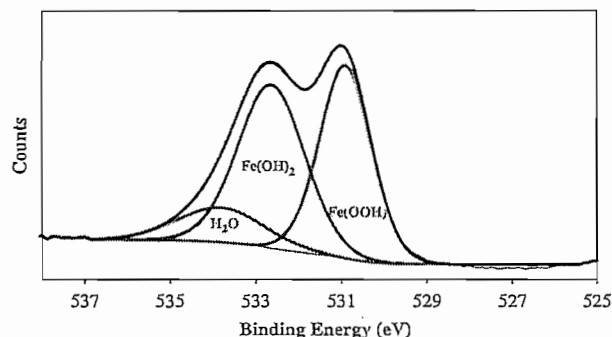


Fig. 8. XPS 1s oxygen peak obtained for a standard steel surface.

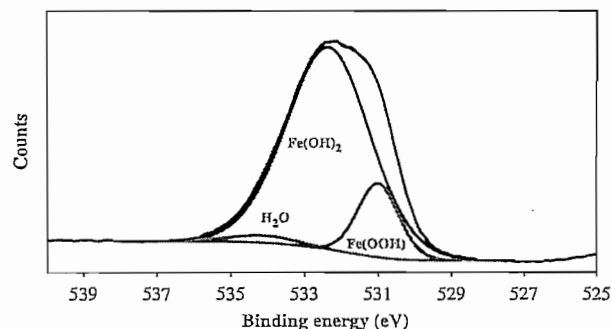


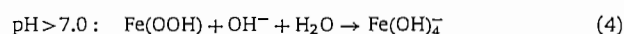
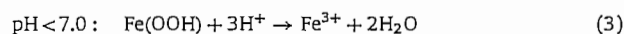
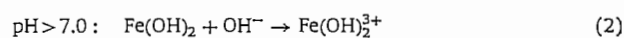
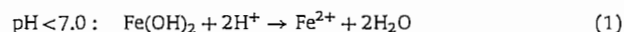
Fig. 9. XPS 1s oxygen peak obtained for a warm water treated steel surface.

Table 3
XPS results and an estimated molecular ratio between $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OOH})$ on the surface of an LCAK steel sample

Name	Binding energy (eV)	Chemical surface species	Standard % area	Warm water % area
O 1s	534	H_2O	4.238	3.556
O 1s	532	$\text{Fe}(\text{OH})_2$	49.175	78.064
O 1s	531	$\text{Fe}(\text{OOH})$	46.587	18.380
Ratio		$\text{Fe}(\text{OH})_2/\text{Fe}(\text{OOH})$	1.05	4.2

treating the LCAK sample in the solutions at pHs 3 and 8, the spectroscopic results obtained (Figs. 10 and 11) were similar. The XPS results of the iron 2p peaks indicate $\text{Fe}(\text{OOH})$ species associated on top of the metallic iron. This is evident from the larger $\text{Fe}2p_{1/2}$ (oxide) and $\text{Fe}2p_{3/2}$ (oxide) peaks at 45° take-off angle. The angle resolved XPS spectra (Fig. 12) obtained for the oxygen 1s peak indicated that the Fe^{2+} or $\text{Fe}(\text{OH})_2$ species are found on the outside surface layer.

In contact with acidic and basic solutions, the $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OOH})$ surface species on the standard LCAK substrate may react as follows [23]:



Reaction (1) and (2) represent the basic and acidic reactivity of the $\text{Fe}(\text{OH})_2$ surface species, respectively and Eqs. (3)

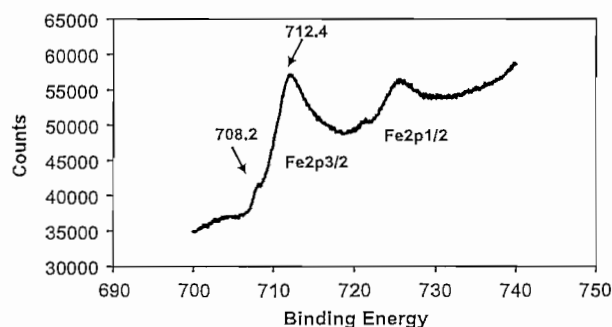


Fig. 10. XPS survey spectrum of the iron surface layer produced in an aqueous solution at pH 3.

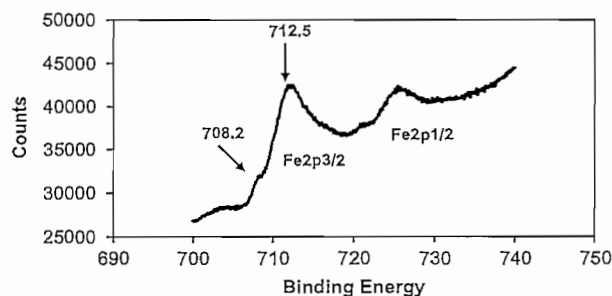


Fig. 11. XPS survey spectrum of the iron surface layer produced in an aqueous solution at pH 8.

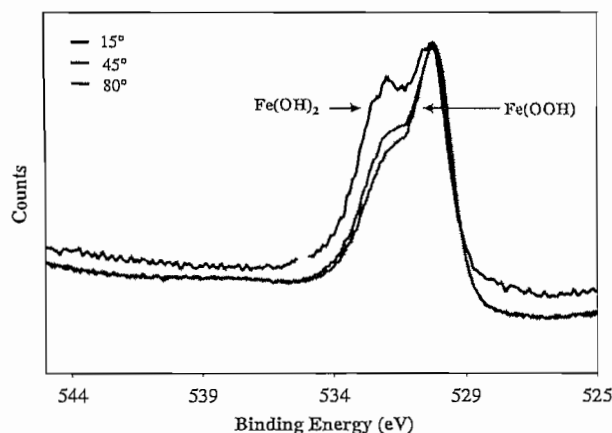


Fig. 12. XPS 1s oxygen peaks obtained for a standard steel surface at pH 4 at take-off angles of 15°, 45° and 80°.

and (4) are representative of the basic and acidic reactivity of Fe(OOH).

The standard LCAK steel surface, being shown to have a Lewis base character, may thus react with acidic organic compounds through Lewis acid–base reactions. As indicated in Table 3, the ratio between the Fe(OH)₂ and the Fe(OOH) groups on the surface is 1.05, thus close to 1:1. The Fe(OOH) species were previously characterized as having Lewis acid character [25]. It thus seems that the Fe(OH)₂ species on the standard LCAK steel surface must result in the Lewis basic character and that the presence thereof dominates the characteristics of the surface. The main surface reaction for the standard LCAK steel surface thus as given in reaction (1).

Table 4
Summarized iron species at different pH values

pH	Iron species	References
0.8	Fe ²⁺ , Fe ³⁺	[26]
2.5	Fe ²⁺ , Fe ³⁺	[26]
3.6	Fe ²⁺ , Fe(OH) ²⁺	[26,27]
4.1	Fe ²⁺ , Fe(OH) ⁺ , Fe(OH) ₂ ⁺ , Fe(OH) ₂ ²⁺	[26–28]
9.1	Fe ²⁺ , Fe(OH) ⁺ , Fe(OH) ₂ , Fe(OH) ₃ ⁺	[26–28]
10.5	Fe(OH) ₂ , Fe(OH) ₃ , Fe(OH) ₄ [−] , FeOOH	[26–28]
12.1	Fe(OH) ₂ , Fe(OH) ₄ [−]	[26–28]
13.1	Fe(OH) ₃ [−]	[28]

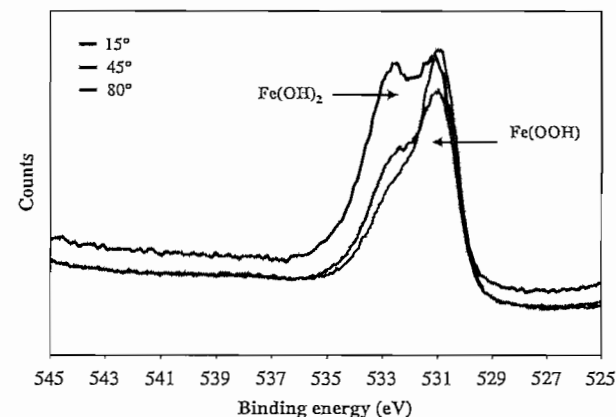


Fig. 13. XPS 1s oxygen peaks obtained for a standard steel surface at pH 13 at take-off angles of 15°, 45° and 80°.

The possible iron species formed during the surface treatment of the LCAK steel surface with acidic and basic solution are shown in Table 4 [26–28]. According to the reports of Hui et al. [29], in the pH range from 5 to 9, Fe(II) ions exist in the form of Fe²⁺, FeOH⁺, Fe(OH)₂ and Fe(OH)₃. At pH 5, the species of Fe(II) ions in the system comprise both Fe²⁺ and FeOH⁺, but the concentration of Fe²⁺ ions predominates. At pH 7, the species of Fe(II) are Fe²⁺, FeOH⁺ and Fe(OH)₂ but the concentration of FeOH⁺ ions is the largest (about 60%). And at pH 9, the amount of Fe(OH)₂ instead of FeOH⁺ and Fe(OH)₃ predominates [26,30]. Fe(OH)₂ and Fe(OH)₃ are thermodynamically stable at pH > 7 [29].

3.5. The molecular orientation of Fe(OH)₂, Fe(OOH) and adsorbed H₂O on standard LCAK substrate

The angle resolved XPS results on treated standard LCAK steel surface at pHs 4 and 13 are shown in Fig. 12 and 13, respectively. The graphs show that despite different surface treatment with acidic and basic solutions, the oxygen containing species remain Fe(OH)₂ and Fe(OOH). The XPS angle resolve technique indicates that the OH surface species associated with Fe²⁺ concentrate towards the outer surface layer, while OOH surface species associated with Fe³⁺ do not change in concentration with the change in take-off angles and thus surface depth.

3.6. Correlation with adhesion measurements

Standard LCAK steel samples and warm water treated samples were coated with alkyd coating, conditioned and tested according to the procedure mentioned previously. In Figs. 14 and 15, the

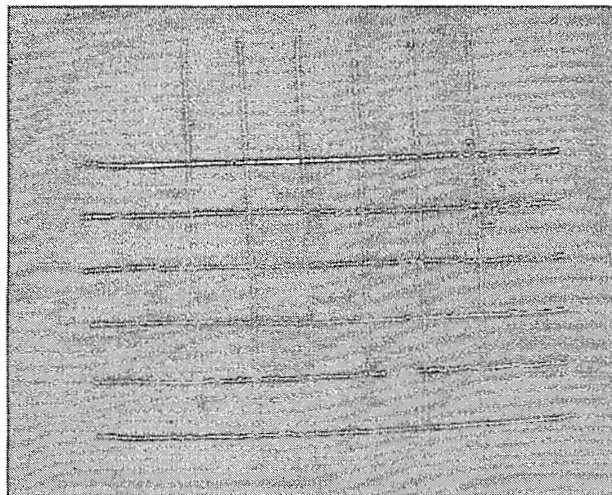


Fig. 14. Paint adhesion results obtained on standard painted LCAK steel sample.

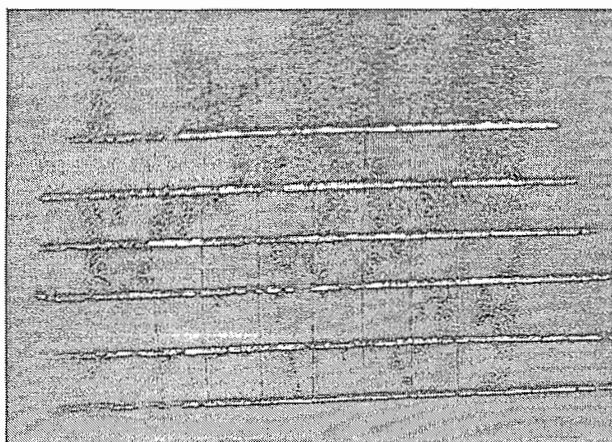


Fig. 15. Painted adhesion results obtained on warm water treated LCAK steel sample.

results of the paint adhesion test done on these samples are shown, with the warm water treated LCAK steel substrate indicating where the paint was removed (Fig. 15). The eight-point ASTM test yielded good adhesion and poor adhesion for standard and warm water treated substrates, respectively. These results agree with the probe molecule adsorption results shown in Figs. 4–6.

4. Conclusions

The LCAK sample is covered by a thin oxide layer before it is introduced to an aqueous solution as the oxidation of iron in air is fast. In contact with an aqueous solution, metallic iron within LCAK sample undergoes oxidation to form a combination of iron oxides and hydroxides. The main oxidation products before acidic and basic treatment are a mixture of $\text{Fe}(\text{OOH})$ and $\text{Fe}(\text{OH})_2$.

Contact angle measurements and XPS analysis were performed on a standard LCAK substrate and a warm water treated

LCAK substrate to determine the surface chemical properties. The contact angle results of the two substrates indicated that the surfaces exhibited opposite surface chemical properties in terms of Lewis acid–base theory. This is in agreement with FTIR analysis of adsorbed $\text{B}(\text{OCH}_3)_3$ on the samples after treatment with acidic and basic solutions. The treated standard LCAK substrate exhibited Lewis base surface properties, while warm water treated LCAK substrate exhibited Lewis acid surface properties.

The XPS study of the oxygen 1s peak indicated that the $\text{Fe}(\text{OH})_2$ to $\text{Fe}(\text{OOH})$ ratio of approximately 1:1 for the standard LCAK steel surface exhibited Lewis base properties. These Lewis base properties are attributed to OH groups being available on the outside surface. The warm water treated surface, with an $\text{Fe}(\text{OH})_2/\text{Fe}(\text{OOH})$ ratio of 4.2 exhibited Lewis acid properties, which may be due to the better availability of OOH groups on the outside surface. Further studies to verify the three-dimensional structures of these surface groups are planned to explain the properties.

With respect to alkyd paint adhesion, LCAK surfaces followed a behavior reflecting the participation of its Lewis acid–base nature. A Lewis base surface will engage sufficiently strong chemical bonds with some acidic groups of the alkyd coating. As a result, strong durable alkyd coating on LCAK are obtained.

These methods of observing the Lewis acid and Lewis base properties of interfaces are believed to have important application in the study of coating system formulations, such as adhesives for automotive, coating for roofing and composites materials. Apart from identifying the Lewis acidic or basic nature, it may be used to develop techniques to modify the surface in order to obtain better adhesion of either basic or acidic adsorbents.

Acknowledgments

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