EFFECTS OF SOME BITUMEN COATING TREATMENTS ON THE CORROSION AND MECHANICAL BEHAVIOUR OF LOW CARBON STEEL

BY

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DECLARATION

I declare that the work in the dissertation entitled "EFFECTS OF SOME BITUMEN COATING TREATMENTS ON CORROSION AND MECHANICAL BEHAVIOUR OF LOW CARBON STEEL" has been performed by me in the Department of Mechanical Engineering under the supervision of Professor S.Y. Aku, Dr. D.S. Yawas and Dr. M. Dauda The information obtained from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at any university.

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CERTIFICATION

This dissertation entitled "EFFECTS OF SOME BITUMEN COATING TREATMENTS ON CORROSION AND MECHANICAL BEHAVIOUR OF LOW CARBON STEEL" by Thomas Ndyar GUMA, meets the regulations governing the award of the degree of Doctor of Philosophy (Mechanical Engineering) of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

The research work highlights the problem of corrosion of low carbon steel as a prime structural material in relation to the Nigerian economy. The work contributes to provide detailed analyses that can be used for sourcing, grading, modification and engineering coat-application of abundant bitumen resources in Nigeria to economically reduce corrosion of structural steelworks in the country's petroleum-dependent economy that is subject to costly effects of corrosion. Low carbon steel rods and three bitumen samples were collected from different critical sources in Nigeria and characterized. Resistance to corrosion by various coating treatments of the bitumen samples and chemical fractions separated from them, and effects of treatment concentrations of sodium benzoate as a standard corrosion inhibitor on mechanical properties of the steel were separately experimentally investigated. Micro-structural make-ups of the coating treatments were also investigated through X-ray diffraction analysis. Analyses of the overall results indicated that bitumens from the sample sources are of high quality as per international standard (IS) for 60/70 and 80/100 penetration grade bitumen. Coat-treating the steel with the bitumen samples in the range of 0.81 to 2.1mm coating thicknesses was found to produce appreciable corrosion inhibition of the steel and affected its mechanical properties. Within the coating thicknesses; resistance to tensile strength, fatigue strength, hardness, and impact strength deteriorations of the steel varied within different bands from 53.35 to 100%. Furthermore, the inhibition performance (IP) levels for the steel were found to vary with the bitumen samples and depended mainly on the asphaltene contents of the samples. By comparison with the coatings, sodium benzoate treatment concentrations in the range of 50 to 250ppm of the same test medium also produced appreciable good results with the highest inhibition efficiency of 27.4% at 250ppm concentration. Microstructurally, about 3.75 to 4.84% by weight of the coatings were found to consist of distinct mineral phases that varied in types and amounts with even bitumen from the same source.

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NOMENCLATURE AND ABBREVIATIONS USED

BISRA	=	British Iron and Steel Research Association
UU	=	Un-coated and un-corroded specimen
UC	=	Un-coated but corroded specimen
TU	=	Coated and un-corroded specimen
TC	=	Coated and corroded
KRPC	=	Kaduna Refining and Petrochemical Company
ASTM	=	American Standards for Testing Materials
Ondo S-A	=	Bitumen sample collected from a waterlogged area at Agbabu village, Ondo State, Nigeria
Ondo S-B	=	Bitumen sample collected from underground through an extraction hole at Agbabu village in Ondo State, Nigeria
KPB	=	A bitumen sample collected from synthetic bitumen produced with the blend of Basara and Nigeria crude feedstock at KRPC.
σ	=	Stress, Standard deviation of inhibition data obtained from test results of a bitumen sample's corrosion inhibition of a mechanical property of low carbon steel
ILO	=	International Labour Organization
R	=	The range of inhibition data obtained from test results of a bitumen sample's corrosion inhibition of a mechanical property of low carbon steel
d	=	Minimum diameter of a fatigue specimen
$\overline{IP}$	=	The average inhibition performance of the data obtained from test results of a bitumen sample's corrosion inhibition of a mechanical property of low carbon steel
g	=	Acceleration due to gravity
V	=	The coefficient of variation of inhibition data obtained from test results of a bitumen sample's corrosion inhibition of a mechanical property of low carbon steel
Vi	=	Volume of a steel slide without bitumen on it
V_2	=	Volume of a steel slide with bitumen on it

l	=	Length of fatigue specimen
m	=	Attached mass to bend fatigue specimen
M_2	=	Mass of a steel slide with bitumen on it
M_1	=	Mass of a steel slide without bitumen on it
ppm	=	Parts per million
η	=	Inhibitor efficiency
S^{UC}, S^{UU}, S^{TC}	=	Strains developed in the Untreated but Corroded, Untreated and Uncorroded, and Treated and Corroded specimen respectively
W_1, W_2	=	Corrosion rates in the presence and absence of inhibitor respectively
WCF	=	Specimen treated in a dissolution prepared without involving any chemical fraction extracted from the as-procured bitumen sample
ρ	=	The density of specimen in grammes/cubic centimetres
UNEP	=	United Nations Environment Programme
US	=	United State of America
ΔT_i	=	The difference in corresponding mechanical property values as the case may be, appropriately between the UC curve and TC curve for the case of a given bitumen sample and coating thickness at some specified conditions
ΔC_i	=	The difference mechanical property value between the UU and UC curves for the case of a given bitumen sample and coating thickness at some specified condition
ΔU_i	=	The difference in micro-hardness or impact strength values as the case may be between the un-coated and un-corroded (UU) specimen and the corresponding treated and corroded (TU) specimen as appropriate for the case of a given bitumen sample, coating thickness and the mechanical property
n	=	Number of sample data values considered
C	=	Carbon
H	=	Hydrogen
N	=	Nitrogen

O	=	Oxygen
NA	=	Naphtene aromatics
AS	=	Asphaltenes
RE	=	Resins
SAT	=	Saturates
S	=	Sulphur
Al	=	Aluminium
Mn	=	Mangenese
Ti	=	Titanium
η	=	Corrosion inhibition of efficiency of sodium benzoate
Ca	=	Calcium
Fe	=	Iron
Cu	=	Copper
Ni	=	Nickel
P	=	Phosphorus
Ag	=	Silver
Si	=	Silicon
Mo	=	Molybdenum
Eu	=	Europium

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Corrosion is an unintentional attack on a material as a result of interaction with its environment resulting in deterioration of its properties. To the engineer, the term is applicable to metals only and the term ‘deterioration’ to other materials like wood, concrete and ceramics. Although there are different forms of corrosion, the common and usual form that is responsible for a majority of failure incidents of structural works is uniform or nearly uniform corrosion. Rusting of structural steelworks is the most important corrosion problem. Rusting is a uniform or nearly uniform form of corrosion and accounts for about 90% of all corrosion problems worldwide (Uhlig, 1971; Higgins, 1993 and Callister, 2004).

The process of rusting results in gradual inward wastage of the outer layer of a steel part or component with time and corresponding reduction in its cross-sectional area, appearance, engineering properties and service attributes. If the process remains unchecked for a sufficiently long time, it will eventuate into poor service performance or even complete failure of the part or component. Mechanical properties such as tensile strength, fatigue strength, impact strength and hardness of a structural material such as steel are most cherished and must therefore be preserved or properly protected in its usage from corrosion for its continuous satisfactory service performance. The performance of steel and that of most other structural materials with regard to each of these properties is however different under different types of mechanical tests, service conditions including corrosive environments. A comprehensive methodical corrosion protection strategy would therefore require specific information on test-performance of

the material with regards to each property instead of the general information usually given for the degree of rusting in terms of penetration rates in mm/yr (Jackson and Ravindra, 1996; Cotterel, 1985; Raghavan, 1989 and 1990; Higgins, 1993; and Callister, 2004).

Bitumen is a highly viscous, black, sticky and chemically complex material that is entirely soluble in carbon disulphide. The quality of bitumen can vary widely from source to source with different levels of service benefits; hence handling, design reliability, safety, efficiency and modifications in technological applications of bitumen demand that proper test-obtained information on the basic properties of a given harvested one should be obtained and applied instead of the average property values that are available for bitumens of good quality (Illston *et al,* 1979; Jackson and Ravindra, 1996).

The most important method used to counteract corrosion of steel is by painting or organic coating. It is estimated that about 90% of all steel surfaces are corrosion-protected by organic coatings. Bitumen coatings are heavy bodied materials and have excellent resistance to industrial pollution. Bitumen is used in various coatings and other forms to protect steel in corrosion-preponderant industries such as petroleum or other chemical and water industries and other technological applications (Illston *et al*, 1979; Jackson and Ravindra, 1996). Bitumen is however produced and supplied in various grades around the world. Each grade has particular uses, distinct handling and service performances. Not all bitumen grades are good or used for coating. Generally, hardness and consistency determine the suitability of a grade for coating. Nigeria's natural bitumen from various locations is yet to be properly graded and exploited for economic and technological development. Yet, there is scarcity of comprehensive

information on codes of practice with the Nigerian bitumen by standards organizations. Bitumen produced at KRPC is grossly inadequate for the needs of consumers in the country or elsewhere. Nigeria loses about 300 billion Naira on bitumen importation annually. It will be contrary to engineering principles to harvest un-graded bitumen from any source in the country and coat a metal to any thickness or on the basis of bitumen of suitable grades for corrosion protection or other engineering applications. Proper engineering principles demand that a series of all necessary tests and evaluations be conducted on such bitumens to establish their grades, suitability levels and handling properties before using them or processing them further to meet the required service properties or standards (Johnson, 1965, Srivastava and Van Roijen, 2000 and *Nigeria Loses Over 300 Billion Naira*, 2014).

Because of its viscosity, bitumen cannot be efficiently and economically coat-applied at room temperature; so it is usually heated to 150 to 250^{o}C to lower its viscosity for industrial applications by spraying, rolling, mopping, and dipping methods (Illston *et al*, 1979; Hall, 1986; Painting and Decorating Contractors of America, 1995).

In Nigeria, natural bitumen has been found in Ondo, Lagos, Ogun, Edo and Enugu States with a proven reserve of about 14.86 billion barrels (2.599 Giga tonnes). Ondo State is however the most noted area of bitumen activities in the country and has the offices of the Nigerian Bitumen Development Project located at Akure and Ore. Bitumen is also a by-product of the production processes of Kaduna Refining and Petrochemical Company (KRPC). This source of synthetic bitumen has an installed capacity of 4,000 barrels of bitumen per day (Sheikh, 2003: Federal Ministry of Solid Mineral Development, 2006 and *Nigerian Bitumen*, 2011). The bitumen content and quality of Nigerian tarsand is not the same but varies from location to location.

Tarsands with 5 to 10% by weight bitumen content are designated as good or medium grade. The average bitumen content of Nigerian tarsand is about 20%. Very rich natural bitumen deposits are found in Ondo state around the regions of Agbabu, Idiobilayo, Foriku, Aiyibi and Okitipupa. The social, economic and technological benefits of bitumen resources exploitation to the country are enormous (Oshinowo *et al*, 1982; and Sheikh, 2003; Federal Ministry of Solid Mineral Development, 2006).

Corrosion testing to obtain ideal design-effective data applicable to a given metal and its given service environment is a complex and technologically encompassing subject. This is because many experts have argued that there is no standard corrosion test that is ideal to obtain ideal practicable results because of unpredictable variability of environmental conditions where metals are applied; from point to point, place to place and time to time. Moreover, appreciable losses from corrosion generally occur only over a long period. Data from field and service corrosion tests are however more realistic for design use but these tests take several years to obtain meaningful results and their costs are comparatively much higher and can be prohibitive. To simulate precisely a corrosive field condition for the purpose of laboratory corrosion testing will often be impractical. Experience has however shown that short period tests or accelerated tests and extracted results are also feasible for evaluating metals and coatings for design use. Such design-effective data must incorporate some factors of safety relative to a reasonably adjudged ideal data for the applicable metal and its service environment by standardized or properly designed test conditions (Doyle, 1969; American Society for Metals, 1975; Khanna, 1999; Bartholomew and Shifler, 2003).

Although the most steel-corrosive natural environments include acidic soils, highly saline soils and heavy clays of high electrical conductivity, organic deposits such as silt

and harbour mud, sea water, the material rusts at almost incredible rates on surf beaches in the tropics where it is exposed to continuous spray of sea salts particularly sodium chloride (Laque; 1975; Illston *et al*, 1979; Cotterel, 1985). The rusting rate increases with the salt and moisture contents of the air but decreases with the distance from the surf beach. At a very high sodium chloride content of 11.1% and 100% relative humidity, a rate of 0.95mm/yr was obtained for ingot iron by Ambler and Bain (2012a) at 50 yards from the tropical surf beach at Apapa in Lagos, Nigeria. It is based on such facts that a majority of accelerated or laboratory corrosion tests are carried out to simulate corrosive environments with adjudged suitable aggressiveness for specimen exposure (Bartholomew and Shifler, 2003; Ambler and Bain, 2012).

1.2 Statement of the Problem

Steel is by far the most important engineering alloy and lots of money is used, far more than for any other material, in protecting it from corrosion. The amount of steel which is allowed to rust away for lack of adequate protection amounts to 1000 tonnes every single day (Cotterel, 1985; Higgins, 1993). Corrosion of steel increases with decrease in the amount of carbon and/or alloy elements it contains. Low carbon steel contains only up to 0.3% of carbon and no or negligible amounts of alloy elements and is not heat-treatable to enhance its properties and corrosion resistance. Furthermore, low carbon steel is the most susceptible type of steel to corrosion ravage and failure and the most used on tonnage basis (Raghavan, 1990 and Higgins, 1993). The steel accounts for about 90% of all steels used for structural works because of its outstanding fabrication and formability properties, coupled with its high strength to weight ratio. These make corrosion of low carbon steel the most important corrosion problem worldwide (Cotterel, 1985; Raghavan, 1990 and Higgins, 1993).

Corrosion costs for industrialized nations are put at 5% of their annual gross domestic products (GDP). In developing countries, the general level of corrosion-consciousness and counteractions are minimal and the deleterious phenomenon has more or less silently been taking its toll indirectly or directly on their economies and people's lives in many quarters. Corrosion is preponderant in the oil and gas industry. The total cost of corrosion to the industry worldwide is huge and staggering. A figure of 300 billion US dollars was mentioned in the United States of America alone in 1998. It was estimated that only 45% of this amount was economically justifiable using the existing technologies of corrosion prevention. The cost of pipeline corrosion alone can also be huge. For example, corrosion and its related effects cost the United States of America transmission pipeline companies as much as 8.6 billion dollars per year (Ali, 1998; Callister, 2004; Yawas, 2006 and *Corrosion Costs US Transmission Companies*, 2008).

Nigeria's economy is about 85% petroleum-dependent. The country is a developing nation that is searching for ways to catapult her to the status of an industrialized nation without necessarily preparing for it. No government in Nigeria has yet come to grips with the reality of the devastating effect of corrosion on the country's economy. The country is endowed with abundant critical and strategic resources that can help her to easily attain the industrial status if they are managed properly. So far, the utilization of these resources as raw materials is dependent wholly on the industrialized economies. The petroleum industry upon which the Nigerian economy is so dependent is prone to ravages of corrosion. About 80% of her refinery equipment and transmission pipelines are made of carbon steel particularly of the low carbon type. These pipelines pass through the sea, rivers, underground or surface water in urban and rural areas. Their deterioration and other aspects of plants in the economy as a result of corrosion is a huge cost to the country in terms of subsequent wastages from oil leakage and spillage,

product contamination, replacement of parts, protection and maintenance, contravention of environmental and safety laws due to pollution, fire and general losses. Yet all the materials of construction in the country are imported, and an enormous amount of foreign exchange is lost to corrosion in this country (Shreir, 1979b; Ali, 1998; Wami, 1998 and Yawas, 2006). There is therefore strong need for concern posed by professional, technological and economic challenges on how best to mitigate the problem.

1.3 Aim and Objectives

The aim of the study is to determine the effects of some bitumen coating treatments on corrosion and mechanical behaviour of low carbon steel using bitumen from Nigerian sources. The specific objectives of the study are:

i. To establish the properties of bitumen sourced from Agbabu in Ondo State and KRPC.

ii. To develop coatings of various thicknesses on the steel and determine their effects on corrosion resistance.

iii. To carry out the structural analysis of coatings and establish the prospects of the bitumens as corrosion inhibitors.

iv. To determine an experimental procedure for determination of variations in inhibition performance levels of the bitumen samples.

v. To study the effects of coating thicknesses and sodium benzoate of various concentrations on the inhibition levels in sodium chloride environments causing accelerated corrosion.

1.4 Significance of the Study

The significance of the study is basically in five dimensions.

i. The enormity of effects and implications of corrosion on the Nigerian economy poses professional challenges to technologically combat it with novel approaches. Nigeria is blessed with large reserves of natural bitumen whose bitumen content and quality vary from surface to underground levels and from location to location. The potential for synthesizing large quantities of bitumen from crudes need to be studied and documented for utilization of this resource for corrosion protection of steel.

ii. This study will provide requisite and basic information on the characteristics and corrosion resistance levels by coatings of bitumens from various Nigerian sources. The information will be useful towards the establishment of design-effective codes of practice for coat-utilization of the country's abundant bitumen in the form wrappings and tapes, admixtures in concrete encasements, bituminous paints and coating supplements to other corrosion protection methods to reduce corrosion problems.

iii. Documented information from the study will be publicized and this can prompt some profitable investments in bitumen-coating of steels with bitumen sourced in Nigeria as a raw material especially in the country by governments, corporate bodies, interest groups and individuals. This will contribute to the development of the Nigerian economy in several ways including creation of employment and conservation of foreign exchange used on importation of corrosion protection materials.

iv. The study will stimulate parallel and further researches such as actual service and field tests to augment laboratory results.

v. The study will be a useful reference material for related research on corrosion inhibition of steel.

vi. The study will contribute as an eye opener towards the use of Nigeria's abundant bitumen and other resources to reduce the problem of corrosion and other technological problems in the country.

1.5 Scope of the Study

The study entails:

i. Procurement of two clear natural bitumen samples at Agbabu village in Ondo State and a synthetic sample at KRPC, Kaduna, in Nigeria and characterization of their basic physico-chemical properties.

ii. Procurement of 25 low carbon steel rods at least four metres long from the iron and steel market in Nigeria and ascertainment of their chemical composition and micro-structure.

iii. Production of specimen for determination of mechanical properties of the steel.

iv. Micro-structural examination of corroded specimen.

v. Appropriate heat treatments of specimen.

vi. Development and use of coating procedure.

vii. Design and use of accelerated corrosion testing.

viii. Statistical determination of the working bitumen coating thickness on the specimen by the method of dimensional change.

ix. Assessment of coatings' corrosion resistance from tests of mechanical properties

x. X-ray diffraction analysis of the coatings.

xi. Comparative assessment of corrosion resistance of chemical fractions separated from the bitumen samples to deterioration of the steel's properties through impact and hardness test results.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Corrosion of Steel

The extent of corrosion of a metal depends on a number of factors. The most important of these are its composition and surface condition, the corrosivity level of the environment it is exposed to and the local conditions. A fundamental approach to any study on corrosion protection of a given metal requires consideration of these factors, since they affect it generally and hence determine any of its corrosion prevention or control approaches as well as test methods, results and analysis (Johnson, 2001 and Callister, 2004).

2.2 Forms of Steel Corrosion

The different forms of forms of steel corrosion include: (Shreir, 1979b and Johnson, 2001).

i. Uniform or nearly uniform corrosion, in which all areas of the alloy corrode at the same rate. For example, oxidation and tarnishing, rusting, active dissolution in acids, chemical and electrochemical polishing etc.

ii. Localized corrosion in which certain areas of the alloy's surface corrode at higher rates than others due to heterogeneities in the metal, environment or in the geometry of the structure as a whole. Attack ranges from being slightly localized to pitting. For example, crevice corrosion and bimetallic corrosion.

iii. Selective dissolution, in which one component of the alloy usually the most active is selectively removed from the alloy. For example, dezincification, dealuminification, and graphitization.

iv. Co-joint action of corrosion and a mechanical factor, in which localized attack or fracture due to the synergistic action of the mechanical factor and corrosion

occur. For example, erosion corrosion, fretting corrosion, impingement attack, cavitation damage, stress corrosion cracking, hydrogen cracking and corrosion fatigue.

All these forms of corrosion except uniform or nearly uniform corrosion can be anticipated, prevented or reduced by correct design by the engineer. The most important form of steel corrosion to control or prevent is rusting (Shrier, 1979b).

2.3 Environmental and Metallurgical Factors in the Corrosion of Steel

2.3.1 Atmospheric environment

Steel and other metals are more frequently exposed to the atmosphere than to any other corrosive environment. On a tonnage basis, atmospheric corrosion accounts for the greatest losses. This type of corrosion is also the oldest corrosion problem known to mankind. The principal reason for this lies in the complexity of the variables, which determine the kinetics of the corrosion reactions. Thus corrosion rates vary from place to place, from hour to hour and from season to season. The approximate nominal composition of the atmosphere at a temperature of 38°C and pressure of 100KN/m^2 as given by Meetham (1968) is shown in Table 2.1 in the Appendix. The composition is global and for components is reasonably constant for all locations, but water vapour content vary according to the climatic region, season of the year, time of day, etc. Rusting of bare steel is controlled by the climatic condition at the exposure site. The main factors are the availability of moisture, and the extent to which the air is polluted, but other less important ones, such as temperature, exposure conditions, and mass of steel (Uhlig, 1971 and Shreir, 1979a).

For a given atmospheric condition, corrosion will be more severe the more humid and oxygenated it is. This is why exposed and unprotected steel structures are quite durable in arid regions but rapidly attacked in humid climates. The quantity of moisture required for rusting to occur need not be great. The corrosion reactions will proceed, albeit slowly on a steel surface in such minute quantity as to be invisible. The moisture can reach the exposed steel surface, directly in liquid form as a result of precipitation processes that is rain and dew (Johnson, 1965). The vapour that is always present in air can also, under certain conditions cause steel to rust at relative humidity well below saturation. This important fact was demonstrated by Vernon (1935) in a series of classical experiments. He showed that rusting is minimal in pure air of less than 100% relative humidity but that in the presence of minute concentrations of impurities, such as sulphur dioxide, serious rusting can occur without visible precipitation of moisture once the relative humidity of the air rises above a critical and comparatively low value. This value depends to some extent upon the nature of the atmospheric pollution, but when sulphur dioxide is present, it is in the range of about 70-80%. Below the critical humidity rusting is inappreciable even in polluted air. The presence of moisture on steel above the critical humidity but below the saturation point may be caused by an adsorption mechanism or by the presence of particles of deliquescent salts on the surface of the metal. Once rusting has begun, the composition of the rust already formed will influence the relative, humidity at which further rusting will occur, because rusts formed in polluted atmospheres contain hygroscopic salts (Shreir, 1979a).

Although humidity plays a vital part, the impurities in the air are decisive in determining the rate of rusting in atmospheres of the requisite humidity; in their absence rusting is not serious even in highly humid air. Typical concentrations of atmospheric impurities of 350µg/m^3 during winter and 100µg/m^3 during summer in

industrial regions; 100µg/m^3 during winter and 4µg/m^3 during summer in rural regions; sulphur trioxide of about one percent of sulphur dioxide content; hydrogen sulphide of about 1.5 to 90µg/m^3 as measured in spring in industrial regions and 0.15 to 0.45µg/m^3 in rural regions; ammonia of 4.8µg/m^3 in industrial regions and 2.1µg/m^3 in rural areas; chlorides of 8.2µg/m^3 in winter regions and 2 to 7µg/m^3 in summer as well as air sampled rural coastal annual average of 5.4µg/m^3 has been reported by (Shreir, 1979a). Although the most important impurity in industrial atmospheres is sulphur dioxide, chlorides and ammonium salts also may have effects. Generally, near the coast chlorides have the most pronounced effects. In the presence of chlorides, rusting can continue at relative humidity as low as 40%. As a rule, steel rusts at almost incredible rates on surf beaches in the tropics where it is exposed to a continuous spray of sea salts on the surf. This is apparent from the results of some tests made with ingot iron exposed for one year in Lagos, Nigeria on behalf of the former Tropical Testing Establishment, Ministry of Supply Britain, and given in Table 2.2 in the Appendix. In most districts, sulphur dioxide and dust particles are the main corrosive pollutants Chandler and Kilcullen (1968) have demonstrated that there is direct relationship between sulphur dioxide in the atmosphere and the corrosion of steel exposed to it as shown in Figure 2.1.

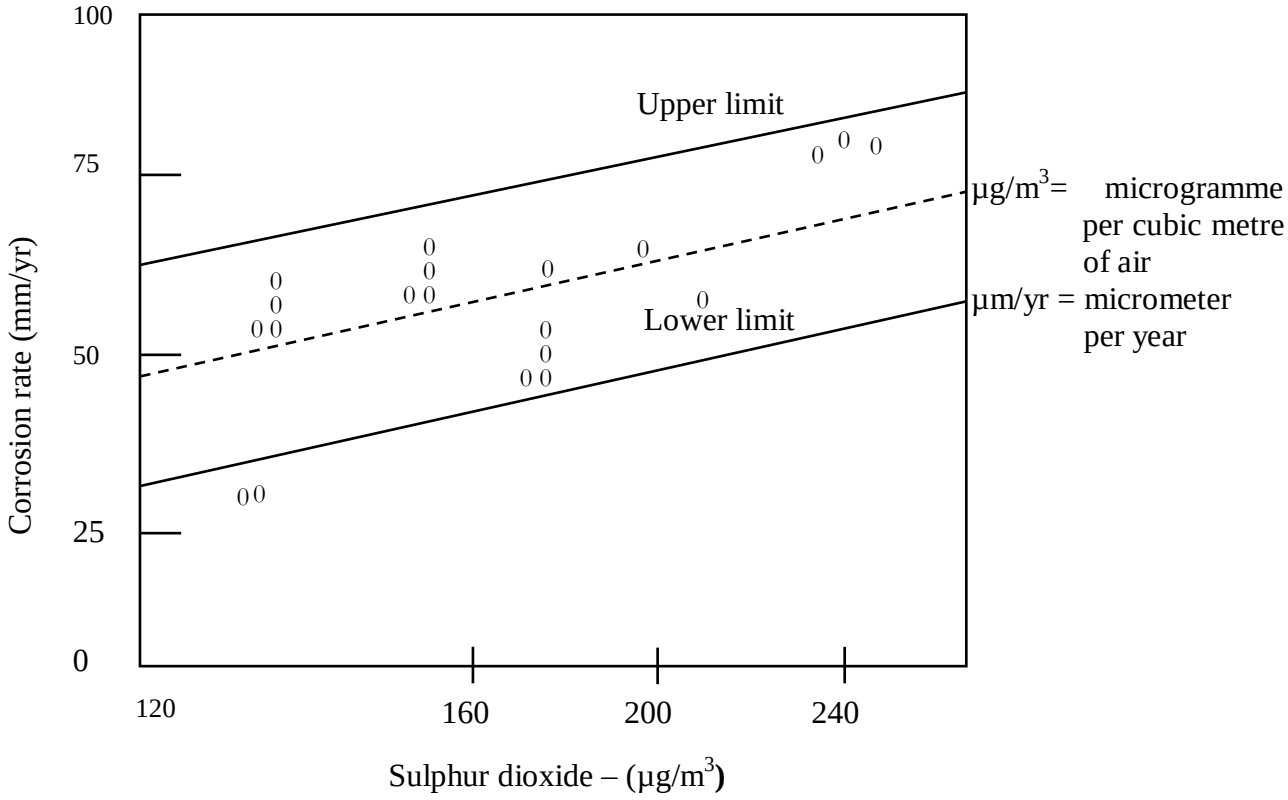


Figure 2.1**:** Relationship between sulphur dioxide and corrosion of steel (Chandler and Kilcullen, 1968)

Sulphur dioxide in the air originates from the combustion of fuel and influences rusting in a number of ways. For example, Russian workers consider that it acts as a cathodic depolarizer, which is far more effective than dissolved oxygen in stimulating the corrosion rate. However, it is the series of anodic reactions culminating in the formation of ferrous sulphate that are generally considered to be of particular importance. Sulphur dioxide in the air is oxidized to sulphur trioxide, which reacts with moisture to form sulphuric acid, and this in turn reacts with the steel to form ferrous sulphate. Examinations of rust films formed in industrial atmospheres have shown that 5% or more of the rust is present in the form of iron sulphates and hydrated ferrous sulphate has been identified in shallow pits. Workers who have studied atmospheric corrosion processes are generally agreed that the loss of iron as a sulpahte accounts in

only a small measure for the effects of sulphur dioxide (Shreir, 1979a). There is no complete agreement on the detailed mechanism but once ferrous sulphate has been formed it is able to promote further rusting. This has been demonstrated by Schikorr (1963) by allowing steel to rust in an atmosphere containing sulphur dioxide and then transferring it to a clean atmosphere where the corrosion continued at enhanced rate, at least for a time. There is cyclic variation in the amount of sulphate found in rust formed on steel exposed at different times of the year, and the amount depends on the month of the year rather than on the period of exposure, at least for periods up to two years as demonstrated by Chandker and Stanners (1963) at Battersea atmospheric environment. The variation is shown in Figure 2.2. Consequently, the month of exposure can have an important influence on the corrosion rate up to a year or so as shown in Table 2.3 in the Appendix.

In one test, specimen exposed for two months from September corroded at 0.035 mm/year compared to 0.0136mm/year for specimen exposed from May, and the amount of rust formed on steel follows this cyclic pattern over periods of up to two years and possibly for longer periods (Shreir, 1979a).

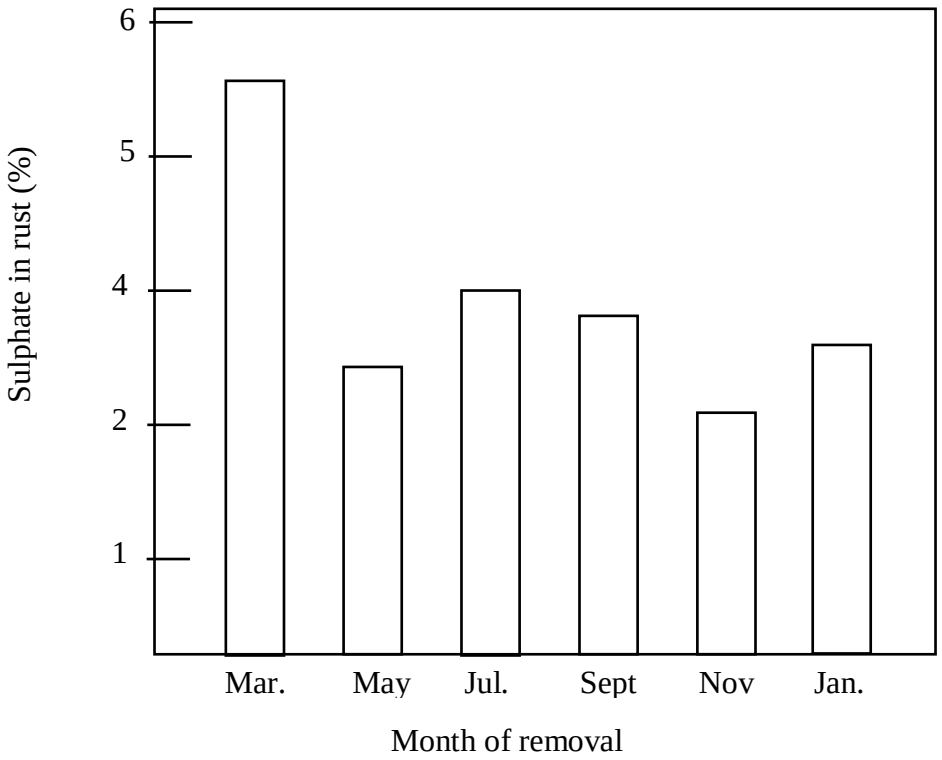


Figure 2.2: Sulphate in adherent rust on steel exposed at Battersea in January (Chandler and Stanners, 1968)

The effects of ammonium contamination have also been studied and some workers consider that it has a significant influence on the corrosion of steel. Dust particles also play an important role. They act as nuclei for the initial corrosion attack and as some particles are hygroscopic; their presence tends to increase the periods of wetness of the steel surface (Shreir, 1979a).

Although ambient temperature would be expected to have an influence on the rate of rusting, its effect is not clearly defined despite the efforts of workers to establish a relationship. However, it has an effect on relative humidity and consequently an indirect effect on corrosion. However, fluctuations in temperature may be more important than average temperatures because they influence condensation and the rate

of drying of moisture. Shreir (1979a) and Higgins and Morrow (1977) have found that within the limits of atmospheric temperatures, every 10°C rise in temperature increases the rate of rusting.

The absolute values for the rate of rusting would be affected by the mass of the specimen itself and by other factors such as the orientation of steel, climatic conditions prevailing at the time of exposure, and the duration of exposure. The Orientation of the steel influences the rate of rusting through its effects on the amounts of moisture and pollutants that can reach its surface. For a given exposure, corrosion will be more severe the more humid the prevailing atmosphere. Corrosion on the skyward or the sunny side of a steel surface that is the side which is not shaded is less severe than on its ground-facing or shaded side. This is because the moisture on the sunny surface is more rapidly evaporated due to the drying action of the sun and often of wind; while the other side is shielded from the drying action, so that moisture tends to remain in contact with the steel side for longer periods (Shreir, 1979a and Johnson, 1965). Moreover, harmful solid particles and soluble salts are not leached away on the latter side. In agreement with this consideration, the results of tests at Derby in Britain by Dearden (1948) have shown that steel specimen exposed at 45° to the horizontal corroded 10-20% more than corresponding vertical steel specimen, and 54% of the total loss was on the underside. In American tests on specimen exposed at 30° to the horizontal, 62% of the loss was on the underside.

The rate of rusting of steel in the atmosphere is affected to some extent by the mass of the part concerned, because this determines the speed at which the surface temperature adjusts itself to fluctuation in ambient temperature, the amount of condensation during humid periods, and the time during which dew or rain remains in contact with steel. In

a test over twelve months at the National Chemical Laboratory in Britain under sheltered conditions, thick steel plates rusted more than thin ones as shown in Table 2.4 in the Appendix (Shreir, 1979a).

Millscale on steel may decrease the corrosion rate over short periods. However, over longer periods the surface condition is not usually a determining factor as can be seen from Table 2.5 in the Appendix, which shows the results of five-year tests at Sheffield England by Shreir (1979a).

It is important to know whether the rate of rusting of steel outdoors increases, remains constant or decreases with increasing 'duration of exposure. The position over a long period is adequately illustrated by the curves drawn in Figure 2.3 showing the results of tests carried out for 15 years in a rural environment at Llandwrtyd Wells, and in an industrial atmosphere at Sheffield, all in the United Kingdom. At both sites the rate of rusting fell considerably after the first year or two, but then remained fairly constant for the rest of the test period. In actual figures the average rate of rusting over the first two years was 0.058mm/year for Llandwrtyd Wells and 0.118 mm/year for Sheffield; the corresponding rates in the same units over the last 10 years were 0.015 and 0.025 respectively (Sixth Report of the Corrosion Committee, 1959).

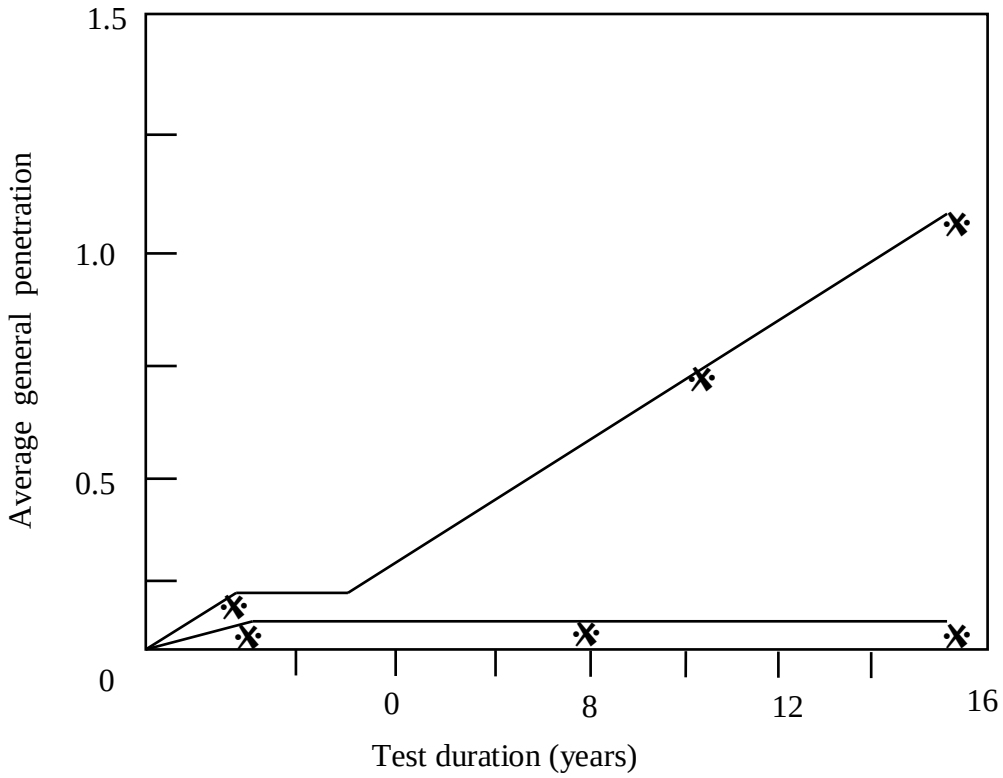


Figure 2.3**:** Rusting of mild steel (0.02% Cu) in the open air at Sheffield and Llanwrtyd Wells (Sixth Report of the Corrosion Committee, 1959)

From the foregoing discussions, it can be appreciated that different places, sites, or points around the globe have different atmospheric characteristics at different times or periods, which affect corrosion of steel, due mainly to variations in climatic conditions and levels of pollution of those places or sites. An exact detailed classification of the atmospheric environment for corrosion behaviour of steel, for all times and for every location around the globe would be complex or impossible due to the complexity and variability of all the controlling factors with time and location. Exact atmospheric conditions at a location may involve reliable instantaneous or automatic technological monitoring and analysis of the level of chemical pollution and climatic conditions of the location. However, laboratory, field and service studies over the years have enabled

engineers to identify four important influential atmospheres in corrosion behaviour of steel; these are; inland rural atmospheric, inland industrial atmospheric, nominal marine atmospheric and marine industrial atmospheric environments.

The inland rural atmospheric environment is any region of the atmosphere of more than two kilometers away from the coast that is not affected by industrial activities. These are essentially inland unpolluted environments. In other words, this environment is more or less nominal, and hence moisture containing dissolved oxygen is the primary corrosive agent. The only possible pollution of the environment could be from distant sources according to prevailing wind direction or topography. This is generally considered negligible. Steel corrosion here tends to be low, usually less than 0.05mm/year in exposure outdoors. The results obtained for mild steel (mm/year) for some sites in the environment are Godaiming (0.048); and Llanwrtyd Wells (0.069) in Britain, Teddington Khartoun in Africa (0.003), Abisko in North Sweden (0.005), State College Pa in the United States of America (0.043), and Berlin-Dahlem in Europe (0.053). Exposure indoors here, such as offices, stores, workshops, industrial production and assembly warehousing, hospitals, schools, hotels, and residential apartments have very much lower steel corrosion rates and risks compared to the outdoors (Shreir, 1979a and Johnson, 2001).

An inland industrial atmospheric environment is any area around industrial and, or high urban activities in rural areas. Such activities include petrochemical, automobile, textile, and cement manufacturing. These are areas of high air-borne sulphur dioxide or other pollutants from industrial or domestic sources. The sulphur dioxide sources are twofold. Firstly, from the aerial oxidation of hydrogen sulphide (H_2S) produced naturally and secondly from the combustion of sulphur-containing fuels. The average

steel corrosion rates here are significant, and are usually between 0.05 and 0.lmm/year, depending on the level of sulphur dioxide, type of steel and whether exposure is outdoor or indoor. Some industrial areas here such as breweries, diaries, laundries, food processing plants or kitchens do not produce much sulphur dioxide but the corrosion is equally significant, because of frequent condensation there (Johnson, 2001; Shreir, 1979a). The corrosion rate (mm/year) for mild steel obtained by British Iron and Steel Research Association – BISRA (In: Shreir, 1979a) for some sites in this type of environment in Britain are; Motherwell (0.095), Woolwich (0.102) Sheffield (0.135), Frodingham (0.160), Derby (0.170); and for Pittsburgh, Pa in the United State of America (0.108).

A nominal marine atmospheric environment is any aero-space region within a two kilometer strip around the coast that is unpolluted by industrial and, or domestic activities. The environment has high air-borne salt levels, particularly sodium chloride (NaCl). In some places, this salt-contained zone may extend to a maximum of three kilometers from the coast. These are areas of frequent heavy condensation and hence the average steel corrosion rates are significant, usually between 0.05 and 0.1 mm/year, largely dependent upon proximity to the sea, type of steel, and whether outdoor or indoor (Johnson, 2001). For mild steel, the rates (mm/year) of rusting in exposure outdoor in this type of environment, obtained around the globe are: Brixham, United Kingdom (0.053), Calshot, Britain (0.079); Singapore (0.015); Apapa, Nigeria (0.028) and Sand Hook, United States of America (0.084). A marine surf beach rate of 0.615 for the steel was obtained in Lagos, Nigeria (Ambler and Bain, 2012).

A marine industrial atmospheric environment, as the name implies, is any area of industrial and high human activities in a marine atmospheric environment. These are

polluted coastal environments coupled with frequent heavy rainfall. These environments produce the highest average steel corrosion rates, ranging from 0.05 to 0.15mm/year (Johnson, 2001). This is mainly because the steel surface is at all times washed by rain and heavily polluted by sulphur dioxide, sodium chloride, and dilutes sulphuric acid (acid rain). The mild steel corrosion rate for exposure outdoor in this type of environment in Congella, South Africa as reported by Shreir (1979a) was 0.114 mm/year.

2. 3.2 Water Environment

A water environment is any area, place, region or point that is entirely occupied by water to saturation all the time. Basically, there are two types of water environments, the sea and fresh water environments. Water environments can also exist as a result of industrial or commercial activities. Steel finds applications in these environments in the form of pipes, bridge structures, tanks and other containers, bodies of ships and other water-going structures, etc. The water environment is complex in diversity, quality or composition and operating conditions. This makes the corrosion of steel by both natural and industrial waters a complicated and many sided phenomenon, which cannot be completely dealt with in this paper. The difficulty arises from the fact that of the main considerations involve the composition and surface condition of the steel, the quality of the water, and the operating conditions; the last is generally the most important. Moreover, in industry the operating conditions vary widely, and many of them need individual study (Callister, 2004; Johnson, 2001; American Society of Metals, 1975 and Harrison and De Mora, 1975).

All ordinary ferrous structural materials, mild steels, low-alloy steels and wrought iron corrode at virtually the same rate when totally immersed in natural waters. As shown in

Table 2.6 in the Appendix, the process of manufacture and the composition of mild steel do not affect its corrosion rate appreciably under water (Uhlig, 1971; Shreir, 1979a and Ross, 1977). The copper content of the tested steels varied from 0.03 to 0.11. The killed steel contained about 0.4% aluminium and 0.04% silicon. In general therefore, the least expensive steel or any other ferrous material of a given cross-sectional thickness having the required mechanical properties is the one that should be specified for water environment.

Although small copper additions generally have no influence on the corrosion rate of steel immersed in water, under certain boiler conditions small amounts of copper of up to 0.3% may have a marked effect on reducing the depth of pitting. This is attributed to the catalytic action of metallic copper on the formation of a protective layer of magnetic nature which diverts the attack sideways producing general rather than pitting corrosion. Generally, over 3% of alloying additions such as chromium are necessary to obtain any marked improvement in the corrosion resistance of steel in waters (Shreir, 1979a and Ross, 1977).

The surface condition of the steel at the time of exposure is of great importance. This is because many natural waters are good electrolytes, so that there is ample opportunity for electrolytic corrosion when steel is permanently in contact with them. The presence of millscale on the surface is more dangerous, for example when steel is immersed in sea-water than when it is exposed to air, for the galvanic cell formed by millscale and bare steel can operate much more freely under the former conditions. This may lead to rapid pitting. Pits of up to 1.25mm depth were found on as-rolled steel specimen after six months immersion in sea-water at Gosport in the United Kingdom. It follows that for many practical purposes, where steel is exposed to water without a protective

coating such as boiler tubes, it is desirable to remove millscale before putting the parts into use (Shreir, 1979a).

Serious pitting may occur in the area of welds particularly in sea-water. Corrosion rates of up to l0mm/year have been reported in weld joints of ice breakers. The severe corrosion has been attributed to galvanic effects between the weld metal and the steel plate. The use of more noble electrodes for welding are reported to overcome this problem (Uhlig, 1971 and Shreir, 1979a).

Saline and acid waters are particularly aggressive to mild steel, so that composition of water is clearly important in determining the rate or rusting of steel exposed to it. Some of the main factors here are the nature and amount of the dissolved solids, which influence the electrical conductivity, the degree of acidity or alkalinity, as determined by pH value and hardness of the water, the carbon dioxide and oxygen contents, and the presence of organic matter. The effect of dissolved solids is complex. The presence of inorganic salts, notably of chlorides and sulphates, should promote corrosion because they increase the conductivity of the water, thereby facilitating the electrochemical rusting process; moreover chlorides at least may be detrimental to the development of the protective films. Alkaline waters tend to be less aggressive than acid or neutral waters, and rusting can be repressed entirely by making the water strongly alkaline. It should be noted that a pH value of 7 gives a neutral liquid that is, the one that is neither alkaline nor acidic. As pH increases from 7 to higher values up to 14, alkalinity of the liquid increases correspondingly, and as pH decreases from 7 to lower values but of more than 0, the acidity of the liquid increases correspondingly. Unfortunately, at pH values just insufficient to give complete passivation to steel, there is a grave danger of severe pitting, even though the total corrosion is reduced and this for many purposes is

a greater evil (Shreir, 1979a; Ross, 1977 and Legrand and Leroy, 1990). The most important property of the dissolved solids in fresh waters is whether or not they are such as to lead to the deposition of a protective film on the steel that will impede rusting. This is determined mainly by the amount of carbon dioxide dissolved in the waters, so that the equilibrium between calcium carbonate, calcium bicarbonate and carbon dioxide, which has been studied by Tulmans and Heublein (1992) and others, is of fundamental significance. Since hard waters are more likely to deposit a protective calcareous scale than soft waters, they tend as a class to be less aggressive than these; indeed soft waters can often be rendered less corrosive by the simple expediency of treating them with lime (Uhlig, 1971; Shreir, 1979a and Legrand and Leroy, 1990).

Oxygen and carbon dioxide are the most important dissolved gases in water. Oxygen is an effective cathodic depolarizer and the cathodic reaction in water is generally oxygen reduction. At ordinary temperatures in neutral or near neutral water, dissolved oxygen concentration results in an acceleration of the corrosion of steel up to a certain concentration but beyond this the rate of corrosion is reduced. In slow-moving distilled water, it has been found that the critical concentration is 12ml. This value increases with temperature and in the presence of certain dissolved salts, it decreases with high velocities. Carbon dioxide affects the acidity of water and as already noted, influences the formation of protective carbonate scales. Another important factor is that most natural waters are far from being sterile. They contain greater or lesser amounts of organic matter, both living and dead. Some of the dead organic matter, for example peat residues, may render the water corrosive by making it acid. In most cases the living organism are probably algae and in fresh waters. Moreover, there are a number of strains of bacteria that can influence the rusting proper under immersed conditions (Harrison and De Mora, 1975 and Shreir, 1979a).

The operating conditions have an important influence. Generally the facts involved are complex; they include temperature, rate of flow, design features and stray currents. The temperature of water affects the rate of rusting in several ways. First, the corrosion process shares the general tendency of chemical reactions to increase in speed with rising temperature. More important, however, are the effects of temperature on the nature and solubility of the corrosion products. For example a rise in temperature will often throw down a carbonate scale; moreover, it increases the rate of diffusion of oxygen through water but decreases its solubility. Some of these effects are conflicting, with the result that under certain laboratory conditions at least the rate of rusting/temperature curve for steel immersed in water passes through a maximum before the boiling point is reached - at about 80°C (Friend, 1940, Laque, 1975 and Shreir, 1979a).

The rate of water flow is also very important. This determines the supply of oxygen to the rusting surface, and may remove corrosion products that would otherwise stifle further rusting. Much supply of oxygen to the cathodic area will stimulate corrosion, but small supply at a slow rate of flow leads to the formation of differential aeration cells. At sufficiently high rates of flow in natural waters enough oxygen may reach the surface to cause partial passivity, in which case the corrosion rate may decrease. In sea-water, owing to the high concentration of chloride ions, the corrosion rate increases with velocity (m/s). In one series of tests, corrosion under static conditions was 0.125 mm/year, 0.50mm/year at 1.52m/s and 0.83 mm/year at 4.572m/s (Shreir, 1979a).

Design must also be considered. Sharp changes in the direction of flow as in a badly designed water box, may lead to severe local damage by impingement attack. Severe galvanic corrosion can result from the injudicious juxtaposition of steel with non-

ferrous metals, such as copper or bronzes. Even when the ferrous and non-ferrous metals are not in direct contact, local corrosion cells can be set up round small particles of non-ferrous metal that have been dissolved by the water and redeposited on the steel. Corrosion cells can also be formed when steel is in contact with solutions of different saline contents; for example ‘long line’ currents have been observed in a lock gate that was in contact with a layer of fresh river water flowing out over a layer of sea-water (Ross, 1977 and Shreir, 1979a).

The sea water environment represents a chemical system on a massive scale covering 71% of the earth's surface and accounting for 97% of the surface water in the global hydrological cycle. The average depth of the sea is 3.7 kilometers but this could be greater than 10 kilometers in deep sea. Sea water is a solution of gases and solids containing both organic and inorganic materials in suspension. This is a well-oxygenated solution buffered at about pH8 containing all the elements, albeit in most instances in very dilute solution. The surface temperature of the sea ranges between -2°C and 35°C, while the temperature of shallow surface layers may run even higher. In a thermodynamic sense, the sea forms an open system as both energy and mass can be exchanged across the boundaries. Sea water is both physically and chemically dynamic in nature leading to heterogeneity within the system. Equilibrium may be attained for some reaction requiring geologic time scales. Short-term perturbations may upset these equilibria. Of greater importance may be the effect of organisms. The concentration and distribution of several elements is controlled not chemically but biologically (Harrison and De Mora, 1975).

The sea environment is one of the most corrosive to steel. This is because almost all agents of steel corrosion are found here in appreciable quantities-water, oxygen, salts

such as sodium chloride, etc; coupled with mechanical actions of impingement. The metal has a remarkably steady rate of corrosion when fully immersed in the water. The average corrosion rates range from 0.05 to 0.15 mm/year depending on the prevailing conditions at the point of immersion (Johnson, 2001). Test results for mild steel, obtained by the Institution of Civil Engineers; at Halifax, Nova Scotia, and Plymouth in Britain, after a 15 year immersion of the metal in the water gave average general penetration for the two sites respectively as 0.108 mm/year and 0.065 mm/year. The effect of exposure period on the corrosion rate of mild steel is clearly shown by results given in Table 2.7 in the Appendix.

In extended exposure periods of up to 16 years in tropical seas, Southwell and Alexander (1970) obtained an average corrosion rate for mild steel as 0.18 mm/year in the first year, falling off to a constant rate after 4 years at 0.025 mm/year. They also quoted pitting rates as 1mm/year in the first year falling dramatically over the second to fourth years and ultimately continuing at a rate comparable with the average rate of penetration, giving an average rate for exposure to 16 years of 0.08 mm/year. However, the pitting rate is generally quoted as several orders of magnitude greater than the average rate of penetration with values of 0.25 to 0.4 mm/year (Shreir, 1979a).

A fresh water environment is any environment that is occupied by water of no or negligibly small salinity, such as most river, lake and commercial waters. These waters contain dissolved solids and gases and sometimes colloidal or suspended matter which may affect the corrosive properties of the water in relation to the steel with which it is in contact. The concentrations of these various substances are relatively low but vary considerable. The important constituents are classified as follows (Shreir, 1979a; Legrand and Leroy, 1990 and Callister, 2004):

i. Dissolved gases which include oxygen, nitrogen, carbon dioxide, ammonia, sulphurous gases, etc.
ii. Mineral constituents which include hardness salts, sodium salts (chlorides sulphates, nitrates; bicarbonates etc), heavy metal, and silica.
iii. Organic matter including those of both animal and vegetable origin, oil, trade waste constituents (including agricultural) and synthetic detergents.
iv. Microbiological forms including various types of algae and slime-forming bacteria.

Some of the organic matter such as oil form films on the water surface which isolates the water from the air, so that in polluted water anaerobic conditions may develop with the encouragement of objectionable bacterial corrosion activities. The various kinds of organic growths, including algae and slime-forming bacteria have a direct or indirect effect on the corrosion of steel. The effects may be of two main types: masking effects of living or dead organisms which are a little different from those of other materials; and the effect of alterations in composition of the water brought about by the organism, algae, for example, may remove carbon dioxide and produce oxygen while other organisms often consume oxygen. The pH of fresh waters is, in fact, rarely outside the fairly narrow range of 4.5 to 8.5. Steel corrosion in fresh waters is much lower than that of sea water, mainly because the concentration of corrosive salts here is much lower than that of sea waters. Moreover, the sea is generally more physically and chemically dynamic than fresh water environments. The average steel corrosion rates in fresh waters range from 0.03 to 0.05 mm/year (Shreir, 1979a).

2.3.3 Soil Environment

Soil is a complex system of solid, liquid and gaseous phases, physically and chemically associated with each other. The solid phase is by far the most heterogeneous component, even in small volumes of soil, being composed of different sized organic particles of silica, silicate, clay, metal oxides, and other minor components all associated, to some extent, with organic material. The organic matter consists of a number of materials ranging from un-decomposed plant or animal tissue through various intermediate levels of decomposition to a comparatively stable amorphous brown and or black material. Compositional variables of a soil include moisture, oxygen, salt content, acidity, as well as the presence of various forms of bacteria. Climatic factors; temperature, rainfall, air movement, sunlight, etc, can cause marked alterations in properties of soil. Steel, particularly plain carbon ones are found most economical for underground structures, especially in forms of long pipelines (American Society of Metals, 1975; Harrison and De Morra, 1975 and Basalo, 1992).

No two soils are exactly alike, and extremes of structure, composition and corrosive activity are found in different soils. The type of soil affects the corrosion rate of steel much more than any variation in the steel material or in its method of manufacture. In general, dry, sandy or calcareous soils with high electrical resistance are the least corrosive. At the other end of the scale are the heavy clays and the highly saline soils, whose electrical conductivity is high. Other steel-corrosive soils include organic deposits such as peat and organic silt and, river and harbour mud. Although it is difficult to assess the corrosiveness of a particular soil before hand, much useful information can be obtained from a well-conducted soil survey on the site. The corrosivity assessment methods include determination of the soil's resistivity, redoxpotential to assess the soil's capability of anaerobic bacterial corrosion, acidity

(pH), and water and oxygen contents. Highly acidic soils, that is, those with pH less than 3.0, can be very corrosive. Bacterial activity often plays a major part in determination of corrosion of buried steel. This is particularly so in waterlogged clays and similar soils where no atmospheric oxygen is present as much. If these soils contain sulphates, for example gypsum and the necessary traces of nutrients, corrosion can occur under anaerobic conditions in the presence of sulphate-reducing bacteria which reduce sulphates in the soil to sulphides which are corrosive to steel. The depth of water table is also important; much depends on whether it is alternately wet or dry. It has however been found that the depth of burial has no consistent effects, which should not be surprising since the average depth of the water table and seasonal fluctuations vary from one site to another (Ross, 197 and Shreir, 1979a).

Finally, extensive field tests made at different sites around the globe indicate that steel's rusting rate could become less and less rapid as time of burial increases, or it could be roughly proportional to the duration of burial; depending on the type or properties of the soil. The maximum general soil corrosion rate reported in tests carried out by the United States National Bureau of Standards on mild steel is 0.068 mm/year. The maximum rates obtained in tests carried out in the United Kingdom by BISRA (In: Shreir,1979a) and the National Physical Laboratory is 0.035 mm/year and 0.050mm/year respectively. However, the pitting rate was much greater with reported maximum pits of 0.25mm/year from American and 0.30 mm/year from British tests. Table 2.8 in Appendix A shows the effect of depth of burial on the rusting of mild steel in different soils as obtained by BISRA (In: Shreir,1979a) at different sites in the United Kingdom.

2.3.3.1 *Effect of steel composition*

Corrosion of steel in soil is generally electrochemical in character but the conditions are such that the corrosion products usually remain in contact with the metal. Moreover, the rate of oxygen supply is often low in comparison with that in air or water. This is probably the main reason why there are no major differences in the general corrosion rates of ordinary steels when buried in most soils. The rates of general attack ate comparatively low, say 0.038 mm/year over a 10-year period of burial in a clay soil, as compared with 0.1 to 0.13 mm/year for complete exposure outdoors in an industrial atmosphere. The cheapest type of steel or iron of a cross-sectional thickness having the required mechanical properties is therefore suitable for underground structures (Uhlig, 1971; Shreir, 1979a and Johnson 2001).

2.4 Protective Methods for Steel Corrosion

2.4.1 Introduction

Any study aimed to determine the suitability of a method for preventing or controlling steel corrosion, will require as well as sound knowledge of the basics of the established methods on the subject. This is necessary for appreciation of:

i. The existing optimal levels attained on the subject

ii. Problems or inadequacies on the subject and hence need for more positive researches.

iii. The research result and the level of suitability of the results for field or service applications.

Since this work is intended to establish the level of efficacy of corrosion protection of low carbon steel by coatings of bitumen from Nigerian resource, these

established methods are explored under this section. The domains of survey include methodical principles, advantages and disadvantages.

2.4.2 Design method

Prevention of corrosion generally begins at the design stage of a project. Faulty geometrical design is a major factor in the corrosion of steel. A design may be sound from the structural and aesthetic points of view, but if it incorporates features that tend to promote corrosion, then unnecessary maintenance costs will have to be met throughout the life of component or part, or early failure may occur. Design can therefore have an important bearing on the corrosion of steel structures (Johnson, 1965; Shreir, 1979b and Johnson, 2001). The most common and easiest way of preventing steel corrosion once the alloy has been judiciously selected for a characterized corrosion environment is by observing important points such as; arrangement of features so that they do not trap moisture and dirt, allowing free circulation of air around the steel structure or part, not exposing steel to contact with water-absorbent material or wood, making parts of the structure accessible for maintenance, selecting structural shapes which will have a minimum exposed surface, avoiding shapes or details which catch dirt or debris, noting that large flat surfaces are easier to protect than more complicated shapes. Ideally locating load-carrying members in the least corrosive locations and elimination or avoidance of pockets, low spots, sharp edges, sharp corners, cavities, crevices, lap joints, bolted joints, box sections which will trap moisture or water in all designs (Johnson 1965; Moore, 1966; Pludek , 977; Shreir, 1979 and Collins, 1981).Observance of some design details for the sake of corrosion protection will involve little or no increase in the cost of a structure and will result in substantially decreased maintenance cost. However the disadvantage of the method include:

i. The method may not be feasible or economical for some practical situations; and in most cases could only reduce corrosion but not prevent it completely.

ii. Occasionally a change in design or materials for the purpose of corrosion control may have serious effects that are not related to corrosion per se, or result in corrosion problems that were previously present in the old system ; and incur much costs.

iii. Very often the effects of corrosion cannot be clarified at the early stage of design because information is lacking either on the precise environmental conditions or on the behaviour of the material in a certain configuration or application under these conditions (Pludek, 1977; Ross, 1977 and Shreir 1979b).

2.4.3 Cathodic protection

Corrosion of steel in aqueous environments or damp soil is primarily electrochemical in nature and is due to a corrosion current passing from anodic areas of the metal into solution and returning to the metal at the cathodic areas. Cathodic protection is used to prevent or reduce the rate of corrosion of steel structures, immersed or imbedded in such environmental electrolytes by impressing a counter current on the metal in a sufficient amount to neutralize corrosion current, or making the structures cathodes. The principle is based on the fact that corrosion and cathodic protection are natural phenomena which occur when any two dissimilar metals immersed in an electrolyte are brought into electrical continuity. The more active metal becomes the anode, while the less active becomes the cathode and receives protection. There are two common techniques of affording cathodic protection. These are; by using sacrificial anodes and by impressing a current (power impressed). Cathodic protection is often applied to coated structures, with the coat providing the primary form of corrosion protection and

the cathodic protection system acts as a supporting protection. The main applications of cathodic protection include: buried pipelines, acid storage tanks, offshore steel structures such as platforms and oil rigs, ships and concrete structures exposed to sea water such as bridges (IIIston *et al* 1979; Shreir, 1979b and Zuhair, 2014).

Cathodic protection is usually the only economic method of protecting major buried or immersed steel and other metallic structures from corrosion. The method is simple and when absolutely correctly applied, corrosion is impossible. It can be applied to any buried steel item without fully excavating the system. The forms of corrosion which can be controlled by cathodic protection are wide including all forms of general corrosion, pitting corrosion , crevice corrosion stress-corrosion cracking, corrosion fatigue, cavitation corrosion , bacterial corrosion, etc. In particular it can be applied in conjunction with some protection coatings to guard against any damage to the coating, or any break or discontinuities that may of necessity or accident exist. At any time, the efficiency of the protection can be checked by measuring the potentials of the reference points, and adjusting to compensate for any changes in local environment. Sacrificial cathodic protection needs no external power source, is cheap, easy to install, has low maintenance cost, and provides uniform distribution of current. The impressed current cathodic protection has higher current and power outputs and adjustable protection levels, can be used for large-area works, require lower numbers of anodes and can be used to protect poorly coated structures.

The method however has noteworthy disadvantages. The structure to be protected and the anode used for protection must be in both metallic and electrolytic contact hence it is applicable only in aqueous electrolyte or some damp soil environments. It cannot be applied in controlling atmospheric corrosion of steel, since it is not feasible to immerse an anode in thin condensed film of moisture or droplets of rain in the atmosphere. The

spread of the protective current is dependent on the resistivity of the environment. As a result, cathodic protection is not practicable for large structures in fresh water and high resistivity soils. Under such conditions a large number of widely distributed anodes would be required. Fortunately, however poor conductance and high resistivity also reduce the risk of steel corrosion taking place, or at least keep it to significant proportions so that protection is not necessary. Specifically, the disadvantages of sacrificial cathodic protection include: limited current and power output, requirement of a large number of anodes for high resistivity environments or large structures, periodic replacement of anodes. The disadvantages of impressed current cathodic protection include: complex equipment and installation costs, possible interference problems with foreign structures and risk of incorrect polarity connections (Shreir, 1979b and Zuhair, 2014).

2.4.4 Corrosion inhibition

Rusting of steel depends on both moisture and oxygen contents and the degree of pollution of an environment. The rate of the process can be affected by modifying the environment. This can be achieved principally, by inhibition of the corrosion process or its agents by addition of certain chemicals or substances that can restrain it, to requisite environments. Corrosion inhibition is an economical method of protecting steel used in certain environments such as boilers and pipe work of central heating systems, re-circulating systems such as internal combustion engines, cooling systems of road vehicles and railway locomotive; steam condensate lines; the oil industry at every stage of production from initial extraction to refining and storage prior to use, storage tanks, domestic and industrial water supplies, store rooms, and packages (Shreir, 1979; Legrand and Leroy, 1990 and Callister, 2004). Many inhibitors such as: acetylenic alcohols, aromatic aldehydes, alkenyphenones, amines, sodium benzoate, nitrites,

toluylalanine, cyclohexylamine, dicyclohexylamine, methycyclohexylamine, phenythiourea, sebacic acid, calcium silicate, sodium phosphate, imminium salts, triazole pyridine and its derivatives, thiourea derivatives, thiosemicarbazide, thiocyanates have been reportedly used to prevent steel corrosion (Kahraman, 2002; Finsgar and Jackson, 2014).The main advantages of preventing or controlling steel corrosion by chemical inhibition are (Ross, 1977; Shreir, 1979; Harrop, 1990 and Legrand and Leroy, 1990):

i. It is the most feasible and economical method of protecting steel that is used in recirculation systems and some other confined environments of liquid nature, from corrosion.
ii. Most inhibitors are cheap and their application is easy and fast, once the right application conditions are established.

Corrosion inhibition process however has the following problems or limitations (American Society of Metals 1975; Ross, 1977; Shreir, 1979b and Harrop, 1990):

i. For effectiveness of inhibition, the process is applicable only where chemical and conditions monitoring is feasible. All inhibitors have a pH range in which they are effective, so close Ph control is often necessary to ensure continued efficiency of inhibitive treatments. To be fully effective, inhibitors require to be present above a certain minimum concentration, otherwise corrosion that occurs with insufficient inhibitor may be more severe than the complete absence of inhibitor. Effective inhibitor application is affected by the liquid composition such as; oil and the water composition ratio, the types of oil and the water composition. Other factors that affect the application include fluid velocity, type of geological formation, solubility and specific gravity of the inhibitor to be used, smoothness of the materials to be protected, and the

prevailing temperature. This makes inhibitor application difficult or complex for many practical situations.

ii. The process is not applicable to prevention of atmospheric corrosion of steel. This is because it is difficult to achieve and maintain the required inhibitor concentration in air due to wind; and hence the inability of the inhibitor to remain suspended in the air at the right concentration for any reasonable time.

iii. Some inhibitors present toxicity hazards to human beings or animals and often there arises the problem of detoxifying or disposal of some inhibitor-treated waters of large volume. For example, waters treated with chromate and phosphate inhibitors, are known to be toxic. The problem of toxicity is complicated by difficulty that arises in describing the precise chemical nature of many inhibitor formulations that are actually used in practice. This is because, with the advancing technology of inhibitor applications there are increasing numbers of formulations that are marketed under trade names; their corrosion prevention capabilities are for various reasons, frequently not disclosed. This makes safeguarding against inhibitor toxicity while using them difficult.

iv. The lives of inhibitors vary from hours to days, months and years depending on the type, and type of environment. It could therefore require some preliminary test in an environment with a particular inhibitor for some time, before a design concentration of the inhibitor for the environment is made. This can incur much cost.

v. Effective protection by inhibitor relies on the continued access of an inhibitor to all parts of steel surfaces, where this condition is difficult to achieve due to the presence of crevices at points, dead-ends in pipes, gas pockets., deposit of

corrosion products, etc, corrosion will then occur at these sites even though the rest of the system remains adequately protected.

vi. Inhibitors that are effective in the absence of conjoint action of mechanical factors such as fretting or cavitations, applied stress and fatigue effects may not be so in the presence of such factors.

vii. Many inhibitors will lose their effectiveness in the presence of effects of some micro-organisms in aqueous solution of inhibitors in some ways by acting as nutrients to them.

viii. Economical factors can prohibit the application treatment for many practical situations.

2.4.5 Protection by metallic coatings

A preventive metallic coating for steel corrosion is an applied adherent metallic coat on the surface of the alloy, which can protect it sacrificially and or mechanically. The coating is intended to perform the function by acting as an impervious interface between the steel and the environment and hence prevent any corrosion activity between them. The coating can also have inhibitive capabilities on steel corrosion. In sacrificial protection, the metallic coat corrodes at a rate higher than that of steel. The metallic coating can be formed by a variety of methods. The choice between these may be dictated by convenience, but successful coats depend on adherence produced by the coating method (Carter, 1977; Barton 1976 and Shreir, 1979b).

There are four commonly used methods of applying protective metallic coatings to steel surfaces, hot-dip galvanizing, metal spraying, electroplating, and sherardizing. The last two process are not used in structural steelwork because of some infeasibilities, or higher costs; but are used for fittings fasteners and other small items. The methods are common because they are the optimal ones, applicable to coating steel with zinc,

aluminium, lead, and tin. These four metals offer the most effective protection of steel, at economical costs since they are the most common and cheap non-ferrous metals (Shreir, 1979b and Johnson, 2001).

2.4.5.1 *Hot-dip galvanizing*

This is the most common method of applying a metal coating to structural steel. It is the most economical method of zinc-coating steel. It is estimated that approximately 40% of the world production of zinc is consumed in hot-dip galvanizing of steel, and this adequately demonstrates the world-wide use of zinc as a protective coating. This is mainly because the metal itself resists corrosion and is available at comparatively cheap price. Hot-dipping is used for the application of other metals such as aluminium, lead/tin but these metals are not commonly used for structural steelworks. The specification of hot-dip galvanized coatings is covered by British Standard-BS729 which requires for sections not less than 5mm thick, a minimum mean zinc coating weight of 610g/m^3 equivalent to a coating thickness of 0.085mm. Galvanizing provides a barrier as well as cathodic protection. It results in coatings of very high corrosion resistance that are also highly resistant to damage during transportation, storage and handling. The finish appearance of the coating is not particularly attractive and its thickness can be variable, thus precluding the use of galvanizing for components which are required to have good visual finish and fine limits. There is also health hazard to the operator as zinc fumes are toxic (Johnson, 2001).

2.4.5.2 *Metal spraying*

Alternative method of applying a metallic coating to structural steelwork is by metal spraying of either zinc or aluminium. The main advantage of metal spraying compared to other metallic coating processes is cheapness. Metal spray coatings can be applied in

shops or on site after a structure has been erected because of portability of spraying equipment and there is no limitation to the work size as there is with hot-dip galvanizing. The surface of the workpiece remains cool during the process so there are no distortion problems. The main disadvantages of the coating process are; the tools are rather awkward to handle as they contain molten metal, the metal used for spraying must be easily fusible, there is good deal of erosion on the nozzle orifice which may affect control of the process, spray coatings are porous due to their structure of overlapping flakes after having solidified instantly on contact with the surface and is more expensive than hot-dip galvanizing (Johnson, 2001).

2.4.5.3 *Electroplating*

Electroplating is application of electro-deposition to produce a thin, coherent and adherent coating of solid metal on a base. The process is used to protect steel from corrosion by producing metallic coatings of suitable metals on it. The process is used to protect steel from corrosion by producing metallic coatings of suitable metals on it. Thickness of electroplated metals on steel varies from 0.00762 to 0.001524mm. Deposit thickness appropriate to various conditions of service of the steel metal are laid down in a number of specifications such as the International Standards, British Standards and American Standards for Testing Materials. Electroplatable metals on steel for corrosion protection include metals that offer sacrificial protection such as zinc, tin, aluminium, copper and bronze; and the noble metals such as lead, nickel, gold, chromium, titanium and platinium. The process requires high-quality surface pretreatment of the base steel, good operator skills to control process variables such as electricity current density. On the side of advantages, protective coatings of the required minimum thickness produced by the electroplating process are generally more adherent, smoother, cleaner, and thinner than those of other coating processes. The

disadvantages of the process include (Ross, 1977; Shreir, 1979b and Degarmo *et al*, 2003):

i. Electroplating relies on electricity; hence it can be accomplished only at a workshop where facilities are installed and electricity is available, but not at worksites.

ii. The process is slower compared to painting, hot-dip galvanizing and metal spraying.

iii. The need for very high quality cleanliness of the steel and proper process control makes electroplating unsuitable for structural steelwork. It is therefore more applicable to small steel parts.

iv. All electroplating contain pores and the only certain way of eliminating them is to plate to an uneconomic thickness to eventually abridge over the pores.

v. Metals in electroplating are deposited in a state of residual stress which can be considerable up to 225MN/m^2, if conditions in the plating bath are not properly adjusted. Such stresses may cause the plating to break away, or result in distortion of the plated steel; and can also have dangerous consequences if the plated part or article is then subjected to tension, fatigue or corrosion during service.

vi. No electroplating bath has perfect throwing power, that is, the measure of the ability of the bath to produce a uniform thickness of the plating. Uniformity in thickness is important, both for economy and adequate protection.

2.4.5.4 *Sherardizing*

Sherardizing is zinc-coating steel by a diffusion process. By this process, the chemical composition of the steel surface is modified by diffusing zinc into it. This is accomplished by first cleaning the steelworks thoroughly, by pickling and sandblasting.

The works are then placed in a suitable steel drum with zinc dust and heated to a temperature of about 260 to 315^{o}C, depending on their sizes and shapes whilst the drum is being rotated so as to promote tumbling of the contents. This results in coatings on the works that are not pure zinc, but an alloy of about 90% zinc and 10% iron; which is highly resistant to corrosion. The process is especially suited for screws, bolts and nuts, chains, pipe fittings, nails, and such other high strength articles that may conveniently be placed within the drum. The cost varies with character of the steelwork coated. The protective coating that is produced by the process is the most adherent, thinnest, more uniform thickness and damage-tolerant with long-term-corrosion protection compared to those of galvanizing and spraying processes; but the cost involved is highest. Coating thickness usually varies from 0.012 to 0.04mm, and the coating is continuous and uniform even on threaded or irregular parts. Sherardizing is limited to works of small size. It is more laborious and takes longer time than hot-dip galvanizing and metal spraying. The process is covered by BS 4921 (Price, 1963 and Jackson and Ravindra, 1996).

2.4.5.5 *Overall advantage and disadvantage of metallic coatings*

Metallic coatings are much more resistant to degradations such as cracking, blistering and peeling compared to paint coatings. They are strong and insensitive to light and moderate heat and for the most part they are more wear resistant than paints and are amenable to soldering. On the other hand, if corrosion has started, it will proceed at a faster rate because of the galvanic conditions which are set up and because it is not possible impregnate metallic coatings with inhibitive compounds that are present in paints. The equipment for applying metallic coatings is more elaborate than that for painting, which puts up costs and may make it difficult to replace coatings which have failed on structures, as compared with the relatively straightforward task for repainting.

The coatings also change the chemical, physical and mechanical properties of steel (IIIston *et al,* 1979b).

2.4.6 Paints or organic coatings

Paint or organic coating is the principal method of protecting structural steelwork from corrosion. About 90% of all steels are corrosion-protected by paint or organic coatings. A paint or organic coating is required mainly to prevent corrosion of the substrate in the presence of moisture and corrosive electrolytes over an indefinite period; and to stifle corrosion in the event of its onset because of any incomplete covering, mechanical damage or breakdown of the coating through age and factors of exposure to the environment. There are laid down types of paint or organic coatings for different soil, water, atmospheric and other comparable environments and procedures for applying them by different, industries, organizations and authorities such as the International Standards Organization, American Standards for Testing Material, National Association for Corrosion Engineering, British Standards, Army, Navy, etc which must always be consulted and properly used (Diamant, 1967; IIston *et al*, 1979; Shreir, 1979b and Johnson, 2001). The comparative advantages of using paint or organic coatings for corrosion protection of steel include the following (Laque, 1975: Pludek, 1977 and Shreir, 1979b):

i. A wide range of solid and liquid materials of organic or inorganic nature are available and are used, or can be exploited for formulating paints of desired characteristics. This flexibility is not common with any other coating method.

ii. A painting system can be formulated anywhere, anytime under normal conditions for a particular application, and the formulation is modifiable to meet any change in the service requirement.

iii. Painting is generally more economical, easier and faster to accomplish than metallic and other coating methods.

iv. A wide range of paint application methods, ranging from hand brushing to fully automated ones are available, which can be conveniently or suitably exploited for particular situations of the work.

v. The protection provided by a properly selected and applied paint, is reasonable during its life.

vi. Painting is the most important method of protecting steel from atmospheric corrosion. It is applicable to almost all other environments.

vii. Maintenance work with paints is easier and cheaper and can be carried out at a worksite without necessarily bringing the work to the workshop.

viii. The material, equipment, and labour costs incurred in procurement, paint formulation, surface preparation of the work, and maintenance are in totality minimal for painting compared to other coating costs.

ix. Painting is applicable to jobbing, or batch, or mass works at economical cost.

Despite these advantages, painting systems have some disadvantages which include (Laque, 1975; Pludek , 1977 and Shreir,1979b):

i. Some of the paints contain toxic materials that are health-hazardous to personnel if exposed to them for some time through inhalation or skin contact. For example, lead contained primers used for corrosion protection of steel.

ii. The protection lives of paint coatings are generally less than those of metallic and some other coatings of the same thickness, under the same environmental conditions.

iii. Most paint coatings are more porous, and are generally less adherent rougher, and less hard, compared to most properly applied metallic coatings which also posses other characteristics that are much better.

iv. Formulation of a paint of suitable or desired characteristics requires knowledge of chemical compositions of its ingredients and their compatibility.

v. Some paints are prone to fire and explosion hazards.

2.4.7 Encasement

Encasement is often used as a protective method against corrosion of steel parts or structures in certain environments, where the method is found to be the only feasible one. The method is used to provide permanent or semi permanent corrosion protection of steelwork by encasing or sheathing the entire or part of the work with a suitable non-corrodible material. Concrete encasement, and reinforced bitumen coatings (wrappings) are the optimal encasements for the protection (Johnson, 2001; Shreir, 1979b and Callister, 2004).

2.4.7.1 *Concrete encasement*

Concrete encasement of steel sections is most frequently used for protection of; waterfront steel structures in the tide zone and below the waterline, buried pipe structures, lining pipes, structural elements which will be inaccessible in the final work and for structures subjected to particular corrosive atmospheres such as those exposed to locomotive blasts or those in chemical plants (Johnson, 2001). The disadvantages of the method include (Johnson, 1965; Basalo, 1992; Perkins, 1997; Callister, 2004 and Uche, 2006):

i. The method is slow and laborious for mass work.

ii. In reality, even a well-constructed concrete encasement will not protect steel from corrosion completely, due to electrolyses. This is because most concretes are somehow porous.

iii. It can mostly be accomplished at the worksite. This requires moving materials, equipment, and workmen to sites; and hence addition of incurred costs.

iv. For stability, integrity, feasibility and convenience; concrete encasements are ground-based but not aerial-based. This makes application of the method difficult and costly if not feasible when the structure to be protected is very tall and the protection is to be provided at sections of the structure that are high above the ground. This difficulty may exacerbate if the structure is slanted.

v. It is more applicable to immoveable installed structures. Where the steel may be required to discharge stray current to the ground, some form of suitable cost-incurred grounding system must be provided.

vi. Generally the costs involved are very high compared to paint and metallic coatings.

2.4.7.2 *Reinforced bituminous coatings (wrappings)*

The coatings provide excellent protection against corrosion, and are widely used for the encasement of buried steel members in highly corrosive soils such as river bottoms marshlands, cinder fills, fills containing organic debris such as garbage and in tidal regions. Wrappings are particularly used to protect, pipes, the tie rods and fittings that anchor retaining structures, and elsewhere where high-quality long-lasting protection is desired. The coatings have the advantages of impermeability to water, high electrical resistance, good adhesion and resistance to bacteria. They are however, not commonly used for protecting structural steel from atmospheric corrosion, because of higher costs

involved compared to painting galvanizing and metal spraying and somewhat appearance (IIIston *et al*, 1979; Shreir; 1979 and Basalo, 1992).

2.4.8 Corrosion monitoring

The rate of corrosion dictates how long any process plant can be useful or safely operated. Corrosion monitoring refers to corrosion measurements performed under industrial or practical operating conditions. Its main purpose is to acquire data on the rate of material deterioration. A number of different technologies of directly monitoring corrosion are available and include; electrical resistance (ER), linear polarization (LPR), Galvanic, ceion, continuous temperature analysis, continuous chemical analysis, electronic hydrogen analysis, and weight loss coupons techniques. Non-destructive techniques including radiography, ultrasonics, eddy current testing, magnetic particle inspection and dye penetrant inspection are also available and can be used to indirectly monitor corrosion. Each method has its own relative advantages and limitations (Bartholomew, 2003 and Protan, 2014). The overall benefits of corrosion monitoring include (Bartholomew and Shiffler, 2003 and Protan, 2014):

i. Provision of early warnings that damaging process conditions exist, which may result in a corrosion-induced failure or malfunction to enable preventive action to be taken when corrosion rates approach unacceptable levels.
ii. Provision of understanding on the correlation of changes in process parameters and their effects on system corrosivity.
iii. Diagnosis of a particular corrosion problem, identification of its cause and rate-controlling parameters, such as pressure, temperature, Ph, flow rate, etc.
iv. It enables evaluation of the effectiveness of a corrosion control/preventive technique such as chemical inhibition and determination of optimal applications.

v. It provides management information relating to the maintenance requirements and ongoing conditions of a plant.

vi. It is the most common and economical means of ascertaining deterioration of *insitu* structural materials where accessibility is difficult.

vii. It can assist in optimizing maintenance and inspection schedules.

viii. It can be used to apply corrosion control selectively, when and where it is actually needed and use corrosion prevention systems (chemical inhibitors, coatings, resistant materials, etc).

ix. Most of the instruments and techniques used in corrosion monitoring are simple and the skills required to get true results are not much.

Corrosion monitoring however has the following shortcomings:

i. Corrosion monitors are most accurate and effective only when monitoring uniform or nearly uniform corrosion and least effective and accurate in monitoring mechanical phenomena, pitting or localized corrosion, stress corrosion cracking, thermal effects etc.

ii. Most of the techniques used in corrosion monitoring are more reliable and applicable to confined environments or *insitu* materials where the monitored variables do not change appreciably.

iii. For a large part, structure or system, whose corrosion rates are different at different points on it; applying corrosion monitoring to obtain reliable results becomes more tedious.

2.5 Bitumen Coatings in Corrosion Protective Applications

Bitumen is a complex mixture of molecules of a predominantly hydrocarbon nature which vary widely in their composition. They contain amongst others, minor amounts

of heteroatoms containing sulphur, nitrogen and oxygen and trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium which occur in the form of inorganic salts and oxides. The chemical composition of bitumen depends on its natural origin or the nature of the crude oil and the processes used during its manufacture. Besides, elemental composition of bitumen provides little information of what types of molecular structures are present in bitumen. This knowledge is necessary for fundamental understanding of how the composition of bitumen affects its physical properties and chemical reactivity (Srivastava and Van Roijen, 2000).

Bitumen used in most applications is produced by fractional distillation of crude oil and only a small amount comes from natural resources like Tinidad lake asphalt. Usually the distillation is done in two steps. First, the crude oil is heated up to 300-350^{o}C and introduced into an atmospheric distillation column. Lighter fractions like naphta, kerosene and gas oil are separated from the crude oil at different heights in the column. The heaviest fractions left at the bottom of the column are called long residue. The long residue is heated up to 350-400^{o}C and introduced into a distillation column with reduced pressure called vacuum column. By using reduced pressure, it is then possible to further distillate lighter products from the residue because the equivalent temperature that is temperature under atmospheric conditions is much higher. If a second distillation is carried out under atmospheric conditions with increment in the temperature above 400^{o}C, thermal decomposition of the long residue occurs. The residue at the bottom of the column is called short residue and is the feedstock for manufacture of other bitumen grades. The viscosity and other properties of the short residue depend on the origin of the crude oil, the temperature of the long residue, the temperature and pressure in the vacuum column and the residue time. Usually, the conditions are such that short residue is produced with a penetration between 100 and 300mm. Bitumen manufactured from

short residue is called straight run bitumen (Srivastava and Van Roijen, 2000 and Bitumen Suppliers Limited, 2012).

Bitumen occurs naturally within the soil or is synthesized in available variety of grades around the world. Specifications vary to meet the needs of the consuming industries and are based on physical tests that define the safety, solubility, physical properties and durability of bitumens. The physical properties are designed to define performance characteristics that are required under climatic and loading conditions that the bitumen will experience. However, not all grades of bitumen are good for coat-protective applications due to the foregoing discussions.

2.5.1 Grades of bitumen

The principal grades of bitumen are:

i. Penetration or paving grade bitumen. This is the most commonly and widely used bitumen for road engineering and industrial applications. It is essentially the parent bitumen or original form of bitumen from which the other forms of bitumen are produced by further processing to meet better service requirements that take into account different climatic conditions. Penetration grade bitumen (Pen) is divided into Pen 40-50, 60-70, 80-100, 120-150 and 200-300 grades based on bitumen penetration test procedure in accordance with ASTM D5. Each bitumen grade has other distinct properties such as viscosity, flash point, specific gravity, elasticity and/or plasticity, adhesion and cohesion, softening point, weather or oxidation resistance, breaking point, etc; so, their performances are different under the same service application. The differences in properties between high and low penetration grade bitumen are mainly caused by different amounts of molecule structures with strong interaction. Low penetration grade bitumen contains more of these molecule structures. This is

the main reason why their properties are much higher than for high penetration grade bitumens. Pen 40-50 is the hardest grade and is most suitable for application in hotter climates while the Pen 200-300 in cold climates. The hardness of bitumen decreases with increase in its penetration, so the Pen 200-300 is the softest. For service performance by any arbitrary parent bitumen, its properties need to be established for optimally using it.

ii. Cut back bitumen. This consists of short residue (original form of bitumen) that has been diluted in solvent oil such as white spirit, diesel, kerosene, gasoline and gasoil to make it more fluid to reduce its viscosity for applications at ambient temperatures. Cutbacks are classified according to the time it takes for them to cure, or become solid due to evaporation of the diluents. Classifications are rapid curing (RC), medium curing (MC) or slow curing (SC).

iii. Bitumen emulsions. These are dispersions of about 30-80% by bitumen volume in water. Hot bitumen, water and emulsifier are processed in a high speed colloid mill that disperses the bitumen in water in the form of small droplets. The droplets are normally 5-10 micrometres in size range but may be even smaller.

iv. Modified bitumen. These are formulated with additives to the original form of bitumen to improve their service performances by changing such properties as their durability, resistance to ageing, adhesive or cohesive strength, elasticity and/or plasticity.

v. Industrial or oxidized bitumen. This is made by blowing air through hot paving grade bitumen. The process results in harder bitumen that softens at a higher temperature than at which penetration grade bitumen softens. Industrial bitumens also have more rubber-like properties and their viscosities are much

less affected by changes in temperature than is the case with penetration or paving grade bitumen.

vi. Multigrade bitumen. This is chemically modified bitumen that has the properties of hard paving grade bitumen at high service temperatures coupled with the properties of soft paving grade bitumen at low temperatures. In other words, it has properties that span at least two grades. Multigrade bitumens provide improved resistance to deformation and reduce the detrimental effects of high service temperatures, whilst providing reduced stiffness at low service temperatures than exhibited by a similar normal paving grade bitumen.

Bitumen is in most cases not used in its original form, but modified or supported because of certain characteristics of the material (Illston et al, 1979; Hall, 1986). These characteristics include (Jackson and Ravindra, 1996):

i. Its ability to exist in solid, semisolid, or very high and low viscous liquid state; and change its hardness or consistency with temperature. At $20^{o}C$, the viscosities of some types of bitumen range from 10^{3} to 10^{8} Poise depending on the type; compared to water 10^{-2} Poise, diesel 10^{-1} Poise and engine oil 10 Poise.

ii. It's not being mechanically tough enough to withstand much wear or stress.

iii. Its ability to crack under cold weather

iv. Its poor resistance to organic solvents

v. The engineering properties of bitumen are dependent on both temperature, T, and the duration or time of loading t, and of the stress applied, 6. In contrast to many traditional structural materials, such as steel, whose properties are for practical purposes constant, the behaviour of the material under stress varies

from elastic to viscous, according to the condition of stressing. Under stresses of short duration and at low temperatures, bitumen behaves purely elastically, whereas, under conditions when the stress is applied for long periods and/or at high temperatures, the behaviour is purely viscous. Between these two extremes, and this is the range of practical interest for most applications, the behaviour is intermediate or visco-elastic.

One reason that is attributed to all these above characteristics is that bitumen is not well-characterized chemical despite its wide use. The material is a complex mixture of organic and inorganic compounds and their complexes (Jackson and Ravindra, 1996; Usmani, 1997a).

2.5.2 Bitumen coatings

The choice of the coating material to protect steel is dictated by both economics and service requirements. To ensure the integrity of a coating during application, handling and in service, it is essential that it possesses a number of key properties which include: ease of application, strong adhesion to steel, resistance to impact at low temperatures, resistance to flow at low temperatures, negligible water absorption, electrical resistance, chemical stability, resistance to root penetration, resistance to bacterial attack, resistance to marine organisms, resistance to soil stress, resistance to weathering, resistance to abrasion, non-toxicity and cathodic disbondment resistance. These requirements are to a great extent determined by the physicochemical properties of bitumen. As earlier pointed out under section 1.1 of the introduction to this work, bitumen has been in use for protecting steel and other materials from corrosion, and coatings based on it show excellent resistance to industrial pollution. Whilst bitumen itself does not possess any inherent corrosion inhibiting properties, it is effective because of its impermeability to water, oxygen, and other agents of corrosion

promoting agents and stops them from reaching the metal surface. Bitumen is not totally impermeable to the agents for every thickness, but any desired degree of impermeability can be achieved by applying a sufficiently thick layer of hard grade bitumen. Proper engineering principles demand that such a layer must be applied with the understanding of the minimum thickness that is sufficient to completely inhibit corrosion of the substrate steel when using any arbitrary bitumen whose grade is not known. Such thickness can only be obtained by proper tests (Srivastava and Roijen, 2000 and *V Pipe coating.pdf*, 2014).

By adjusting the proportions of the various constituents of bitumen, it is often prepared with sufficient plasticity to prevent cracking under cold weather and a sufficiently low melting point that it may be applied to metalwork by hot-dipping at about 150-200^{o}C. Bitumen is usually coat-applied as enamels. As bitumen is not mechanically tough enough in itself to withstand much wear or stress, it is usually applied by 'hot wrapping' in which a fiberglass swethe is passed through the couldrop of molten bitumen and then wound round the steel or other material to be protected. Inorganic or polymer weaves are not used for wrapping, ordinary sacking or bessian is subject to decay and in so doing creates conditions suitable for both direct acidic attack and bacteria corrosion. This mode of protection is particularly to exterior pipelines both above and below ground level, and by it much thicker coatings can be achieved than is possible with unsupported bitumen. A second technique that is used for producing thick coatings is by the addition of about 30% of inorganic filler such as powdered limestone or asbestos to the bitumen, the resulting composition is known as mastic coatings (Illston *et al*, 1979 and Hall, 1986).

The principal limitation of bitumen is its vulnerability to heat. Many bitumens will soften and creep on inclined surfaces if exposed to strong sunshine and are therefore

unsuitable for applying to pipes carrying hot liquids. They should also be used with caution in conjunction with oil paints, as for example when bituminuous coating might be applied on top of a red lead primer. The reason for this is that chemicals in the bitumen can have the effect of preventing hardening in oil-bound paints and the result may be a failure in adhesion of the combined coating. It should also be noted that bitumen is unlovely in appearance, which often restricts its use to buried metalwork and industrial protection systems in which aesthetic values are not a high priority (Illston *et al*, 1979 and Jackson and Ravindra, 1996).

Bitumens used in the coatings industry are coal tar and asphalt. Although these materials are distinctly different physically and chemically in appearance they are identical black tar materials. Coal tar enamels or pitches, are derived from coking of coal. Asphaltic coatings generally have much greater ultraviolet resistance than coal tar, and therefore, they are suitable for above-grade, atmospheric weathering applications. However, coal tar coatings are vastly superior to asphaltics in moisture and chemical resistance, and so they are used most commonly below grade or in water immersion services (Painting and Decorating Contractors, 1995). Thermoplastic bituminuous coatings are applied as hot melts, solvent curbacks, or water emulsions as described below (Painting and Decorating Contractors, 1995):

i. The hot melt method involves heating the bitumen to a temperature of approximately 177-246^{O}C to reduce viscocity for application. The hot melt can then be applied by mop or swap by brush, roller or spray, or by flow coating of the interiors of pipes and small vessels. In general hot melt applications provide the best moisture and chemical resistance, followed in order by solvent cutback and water emulsions.

ii. The solvent cutback method involves dissolving asphaltic or coal tar bitumen in a suitable aliphatic or aromatic hydrocarbon solvent to lower viscocity for application by spray, brush or roller. The solvent then volatizes and the bitumen resolidifies into a film. The coating thickness and moisture resistance of a solvent cutback generally are less than that achieved by hot melt application, but the convenience of not having to heat the bitumen at the job site immediately before application is a major advantage.

iii. Water emulsions are prepared by suspending minute particles of the bitumen in water using emulsifying agents together with inert fillers, such as coal dust, powdered silica, mica, and limestone dust. After application, the water evaporates and coalescence occurs to form a protective film. Emulsions of both asphalt and coal tar can be applied by brush, roller or spray.

Bitumen water emulsions are VOC-complaint. 'VOC' means Volatile Organic Compound. However some solvent cutback applications may not be VOC-complaint due to the use of solvents. While hot-melt bitumens generally are VOC-complaint, they may release volatile organic compounds into the atmosphere during heating and application. This depends on the type of bitumen and the heating temperature. Furthermore, volatile phenol-containing compounds produced during the heating of the bitumen are considered carcinogenic and skin irritants. Therefore suitable protective clothing and appropriate respirators must be used. Because of their chemical make-up, coal tar and asphalt coatings generally are incompatible and should not be used as mixtures or applied one over the other (Painting and Decorating Contractors, 1995).

2.5.3 Modification of bitumen

To mitigate temperature dependence and other shortcomings of bitumen, it can be modified by many types of polymers, for example, thermoplastics, thermosets, and rubber polymers. Because of cost consideration, polypropylene and styrene-butasdiene-styrene (SBS) modifications find applications in paving and coating. Amorphous polypropylene (APP), a waste by-product in the manufacture of isotactic polypropylene (IPP), was initially used in Europe to modify asphalt for roofing membranes and other applications. The technology is now applied in many countries such as United States of America. Copolymer polypropylene containing 2-10% ethylene has been found to increase clarity, toughness, flexibility, and lower melting points of bitumens. Thermoplastic block copolymers with styrene endblocks and rubber midblocks, for example, butadiene (SBS), isoprene (SIS), and their hydrogenated versions (SEB, SEPS) are common modifiers of asphalt (Usmani, 1997b). Polymer modification of bitumen is achieved by polyblending with rubber polymers, for example, SBS, SEBS, SIS, and ethylene/vinyl acetate/carbon monoxide (E/VA/Co) at 2-5% by weight polymer level in paving applications. For coatings, both rubber and polypropylene modifications are used but at a much higher polymer loading. Typically 11-15% by weight SBS rubber polymer (linear, radial, or combination) or 20-25% by weight polypropylene (APP/IPP or copolymer PP/FPP) based on bitumen is used for coating. Bitumen is also often coordinated with resins such as phenolies, alkyds, urea formaldehyde or polystyrene to increase the strength of bituminous finishes. Such finishes are used for treating the external surfaces of pipelines employed to carry water, gas or oil (Zielinski, 1997 and Usmani, 1997b).

2.5.4 The health question of bitumen

Bitumens are handled and applied at high temperatures, which can be above their flash points, and this present potential hazard from skin burns and inhalation of substances such as sulphur compounds from hot storage tanks. Skin burns should be plunged into cold water and once cooled; no further harm will be done as the bitumen provides a sterile covering until it becomes detached (Jackson and Ravindra, 1996). Bitumens contain compounds which are potentially carcinogenic but the concentrations of these compounds in the bitumens have been found to be negligibly minute and thus do not necessarily constitute a health risk in practice, although appropriate precaution should always be taken (Jackson and Ravindra 1996; Kalinger *et al*, 1997).

The unmistakable odour of bitumen, which can be carried over great distances, may result in a variety of complaints ranging from slight discomfort to mild nausea or feeling ill. The pungency of the odour varies with a number of factors, including the source of bitumen (composition), temperature of the bitumen, ambient temperature, prevailing winds, and the type and condition of the melting equipment. The fumes emitted by bitumen tend to be concentrated at the locations where it is being heated, discharged into carriers, and applied. Unfortunately, current technology for heating bitumen, relying on external heating sources and exhausting fumes into the air, makes its aroma an unavoidable eternality that must be taken into consideration each time they are heated and applied. Complaints from individuals regarding the noxiousness of the fumes, particularly on such sensitive projects as school and health care facilities, have, in some instances, led to costly interruptions, severe restriction to work schedules, and in extreme cases the complete cessation of activities (Kalinger *et al*, 1997).

In response to the above reported complaints and high costs imposed by them on contractors involved in the use of bitumen, a research project was designed to

investigate potential ways of reducing or mitigating the adverse effects with respects to the odour produced while heating the material. The project consisted of laboratory testing and field trials of commercial fragrant compounds to determine their effectiveness in masking the odours associated with heated bitumen. The results of this research indicated that these compounds can be successfully employed to screen the aroma of hot bitumen and reduce the discomfort of individuals who find it offensive (Kalinger *et al*, 1997).

2.6 Some Previous Researches in Relation to Bitumen Treatment

Some of the previous researches on bitumen treatment particularly those conducted using bitumen obtained in Nigeria include works of Ause (2007), Alabi (2009), and Oloche (2001). Ause (2007) showed that bitumen is a suitable austempering medium. The results of his work which investigated the possibility of using bitumen as a quenching medium for austempering steel and ductile cast iron showed that bainite structure was formed when 0.55%C steel, 0.73%C steel, and ductile cast iron were austempered in hot bitumen at 350^{o}C. The hardness values of the austempered 0.55%C steel and 0.75%C steel increased from 200HV to 430HV and from 200 HV to 548HV respectively over the as received samples. The impact strength of the as-cast ductile cast iron also increased from 171 to 291J after austempering in bitumen. Alabi (2009), showed that the wear resistance of bicycle axles can be improved greatly by bitumen treatment. His simulated wear resistance tests of bicycle axles (0.45%C steel material) showed that improvements in impact strength, tensile strength and hardness recorded for the axles austempered in hot bitumen at 290^{o}C for three hours produced optimum values of the mechanical properties of the steel material. Hardness of 496.2HV, impact strength of 149J, and tensile strength of 706.2N/mm^{2} as obtained at the maximum condition were 14.97%, 11.19% and 30.08% higher than the maximum hardness,

impact strength, and tensile strength respectively obtained for austempered samples of the steel in water at 200-500^{o}C. The property values were also 24.52, 4.93 and 25.79% higher than the corresponding values of hardness, impact strength and tensile strength respectively obtained for the as-received steel samples. Result of the wear rate test showed a significant decrease in the wear rate of the bicycle axle's austempered in bitumen at 290^{o}C for three hours as the load on them increased from 4 to 20Kg at an axle speed of 25km/hr for 12 hours. This showed an improvement of about 75% in wear rate over the as-received bicycle axles under similar service conditions. Oloche (2001) studied the effects of three quenching media; air, water and bitumen, on the mechanical properties of mild steel. His results showed that the highest impact strength and hardness values were recorded for samples austempered in hot bitumen at 300^{o}C for two hours (Alabi, 2009).

It is however noteworthy that the results achieved by the researchers are through the heat treatment process method of altering the mechanical properties of the steel material for corrosion resistance. In that regard and in as much as these heat treatment processes involving bitumen treatment can enhance mechanical properties of the steel samples used in the researches and can make the samples better for corrosion resistance, heat treatment processes are costly. This is because of the cost of energy required to heat steel parts or components which may also be heavy and/or awkward, to high temperatures between 850 to 1200^{O}C and maintain them there for about two hours and their handling. Costs of quenchants also contribute to final costs. (Callister, 2004). Therefore, corrosion-protective methods involving heat treatments are not cost-affordable in most cases particularly for mass corrosion protection of structural steels according to Cotterel (1985) and Callister (2004). Furthermore, the austempering time of two hours in the case of Oloche's study is quite uneconomical compared to the

general organic coating and painting time that is usually less than a minute (Illston *et al*, 1979; Hall, 1986). Moreover, the steel specimen used in the researches were heat-treatable or prepared for that but low carbon steel per se is not. Further information obtained shows that in organic coating treatment or painting of steel, the time involved in the processes and the temperatures to which the steel is heated are generally much lower than the time and temperature that can induce any meaningful micro-structural transformation in any steel to alter or enhance its engineered mechanical properties when the steel is cooled to room temperature. Moreover, the temperatures to which the bitumens were heated in the tests by the researchers were all much higher than the 150-250^{o}C temperature values stipulated by Illston *et al* (1979), Hall (1986), and Painting and Decorating Contractors of America (1995) for bitumen-coating steel which also imply higher heating cost for mass treatment.

2.7 Appraisal of Corrosion Damage to a Metal

There are many ways of determining the extent or progress of corrosion. The choice may be determined by either convenience or on the basis of some special interest in a particular result of corrosion or in a particular stage of a corrosion process. These include; determination of corrosion rate, changes in mechanical properties, level of the corrosion produced, and changes in the physical properties of the metal. Whenever changes in mechanical properties such as performance in tension, fatigue and impact tests are to be used as a measure of corrosion damage, it is necessary to provide test data on the relevant properties of the un-corroded metal. When tests extend over long periods during which the metals or alloys being tested may be subjected to changes in mechanical properties due to ageing effects, entirely aside from corrosion, it will be necessary to provide sets of specimen that can be used to remove the effects of ageing from test results (Shreir, 1979b: Bartholomew and Shifler, 2003). In calculating the

strength properties of the corroded metal, the engineering stress-strain analysis which uses the original area and length of the specimen should be used in preference to the true stress-strain analysis since the true strain is of little significance in failure analysis (Raghavan, 1990). In determining corrosion damage to the hardness of a material better results are obtained by properly conducted micro-hardness tests. This is because indenters of micro-hardness testing facilities are more sensitive to even very small changes in hardness of a material in comparison to others. Micro-hardness tests employ principally Knoop and Vickers' tests, but results from Knoop tests are considered more precise than the Vickers' tests (American Society for Metals, 1975).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Procurement of bitumen samples

Since the bitumen content of Nigerian tarsand varies from the topsoil downwards and from place to place (Sheikh, 2003; Federal Ministry of Solid Mineral Development., 2006; *Nigerian Bitumen,* 2011), it is imperative for estimation of material characteristics, to specify the collection points of the natural bitumen samples. Field survey showed that clear natural bitumen can be found in waterlogged or marshland on the surface and underground. Accordingly, the natural bitumen samples were collected only at some of designated points with more or less clearest bitumen deposits. These points are standard drilled extraction holes or clear outcrop deposits in waterlogged areas. Two clear natural bitumen samples for the corrosion tests were collected at Agbabu village after Ore, in Ondo state. The first sample was about seven metres from underground through a standard extraction hole drilled by early explorers for bitumen in 1903 in front of the family house of Chief A.O. Akinyele at Agbabu. The second sample was from an outcrop in a waterlogged area about 10 kilometres from the first sample on the outskirt of Agbabu near Agbabu-Ore road. Both were by courtesy of the village Head of Agbabu. The two samples were assigned identification names Ondo S-B and Ondo S-A respectively. The reason for collecting two samples was to find out whether there are any significant differences between them. Another bitumen sample from 'Short Residue 2', manufactured with the blend of Iran's Basra and Nigerian crudes as feedstock by KRPC was collected at the company courtesy of the Executive Director of the Company. Short Residue 2 is the vacuum residue produced after fractional distillation of the blend. The sample's identification name is 'KPB'. Plate I

shows the sceneries of a scientific expedition to Ondo State and collection of Ondo S-A, and Ondo S-B.

A pipe outlet from the extraction hole

Pipe hole through which the bitumen was extracted



Plate 1a: Inspecting an extraction hole at Agbabu village where Ondo S-B bitumen sample was collected



Various vegetative growths and remains amidst the bitumen outcrop

Bitumen outcrop on the ground surface

Plate 1b: Bitumen outcrop on ordinary sand on the outskirt of Agbabu village



Bitumen as it was hand-collected and lifted up from the waterlogged area

Plate 1c: Collection of a bitumen sample in waterlogged area on the outskirt of Agbabu village

Plate 1: Some sceneries of a Scientific Expedition to Nigerian Tarsand in Ondo State and collection of Ondo S-B and Ondo S-A

3.1.2 Procurement of low carbon steel

Corrosion tests and analysis of the results demand that the specimen materials used should be consistent in micro-structure and chemical composition for easier analysis. The material was procured from the iron and steel market in suitable and available rods of 20mm to 30mm diameter and as-rolled, for machining into the smaller diameter test specimen. 25 steel rods, each over four metres long, were bought from the same supplier in the market in Nigeria. They were personally observed to be rusty-brown typical of low carbon steel material. Discussion with the supplier indicated that the material was imported into the country for general uses. Plate II shows a heap of the procured rods of the steel.



Plate II: A Heap of the As-procured Low Carbon Steel Rods

3.2 Methodology

3.2.1 Determination of the physicochemical properties of the bitumen samples

The physicochemical properties were determined using facilities, methods, and analyses available at the Centre for Energy Research and Training (CERT) of Ahmadu Bello University (ABU), Zaria, the KRPC; and the National Steel Raw Materials Exploration Agency, Malali, Kaduna, Nigeria. The physico-chemical properties were determined in accordance with respective standard methods or procedures of the

Institute of Petroleum London (IP) in conjunction with British Standards (BS) or the International Standards Organization-ISO (Institute of Petroleum London., 1993).

3.2.1.1 *Composition by elemental weight*

The chemical composition of each sample by percentage weight was determined principally using the Instrumental Neutron Activation Analyser (NAA) based on the principle of Molnar (2010) at the CERT. By this analyser, high fluxes of neutron energy from the fission of uranium (^{235}U) produced by the Nigeria Research Reactor-1 (NIRR-1) bombarded the given bitumen sample. The chemical analysis was based on the principle that amplitudes of scattering neutrons do not vary uniformly with the atomic number of each element bombarded. The nuclear energy from the reactor scatters each metallic element to respectively suitably more enriched isotopes which have scattering amplitudes that are different but identifiable according to the proportion of the amount of each element in the bitumen sample. These characteristics were then determined by computerized instrumentation at the Centre to reveal the types and amounts in parts per million (ppm) of some of the chemical elements present in the sample. The results were then converted to percentages of the elements. The NAA method can detect up to only 40 types of elements (Jonah *et al*, 2006 and Molnar, 2010), so other elements that were not detected and are commonly found in various proportions in bitumens such as carbon, sulphur, hydrogen and oxygen were determined using the methods of gas chromatography through KRPC. In principle this was achieved by heating the bitumen samples to a temperature range of $1000^{O}C$. Separately degrading them oxidatively with oxygen. This produced volatile reaction products that contained the elements to be determined among others. The products were carried along an arranged path by helium and processed to remove unwanted products. The wanted products were automatically detected and quantitatively analyzed into

elemental contents of the samples with the Perkin Elmer chromatograph and auxiliary facilities in accordance with Berezkin (2012). If a sample contains carbon, hydrogen, nitrogen, sulphur, etc, its oxidative degradation formula according to Berezkin (2012) can be given as:

$$C_k H_l N_m S_n \text{-------} \xrightarrow{\text{oxidation}} KCO_2 + \tfrac{1}{2} lH_2O + \tfrac{1}{2} mN_2 + nSO_2 \text{----------} \quad (3.1)$$

3.2.1.2 *Flash point*

The tests were conducted in accordance with procedure number IP-36/84 (1989) of the Institute of Petroleum London in conjunction with the British Standards – BS 36,1993 (Institute of Petroleum London, 1993). A test cup, thermometer, and Bunsen burner were used for the experiment. Ondo S-A was poured into the test cup to a standard level and heated at a constant temperature increment rate of 5^0C/min, with the Bunsen burner while periodically passing a small flame across the surface of the bitumen. The flash point was taken as the temperature at which vapour was given off by the bitumen. The temperature at that instance was then determined by reading a mercury-in-glass thermometer inserted in the bitumen bath. The procedure was repeated for Ondo S-B, and then KPB. Plate III shows an instant of the experimental process of determining the flash point in the laboratory.



Plate IIIa: Standard cup used for determining the flash point

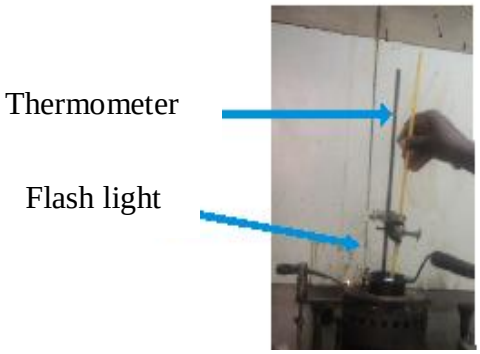


Plate IIIb: Flashing the bitumen as it was being heated in the test cup

Plate III: Experimental Process of Determining the Flash Point of a Bitumen Sample in the Laboratory at KRPC

3.2.1.3 *Penetration*

The tests were conducted in accordance with procedure number IP-49/86 (1989) of the Institute of Petroleum London in association with the International Standards Organization (Institute of Petroleum London, 1993).The method is based on how far a standard needle specified by ISO 683/XIII and Rockwell hardness C54-C60 penetrates vertically into a bitumen sample under standard conditions of load, temperature and time. The conditions are 100g, 25^0C and five seconds respectively. By procedure, Ondo S-A was heated to 75-100^OC to soften it and poured to a depth of 15mm into a cylindrical flat-bottomed glass container. The container was immersed in a bath containing water and maintained at a temperature of 25^oC for 30 minutes. The temperature and time were monitored by an automatic temperature indicator on the bath and a watch respectively. The standard one-millimetre diameter needle with a load of 100g was allowed to touch the surface of the bitumen in the container. The needle was then released to sink under gravity into the sample for five seconds and its penetration

obtained from the indicator scale on the penetrometer. This was repeated with Ondo S-B and then KPB. The overall procedure was repeated twice and the average reading taken in each bitumen case, since penetration is measured in units of 0.1mm. The obtained result in millimeter in each case was divided by 0.1. Plate IV shows an instant of the experimental process of measuring the penetration of a bitumen sample.

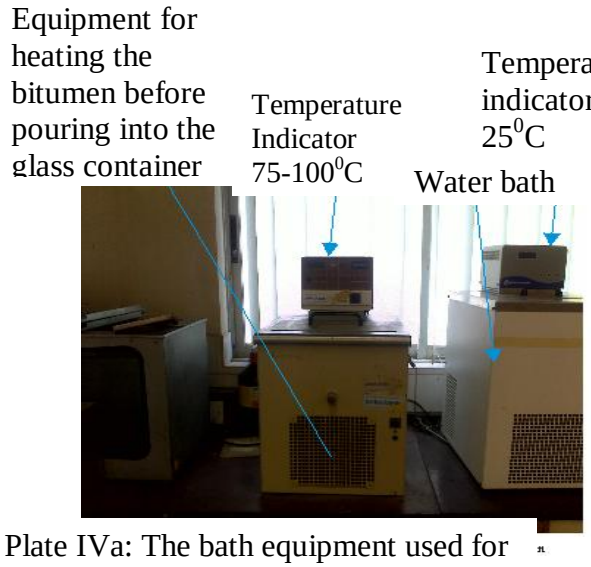


Plate IVa: The bath equipment used for heating maintaining a bitumen sample at 25^{0}C

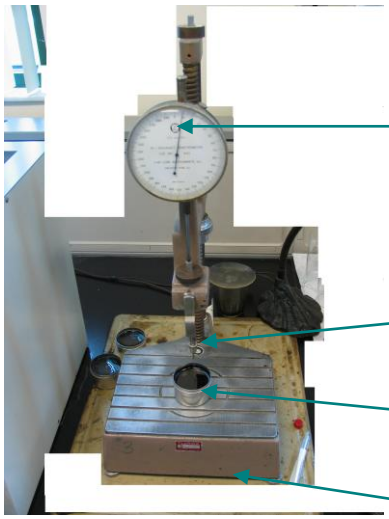


Plate IVb: The digital Setamatic penetrometer used for determining the Penetration of bitumen sample

Plate IV: Process of Measuring the Penetration of a Bitumen Samples in the Laboratory at KRPC

3.2.1.4 *Oxidation or weathering resistance*

Bitumen is known to be vulnerable to high temperatures and these are usually design – avoided in bitumen work. However, large and quick temperature drops from hot to cold weather conditions are particularly known to result in stresses in bitumen and bad cracking of some bitumen work has been noted to be associated with such drops (Bondt and Roijen, 2004). The tests were thus conducted during cold weather to obtain design-meaningful results and in accordance with the procedure used by Mumah and Muktar (2001). A portion, each of Ondo S-A, Ondo S-B, and KPB was heated to 100^{o}C to soften it and simulate its hot weather temperature and poured separately to the same 32.9mm-level into transparent glass containers of similar cross-sectional and volume

sizes. The initial thickness of bitumen in each container at room temperature was noted. The containers were then exposed to the atmosphere at the beginning of very cold weather conditions on a fence top outside the laboratory in February 2009 at the Nigerian Defence Academy, Kaduna, Nigeria. Measurements were made of the thickness of the bitumen in each of the containers every week for a period of five weeks using a vernier ruler graduated in millimeters Plate V shows the glass containers in exposure condition during the test period.

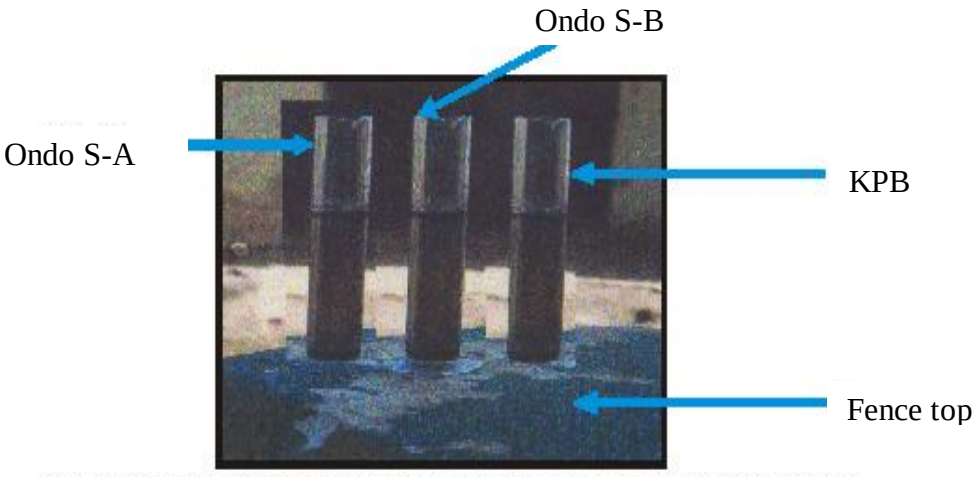


Plate V: Containers in Exposure Condition for the Weathering Test at Nigerian Defence Academy, Kaduna

3.2.1.5 *Softening point*

The tests were conducted in accordance with procedure number IP-58/86 (1989) of the Institute of Petroleum London in conjunction with the British Standards – BS 58,1993 (Institute of Petroleum London, 1993). Ring balls, centering guides and a mercury-in-glass thermometer were used for the test. A portion of Ondo S-A was heated to 75–100^{O}C to soften it, and it was poured into the ring and allowed to cool; so that a flat disc of the bitumen was enclosed completely in the ring. The ring was fitted to an opening on a metal carrier and immersed and maintained in water at a temperature of 25^{0}C for 30 minutes. A standard steel ball of 9.53mm in diameter was placed centrally on top of the bitumen in the ring. The water was then heated at a constant rate until the

ball fell through a standard height of 25mm of the ring. The temperature at that instant was recorded. The test was repeated with Ondo S-B, and then KPB. Plate VI shows an instant of the laboratory process of determining the softening point of a bitumen sample.

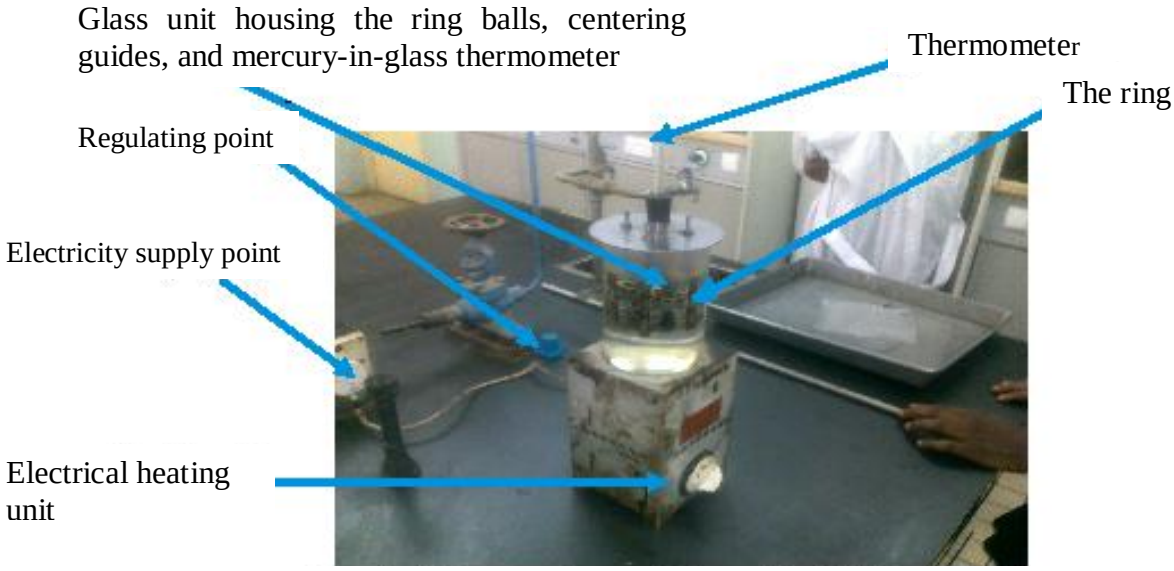


Plate VI: A laboratory process of determining the softening point of a Bitumen sample in the Laboratory at KRPC

3.2.1.6 *Relative density*

A 250-milllitre glass container of internal diameter 75mm, an electronic digital weighing scale, a steel ruler, and a small steel slab that could be contained in the container were used for determining the relative densities of the bitumen samples. By procedure, the slab was immersed in water poured to a 20mm-depth level in the container and the change in volume of water in the container (V_1) determined in cubic centimetres. The container with its contents was then weighed on the scale and its mass (M_1) was noted in grammes. The slab was gently removed from the container and all water on it allowed to drain into the container and wiping it dry with a towel. A small portion of Ondo S-A at 25^{O}C room temperature was detached from the sample and placed on the slab, and the previous procedure was repeated to obtain another volume

(V_2) and mass (M_2). The relative density of Ondo S-A (ρ) was thus determined as (Raghaven, 1990):

$$\rho = \frac{M_2 - M_1}{V_2 - V_1} \qquad (3.2)$$

This was similarly repeated for Ondo S-B and then KPB (Guma, 2014). Plate VII shows an instant of the weighing processes in determining the relative density of a bitumen sample.

Digital scale



Glass container with water and bitumen on the steel slab in it

Plate VII: A weighing process of Determining the Relative Density of a Bitumen Sample at College of engineering, Kaduna Polytechnic

3.2.1.7 *Viscosity*

The Saybolt viscometer is the most commonly used instrument for measuring viscosity, and it provides a means to determine the time for 50ml of a material to flow through a specified orifice at a predetermined and maintained temperature. Baths with different heating capacities including the KV bath by Stanhope-seta of UK model 84000P, serial No.1005582 and the viscometer were used for the test. In using them, a portion of Ondo S-A was heated in a sealed container for three hours at a temperature above the temperature in which the viscosity was to be determined. Care was taken to prevent

local overheating and loss of volatile constituents. It was then allowed to cool to a temperature slightly above the one at which its viscosity was to be determined. After cleaning the viscometer cup with carbon tetrachloride, a cork was inserted in the bottom of the cup and the prepared portion poured into it to such a height that the leveling peg on the bath was just immersed when the bath was vertical. The viscometer was then immersed in the bath under controlled condition of constant bath medium temperature that did not vary more than $\pm 0.01^{o}C$ over the length of the viscometer. The time in seconds it took the bitumen to rise to a standard level of 50ml as indicated by sections in the cylinder of the viscometer was recorded as the viscosity in accordance with procedure number IP-319/84(89) of the Institute of Petroleum London in conjunction with International Standards Organization – ISO 3104 (Institute of Petroleum London., 1993). The bath water was heated with electrical heaters. The viscosity of the bitumen in Poise at $60^{0}C$, $100^{0}C$, $150^{0}C$, and $250^{0}C$ was recorded. This procedure was repeated with Ondo S-B and then KPB samples. The experimental process of determining the viscosity of a bitumen sample is as shown in plate VIII.

Temperature indicator at which the viscosity was determined

The housing bath

Viscometer installed in place in the bath



Plate VIII: A laboratory Process of Determining the Viscosity of a Bitumen Sample at KRPC

3.2.3 Production of the working drawings for each standard specimen type for corrosion-mechanical tests

For reproducibility and appropriate correlation of test results for low carbon steel, specimen for each type of test were designed to be produced in strict adherence to the respective standard or consistent dimensions and profiles. The working drawings of the standard specimen for the ASTM E8 (2004) tension, ASTM E92-82 (2003) fatigue, and ASTM E23 (2005) impact standard test methods for metallic materials were produced in accordance with the standards of the American Society for Testing Materials (ASTM) West Conshocken Pa Vol. 03.01. Each of the hardness specimen was specified to be 25 millimetres in diameter with a flat smooth circular surface and thickness of 8mm in accordance to ISO 4545-1 (2005) and ASTM 384 for Knoop microhardness test of metallic materials (New Standards Enclyclopedia, 2008). The dimensional specifications of each type of the standard specimen are as shown in Figure 3.1.

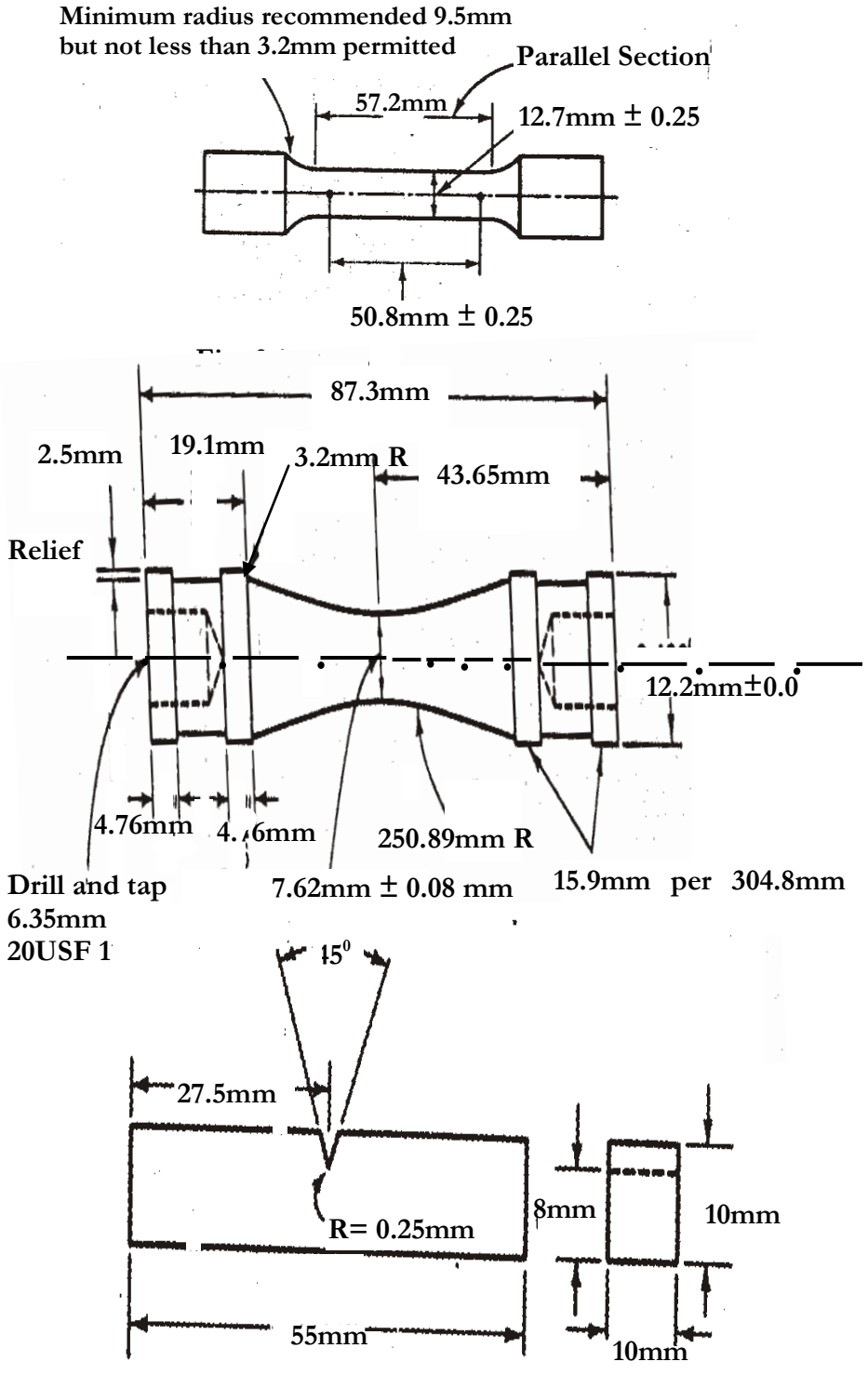


Figure 3.1: Dimensional Specifications of ASTM Standard Tensile, Fatigue and Impact Specimen (New Standards Encyclopeadia, 2008)

3.2.4 Determination of the chemical composition by weight of the steel rods

The chemical composition of steel rods that were found to be similar and consistent in micro-structure typical of a low carbon steel in section 3.5 were determined using the Japanese-made Shimadzu-model-PDA-7000 optical emission spectrometer metal analyzer at the Research and Development Unit of the Defence Industries Corporation of Nigeria (DICON). Three specimen as a set, each 35mm long, suitable for accommodation on the specimen stand of the analyzer were sawn out at three different locations near the ends and the middle of each rod. The rust on each specimen was then brushed off with a polishing paper in order not to include the chemical composition of the rust in the chemical analysis of the specimen. One specimen in a set was loaded on the specimen stand of the analyzer and the equipment was switched on. This created an arc or spark discharge that resulted in vaporization of material from the surface of the steel specimen. The atoms and ions contained in the atomic vapour were excited into emission radiation. The emitted radiation passed to the spectrometer optics via an optical fibre, where it was dispersed into its distinct spectral components that were each the characteristic of a chemical element of the steel specimen. These spectral components were automatically and appropriately analyzed by the designed capability of the integral computer accessory of the unit into percentage elemental weight quantities and the results were printed out by the printer unit. This was repeated with each specimen in the set and for all rod sets. Rods whose elemental chemical compositions were found to have very minimal differences from one another and also from the three locations on the rod were accepted. The minimal range in carbon content of the rods was used for analysis of composition. Any rod whose composition was found to deviate by more than one percent from the rest, even from one result from one

of its specimen was discarded. Plate IX shows the set up for the tests using the analyzer.

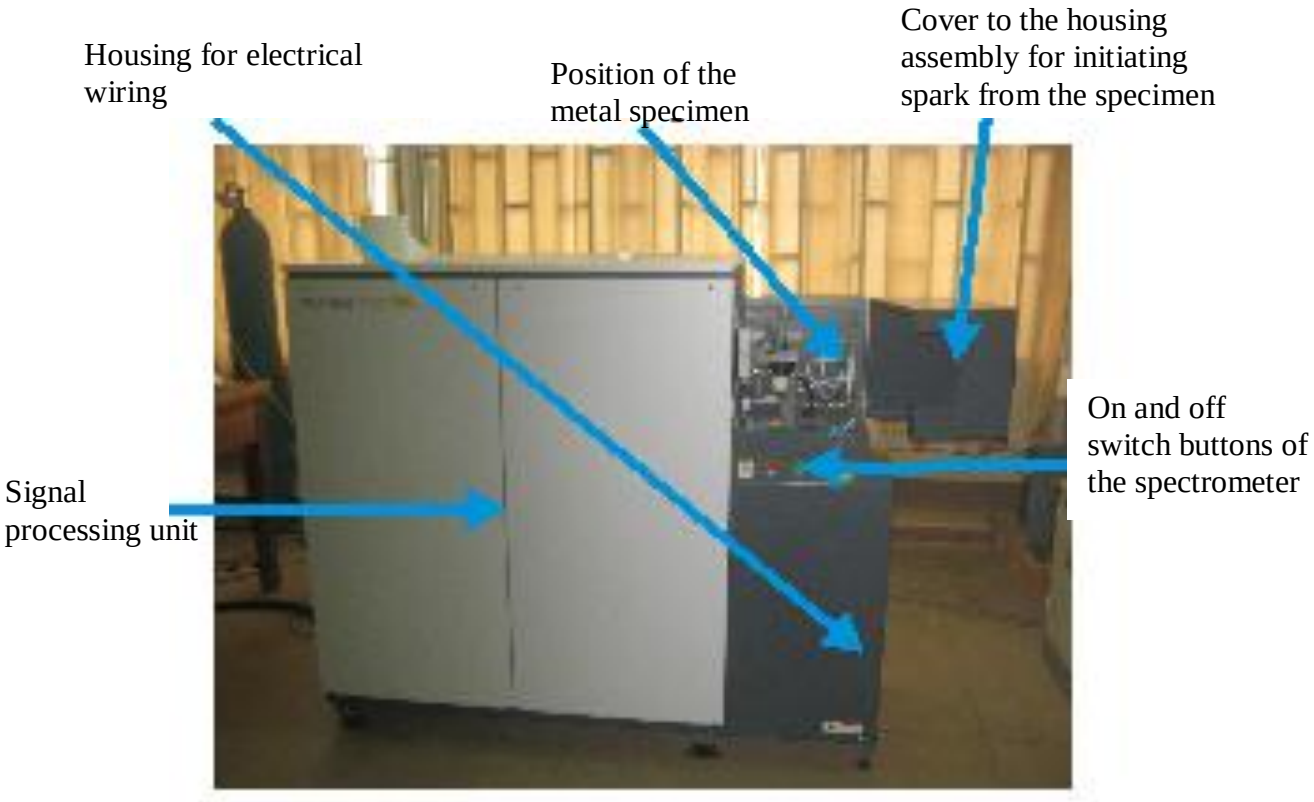


Plate IX: Side view of the Japanese-made Shimadzu-PDA-7000 model optical Emission Spectrometer metal analyzer used to analyze the various elemental weight composition of the procures steel rods at R and D unit of DICON Kaduna

3.2.5 Determination of microstructure of the low carbon steel rods

The microstructures of the low carbon steel rods were determined using a metallurgical microscope in the Department of Metallurgical and Materials Engineering, ABU, Zaria. Procedurally, a representative steel piece of 15mm by 15mm thickness in accordance to ASTM E 408 procedures was machined off near one end of the rod, at the middle and near the other end of one of the procured steel rods (Rajan *et al*, 1997 and New Standards Enclyclopedia, 2008). This was repeated with the remaining rods. Three specimen with identifications as sections A, B, and C were thus produced as a set for the test specimen of each rod. The choice of three specimen was to find out if there

were significant microstructural variations within each rod and among the rods. Each specimen was then machine-polished using polishing paper grades 250 and 300 in that order and finishing with grade 400 paper. After scratches down to the fine grade of 400 were removed, each specimen was cleaned and then polished by rubbing it on soft moist velvet cloth with fine alumina polishing paste to a mirror finish. This produced a smooth but a smeared surface layer which was removed by etching for 10-30seconds in nital (2ml nitric acid in 98ml industrial alcohol). Each specimen was then subjected to a magnification of 200 using the microscope in accordance with magnification stipulation of between 20 times and 2000 times for micro-examination. The micro-structures accessed by the microscope were then processed and printed out by the computer accessory of the microscope. The process was carried out in accordance with ASTM E 408 procedure (American Society for Metals, 1975; Rajan *et al*, 1997; Khanna, 1999 and New Standards Enclyclopedia., 2008). Any rod whose specimen microstructure was observed to deviate from the rest even at one of its sections was discarded. Some of the prepared specimen and the set up for their micro-examination in the laboratory are shown in Plates X and XI respectively.



Plate X: Prepared set of specimen for micro-examination

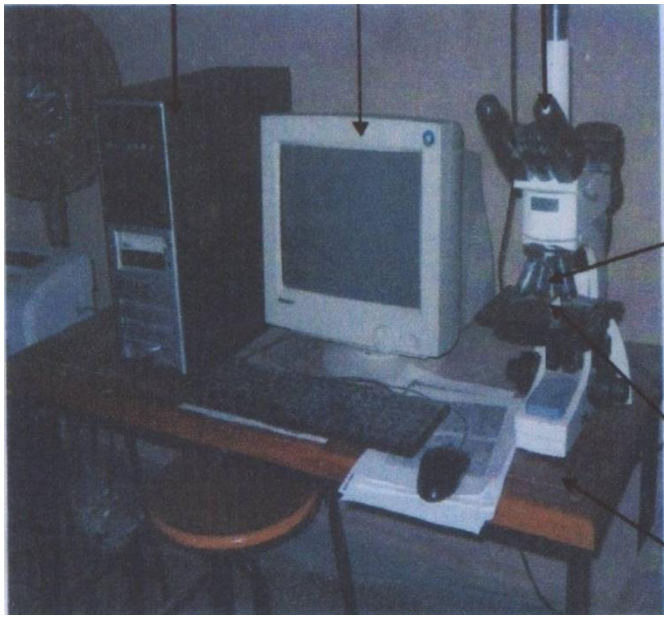


Plate XI: Setup process for micro-examination in the materials laboratory of the Department of Metallurgical and Materials Engineering, ABU Zaria

3.2.6 Production of specimen for tests

The types of specimen as specified in section 3.4 were machine-produced using facilities in the Department of Mechanical Engineering ABU, Zaria. Each type of specimen was produced by first turning a piece out of the procured low-carbon steel rods on the engine lathe to the desired overall size and dimensions required for the specimen. The shoulders of each tensile specimen where then mill-finished while the

notch on each of the impact-test specimen was produced using a special milling cutter. The hardness specimen were produced by sawing out suitable pieces out of the rods, properly facing the ends of each piece and turning it down to 25mm diameter using the lathe. The numbers of the different types of specimen produced are as shown in Table 3.1, while Plate XII shows the processes of machine-producing the specimen.

3.2.6.1 *Fatigue specimen*

The ASTM E92-82 fatigue specimen shown in Figure 3.1 has a curved shape at its middle so it was not possible to produce it conventionally on the ordinary engine lathe. The specimen were each first produced as initial workpieces on the ordinary engine lathe from the procured rod stocks. Their ends were properly faced to their overall accurate cylindrical shape of length 87.3mm and diameter 12.5mm. A hole of diameter 6.35mm and depth 14.34mm was drilled longitudinally and tapped at the end of each specimen. The specimen dimensions were ascertained using a vernier calliper, a depth gauge and a micrometer. This was carried out in the production laboratory of the Department of Mechanical Engineering, ABU, Zaria. A copying engine lathe that was available in the same laboratory was used to produce the curved section of the ASTM E92-82 specimen from the prepared workpieces. A master or template that was the replica of the size and shape of the ASTM E92-82 fatigue specimen was used on the copying lathe to machine into shape the curved section. The template was previously produced in London, England by numerical machining. The copying lathe had provision for accommodating any desired suitable template. The template or master fatigue specimen was fixed into position on the lathe. The workpiece produced on the ordinary lathe was held into the chuck of the copying lathe. Electrical power supply for operation of the lathe and hydraulic control system were switched on. This caused the template to rotate and actuate a hydraulic control system via kinematic linkage with a

tracing follower of the system. The hydraulic control system which was an integral structural component of the lathe regulated the servovalves of the system and caused the system to move the tool slide to move the turning tool on it in a programmed and coordinated fashion whilst the tool turned the middle of the workpiece into the desired profile. Small feeds and depths of cut were adjusted from time-time within the length of 49.1mm at the middle of each specimen. Measurements were frequently taken across diameters within the length with a vernier calliper and compared with the diameters of another ASTM E91-82 fatigue specimen that was also previously produced by numerical machining. This continued for the length until the correct profile and dimensions of the section were achieved on the workpiece in accordance to ASTM E92-82 fatigue specimen.

Table 3.1: Number of Specimen Produced for the Mechanical Tests with Bitumen Samples

Type of Test	Tensile	Fatigue	Impact	Hardness	**Total**
No of specimen	90	450	90	90	**720**

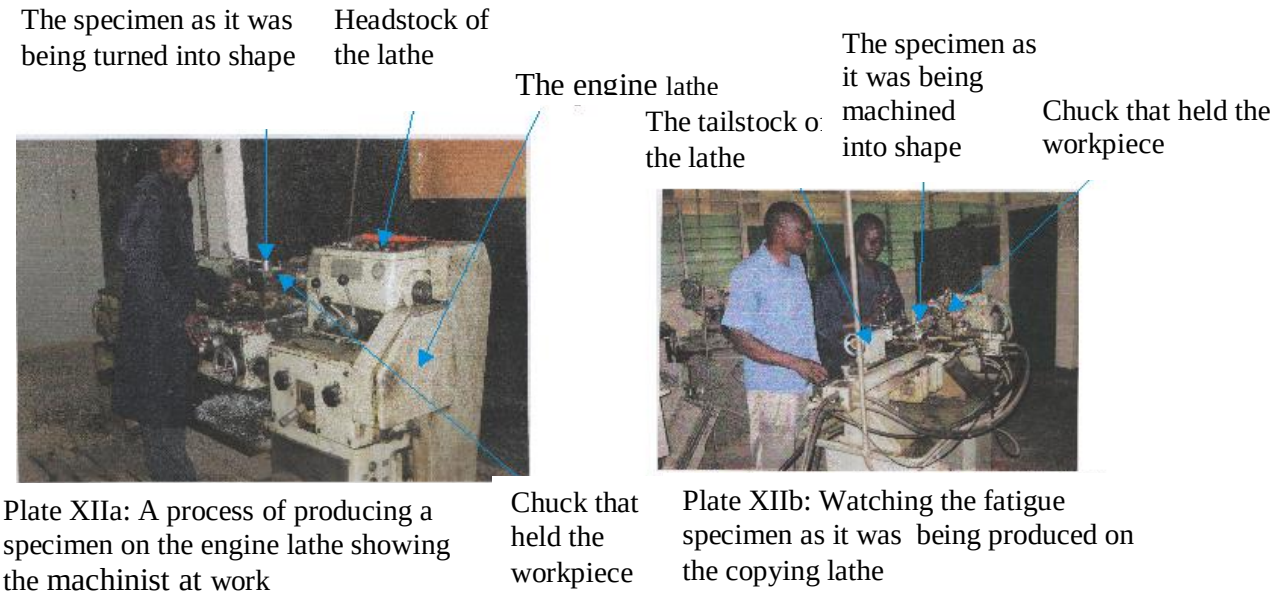


Plate XIIa: A process of producing a specimen on the engine lathe showing the machinist at work

Plate XIIb: Watching the fatigue specimen as it was being produced on the copying lathe

Plate XII: Facilities Used to Produce Different Types of Specimen in the Production Laboratory of the Department of Mechanical Engineering, ABU, Zaria

3.2.7 Polishing the specimen

The exercise was carried out using polishing papers of grades 200 to 400 in the Department of Mechanical Engineering, Nigerian Defence Academy (NDA) and the Airforce Institute of Technology (AFIT), Kaduna, Nigeria. Each specimen was machine-polished with various grades of polishing paper under similar conditions. After scratches down to a fine grade (400 grade paper) were removed, each specimen was cleaned and then polished by rubbing it on a soft moist velvet cloth with fine alumina polishing paste to a mirror scratch free finish. This produced a smooth surface but a smeared surface layer which was removed by etching for 10-30 seconds in nital (2ml nitric acid in 98ml industrial alcohol). The process was carried out in accordance with ASTM E 408 procedure of preparing specimen for corrosion tests (Rajan *et al*, 1990; Khanna, 1999 and New Standards Enclyclopedia., 2008). Plate XIII shows some of the polish-prepared specimen for the different types of mechanical tests.



Plate XIIIa: Tensile

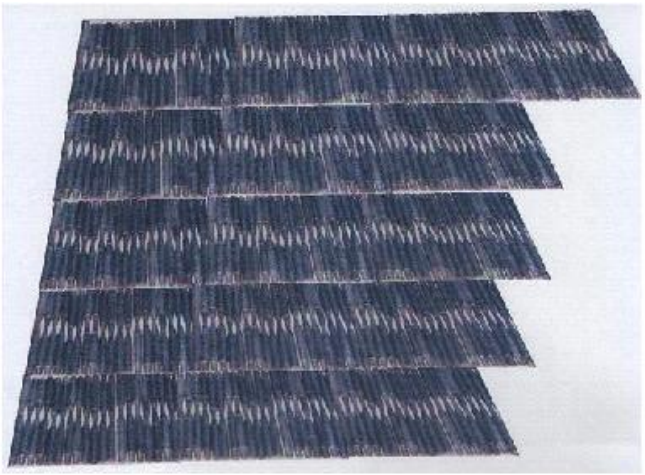


Plate XIIIb: Fatigue specimen



Plate XIIIc: Impact specimen



Plate XIIId: Micro-hardness specimen

Plate XIII: Heaps of polished specimen for the various types of test of the mechanical properties at Airforce Institute of technology Kaduna

3.2.7.1 *Surface finish assessment*

Each polished specimen was checked for uniformity in surface finish using a profilometer available in the Department of Mechanical Engineering Ahmadu Bello University, Zaria. The profilometer was used to determine and compare the surface finish of the specimen at several points to find out whether there was any variation in the surface finish of the specimen. Any specimen whose surface finish was found rougher in relation to those whose finishes were considered satisfactory was re-polished and re-measured until it was ascertained satisfactory. The results obtained with each specimen were averaged and compared with one another to find out whether there was also any variation in the surface finishes among the specimen that were expected to have similar surface finish. The result showed an overall average surface finish of 25 microns for 720 specimen and with minimal variations of less than 0.2% on and among the specimen. Plate XIV shows the process of checking the surface finish of a polished specimen with the profilometer.

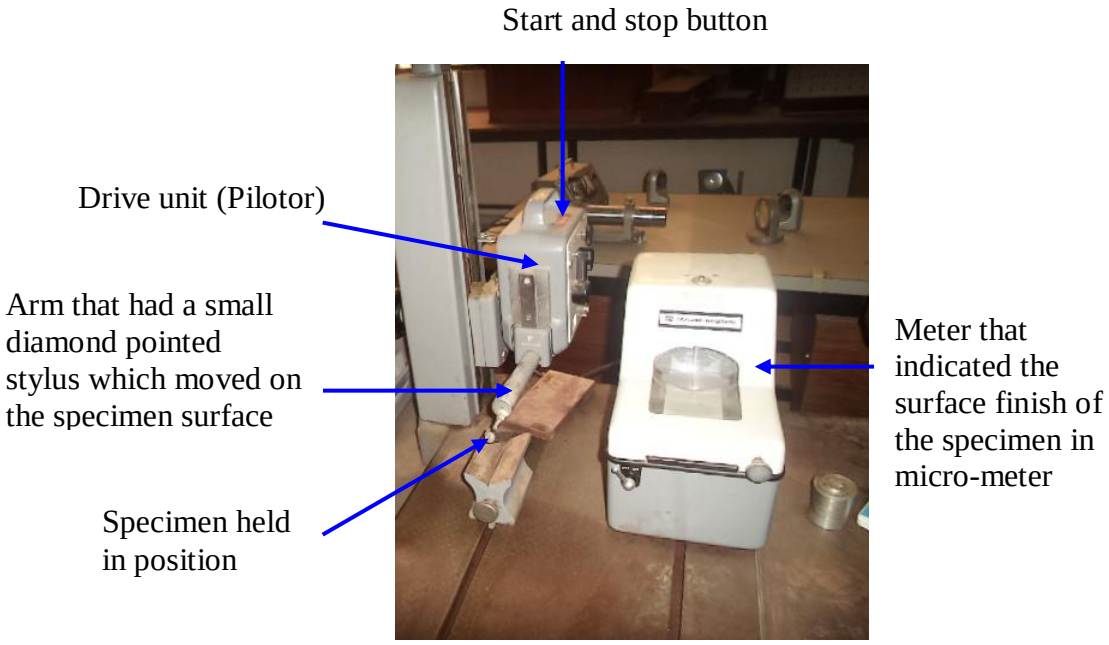


Plate XIV: An Instant of checking the surface finish of a hardness specimen in the laboratory at the Department of Mechanical Engineering, ABU, Zaria.

3.2.8 Normalizing heat treatment

Each specimen for each type of mechanical test was normalized to relieve it of any machining stresses to its as-procured material status by heating it through the eutectoid transformation temperature (800^0C) which is 50^0C into the single phase austenistic field; holding it there for one hour to dissolve its cementite and disperse its carbon uniformly and then cooling it in air to room temperature; in accordance with procedures used by Cotterel (1985), Rajan *et al* (1990) and Alabi (2009). The specimen were heated in sets under similar conditions. Each set consisted of all specimen of the same type and crucible tongs were used to handle the specimen in the heating process. The holding time was monitored using a watch. The process was carried out at the National Metallurgical Development Centre, Jos, using a tubular heat treatment furnace. The normalizing temperature was pre-determined at 800^0C and set on the furnace. Plate XV shows an instant of the process of normalizing the specimen with the tubular furnace.

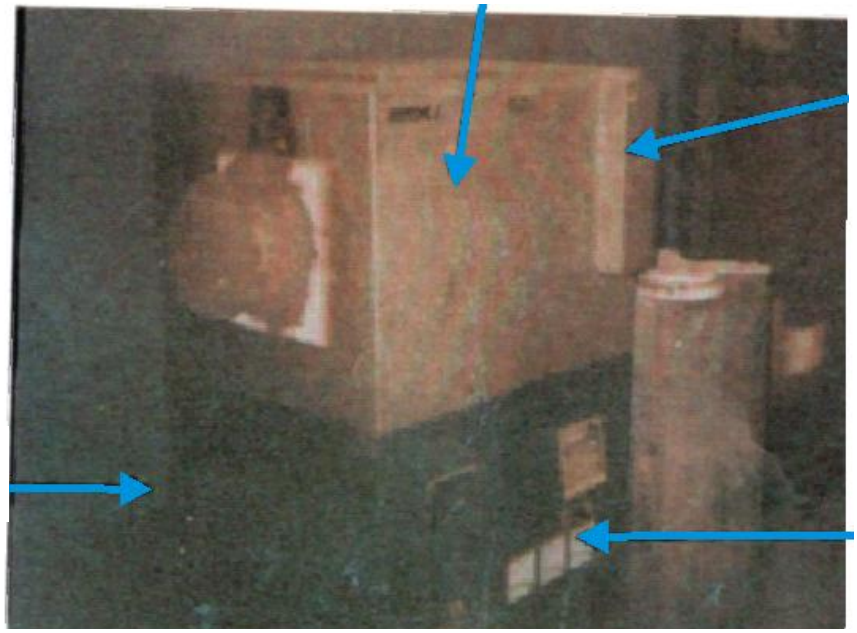


Plate XV: The tabular heat treatment furnace used for the normalizing process at the National Metallurgical Development Centre, Jos

3.2.9 Design of accelerated corrosive condition for steel specimen

Personally monitored information from daily forecasts of weather around the globe through the Cable Network News (CNN) television over the last seven years shows that the average global room temperature is about 25^0C and the highest outdoor temperature anywhere around the globe is about 60^0C. The corrosive environment was designed and used at a determined average prevailing room temperature of about 38^0C with a thermometer at Kaduna Polytechnic, Kaduna, Nigeria, and an aerating pressure of 0.0158 bars above one atmosphere. An overall corrosive medium of 30% NaCl+5% concentrated H_2SO_4 +air of 100% relative humidity at 38^oC under continuous aeration and circulation was used for specimen exposure. The medium was designed to simulate the corrosive factors of the tropical atmospheric acidic surf beach environment of 100% relative humidity with a high factor of aggressiveness in accordance to Shreir (1979b) and Johnson (2001). Most accelerated corrosion tests last between 7 and 30 days. For performance evaluation of organic coatings the timescale is higher, usually from 35 to 50 days depending on the type of test, specimen, coating and aggressiveness of the corrosive medium used (Pludek, 1977; Khanna, 1999; Bartholomew and Shifler, 2003). The test exposure duration for a set of given specimen for each of the mechanical tests was thus chosen to be 50 days. All specimen were held in the vertical position and the corrodant circulation was in up and down movement with accessibility to the specimen's entire surface in accordance to Barthlomew and Shifler (2003).

3.2.10 Bitumen-coating of the steel test specimen

The coating treatment was carried out using a 20kg gas-fired heating unit, a steel container, a thermometer, and crucible tongs. It was accomplished by a bath-dipping process of applying bitumen coatings (Illston *et al,* 1979; Hall, 1986). Ondo S-A was heated first in the steel container to a temperature of 150^oC. A mercury–in-glass

thermometer with a maximum temperature of 360^{o}C was used to monitor the temperature. Two pairs of specimen for each of the four types of mechanical tests were each separately dipped at the same time in the bitumen bath for 30 seconds, and then withdrawn and allowed to cool to room temperature in accordance to Illston *et al* (1979) and Hall (1986). A thin-lip crucible tong was used for grip-handling each specimen on its head. Eight assistants were engaged, each to handle a specimen. For the same temperature, this was repeated for a set of eight fatigue specimen. The bath temperature which was monitored by a thermometer was raised in five steps up to 230^{0}C by increasing the duration of heating or adjustment of the control valve of the heating unit to burn more gas. In each step, the same process of dipping and withdrawing was repeated for eight fatigue specimen. This produced more or less similar uniform thickness of coatings that were observed to have good adhesion on specimen treated at the same temperature, but different thicknesses among those at different temperatures of treatment. The overall procedure as described here for Ondo S-A was similarly repeated using Ondo S-B and then KPB. The temperatures chosen for coating the specimen were all in the range of 150-246^{o}C recommended by Illston *et al* (1979); Hall (1986); and Painting and Decorating Contractors of America (1995) for heating and applying most bitumens. Table 2.2 shows the total number and types of specimen prepared for each bitumen sample, while Plate XVI shows an instant of coating the specimen. The tensile specimen were coat-treated in a day followed by the impact and micro-hardness specimen. 10 fatigue specimen on different days at five-day intervals. This was to avoid handling large number of specimen at a time during corrosion and tests of their mechanical properties.

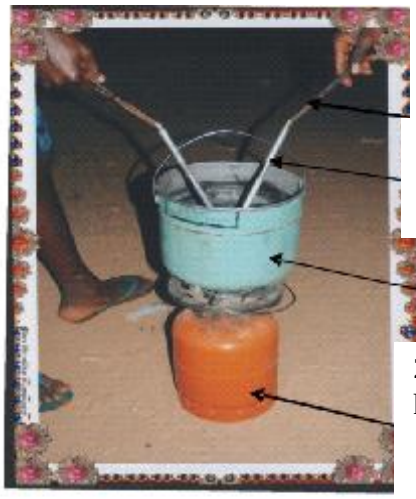




Plate XVI: An Instant of Bitumen-coating Process Showing a Five-set Coat-treated Fatigue Specimen of the same Coating Thickness

Table 3.2: Total Number of Test Specimen Prepared for the Accelerated Corrosion Tests

Bitumen Sample	Type of Test	UU	UC	TU	TC	**Total**
Ondo S-A	Tensile	4	2	12	12	**30**
	Fatigue	20	10	60	60	**150**
	Impact	4	2	12	12	**20**
	Micro-hardness	4	2	12	12	**30**
	Tensile	4	2	12	12	**30**
	Fatigue	20	10	60	60	**150**
Ondo S-B	Impact	4	2	12	12	**30**
	Micro-hardness	4	2	12	12	**30**
	Tensile	4	2	12	12	**30**
	Fatigue	20	10	60	60	**150**
KPB	Impact	4	2	12	12	**30**
	Micro-hardness	4	2	12	12	**30**
Total		**96**	**48**	**288**	**240**	**720**

Table 3.3: Number of Specimen Coat-treated with each Bitumen Sample and Different Temperatures for the Specified Status of Corrosion and Mechanical Tests

Tensile test							
Temperature of treatment (^oC)		150	170	180	200	220	230
Ondo S-A	TC	2	2	2	2	2	2
	TU	2	2	2	2	2	2
Ondo S-B	TC	2	2	2	2	2	2
	TU	2	2	2	2	2	2
KPB	TC	2	2	2	2	2	2
	TU	2	2	2	2	2	2
Fatigue test							
Temperature of treatment (^oC)		150	170	180	200	220	230
Ondo S-A	TC	10	10	10	10	10	10
	TU	10	10	10	10	10	10
Ondo S-B	TC	10	10	10	10	10	10
	TU	10	10	10	10	10	10
KPB	TC	10	10	10	10	10	10
	TU	10	10	10	10	10	10
Micro-hardness test							
Temperature of treatment (^oC)		150	170	180	200	220	230
Ondo	TC	2	2	2	2	2	2
S-A	TU	2	2	2	2	2	2
Ondo	TC	2	2	2	2	2	2
S-B	TU	2	2	2	2	2	2
KPB	TC	2	2	2	2	2	2
	TU	2	2	2	2	2	2
Impact test							
Temperature of treatment (^0C)		150	170	180	200	220	230
Ondo	TC	2	2	2	2	2	2
S-A	TU	2	2	2	2	2	2
Ondo	TC	2	2	2	2	2	2
S-B	TU	2	2	2	2	2	2
KPB	TC	2	2	2	2	2	2
	TU	2	2	2	2	2	2

UU = Un-treated with bitumen but un-corroded, UC = un-treated with bitumen but corroded, TU = Treated with bitumen but un-corroded, and TC = treated with bitumen and corroded.

The use of the UU specimen was to separate any natural aging effects in the steel specimen due to time lapse from the day the specimen type were produced to the end time of accelerated corrosion of other specimen of the same type, while that of the TU specimen was to determine if the bitumen itself, the coating process and the time lapse after coating and testing had effects on the mechanical properties of the specimen, so as

to separate them from those of the test corrosion during analysis of results. Testing fatigue endurance of a metal of the same dimensional specification generally takes longer time than the case of its other basic mechanical properties (Selby, 1989). Therefore only 10 fatigue specimen were coated on different days for sequential testing their fatigue endurances. The details of the number of specimen treated with each bitumen sample at various temperatures for the specified status of corrosion (TC or TU) and mechanical tests are as shown in Table 3.3.

3.2.10.1 *Determination of the working bitumen coating thickness on specimen*

Determination of working coating thickness is a complicated task in the product finishing field. This is because coatings are generally discontinuous with different defects such as porosities, segregations, holidays, and thinned areas; and the substrate itself may not be flat and straight with parallel edges but characterized with curved surfaces. Moreover, the nature of the surface-roughness interface between the coating and the substrate can also affect the repeatability of coating thickness measurements (Von Fraunhoffer, 1975 and *Coating Thickness Measurement,* 2012). The working thicknesses of all bitumen coatings produced on the steel specimen were determined statistically with measurements obtained through the method of dimensional change with a micrometer in accordance with Von Fraunhoffer (1975) using two specimen coatings for each bitumen sample. This was achieved by first determining the diameter of a given untreated specimen type at 10 different mapped out sections along its length perpendicular to its axis using a steel ruler and micrometer and finding the average diameter, and repeating this procedure at similar sections after coat-treating the specimen at a given temperature and allowing them to cool to room temperature. The average coating thickness of treatment at a given temperature on a specimen was then taken as the difference between the two averages and the working thickness was taken

as the overall average of all average coating thicknesses achieved on different specimen at the same temperature with all the bitumen samples. A steel ruler, a depth gauge and a hand-held outside micrometer with a measuring range of 0-13mm, main pitch of 0.005mm, and minimum resolution of 0.01mm was used for the exercise (Micrometer, 2012).

3.2.11 Accelerated corrosion tests

Each test was conducted using a corrosion studies kit and digital weighing scale available at the College of Engineering, Kaduna Polytechnic. The corrodant was prepared by dissolving 461.5385 grammes of sodium chloride in 1000cm^3 of water, and mixing the solution thoroughly using a hard wooden rod. 76.923 grammes of concentrated sulphuric acid were added to it to get the overall corrodant of 30% NaCl + 5% concentrated H_2SO_4 + 65% water (100% relative humidity). The kit has an air compressor that was operated to supply air at a constant pressure of 0.0158 bar through similar small plastic hoses that could each be immersed in the corrodant contained in transparent containers in which the specimen are properly placed. The kit had 10 similar work stations and 10 similar plastic hoses each for a container. One container was found to be capable of containing up to 60 fatigue specimen and 120 of each of the tensile, impact and hardness specimen at a time. It had the advantage that once the air was compressed by the compressor and stored, it would continue to function as desired up to a week when in use, even if there was no electricity supply to power it. The desired pressure can also be observed or read directly from the pressure gauge of the compressor. In using the kit, the prepared overall corrodant was poured almost to the brim into suitable transparent containers into which the specimen to be corroded had been carefully placed. The containers had some shallow circular depressions of 10 to 12mm in diameters around their bottom cavities in which small quantities of araldite

adhesives where smeared to facilitate slightly stick-holding the specimen at their bottoms to keep them in vertical position during corrosion. A suitable cover plate to each container had six uniformly spaced perforations around it, and close to its edge was part of the kit accessories. Through the centre of the plate, a plastic hose passed to supply air from the compressor to the container as shown schematically in Figure 3.2. By this, air from the compressor bubbled through the corrodant and caused it to move slowly in an up and down fashion over the specimen, washing continuously and uniformly the specimen in simulation of their exposure to natural atmospheric conditions. In this way each set of specimen in the container was allowed to rust continuously from the days they were coated for 50 days as designed. Plate XVII shows an instant of accelerated corrosion of the specimen with the kit. At the end of the corrosion they were carried in the containers in which they were corroded to test locations. Each specimen was held on its head with a thin-lip crucible tong and removed, hand-held, loaded into position on the appropriate testing machine and tested accordingly with the coating on it in accordance to Shreir (1979b) and Johnson (2001). Rubber gloves were worn on hands during handling. A dry towel, bristle brush, hypo detergent, kerosene, and carbon disulphide were used to clean off bitumen that got stuck to the machine frames, specimen-holding chucks and parts of specimen to be held before and after each test.

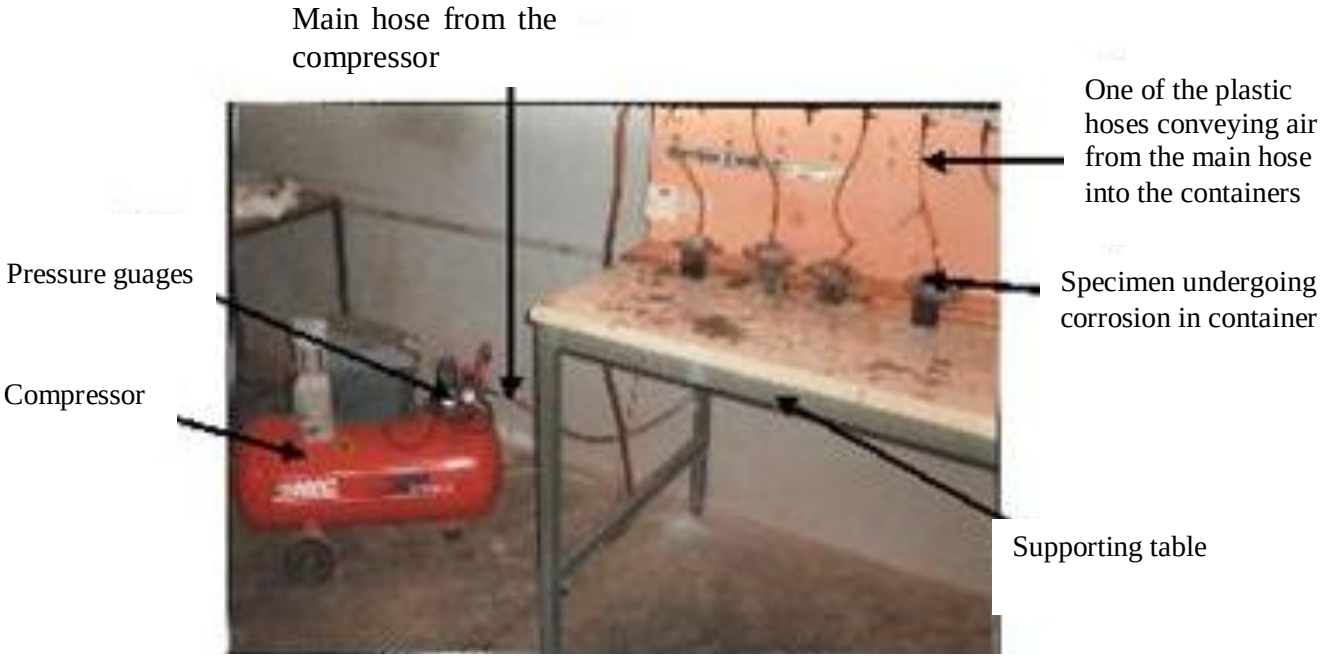


Plate XVII: An instant of experimental set-up arrangement showing corrosion in progress in the laboratory at College of Engineering Kaduna Polytechnic, Kaduna

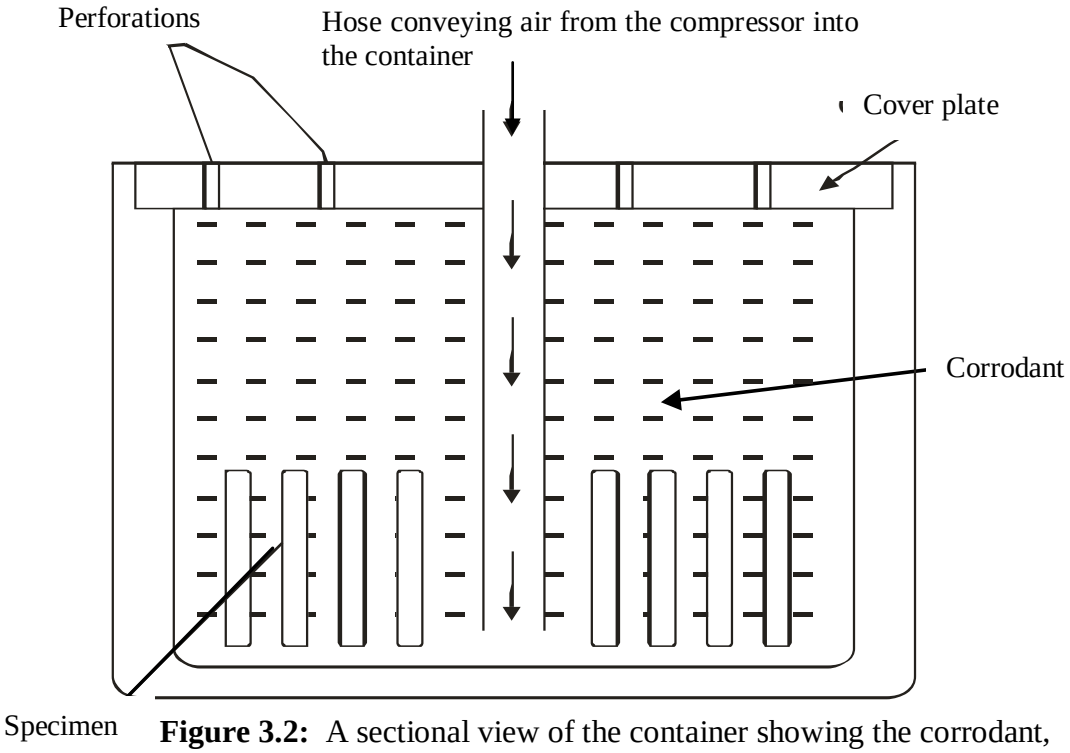


Figure 3.2: A sectional view of the container showing the corrodant, specimen and the air-conveying hose

The experiments on mechanical properties of the specimen were conducted in the Strength of Materials Laboratories of the Departments of Mechanical, and Metallurgical and Materials Engineering, ABU, Zaria; and the Airforce Institute of Technology, Kaduna, Nigeria. In each experiment, data was collected for specimen of indicated status of treatment and corrosion: UU, UC, TU, and TC. For each mechanical property and bitumen coating thickness used, the obtained data was used to determine the effects of corrosion by changes in properties of the corroded steel specimen relative to the un-coated and un-corroded specimen. The different types of tests conducted were tensile, fatigue, hardness and impact tests.

3.2.12 Test of mechanical properties

3.2.12.1 *Tensile tests*

The tensile test was conducted at room temperature using the Hounsefied tensometer manufactured by Tensometer Limited of England. Each tensile specimen of known status of bitumen treatment and or corrosion was slowly subjected to increasing force until fracture occurred. The load and extension were recorded automatically by the tensometer on special graph paper. The plot on the graph paper was used to obtain each load and converted it to stress by dividing the load by the initial cross sectional area over which it acted. The corresponding strain was obtained by dividing the change in length by the initial gauge length. The data was used to plot stress-stain relationship appropriately for each specimen up to the ultimate tensile stress of the specimen. Two of the four un-treated and un-corroded (UU) and TU specimen were tested two months earlier, immediately after machining and normalizing the specimen and the other two along with the remaining specimen in order to know the effects of ageing on the specimen and separate them from those of the accelerated corrosion. The tests were conducted on the same day. Plate XVIII shows the set up for the tensile tests.



Plate XVIII: Top view of the set-up arrangement on the tensometer with a test specimen in the materials laboratory of the Department of Mechanical Engineering, ABU, Zaria

3.2.12.2 ***Fatigue tests***

Fatigue tests were used to investigate effects of each bitumen coating treatment on the fatigue strength of UU, UC, TU, and TC specimen which were subjected to repeated applications of chosen small cyclic loads which were individually incapable of producing detectable plastic deformation until they caused the specimen to fracture. Each load was chosen above the endurance limit of low carbon steel, which is about 230N/mm^2 as given by Selby (1989); in order for fatigue failure to occur. A pair of the five-set un-treated and un-corroded (UU) and the treated but un-corroded (TU) specimen were tested four months earlier immediately after machining and normalizing the specimen or bitumen-coating them as the case was and another pair in each case immediately after the last set of 10 TC specimen were tested so as to separate any effects of ageing on the specimen from those of the accelerated corrosion during

analyses of test results. The endurance of one specimen in each five-set was tested with a cyclic stress of 250N/mm^2. The number of cycles to failure in each case was recorded automatically on the machine. This procedure was similarly repeated using four different stresses of 275, 300, 325 and 350N/mm^2 with the remaining specimen of each five-set. In testing the endurance of a specimen, one end of it was screwed-joined and secured to the end of a small protrusion of the power shaft from the motor and frame of the testing machine on the right hand side, so that the specimen was like a cantilever from the frame as shown in Fig. 3.3 and Plate XIX.

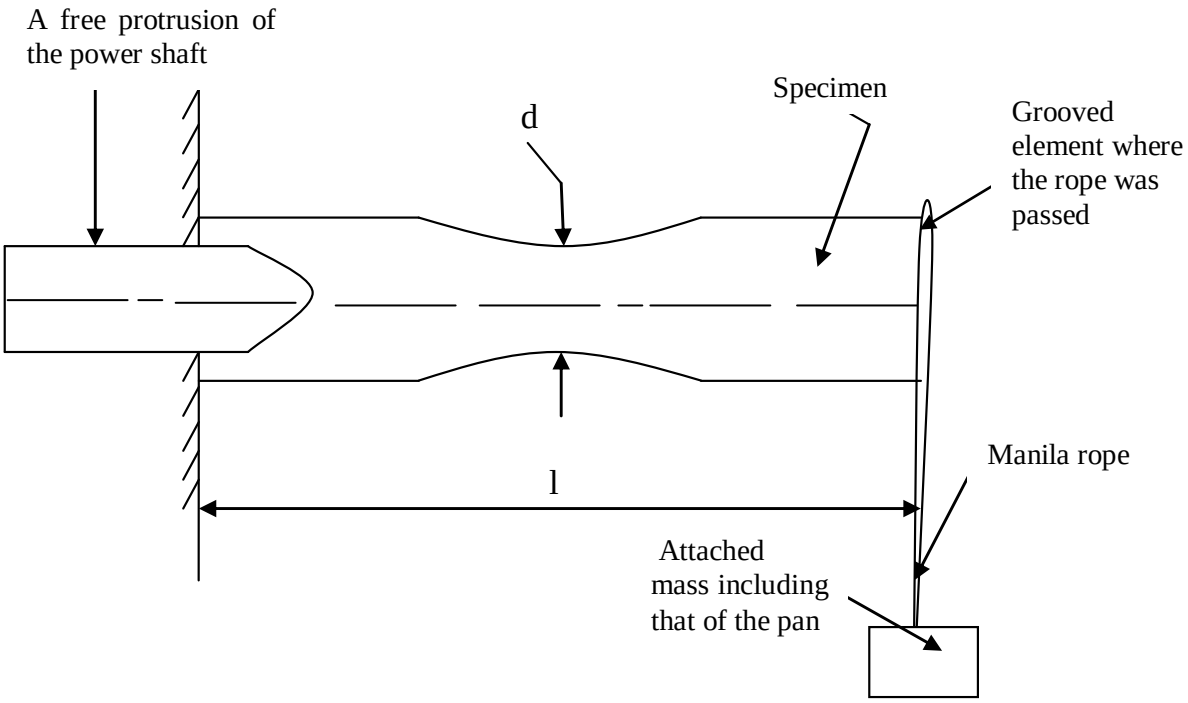


Figure 3.3: A sketch of the specimen loading for the test

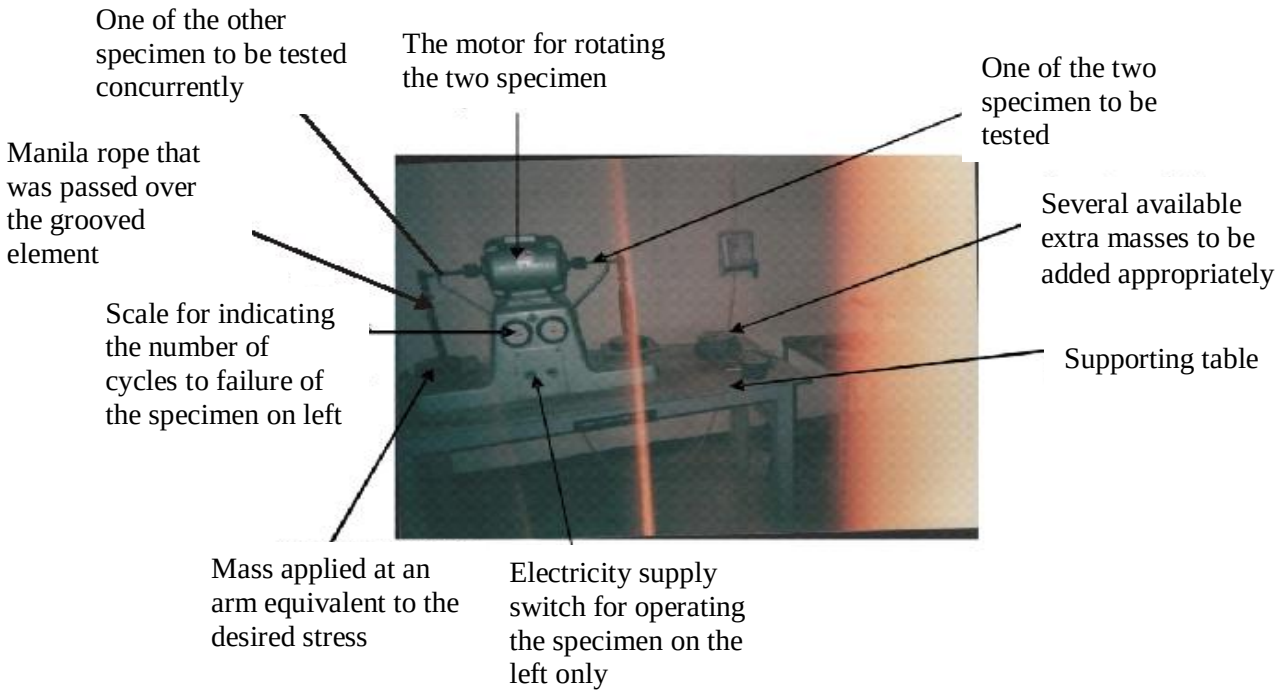


Plate XIX: Set-up Arrangement for fatigue-testing of prepared specimen in the Materials Laboratory of the Department of Mechanical Engineering ABU, Zaria

A stress was applied to the specimen by hanging a predetermined appropriate mass at its free end. This was facilitated by placing the mass on the small circular steel pan which is an accessory of the machine. Two ends of manila rope of relatively negligible mass, length 60cm, diameter 4.76mm, and minimum breaking strength load of 202.5kg in accordance to United States of America specification (Baldo, 2003) were used to hold the pan at two points on its edge along its diameter and the middle of the rope passed over a groove of 10mm depth by 6mm width around a circular steel element of overall solid diameter of 12mm, that was secured to the free end of the fatigue specimen as shown in Figure 3.3 and plate XIX. This caused the mass to induce the largest bending stress in the specimen at its smallest section at its middle, in accordance to Ryder (1983) as:

$$\sigma = 16mgl/\pi d^3 \qquad (3.3)$$

where ‘m’ is the hung mass, ‘l’ = 87.3mm is the length of the specimen, ‘d’ = 7.63mm is the diameter of the fatigue specimen at its smallest section and ‘g’ is the acceleration due to gravity. When the testing machine was put on, the arrangement made the mass to remain stationary whilst the shaft rotated the specimen freely at a very high speed of 917rpm. The rotation caused the stress (σ) to alternate from positive to negative values within the specimen depending on which side of the specimen was above or below its centroidal axis until the specimen fractured. Standard masses of 10g, 20g, 50g, 50kg, 100kg, 200kg, and 300kg were available as part of the accessories of the fatigue testing machine to be selected in appropriate combinations and used. To induce applied stresses of 250, 275, 300, 325, and 350N/mm^2, masses of 25.47, 28.02, 30.57, 33.12 and 35.66kg including the mass of the pan and the grooved element were respectively evaluated from equation 3.2 and used in each case. The testing machine facilitated similar loading arrangement on its opposite side to enable two specimen to be tested concurrently.

3.2.12.3 *Hardness tests*

The micro-hardness of each specimen of indicated status of treatment that is UU, UC, TC, and TU with each of the bitumen samples was determined by appropriately mounting the specimen on a micro-hardness testing facility as shown in plate XX and applying a compressive load of 200g by dead weight at a constant rate to the indenter of the facility, maintaining the load in the specimen for 18 seconds; and smoothly removing it; all in accordance to ISO 4545-1 and ASTM 384 procedures (American Society for Metals, 1975; New Standards Encyclopeadia, 2008). By this, the very-small diamond indenter having pyramidal geometry was forced into the surface of the specimen. The resulting impression was observed under the microscope and measured

electronically in millimeters by the design capability of the facility and shown on its scale. The measurement was then used to evaluate the Knoop hardness number (HK) of each specimen according to the relation (American Society for Metals, 1975; Callister, 2004):

$$HK = {}^{14.2P}/_{l^2}, \tag{3.4}$$

where 'P' is the applied load in kilogrammes (kg) which in the test case was 0.20kg and 'l' is the measured length of the longer diagonal of the indentation in millimetres. This procedure was similarly and appropriately repeated for the remaining specimen of each indicated status of corrosion, and coating thickness with a given bitumen sample. The micro-hardnesses of two of the four un-treated and un-corroded (UU) and treated but un-corroded (TU) specimen were determined two months earlier immediately after machining and normalizing or bitumen-coating the specimen, while the other two in each case when the rest of the specimen were being tested so as to separate any ageing effects on the specimen from those of the accelerated corrosion during analysis of test results. The tests were conducted on the same day. It was not easy to load the specimen on the testing machine with coatings on them, so the coating on the back side of each specimen were cleaned-off with carbon disulphide, a bristle brush and towel.

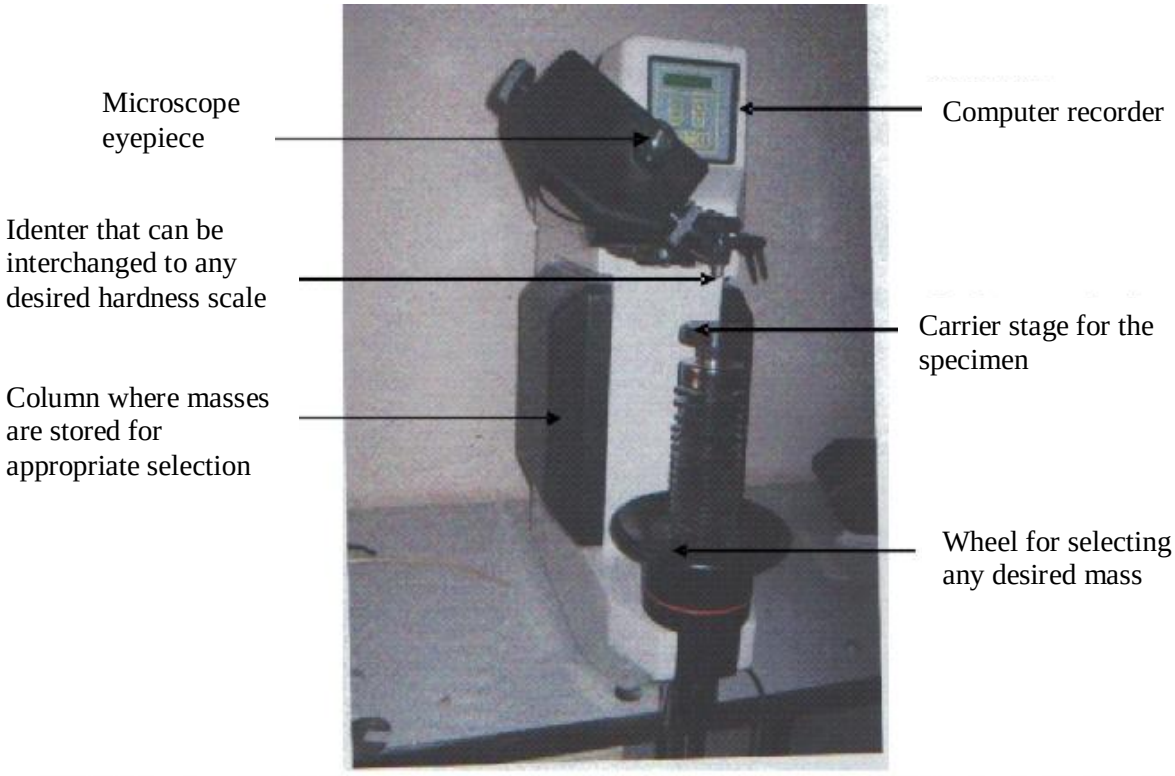


Plate XX: Set-up arrangement for micro-hardness test of a specimen in the Materials Laboratory of the Department of Materials and Metallurgical Engineering ABU, Zaria

3.2.12.4 ***Impact tests***

An impact test of each specimen of indicated status of treatment with a given bitumen sample and or corrosion, that is UU, UC, TU and TC was determined by holding it appropriately in the vice of the impact testing machine. The specimen was struck by two released pendulums each of mass 2.443kg traveling at a standard speed of 5m/s with a kinetic energy of 149.2 Joules in opposite directions from their calibrated standard height to fracture the specimen. The energy remaining after fracture was determined in each case from the height of rise of each pendulum and its weight. The difference between the energy input and energy remaining represent the energy absorbed by the specimen. In that way data was collected from the tests. The experiment was conducted in accordance with stipulated procedures (American Society for Metals, 1975; and Choudary, 2003). Two of the four un-treated and un-corroded (UU) and treated but un-corroded (TU) specimen were tested two months earlier

immediately after machining and normalizing or bitumen-coating the specimen while the other two were tested when the rest of the specimen were being tested so as to separate any effects of ageing on the specimen from those of the accelerated corrosion during analysis of test results. The tests were conducted on the same day. The set up for impact-testing is shown in Plate XXI. It should be noted that each specimen was held in the vice so that it was just a simple beam supported at the ends and hit behind the v-notch.

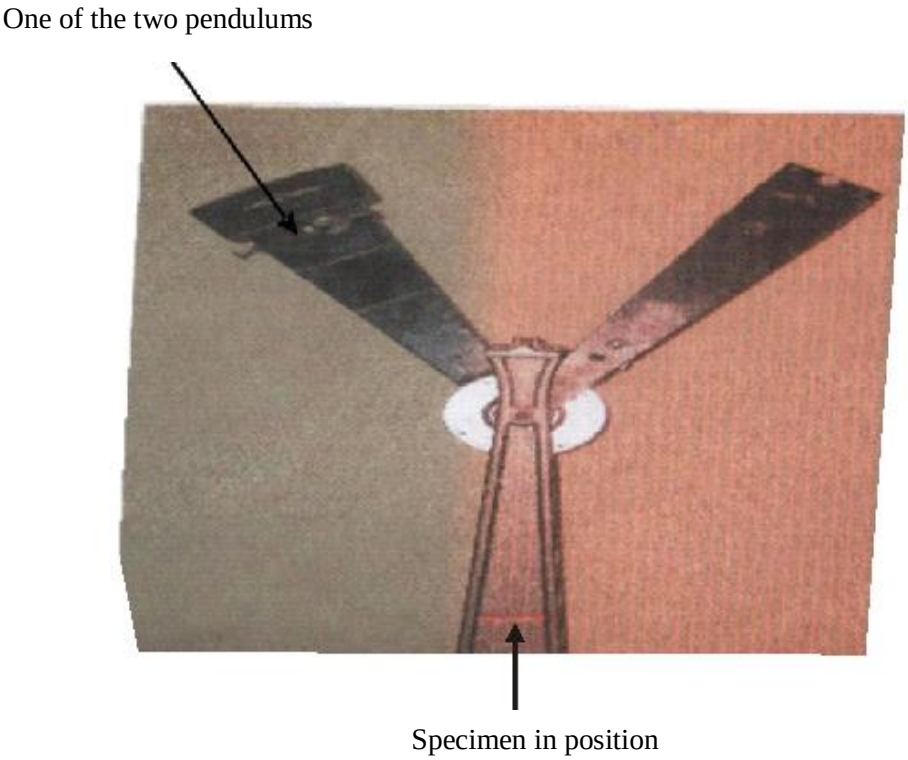


Plate XXI: Set-up Arrangement for Impact Testing of Prepared Specimen in the Materials Laboratory of the Department of Mechanical Engineering ABU, Zaria

3.2.13 Inhibition performance tests on chemical fractions from the bitumen samples

Bitumen is generally divided into two broad chemical compositional groups; asphaltenes, and maltenes. The maltene is further divided into three fractions, namely; naphthalene aromatics, saturates and resins (Srivastava and Roijen, 2000; Mumah and Muktar, 2001; Fan and Buckley, 2011). A 400g-portion of each bitumen sample was

separated through KRPC into its different main chemical fractions by initially precipitating its asphaltenes with n-pentane followed by chromatographic separation of its maltene fractions. The separation was achieved by heating a 400g-portion of a bitumen sample to a temperature of about 300^0C to over 400^0C to a liquid-gaseous state (mobile phase) using a steel container with two parts that could be opened to introduce bitumen into its cavity and fit-close it. One of the parts was the outlet and a control valve to release the heat-prepared sample to flow through the separation column of the liquid-gas chromatograph. The column was packed with alkane, aromatics and a polar solvent at distinct sections to extract saturates naphtalene aromatics and resins respectively. This was done in accordance with the method used by Huang (1997), and Fan and Buckley (2011). The mass percentage of each chemical fraction was then evaluated as follows: asphaltenes = (m_a/m) 100%, naphtalene aromatics = (m_n/m) 100%, resins = (m_r/m) 100%, and saturates = (m_s/m) 100%, where m_a, m_n, m_r, and m_s are the masses of asphaltenes, naphtalene aromatics, resins, and saturates respectively.

Meanwhile, 25 pairs of micro-hardness and 25 of impact test specimen were reproduced from the ascertained low carbon steel, prepared as outlined in sections 3.3, 3.2.6, 3.2.7 and 3.2.8, and used to investigate the capability of each chemical fraction to inhibit corrosion of the steel. Since it is difficult to coat the specimen with each chemical fraction as had earlier been done for each whole bitumen sample because of the nature of each fraction (liquid or semi-solid), 50g of each fraction in a sample was dissolved separately in 30ml of carbon disulphide in a 100ml test tube followed by adding 20ml con. H_2S0_4 to each tube's content to obtain a dissolution involving a specified fraction from each bitumen sample. In this way, solutions were prepared in 12 separate test tubes. Also a solution was similarly prepared in another test tube but without any of the samples' chemical fractions in it (WCF). The solutions were then

left for 24 hours to allow for more proper mixing. A pair of hardness and a pair of impact test specimen were then wholly immersed continuously in each prepared admixture and exposed to the atmosphere in the laboratory for 20 days to undergo corrosion. This was done in line with the procedures used by Anafi and Obi (2004), and Yawas (2005). At the end of the time, the hardness or impact strength of each specimen was determined as outlined in sections 3.2.12.3, and 3.2.12.4 and the respective average pair of values evaluated as the micro-hardness or impact strength of the steel. The procedure was repeated with 12 similar test tubes but with 70g as the mass content of the chemical fraction in each tube.

3.2.14 Corrosion inhibition tests of sodium benzoate of various concentrations and their effects on mechanical properties of low carbon steel

Five pairs of ASTM tensile, five-set ASTM fatigue, five pairs of ASTM impact fracture specimen; and 10 others for the Knoop microhardness test were produced from the low carbon steel for the tests in accordance with specifications given in section 3.2.3. The specimen were similarly prepared to the same consistent average surface finish of 25 microns in accordance with sections 3.2.6, 3.2.7 and 3.2.8. The same corrosive admixture of 30% NaCl + 5% con. H_2S0_4 + 65% air of 100% relative humidity at 38^0C under continuous aeration was reproduced for the test. The pH of the admixture was determined with a pH meter to be 11.2. The prepared corrosive medium was then divided into five equal portions and each portion poured into a separate plastic 1000-ml glass container. Stoichiometric masses of 40g of the procured sodium hydroxide and 122g of the benzoic acid were determined in the laboratory with a digital micro-scale and added together in a 250-ml glass container and gently stirred with a plastic spoon for thorough mixing to get their reaction product as 162g of sodium benzoate

$$NaoH + C_7H_5O_2 \longrightarrow C_7H_5O_2Na + H_2O \quad (3.5)$$
40g 122g 162g

With the same digital scale 0.01539, 0.03078, 0.04617, 0.06156, 0.07695 grammes of the produced benzoate were determined. Each mass was then added separately to one of the prepared corrosive medium in the glass container to get respectively 50, 100, 150, 200 and 250ppm of the sodium benzoate treatment concentrations of the medium. Each container of the treated media was then labeled with the treatment concentration value on it for identification, using a piece of paper with the concentration quantity written on the paper and gummed to it. A pair of impact fracture, tensile, hardness, and five-set fatigue specimen as an overall set was immersed in the treated medium in each container under similar corrosion exposure to the bitumen-coated specimen using an Armfield corrosion study kit as in section 3.2.11. The duration of exposure was also 50 days with the media at room temperature. At the end of the 50 days, the specimen were all removed with crucible tongs, and each was cleaned with a towel and subjected to the appropriate mechanical property test using the relevant facility as in section 3.2.12.

3.2.15 X-Ray diffraction analysis of the microscopies of the bitumen coatings

The levels of material structure which are of interest in material science and engineering are the microstructure, the substructure and the crystal structure. The mechanical, physical, chemical, electrical and magnetic properties of a material such as strength, wear resistance, hardness, corrosion resistance, high and low temperature behaviour and defects such as porosities, segregations, discontinuities, etc are strongly dependent on its micro-structure (Raghavan, 1990; *Basics of X-ray Diffraction*, 2011; *X-ray Diffraction,* 2012). Microscopy is the technical field of using microscopes to view samples that cannot be seen with the unaided eye, to understand and provide basic information on their microstructures. There are three well-known branches of

microscopy: optical, electron, and scanning probe microscopy. Characteristic distances observable by optical microscopy are around 100nm, by electron microscopy 0.15-2.5nm, and by X-ray diffraction 0.01nm; and scanning probe microscopy has minimum scan-spot size and other limitation resolutions to about 1.5mm. Most of our knowledge about atomic positions and intermolecular distances is gained from X-ray diffraction measurements. X-ray diffraction (XRD) is a high-tech, non destructive technique for analyzing a wide range of materials including fluids, metals, minerals, polymers, catalysts, plastics, pharmaceuticals, thin-film coatings, ceramics, solar cells and semi conductors. The technique finds innumerable practical applications in various industries, including microelectronics, power generation, aerospace, and many more. The XRD analysis can easily detect the existence of defects in a particular crystal, its resistance level to stress, its texture, its size and degree of crystallinity and virtually any other variable relating to the sample's basic structure (Von Fraunhoffer, 1975; Bodor, 1991; *Basics of X-ray Diffraction*, 2012; *X-ray Diffraction*, 2012). The prime objective in this section is to present:

i. A study of the micro-structural make-ups of the bath-dip-produced coatings with the bitumen samples.

ii. Information that can be useful in any methodical modification strategy of the bitumens to improve their coatings for better service performance and relevant researches on bitumen and other coating technologies.

Since the properties of bitumen change with temperature (Jackson and Ravindra, 1996), the XRD was taken with coatings produced at 230^{o}C for which the highest change in temperature occurred in heating the bitumen from room temperature and cooling it back to room temperature, among the coating temperatures used. Some quantity of KPB

bitumen was heated in a steel cup with a Bunsen burner to a temperature of 230^{o}C. A mercury-in-glass thermometer with a scale range of 360^{o}C was used to monitor the temperature. The specimen loading glass slide of the diffractometer's goniometer was held with the tong and about 75% of it dipped in the bitumen bath at that temperature for 30 seconds and withdrawn and allowed to cool to room temperature for 30 minutes to produce coating (No. 1) of KPB on it in accordance with Illston *et al* (1979) and Painting and Decorating Contractors of America (1995). The other part of the specimen slide that was not dipped in the heated bitumen was used to hold it in the goniometer's slide attachment slit. The XRD was taken at room temperature using the Japanese-made Shimadzu-1200 model diffractometer at the National Steel Raw Material Research and Development Council, Malali, Kaduna; with counter monochromatic Cu-Kα radiation (from a Cu tube) of wavelength-0.15406nm in accordance with Raghavan (1999). The voltage and current settings were 40KV and 30mA, respectively. The coating was examined in a continuous mode over the maximum angle range of the goniometer from $2\boldsymbol{\theta}$ = 0 to 120^{o}. The scanning speed, sampling pitch and preset time were $2\boldsymbol{\theta}$ = 7^{o}/min, 0.02 degrees and 0.17seconds respectively. With these, the diffractogram, reference peak intensities, reference high and low intensity peaks and, the performed search/match and accept information on the coating; were produced with the diffractometer's computer. The procedure was repeated with another portion of KPB after properly cleaning the cup with kerosene, water and detergent to produce another coating (No. 2) with another portion of KPB. The coating was then scanned with a range of 2θ from 3 to 60^{o} which also covered the major characteristic reflection for all conditions in the coating; and scan speed of 5 deg/min, sampling pitch of 0.02 deg, and preset time of 0.24sec respectively. The described test procedure for coating (No.1) with KPB was repeated with Ondo S-A after similarly cleaning the cup off of the KPB.

In this way diffraction data were collected from the tests. Plate XXII shows the Shimadzu-1200 model diffractometer and its computer accessories as it was used.

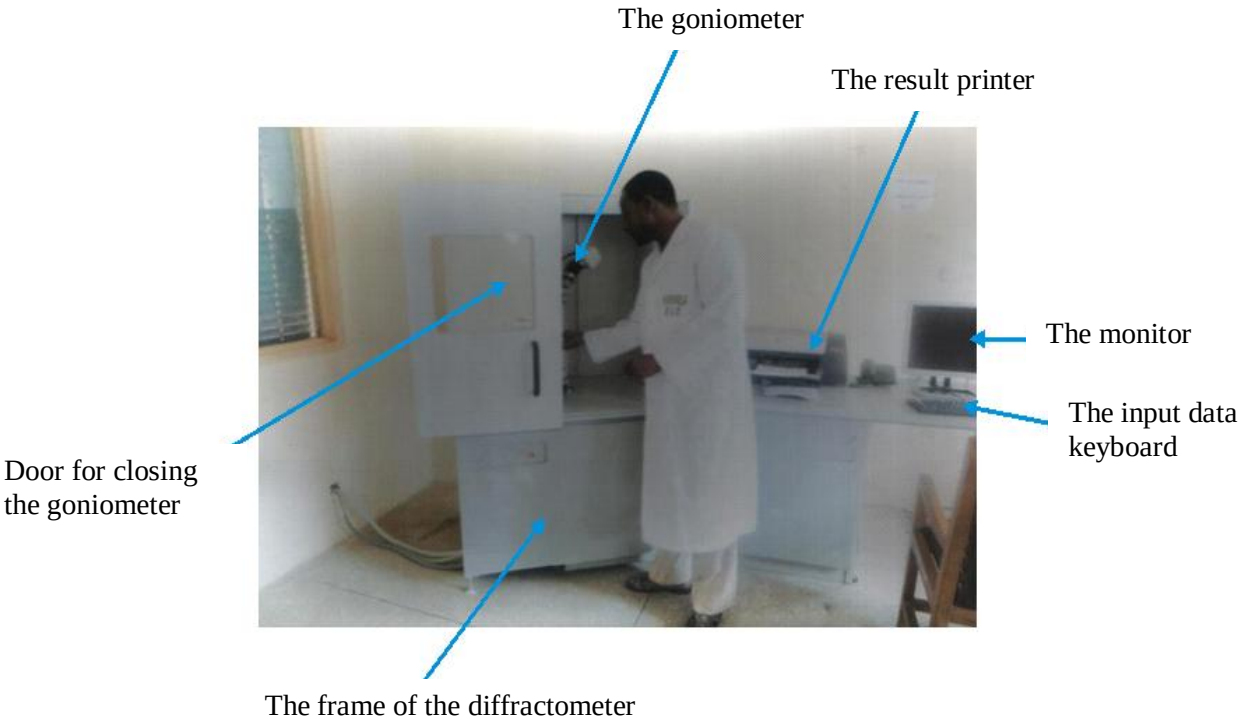


Plate XXII: Process of Loading Specimen on the Goniometer of the Diffractometer in the Laboratory at the National Steel Raw Materials Exploration Agency, Malali, Kaduna

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

The results of all conducted tests in chapter three are presented as follows:

4.1.1 Physicochemical properties of the bitumen samples

The results of physicochemical properties of the bitumen samples as conducted under section 3.2.1 are presented in Tables 4.1to 4.5.

Table 4.1: Elemental Chemical Composition of the Bitumen Samples by Percentage Weight

Bitumen sample used	Percentage Composition by Element								
	C	H	N	O	S	A1	Mn	Ti	V
Ondo S-A	87.78	9.35	0.13	1.25	1.32	0.09	0.05	0.02	0.05
Ondo S-B	86.91	9.37	0.66	1.74	1.23	0.07	0.04	-	-
KPB	83.49	10.51	0.72	1.62	1.14	-	2.04	-	0.02

Table 4.2: Extracted Chemical Fractions by Mass of the Bitumen Samples (%)

Bitumen sample	Chemical fractions by mass (%)			
	Asphaltenes	Maltenes		
		Naphthalene aromatics	Resins	Saturates
Ondo S-A	18.1	59.0	10.9	5.2
Ondo S-B	18.6	58.3	11.1	6.1
KPB	19.8	58.1	11.5	7.8

*The mass of each portion of bitumen sample used for the extraction of the chemical fractions was 420g.

Table 4.3: Penetration, Flash point, Softening Point, and Specific gravity of the Bitumen Samples

Property	Ondo S-A	Ondo S-B	KPB
Penetration (mm)	120	116	85
Flash point (^{o}C)	260	269	320
Softening Point (^{o}C)	36.5	37	45
Specific gravity	0.92	0.95	1.08

Table 4.4: Weathering Resistance of the Bitumen Samples

Time of Exposure	Thickness of Bitumen (mm)		
	Ondo S-A	Ondo S-B	KPB
0 week	32.9	2.9	32.9
First week	32.8	32.8	32.9
Second week	32.5	32.6	32.7
Third week	32.2	32.3	32.4
Fourth week	31.9	31.9	32.1
Fifth week	31.7	31.8	32.1

Table 4.5: Viscosities at specified Temperatures of the Bitumen Samples

Temperature	Viscosity (Poise)		
	Ondo S-A	Ondo S-B	KPB
60	5190.4	5200.4	6270.4
100	120.4	125.04	249.04
150	7.04	7.302	8.102
250	0.12	0.13	0.94

4.1.2 Microstructure of the low carbon steel sample

The microstructure of the procured steel rods that were found consistent at three different sections on each as conducted under section 3.2.5 is presented in plate XXIII.



Plate XXIII: Section A near one end of the rods



Plate XXIII: Section B at the middle of the rods

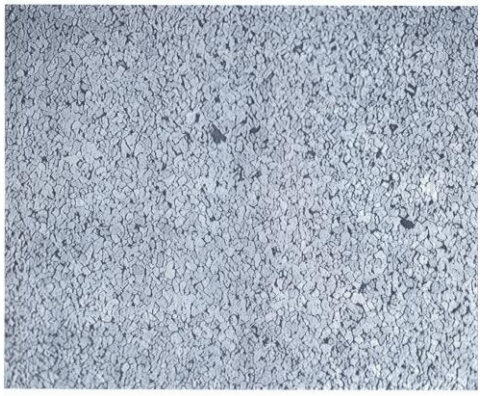


Plate XXIII: Section C near the other end of the rods

Plate XXIII: Revealed microstructure with a magnification of 200 of the procured Low Carbon Steel Rods that were found consistent at three different sections

4.1.3 Chemical composition of the low carbon steel

The overall ascertained consistent and similar chemical composition of each of all low carbon steel rods used for the tests by percentage elemental weight is shown in Table 4.6.

Table 4.6: Overall Average Chemical Composition of all Procured Low-carbon Steel Rods that had Negligible Difference in Composition

Element	Ca	Mn	Mo	Cu	Ni	P	Ec	Fe	Ag	C	Si	S	Re
[%]	0.095	0.28	0.20	0.014	0.31	0.029	0.05	95.68	1.51	0.21	0.59	0.83	0.20

4.1.4 The working thicknesses of coatings achieved with the bitumen samples and different temperatures of treatment

The working coating thicknesses achieved on specimen using each bitumen sample at specified temperatures of treatment are presented in Table 4.7.

Table 4.7: Overall Achieved Working Bitumen Coating Thicknesses on Specimen at Different Temperature of Coating Treatment

Coating temperature (^oC)	150	170	180	200	220	230
Coasting thickness (mm)	2.1	1.46	1.29	1.13	0.93	0.81

4.1.5 Mechanical properties of the steel specimen of specified status of coating treatment and, or corrosion

The test-obtained results are presented as follows:

4.1.5.1 *Tensile tests*

The stress-strain curves for the various coating thicknesses and treatments using data obtained from section 3.2.12.1 are presented in Figure 4.1 and inhibition protection in Table 4.8.

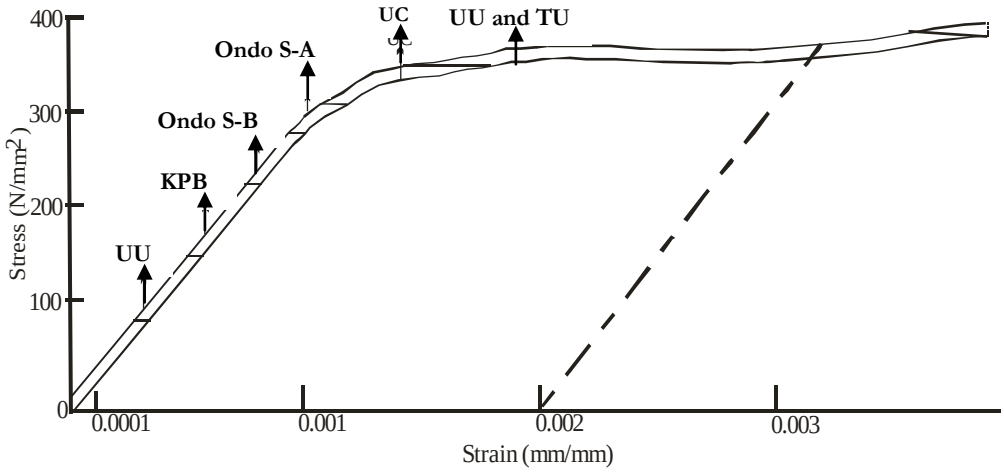


Fig. 4.1a: Case of 2.1mm coating thickness

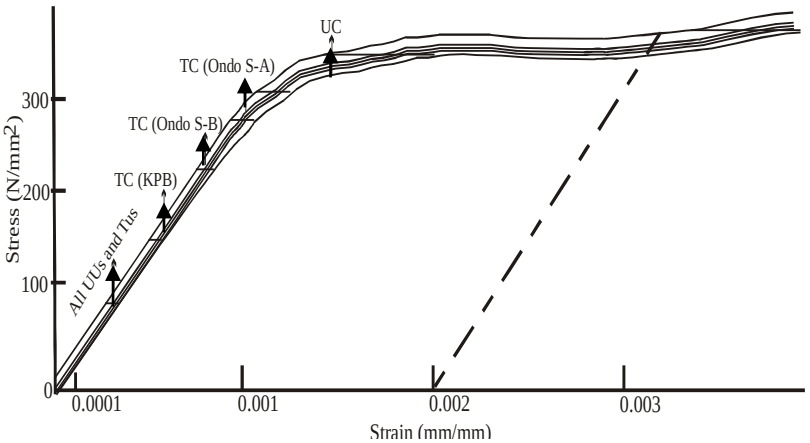


Fig. 4.1b: Case of 1.46mm coating thickness

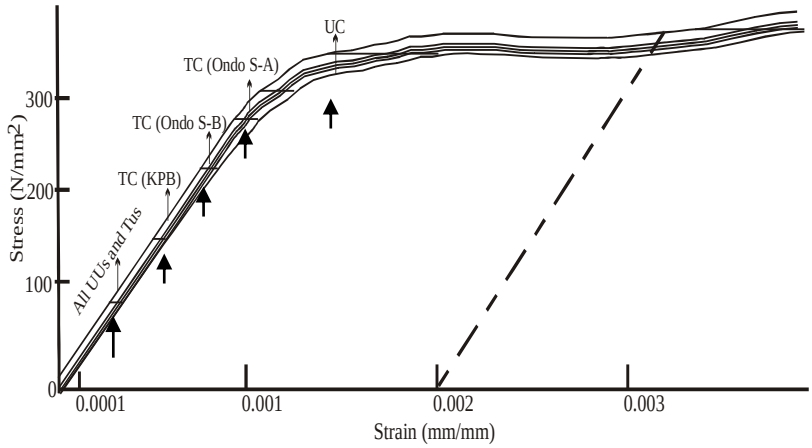


Fig. 4.1c: Case of 1.29mm coating thickness

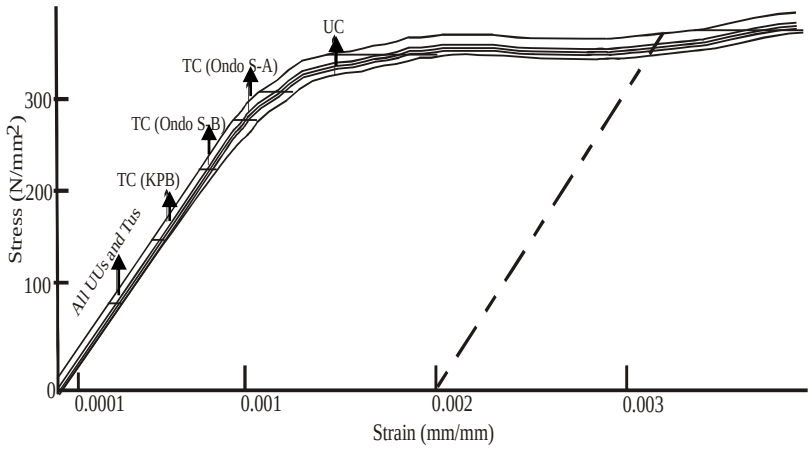


Fig. 4.1d: Case of 1.13mm coating thickness

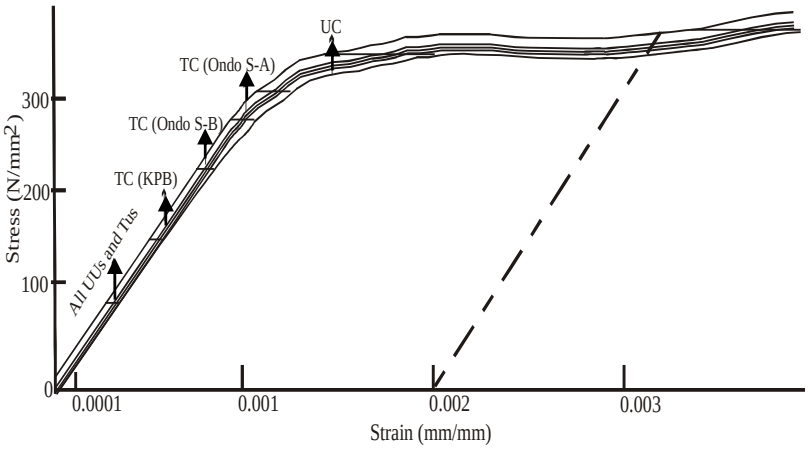


Fig. 4.1e: Case of 0.93mm coating thickness

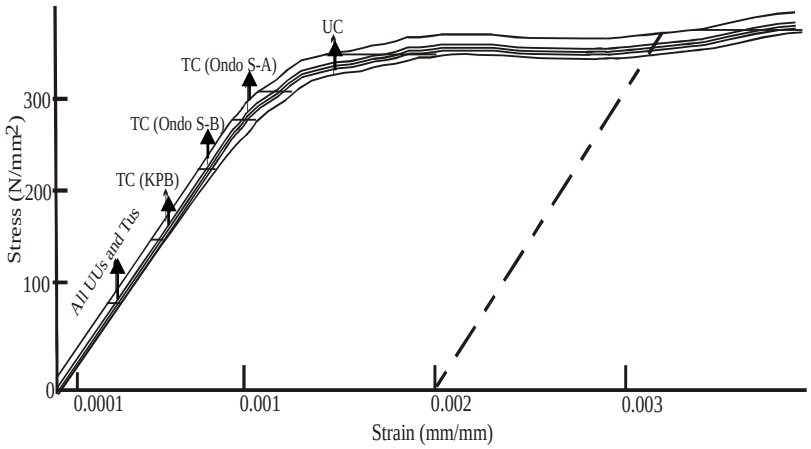


Fig. 4.1f: Case of 0.81mm coating thickness

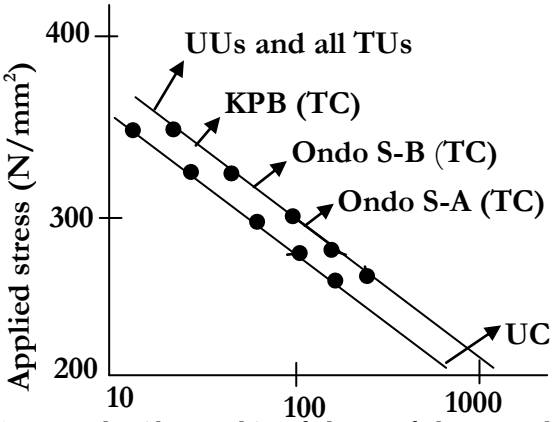
Fig. 4.1: Pattern of stress-strain curves of specimen showing their state of coating treatment with the bitumen samples and or corrosion for the TU and TC specimen.

Table 4.8: Inhibition Performances (IP) by Coating Treatments of Specified Thicknesses on the Tensile Strength Corrosion Deterioration of the Low Carbon Steel using the Bitumen Samples

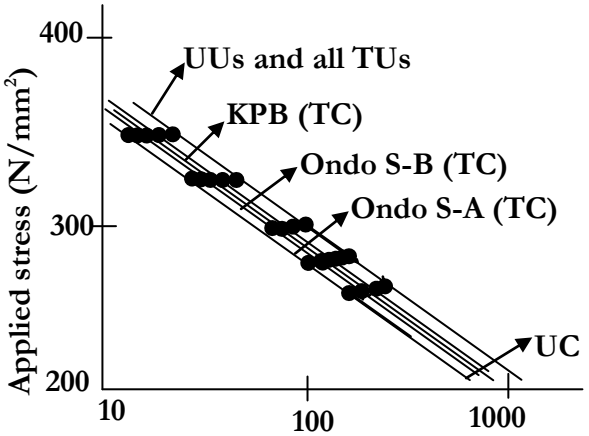
Bitumen sample	Coating thickness (mm)					
	2.1	1.46	1.29	1.13	0.93	0.81
Ondo S-A [%] ⟶	100	91	86	72	67	63
Ondo S-B [%] ⟶	100	93	88	75	69	65
KPB [%] ⟶	100	97	95	81	76	69

4.1.5.2 *Fatigue tests*

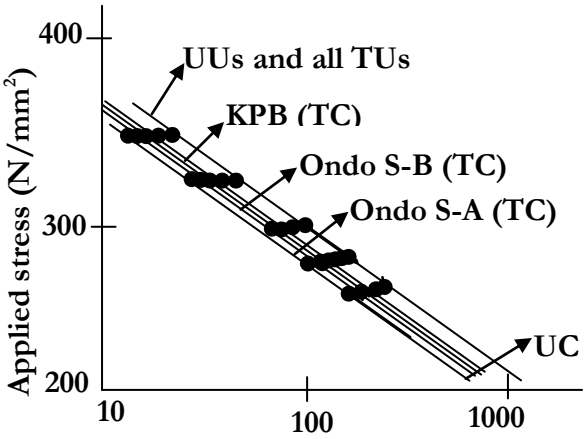
The endurance curves for the various coating thicknesses and treatments using data obtained from section 3.2.12.2 are presented in Figure 4.2 and inhibition protection in Table 4.9.



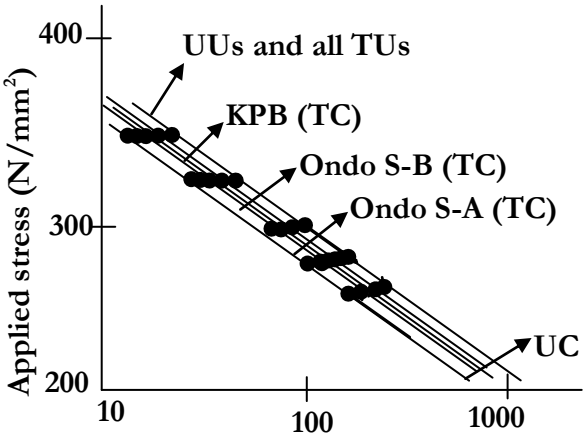
Stress cycles (thousands) to failure on failure semi-log scale
Fig 4.2a: Case of 2.1mm coating thickness coating thickness



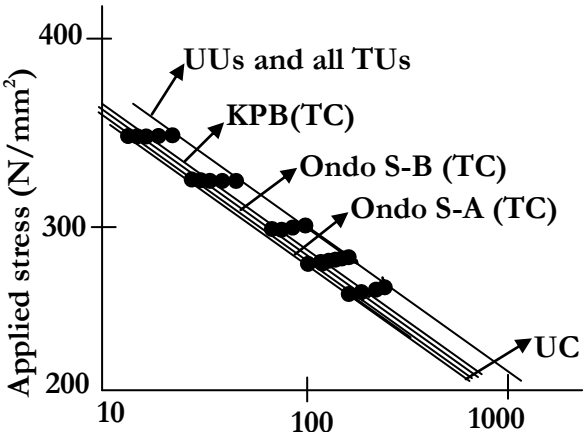
Stress cycles (thousands) to on semi-log scale
Fig 4.2b: Case of 1.46mm coating thickness



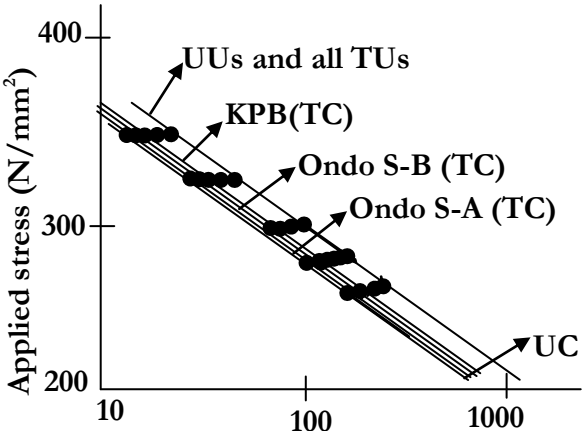
Stress cycles (thousands) to failure on semi-log scale
Fig 4.2c: Case of 1.29mm coating thickness



Stress cycles (thousands) to failure on semi-log scale
Fig 4.2d: Case of 1.13mm coating thickness



Stress cycles (thousands) to failure on semi-log scale
Fig 4.2e:Case of 0.93mm coating thickness



Stress cycles (thousands) to failure on semi-log scale
Fig 4.2f:Case of 0.81mm coating thickness

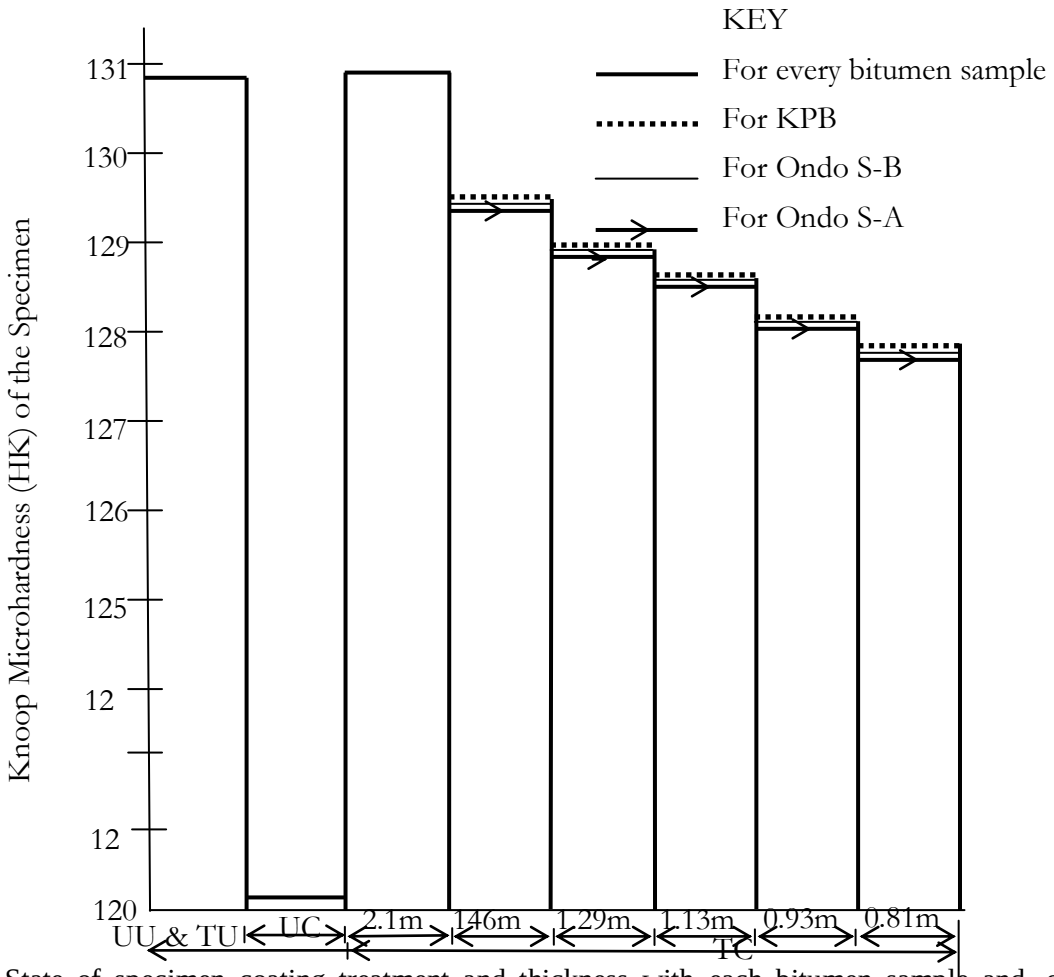
Figure 4.2: Comparative pattern of endurance curves for average pair values of fatigue strength of specimen indicating their state of coating treatment and or corrosion for the specified bitumen samples and thicknesses of coating treatments.

Table 4.9: Inhibition Performances (IP) by Coating Treatments of Specified Thicknesses on the Corrosion Fatigue Strength of the Low-Carbon Steel Using each Bitumen Sample

Bitumen sample	Coating thickness (mm)					
	2.1	1.46	1.29	1.13	0.93	0.81
Ondo S-A [%]	100	82.45	74.53	62.92	56.88	53.36
Ondo S-B [%]	100	83.96	78.14	64.32	59.13	55.21
KPB [%]	100	86.89	80.94	67.81	63.78	59.85

4.1.5.3 *Hardness tests*

The hardness values of the specimen under various coating thicknesses and treatments using data obtained from section 3.2.12.3 are presented in Figure 4.3 and inhibition protection in Table 4.10.



State of specimen coating treatment and thickness with each bitumen sample and, or corrosion showing the coating thickness for the TC specimen.

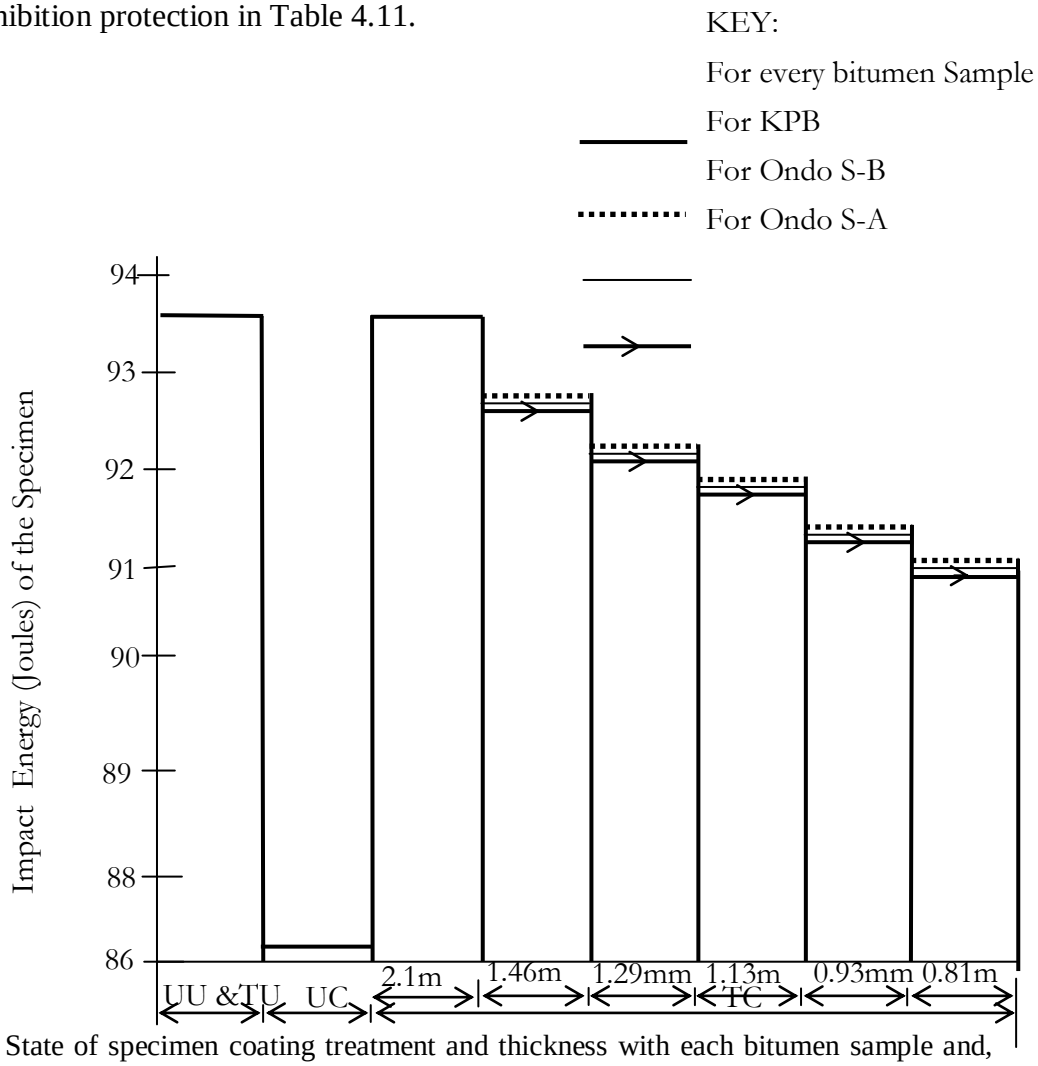
Figure 4.3: Knoop Micro-hardness of Specimen of the Specified state of Coating Treatment with each of the three Bitumen Samples and, or Corrosion.

Table 4.10: Inhibition Performances (IP) by Coating Treatments of Specified Thicknesses on the Hardness Corrosion Deterioration of the Low Carbon Steel

Bitumen sample	Coating thickness (mm)					
	2.1	1.46	1.29	1.13	0.93	0.81
Ondo S-A [%]	100	93.47	89.29	83.71	75.16	69.53
Ondo S-B [%]	100	94.91	92.63	86.84	79.13	72.65
KPB [%]	100	97.42	94.34	89.64	85.32	77.54

4.1.5.4 *Impact tests*

The impact fracture energy values of the specimen under various coating thicknesses and treatments using data obtained from section 3.2.12.4 are presented in Figure 4.4 and inhibition protection in Table 4.11.



State of specimen coating treatment and thickness with each bitumen sample and, or corrosion showing the coating thickness for the TC specimen.

Fig. 4.4: Impact fracture energy (joules) of specimens of the shown state of coating treatment and, level of corrosion using the bitumen

Table 4.11: Inhibition Performances (IP) by Coating Treatments of Specified Thicknesses on the Corrosion Deterioration of Impact Strength of Low-Carbon Steel Using Each Bitumen Sample.

Bitumen sample \ Coating Thickness (mm)	2.1	1.46	1.29	1.13	0.93	0.81
Ondo S-A [%]	100	82.31	78.19	63.56	59.70	57.26
Ondo S-B [%]	100	86.94	80.32	65.28	61.86	58.93
KPB [%]	100	90.47	84.58	70.14	64.63	62.17

4.1.6 Statistical parameters from the coat-protection values of the mechanical properties

The computed statistical parameters that is, the mean, standard deviation, Range, and coefficient of variation of inhibition performances values using results from Tables 4.8 to 4.11 evaluated for each case of bitumen sample are presented in Table 4.12.

Table 4.12: Evaluated mean (IP), standard deviation (σ), Range (R), and Coefficient of Variation (V) of inhibition performances by the bitumen samples from Tables 4.8 to 4.11.

Type of Test	Bitumen samples used	$\overline{IP_i}$ [%]	σ [%]	R[%]	V [%]
Tensile	Ondo S-A	79.6	14.691	37.0	0.18457
	Ondo S-B	81.66	14.054	35.0	0.1720874
	KPB	86.33	12.738	31.0	0.147558
Corrosion Fatigue Strength	Ondo S-A	71.69	17.65	40.61	0.246184
	Ondo S-B	73.46	17.079	44.79	0.232504
	KPB	76.5625	15.456	40.15	0.201857
Micro-Hardness	Ondo S-A	85.192	11.426	40.47	0.1341202
	Ondo S-B	87.693	10.279	27.35	0.1172196
	KPB	90.708	8.34	22.46	0.0919456
Impact Strength	Ondo S-A	73.67	16.821	42.74	0.2283105
	Ondo S-B	74.555	16.281	41.09	0.2183406
	KPB	78.665	15.305	37.83	0.1945525

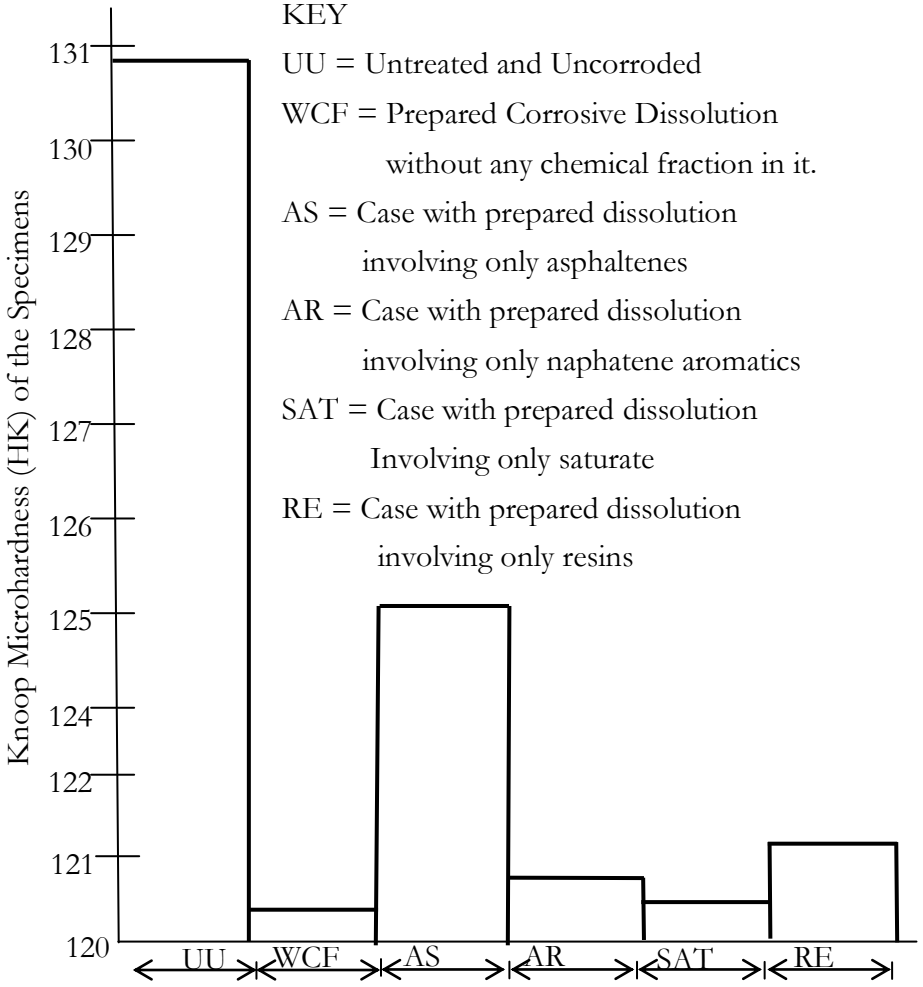
*Mean bitumen coating thickness = 1.283mm

4.1.7 Comparative Assessment of Effects of Chemical Fractions of the Bitumen Samples

The overall comparative effects of separately treating the prepared corrosive solution with 50g and 70g of various chemical fractions separated from the bitumen samples as conducted in section 3.2.13 on the hardness of the steel specimen are shown in Figures 4.5a and 4.5b respectively, while the results for impact fracture strength are in Figures 4.6a and 4.6b respectively.

4.1.7.1 *Hardness tests*

Figure 4.5 below presents the results for the hardness test



State of specimen treatment of the prepared dissolution with the shown chemical fractions

Fig. 4.5a: Case involving 50g of the specified chemical fraction from the bitumen samples in the prepared dissolution

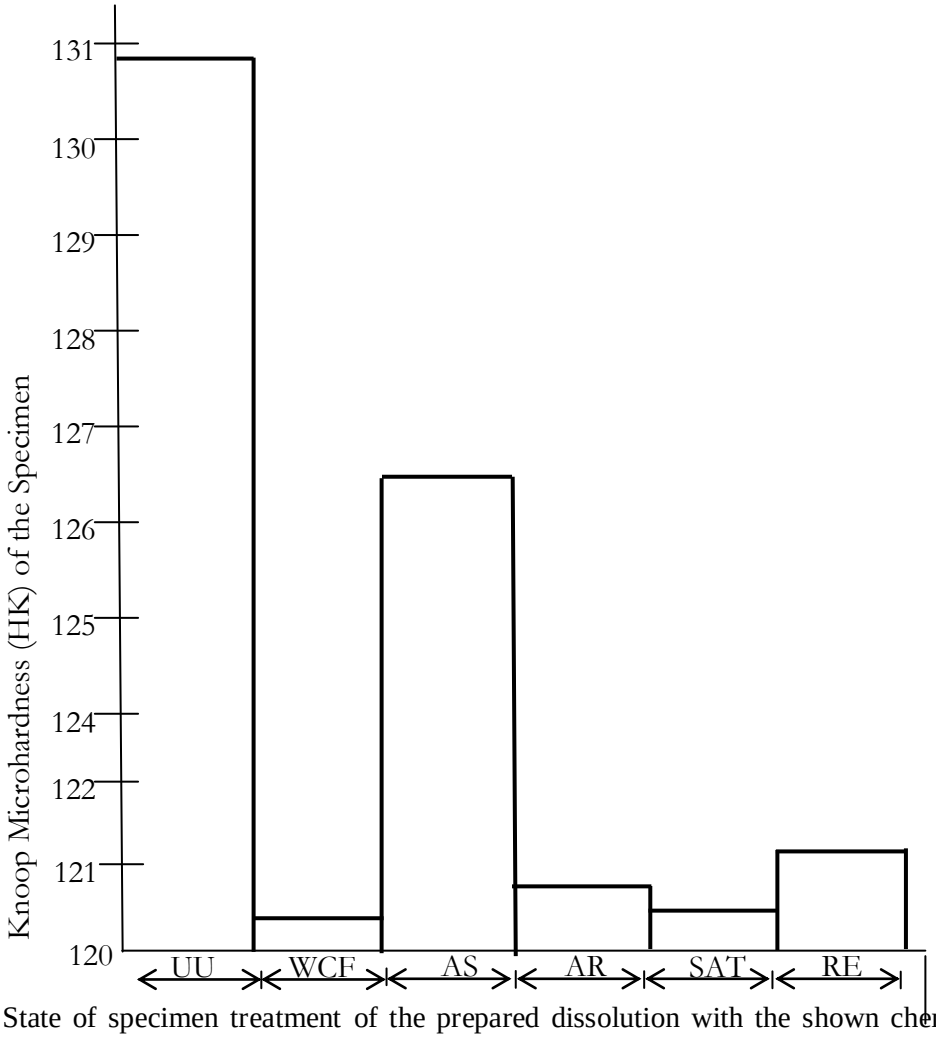
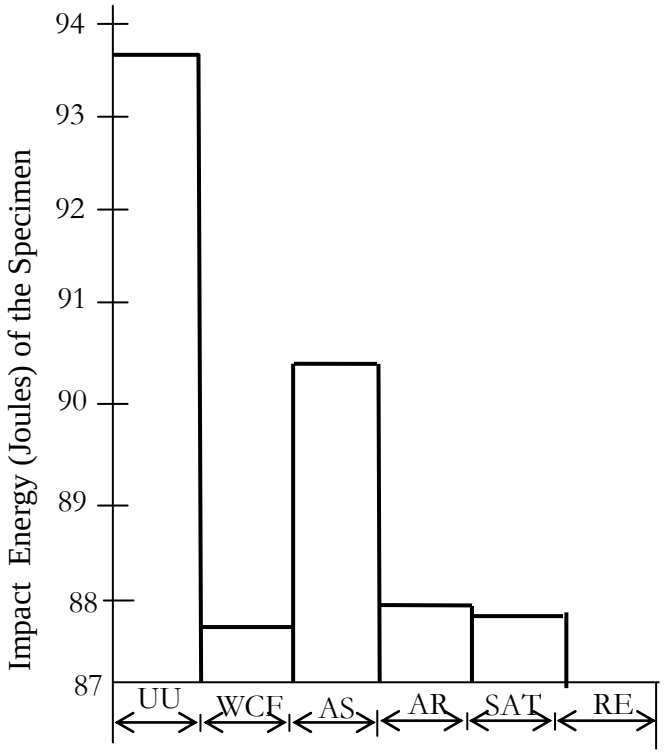


Fig. 4.5b. Case involving 70g of the specified chemical fraction from the bitumen samples in the prepared dissolution

Fig. 4.5: Knoop Micro hardness of Specimen of the Specified Status of Treatment Involving Chemical Fractions Extracted from the Bitumen Samples.

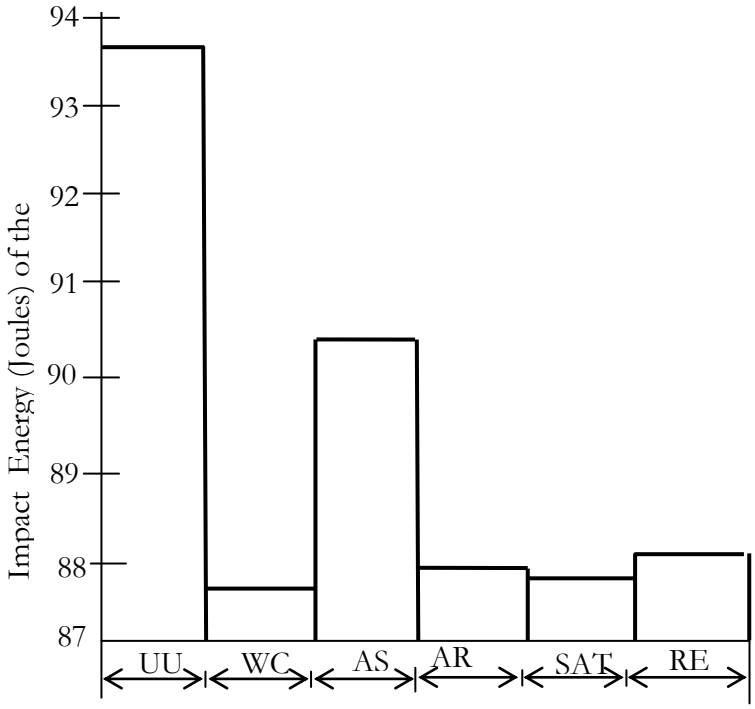
4.1.7.2 *Impact tests*

Figure 4.6 below presents the results fir the impact test



State of specimen treatment of the prepared dissolution with the shown chemical fractions.

Fig 4.6a: Case involving 50g of the specified chemical fraction from the bitumen samples in the prepared dissolution



State of specimen treatment with the prepared dissolution with the shown chemical fraction.

Fig. 4.6b: Case involving 70g of the specified chemical fraction from the bitumen samples in the prepared dissolution

Fig. 4.6: Impact Strength of Specimens of the Specified Status of Treatment Involving Chemical Fractions Extracted from the bitumen samples

4.1.8 Effects Sodium Benzoate Concentrations as Corrosion Inhibitors on Mechanical Properties of Low Carbon Steel

The results obtained from section 3.2.14 are presented in Tables 4.13 to 4.16.

Table 4.13: Tensile Strength

Concentration [ppm] / Applied stress (N/mm^2)	50		100		150		200		250	
	Strain (ε_i)	η (%)	Strain (ε_i)	η (%)	Strain (ε_i)	η (%)	Strain (ε_i)	η (%)	Strain (ε_i)	η (%)
83.5	0.000314	3.5	0.000320	5.09	0.00031962	7.0	0.000319	10.00	0.000318	15.00
140.5	0.000534	3.1	0.000533	6.25	0.000533	6.25	0.000531	12.5	0.000530	15.60
203.5	0.000747	4.2	0.000746	6.38	0.000706	8.51	0.000744	10.6	0.0007474	15.00
258.7	0.000961	4.2	0.000959	6.35	0.000957	7.94	0.000956	11.1	0.0009535	14.00
310.5	0.001174	4.6	0.001173	6.15	0.0001172	7.69	0.001170	10.77	0.001167	15.10
348.3	0.001606	3.8	0.0001606	5.17	0.001602	7.62	0.001598	10.88	0.0001595	15.40
354.6	0.002583	4.1	0.0025103	7.00	0.00250	7.96	0.002583	10.73	0.002424	14.30
358.4	0.004057	3.9	0.0040527	5.22	0.004046	7.81	0.00247	11.33	0.00403	14.99
401.8	0.00427	4.5	0.004265	6.82	0.00462	8.1	0.004037	10.91	0.004246	14.10
405.3	002583	3.7	0.106415	6.5	0.10656325	7.5	0.004256	11.0	0.105632	15.50
	Average value	3.98	Average value	6.146	Average value	7.0	Average value	10.982	Average value	15.20

Table 4.14: Fatigue Strength

Concentration [ppm] / Applied cyclic stress (N/mm^2)	50		100		150		200		250	
	S_i	η[%]	S_i	η[%]	S_i	η[%]	S_i	η[%]	S_i	η[%]
250	201312	1.4	201554	3	201705	4	202023	6.1	202356	8.3
275	165542	1.1.43	165741	2.9	165903	4.2	166164	6.3	166388	8.1
300	93078	1.5	93183	2.9	93267	4.1	93414	6.2	93561	8.3
325	53246	1.3	53291	3	53322	4.0	53392	6.3	53449	8.2
350	29439	1.38	29474	2.9	29503	4.2	29545	6.1	29593	8.3
Average	108523.4		108648.6	2.94	108740	4.1	108907.6	6.2	109069	8.24

Table 4.15: Hardness

Sodium Benzoate Treatment concentration (ppm)	Knoop microhardness (HK)	η [%]
50	121.44	10.8
100	121.69	13.2
150	122.1	17.1
200	122.64	22.3
250	123.18	27.4

Table 4.16: Impact Fracture Strength

Sodium Benzoate Treatment concentration (ppm)	Impact Fracture Energy (Joules)	η [%]
50	87.33	2.4
100	87.44	3.6
150	87.60	5.2
200	87.85	7.9
250	87.97	9.1

4.1.9 X-ray Diffraction Analyses of the Coatings

The diffractograms for: KPB coating No.1 is shown in Figure 4.7, KPB coating No. 2 in Figure 4.8 and Ondo S-A in Figure 4.9. The corresponding reference peak of high and low intensity for KPB coating No.1 is shown in Figure 4.10, KPB coating No.2 in Figure 4.11 and Ondo S-A in Figure 4.12. The overall print out of the search/match and accept result with the integral computer software of the diffractometer for KPB, coating No. 1, KPB coating No. 2, and Ondo S-A are shown in Tables 4.17, 4.18 and 4.19, with the scale factor (S), line match ratio (L), weight percentage by composition (Wt%) and reliability (R) as indicated.

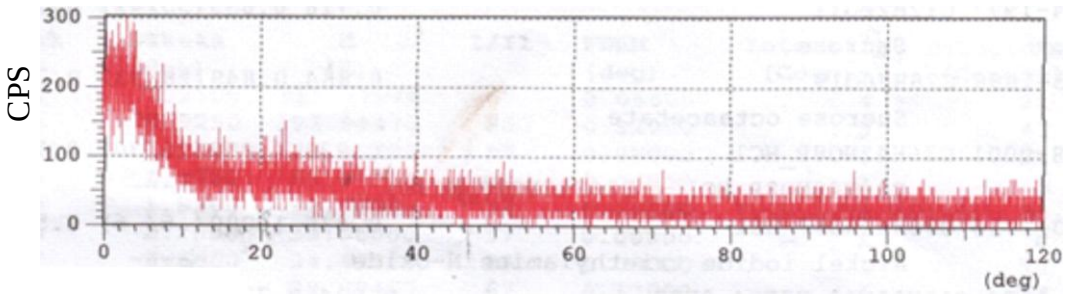


Fig. 4.7: Diffractogram Obtained with KPB Coating No. 1

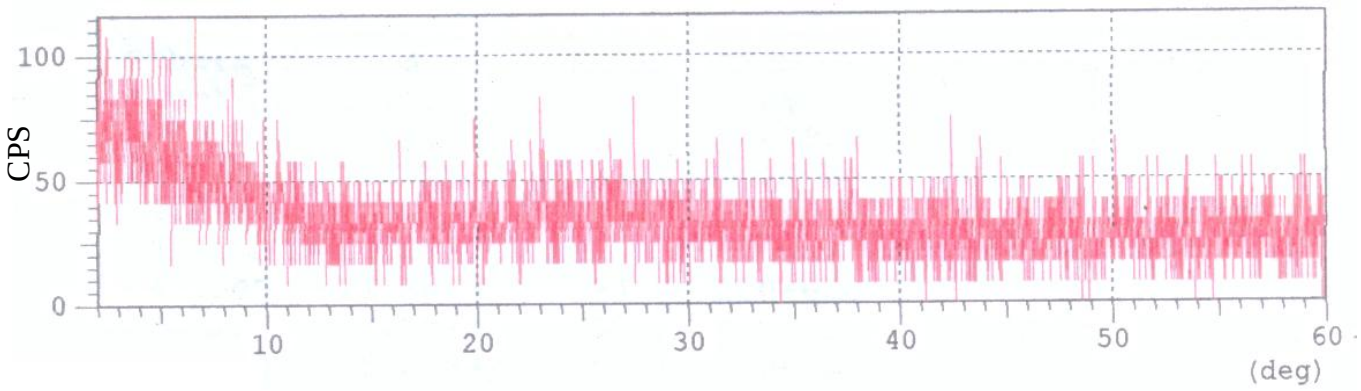


Fig. 4.8: Diffractogram Obtained with KPB Coating No. 2

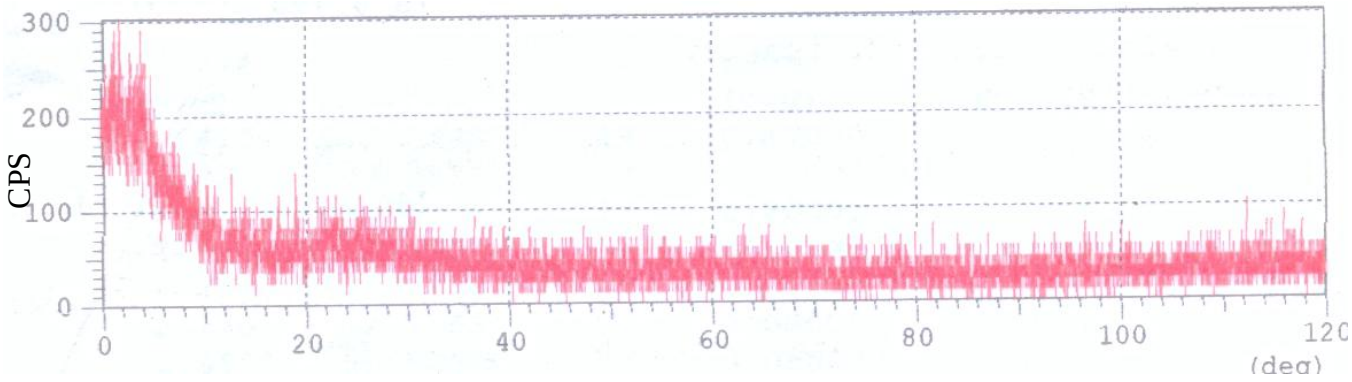


Fig. 4.9: Diffractogram Obtained with Ondo S-A Coating

<Peak Data/Entry>

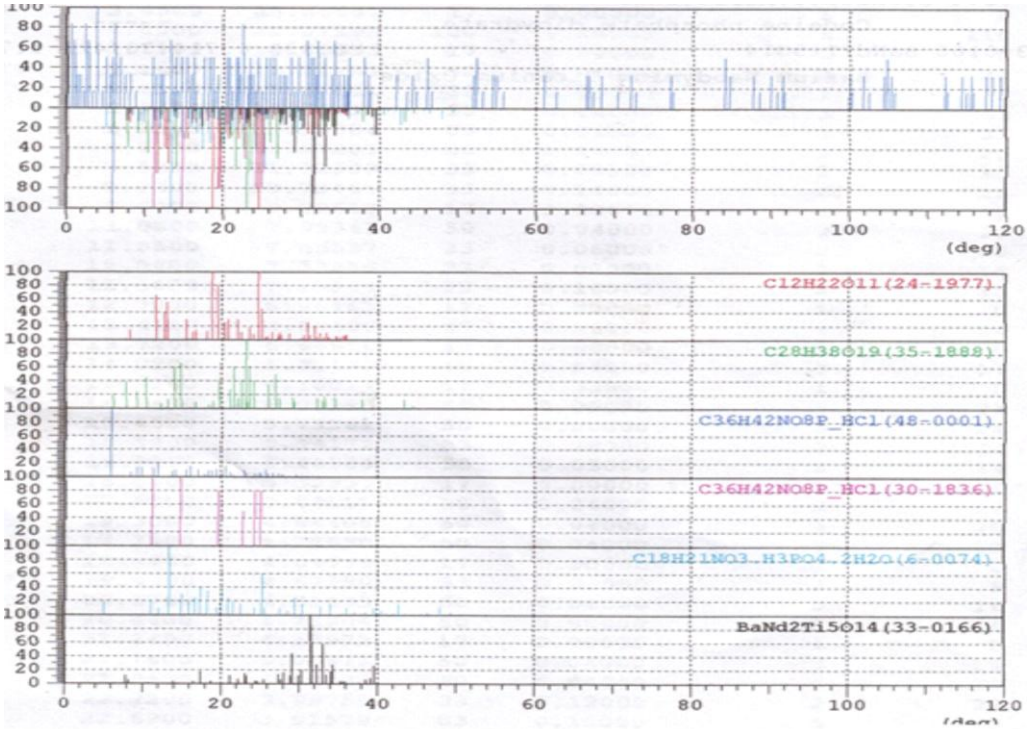


Fig. 4.10: Reference Peaks of High and Low Intensities for KPB Coating No. 1

CPS= Count Peaks

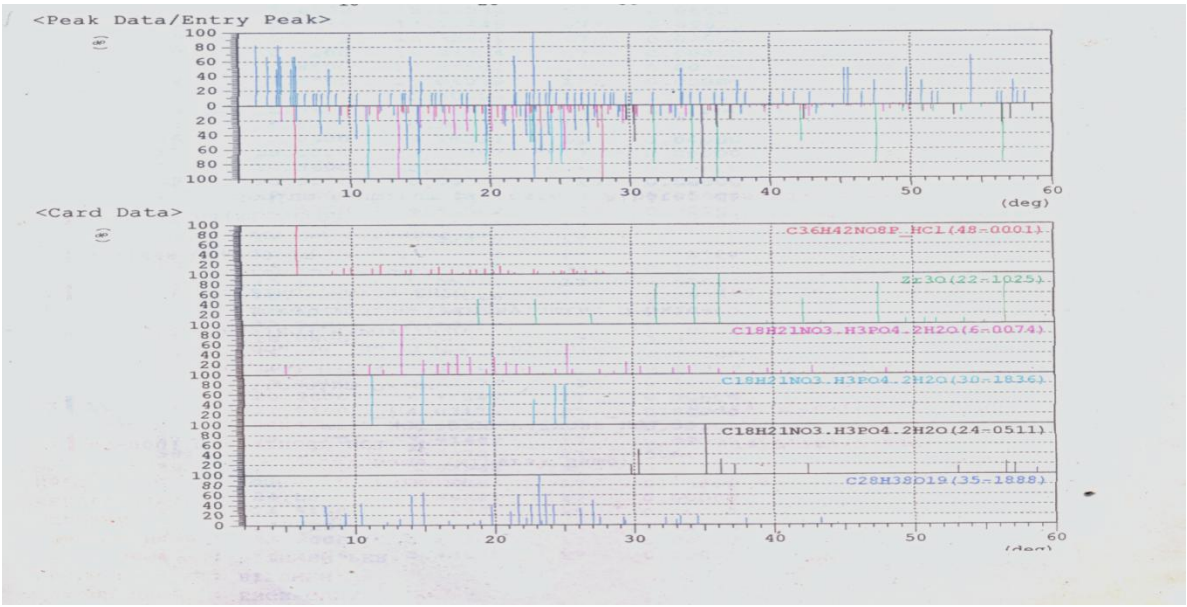


Fig. 4.11: Reference Peaks of High and Low Intensities for KPB Coating No. 2

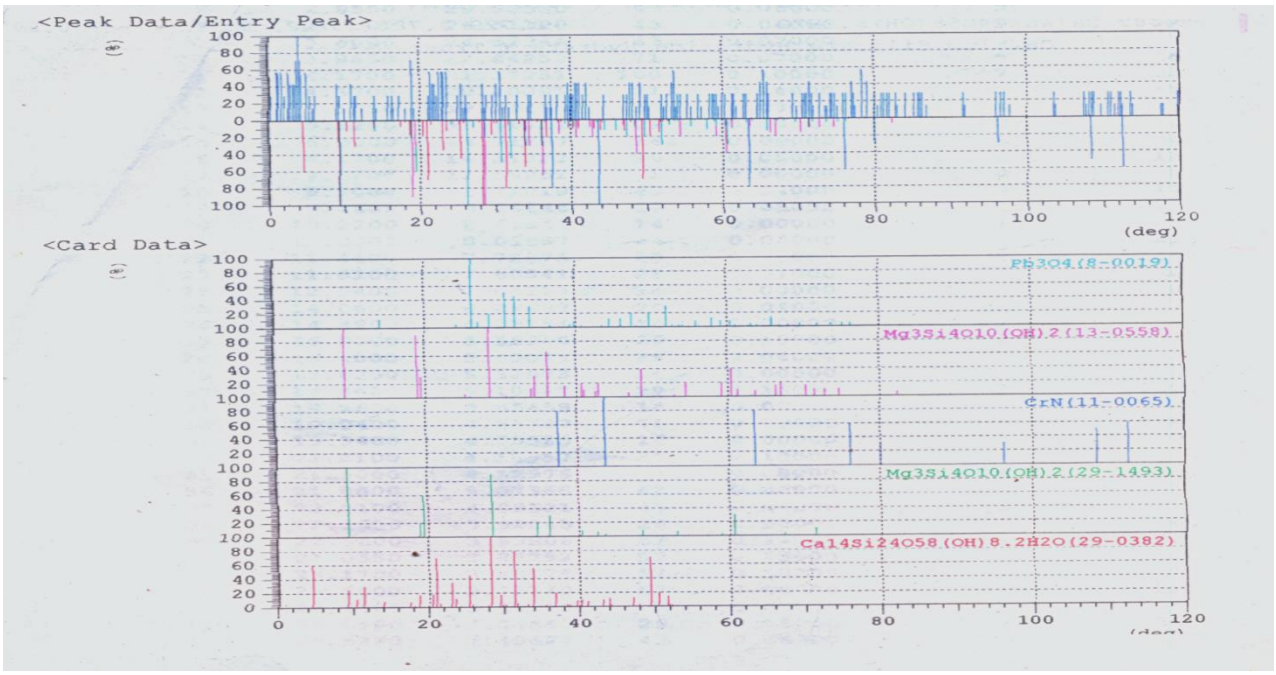


Fig. 4.12: Reference Peaks of High and Low Intensities for Ondo S-A Coating

Table 4.17: The search/match and accept result for KPB Coating No. 1

Entry Card No.	Card No.	Chemical Formula Chemical Name (Mineral Name)	S	L	Wt%	R
1	24-1977	C12H22011 Sucrose	0718	0.833 (35/42)	0.799	0.666
2	35-1888	C28H38019 Sucrose octaacetate	0.834	0.848 (28/33)	0.745	0.632
3	48-0001	C36H42NO8P HCL C36H42NO8P HCL (C36H42NO8P HCL)	0.838	0.838 (25/30)	0.712	0.593
4	30-1836	C36H42NO8P HCL Nickel iodide triethylamine N-oxide	0.476	1.000 (6/6)	0.593	0.593
5	6-0074	C18H21NO3 . H3PO4.2H2O Codeine phosphate dehydrate	0.924	0.775 (31/40)	0.733	0.568
6	33-0166	BaNd2Ti 5014 Barium Neodymium Titanium Oxide	0.833	0.714 (30/42)	0.792	0.566

Table 4.18: The search/match and accept result for KPB coating No. 2

Card No.	Entry Card	Chemical Formula Chemical Name (Mineral Name)	S	L	Wt%	R
1	48-0001	C36H42NO8P HCl	0.874	0.767 (23/30)	0.741	0.568
		C36H42NO8P HCl (C36H42NO8P HCl)				
2	22-1025	Zr3O Zirconium Oxide	0.383	0.750 (12/16)	0.702	0.526
3	6-0074	C18H21NO3. H3PO4. 2H2O Codeine phosphate dehydrate	0.706	0.775 (31/40)	0.672	0.521
4	30-1836	C18H21NO3. H3PO4. 2H2O Nickel iodide triethylamine N-oxide	0.300	0.833 (5/6)	0.622	0.519
5	24-0511	C18H21NO3. H3PO4. 2H2O Iron Chromium Oxide	0.460	0.700 (7/12)	0.739	0.517
6	35-1888	C28H38019 Sucrose octaacetate	0.652	0.758 (25/33)	0.683	0.517
7	10-0393	Na (Si3A1) 08 Sodium Aluminum Silicate (Albite, disorder	0.678	0.738 (31/42)	0.688	0.508

Table 4.19: The search/match and accept result for Ondo S-A coating

Entry Card Card No.	Chemical Formula Chemical Name (Mineral Name)	S	L	Wt%	R
1 8-0019	Pb304 Lead Oxide (Minium, syn)	0.715	0.795 (31/39)	0.812	0.646
2 13-0558	Mg3Si4010 (OH)2 Magnesium silicate hydroxide (Talc-2/ITM/	0.614	0.900 (27/30)	0.708	0.637
3 11-0065	CrN Chromium Nitride (Carlsbergite, syn)	0.444	0.875 (7/10)	0.720	0.630
4 29-1493	Mg3Si4010 (OH)2 Magnesium Silicate Hydroxide (Talc-2/ITM)	0.463	0.800 (12/15)	0.759	0.607
5 29-0382	Ca14Si24O58 (OH)8.2H2O Calcium Silicate Hydroxide Hydrate (Trusc)	0.729	0.786 (33/42)	0.752	0.591

4.2 Discussions

4.2.1 Physicochemical Chemical Properties

Table 4.1a shows the chemical composition of each bitumen sample by elements in weight percentages, while Table 4.1b is by the chemical fractions. It can be observed from the table that aluminium and magnesium trace elements were detected in both Ondo S-A and Ondo S-B, while titanium and vanadium were detected in Ondo S-A but not in Ondo S-B. Furthermore, vanadium was detected in both Ondo S-A and KPB but not Ondo S-B. From the results it can be seen that Ondo S-A had more mineral accessories than Ondo S-B and KPB. The major trace element in Ondo S-A and Ondo S-B is aluminium while that in KPB is magnesium. The main difference in the types of mineral accessories between Ondo S-B and KPB is in the aluminum and vanadium contents. In all cases the trace elements are very minimal in quantity and type. In each of the bitumen samples; carbon is the largest element followed in order by hydrogen, oxygen, sulphur, to hydrogen as the least. KPB has the largest percentages of hydrogen and nitrogen as compared to Ondo S-A. The major difference between the KPB and Ondo natural samples is in the quantity of aluminium and titanium present. Naphthalene aromatics are the largest chemical content of all the bitumen samples, followed by asphaltenes and least by saturates as can be seen from Table 3.1b.The chemical compositions of five natural bitumen samples from other locations in the Nigerian tarsands have been reported, by Sheikh (2003). The chemical elements and percentage ranges of their contents by weight in the samples were 82.96-86.02% carbon, 10.26-10.61% hydrogen, 0.47-0.67% nitrogen, 1.21-1.98% oxygen, and 1.11-1.2% sulphur. It can be observed that the percentages of these elements as obtained for Ondo S-A, Ondo S-B and even KPB are respectively comparable to these ranges. The compositions of very good bitumen produced by Mexican blend, Arkansas Rousiana,

Boscan and California crude sources have the following compositions by elemental weight in the indicated percentage ranges; 83.77 to 86.77% carbon, 9.91 to 10.94% hydrogen, 0.28 to 1.10 nitrogen, 0.99 to 5.25% sulphur, 0.2 to 0.77% oxygen and minute traces of vanadium and nickel (UNEP and ILO, 2004). It can be observed from Table 4.1a that the compositions of all the bitumen samples are comparable to those of these bitumens. Moreover, the general average composition of bitumens of good quality as reported by UNEP and ILO (2004) lie in the range of 79-88% carbon, 7-13% hydrogen, traces to 3% nitrogen; 8% sulphur; 8% oxygen by weight. From these it can also be seen that the compositions of the bitumen samples compare favourably with the UNEP and ILO average compositions. According to Srivastava and Roijen (1988), bitumens generally contain 10 to 20% asphaltenes, 55 to 70% naphthalene aromatics, 10 to 25% resins and 5 to 15% saturates. It can therefore be observed from Table 4.1b that the fractional chemical compositions by Ondo S-A, Ondo S-B and KBP are comparable to the average composition.

The penetration value of Ondo S-A (120mm) is highest followed by Ondo S-B (116mm) and then KPB (85mm). The flash point of KPB (360^{o}C) is highest followed by that of Ondo S-B (269^{o}C) and then Ondo S-A (260^{o}C). The softening points of Ondo S-A (36.5^{o}C) and Ondo S-B (37^{o}C) are almost the same as can also be seen from Table 4.1c while that of KPB ((45^{o}C) is higher than those of Ondo S-A and Ondo S-B. The specific gravity of KPB (1.08) is highest followed by that of Ondo S-B (0.95) and then Ondo S-A (0.92). The values of penetration, softening points and specific gravity of Ondo bitumen samples compare favourably with respective values of 116.34 and 0.91 obtained by Adebayo (2004) at a different location in the Ondo tarsand, outside Agbabu village. The penetration of each bitumen sample falls in the range of 80-120mm as reported by Mumah and Muktar (2001), Adebayo (2004) and Srivastava and

Roijen (1988) for bitumen of acceptable grade. The flash point of each bitumen sample also lies in the range of 245 to 352^{o}C and is similar to results by Mumah and Muktar (2001) and Srivastava and Roijen (1988), for bitumens of good grade. The specific gravity of each bitumen sample compares favourably with that of asphalt standard (1.013) as reported by Adebayo (2004).

All bitumens weather at slow rates. The oxidation test shows that Ondo S-A has the least weathering resistance and weathers (shrink down) by 1.2mm in a five-week period of atmospheric exposure. This is followed by Ondo S-B by 1.1mm and KPB by 0.8mm as can be seen from Table 4.1d. This result is comparable with that of a similar test conducted by Mumah and Muktar (2001) using natural bitumen from rich deposits in other locations of the Nigerian bitumen belt in which they found that the bitumen weathered by 10mm from 35mm initial exposure to 250mm on the fifth week and the weathering resistance was satisfactory for 70/100 penetration (paving) grade bitumen.

KPB is the most vicious of the bitumen samples at all temperatures, followed by Ondo S-B and then Ondo S-A as can be observed from Table 4.1e. At 20^{0}C the viscosities of some types of bitumen range from 10^{3} to 10^{8} Poise depending on the type; compared to water 10^{-2} Poise, diesel 10^{-1} Poise, and engine oil 10 Poise. The viscosities however decreased with increase in temperature (Jackson and Ravindra, 1996). This trend of behaviour was observed with Ondo S-A, Ondo S-B, and KPB as can be seen in Table 4.1e. KPB is the most viscous sample, followed by Ondo S-B, and then Ondo S-A for the temperatures investigated.

Finally, the penetration value of 120mm for Ondo S-A, 116mm for Ondo S-B and 85mm for KPB; flash points of 260^{o}C for Ondo S-A, 269^{o}C for Ondo S-B and 320^{o}C for KPB; softening points of 36.5^{o}C for Ondo S-A, 37^{o}C for Ondo S-B and 45^{o}C for

KPB; specific gravities of 0.92 for Ondo S-A, 0.95 for Ondo S-B and 1.08 for KPB agree with penetration values of 60-70 and 80-100, flash points of 283 and 310, softening points of 45^{o}C and 42 and specific gravities of 1.01 and 0.998 as per international standard –IS 73:1992 for the 60/70 and 80/100 penetration grade bitumens respectively as given by Dixit and Rostogi (2013). The viscosities of 5190 to 6270 at 60^{o}C and 70 to 8.1 Poise at 150^{o}C are comparable to that between 800 to 3600 at 60^{o}C and 25 to 35 at 150^{o}C for all penetration grade bitumens as per IS-73:2006 as given by Jain (2014). The elemental weight compositions of 83.49 to 87.78% carbon, 9.35 to 10.51% hydrogen, 0.13 to 0.72% nitrogen, 1.25 to 1.74% oxygen and 1.14 to 1.32 sulphur of the bitumen samples are comparable to 83% carbon, 8% hydrogen, 6% sulphur respectively as per IS-73: 2006 for 80/100 penetration grade bitumens (Jain, 2014). The asphaltenes contents of 18.1 to 19.8%, naphtalene aromatics of 58.1 to 59%, resins of 10.9 to 11.5% and saturates of 5.2 to 7.89% of the bitumen samples are comparable to asphaltenes contents of 5 to 25%, naphthalene aromatics of 40 to 60% and saturates of 2 to 10% as per international standards IS-73 (2006) for average composition of all penetration grade bitumens (Jain, 2014).

4.2.2 Microstructure of the low carbon steel

Plates XXII show the sizes, shapes and boundaries of the revealed grains of each procured rod that had similar structure. For each plate, it can be seen that there are small-sized dark spots dispersed among the more or less grey crystals. The black spots are the pearlite while the grey crystals are the ferrite. This clearly agrees with Callister (2004), that the microstructure of low carbon steel consists of pearlite and ferrite. The plates show that the structures of the steel rods are similar and there is no clearly detectable sign of any crack or foreign inclusion etc in the steel material. It can also be observed that the pattern of distribution of the grey crystals is more or less the same in

each of the three plates. From this it is conclusive that the steels are indeed of the low carbon type and consistent in structure.

4.2.3 Chemical composition of the steel

The results in Table 4.2 show that the carbon content of the steel is 0.21% and this falls in the range that is less than or equal to 0.3% carbon content specification for low carbon steel in accordance to Callister (2004). The steel is indeed of a plain carbon type since it contains minimal amounts of chemicals such as copper, sulpur and phosphorus that can influence corrosion behaviour of the steel in accordance to Cotterel (1985).

4.2.4 Mechanical properties of low carbon steel specimen of specified coating treatment

4.2.4.1 *Tensile test*

Figures 4.1a to 4.1f show the overall pair stress-strain curves for specified status of coating treatment and corrosion of the steel specimen with various thicknesses of the bitumen samples. The level of inhibition performance (protection) or efficiency (η) was determined appropriately in accordance to the relation given by Wilson *et al* (2012) and Sulaiman *et al* (2013) as:

$$\eta = 1 - W_1/W_2 , \tag{4.1}$$

where W_1 and W_2 are corrosion rates in the presence and absence of inhibitor respectively. Expanding equation 4.1 for the case of stress-strain curves and changes in values we get:

$$\eta = 1 - \frac{(S^{TC} - S^{UU})/S^{UU}}{(S^{UC} - S^{UU})/S^{UU}} = (S^{UC} - S^{TC})/(S^{UC} - S^{UU}), \tag{4.2}$$

where, S^{TC}, S^{UC}, and S^{UU} are strain values of specimen in the presence, absence, and without the coat-inhibitor and corrosion respectively for the same applied stress value. From equation 4.2, the average inhibition performance value (IP) for n different stress values is given by equation 4.3. Using the actual as-obtained data values and the stress-strain curves the average inhibition performance (IP) by each bitumen sample of specified coating thickness on the tensile strength corrosion deterioration of the specimen used, is determined appropriately with 10 different stress-strain values as:

$$IP = \sum_{i=1}^{i=n} \frac{(\Delta T_i/\Delta C_i \times 100)\%}{n}, \quad \text{at } S_i, \qquad (4.3)$$

where ΔT_i is the average pair value difference in corresponding strain values between the UC curve (S^{UC}) and TC curve (S^{TC}) of the bitumen sample at an applied stress value of S_i, and ΔC_i is that between the UU (S^{UU}) and the UC (S^{UC}) curve values for the same S_i; with due consideration to any ageing or other effects in the UU and TU specimen; and 'n' is the number of stress loads considered. The evaluated IP for each case of bitumen sample, coating treatment and thickness is shown in Table 4.8.

In Figure 4.1a there are two stress-strain curves, the uppermost is the average behaviour for each pair of the UU, TU and TC specimen that were coat-treated at 150^{o}C with a thickness of 2.1mm. This implies that corrosion did not occur in the coat-treated specimen and the strain values and the corresponding stresses are the same for each case irrespective of the bitumen used. For each of Figures 4.1b to 4.1f there are five stress-strain curves. The uppermost curve is the average behaviour of each pair of the UU and TU specimen for all bitumen coating thicknesses. This implies that the strain values at the corresponding stresses are the same for each of the specimen irrespective of the bitumen sample and coating thickness used. The next curve to the uppermost one

in each Figure is the behaviour of the specimen coated with KPB and corroded – TC (KPB). This is followed by TC (Ondo S-B), and then TC (Ondo S-A). The lowest of the five curves in each case is for the un-treated but corroded specimen (UC). As the bitumen coating thickness decreases, the curves for specimen of the TC status shift closer to that of specimen of UC status. Each curve starts from an applied stress and strain of 0.0. Up to applied stress of about 300N/mm^2 each specimen is more or less perfectly elastic as characterized by the straight line portions of the curves, although the strains developed are different in each case. On proceeding beyond this stress of 300N/mm^2 defined as the elastic behaviour the material moves into plastic behaviour. Removing the load at some point leaves permanent plastic strain of 0.2% on each specimen at a given stress. The stress at that point is 0.2% proof stress (yield stress) in accordance with Doyle (1969). The stress was found for each case by drawing the indicated broken line. The point that leaves permanent plastic strain 'P' was found at the intersection of the broken line with each curve. Reloading each specimen along this line, the material is elastic until the stress passes the stress which produced permanent strain. From the tests the ultimate tensile strength (UTS) of the UU and all TU specimen was estimated to be about 425N/mm^2.

4.2.4.2 *Fatigue tests*

Figures 4.2a to 4.2f present the graphical pattern of data obtained under section 3.13.2. The comparative endurance curve patterns of each five-set fatigue specimen of indicated status of coating treatment thickness with each specific bitumen sample and or corrosion are shown in these figures, for the specified applied fatigue loads. Using the actual data values as depicted by the endurance curves, the average IP by each bitumen sample coating thickness on the corrosion fatigue strength of the low carbon

steel specimen was determined appropriately as (Wilson *et al*, 2012 and Sulaiman *et al*, 2013):

$$IP = \sum_{i=1}^{i=n} \frac{(\Delta T_i / \Delta C_i \; x \; 100)\%}{n} at \; S \quad , \tag{4.4}$$

where ΔT_i is the difference in corresponding average pair values of the number of cycles to failure between the UC curve and TC specimen, for a given coating thickness and an applied stress value of S, and ΔC_i is the difference between the UU and the UC values for the same S with due consideration to any ageing effects in the UU and TU specimen; and 'n' is the number of stress loads considered. The IP is shown in Table 4.9.

For Figure 4.2a, there are two endurance curves. The uppermost curve is the behaviour of all UU, TU and TC specimen at the coating thickness of 2.1mm irrespective of the bitumen sample used while the lowest is for the UC specimen. This shows that no change occurred in the UU, TU and TC specimen in relation to one another. For Figures 4.2b to 4.2f, there are five endurance curves and the applied cyclic stresses on each fatigue specimen range from 250N/mm^2 to 350N/mm^2. The uppermost curve in each figure is the one for average pair values of two five-set of each of the UU, or TU specimen for the specified coating thickness. This implies that the number of stress cycles to failure at the corresponding stresses is the same for the UU and TU sets of specimen irrespective of the bitumen sample and coating thickness used. The next curve to the uppermost one of each figure is for pair values of two five-set set specimen coat-treated with KPB and corroded. This is followed similarly by that for Ondo S-B and then Ondo S-A, all at the specified coating thickness. The lowest curve is for a pair of two five-set UC specimen. It can be observed from Figures 4.2a to 4.2f that, as the

bitumen coating thickness decreases the curves for the TC specimen shift closer to that of the UC five-set specimen.

4.2.4.3 *Hardness tests*

Figure 4.3 shows graphically effects of coating treatments of various thicknesses and various levels of corrosion versus the Knoop micro-hardness (HK) of the test steel specimen. The IP by each bitumen sample and coating thickness on the hardness corrosion deterioration was determined as (Wilson *et al*, 2012 and Sulaiman *et al*, 2013):

$$IP = (\Delta T_i/\Delta U \times 100)\% \; at \; i, \tag{4.5}$$

where ΔT_i is the difference in average pair values of micro-hardness between the UC and TC; and ΔU that between the UU and UC specimen for the case of a given coating thickness (i) with due consideration to any ageing or other effects in the specimen. The computed IP is shown in Table 4.10.

Figure 4.3 shows that all the UU and TU specimen have the same micro-hardness of 130.78HK irrespective of the bitumen sample and coating thickness used. This value drops to 120.31 for each of UC specimen. With bitumen coating treatment on the specimen to a thickness of 2.1mm and corrosion, the hardness value improves from the UC status to 129.8 HK for the case of KPB-treated specimen, 129.79 HK for the specimen treated with Ondo S – B and 129.75 HK for Ondo S-A. The pattern of the graph of hardness values for the TC specimen decreases thence with decrease in the coating thicknesses shown in brackets to final values of 126.25HK, 126.22HK, and 126.21HK respectively for specimen treated with KPB, Ondo S-B, and Ondo S-A respectively; at the coating thickness of 0.81mm, that is TC 0.81.

4.2.4.4 *Impact tests*

Figure 4.4 shows the effects of coatings of different thicknesses and levels of corrosion on impact energy for the bitumen samples. The average IP for each bitumen sample and coating thickness used on the impact strength corrosion of the specimen is determined appropriately as (Wilson *et al*, 2012 and Sulaiman *et al*, 2013):

$$IP = (\Delta T_i/\Delta U \times 100)\% \quad , \tag{4.6}$$

where, ΔT_1 and ΔU are the average pair values of changes in impact energy between the impact energies of the UC and TC, and UU and UC specimen respectively; for the case of a given coating thickness with due consideration to any ageing or other effects in the UU and TU specimen. The IP is shown in Table 4.11.

From Figure 4.4, each of all the UU, and TU specimen have the same average pair impact energy of 93.63J irrespective of the bitumen sample and coating thickness used. This value drops to 86.1J for each pair value of UC specimen. With coating treatment thickness of 2.1mm and corrosion (TC), the impact energy value of the specimen improves from the UC status back to 93.633J for each bitumen sample used. The impact energy values for TC specimen depreciates thence with decrease with the coating thickness to final values of 90.37J, 90.36J, and 90.35J for those treated with each of KPB, Ondo S-B; and Ondo S-A respectively; at the coating thickness of 0.81mm.

4.2.5 Statistical assessment of corrosion inhibition of the mechanical properties by the bitumen coatings

The inhibition efficiencies of the bitumen coatings shown in Tables 4.8 to 4.11 were analyzed in the statistical aspects of dispersion and presented as in Table 4.12. This is because statistical methods of experimental or production assessments provide the basis for making decisions, determining errors, precision and general validity of

measurements; or performances. Statistical methods are more reliable both in multi-sample and single-sample data analysis. Dispersion is a statistical method of analysis that determines the variability of performance of a process, or material on the basis of data obtained from it. In most production processes, it is desirous that the process itself and the materials used should be consistent or within a specified range of variability in quality (Holman, 1984; Miller and Freund, 1987; Evans and Lindsay, 1996 and Jain and Aggarwal, 2008). With this backdrop, the mean inhibition performance (IP) of a set of inhibition data is defined as,

$$\overline{IP}=\left(\sum_{i=1}^{i=n} IPi\right)\Big/ n\,, \qquad (4.7)$$

where $\overline{IP_i}$ is the inhibition performance data value and n is the number of data values considered in the sample. In this case n equals six. A high value of $\overline{IP}$ for a set of sample data as judged among other ones gives an indication of better corrosion protection performance by the bitumen sample. In quality control the mean of data value is used in one of the principal control charts (Miller and Freund 1987).

The range (R) of a given set of inhibition data was obtained in accordance with Miller and Freund (1987) as:

$$R = IP_{imax} - IP_{imin} \qquad (4.8)$$

In quality control the range is a very common measure of dispersion. It is also used in one of the principal control charts. It will provide knowledge of the total spread of the inhibition data values from a bitumen sample. IP_{imax} is the highest value in the data and IP_{imin} is the least. The higher the value of R for a given data set, the more the given data values are spread away from mean range of ranges of given different data sets and this gives an indication of worse performance by that set among the others. However, care

must be taken when interpreting the range since a single relatively large or small value in data in a set can greatly inflate its value and be comparatively further away from the average value of the set (Miller and Freund, 1987 and Grant and Leavenworth, 1996).

The standard deviation (σ) is a measure of spread of the inhibition data values from a bitumen sample about its mean value. The smaller the value the better the measured, and closer the overall sample data values are to the mean value, and are given by Miller and Freund, (1987) as:

$$\sigma = \left[\frac{\sum_{i=1}^{i=n} (\overline{IP} - IP_i)^2}{n-1} \right]^{1/2} = \left[n \sum IP^2_i - (\sum IP_i)^2 / n(n-1) \right]^{1/2} \text{ for } i = 1 \text{ to } n \qquad (4.9)$$

A large value of σ shows greater spread of the sample data values about the mean value and variability in the coat-inhibition performance by a bitumen sample.

The coefficient of variation (V) is standard deviation per unit mean value and is given by Miller and Freund, (1987) as:

$$V = [\sigma / \overline{IP}] \times 100 \ (\%) \qquad (4.10)$$

The computed values of these statistical parameters using appropriately equations 5.5 to 5.8 and a digital computer are presented in Table 4.8.

From the mean inhibition values presented in Table 4.12, it can be observed that KPB provides the highest corrosion inhibition for each of all the four mechanical properties of the steel at the mean coating thickness of 1.283mm. This performance is followed by Ondo S-B and then Ondo S-A. For each bitumen sample used, the hardness protection of this steel is highest, followed in order by that of its tensile strength, impact strength, to the lowest by that of the corrosion fatigue strength at the mean coating thickness. The overall least protection of any of the four mechanical properties at the mean

coating thickness is 71.69%, from corrosion fatigue strength by Ondo S-A, while the best possible is 90.08% from hardness by KPB.

The standard deviation values for the hardness protection are least as can be observed from Table 4.12. The results show that the protection is least amenable to changes in coating thickness from the mean value as compared to the other mechanical properties. This is also clearly upheld by the least range (R) for the property by the bitumen samples. Thus, by this statistical parameter the performance of the hardness protection by the bitumen sample are the best. On the other hand, the table shows that, comparatively corrosion fatigue strength inhibition performances by the bitumen samples are the least based on the standard deviation and range analysis.

The ranges (R) for the inhibition protection of the tensile and impact strengths are generally in close range or, more or less similar in values as compared to one another as can be observed from Table 4.12. However, the standard deviation values for the tensile strength protection are generally lower and hence better than those for impact strength. This also shows that the protection of the tensile strength has an edge over that of impact fracture strength.

The standard deviation and ranges of corrosion inhibition values also show clearly that protection of hardness and corrosion fatigue strength of the steel by KPB are generally best, and second best for the case of tensile strength of the steel. The values also show that the protection offered by the KPB bitumen sample for the impact strength is comparable with that of Ondo S-A and Ondo S-B as can be observed from Table 4.12. The ranges and standard deviation values also show that the result for protection by Ondo S-B is best for the tensile strength and second best for micro hardness and impact

strength. The result for Ondo S-A is best for impact strength and second best in hardness protection as judged from standard deviation of inhibition values.

From the coefficients of variation values shown in Table 4.12, it can be observed that the values for KPB are generally best followed by those of Ondo S-B and then Ondo S-A.

From Tables 4.8 to 4.11, it is apparent that corrosion inhibition increases with coating thicknesses of the bitumen samples. With the coating thicknesses used for the tests, it has been possible to completely inhibit effects of corrosion on the steel's properties only at the 2.1mm thicknesses. Ideally the metal selected or the protective system applied to the metal should be such that no corrosion occurs at all, but, this is seldom technologically or economically feasible. It is therefore necessary to tolerate a rate and a form of corrosion that will not be significantly detrimental to the properties of the metal during its anticipated life'. Since structural steel is not smooth, organic coating or paint film thicknesses on it do vary over quite small areas; thus for adequate cover, a thickness well over the mean value is necessary. For an adequate barrier against moisture, a minimum paint film thickness of about 0.125mm of oil-based paint has been found necessary for steel but in wet conditions this is not sufficient (Johnson, 2001). Therefore, any coating thicknesses must be exploited higher than 2.1mm to completely inhibit corrosion of the steel. From Tables 4.8 to 4.12 it is very clear that, generally, the inhibition performances of the bitumens are comparable for each coating thickness and mechanical property and the manufactured bitumen has an edge over the other bitumen samples in the performance followed by clear natural bitumen samples from underground and then that from waterlogged areas. This also agrees with comparability of qualities of the bitumen samples by analysis of their physico-chemical properties.

4.2.6 Inhibition performances by extracted chemical fractions

4.2.6.1 *Hardness tests*

Figure 4.5a shows that the average micro-hardness of a pair of untreated and uncorroded (UU) specimen is 130.78HK. This value drops to 120.35HK for a pair of specimen that was submerged in exposure to the prepared corrosive solution without any of the chemical fractions in it (WCF). When the WCF was separately treated with 50g of asphaltenes, 50g of naphthalene atomatics, 50g of saturates and 50g of resins from each bitumen sample, using a different pair of specimen in each case, the average hardness improves from 120.35HK to 125.1HK, 120.7HK, 120.35HK, and 120.89HK of the treatments respectively. On the other hand, Figure 4.5b shows that when the test was repeated using 70g of each chemical fraction in each case, the average hardness improved from 120.35HK to 126.9HK, 120.36HK, 120.38HK and 120.91HK with each case of asphatenes, naphthalene aromatics, saturates and resins treatments of the WCF respectively.

4.2.6.2 *Impact tests*

Figure 4.6a shows that the average impact fracture energy of a pair of untreated and uncorroded (UU) specimen is 93.63J. This value dropped to 87.48J for a pair of specimen that were immerse-exposed in the prepared corrosive solution without any of the chemical fractions in it (WCF). When the WCF was separately treated with 50g of asphaltenes, 50g of naphthalene aromatics, 50g of saturates and 50g of resins from each bitumen sample using a different pair of specimen in each case, the average impact fracture energy improved from 87.48J for the case with WCF to; 90.27, 87.6, 87.55 and 87.8 respectively. On the other hand, Figure 4.6b shows that when the test was repeated using 70g of each chemical fraction in each case, the average impact fracture energy

improved from the 87.48J to; 90.89J, 87.61J, 87.56J and 87.81J with each case of asphaltenes, naphthalene aromatics, saturates and resins treatments of WCF respectively.

Figures 4.5 and 4.6 under section 4.6 indicate that the asphaltene chemical fraction is outstandingly the most contributory to inhibiting corrosion deterioration of each of the two mechanical properties of the steel. The inhibition by a chemical fraction type is the same irrespective of the bitumen sample it is extracted from. Naphtalene aromatics, saturates, and resins each contribute minimally to the overall inhibition performance of a bitumen sample as can be observed from the figures. One would have expected naphthalene aromatics which constitute the largest fraction in each bitumen sample as can be seen from Table 4.1b to contribute most to the inhibition but it is only third to the highest in the contribution, while saturates contribute the least. It can be inferred that the inhibition performance by a chemical fraction is more or less proportional to its molecular weight in accordance to information from Srivastava and Roijen (1988) and Fan and Buckley (2011). It is also observable from the results that although the saturates, resins and naphtalene aromatics content of KPB are also appreciable, effects of its corrosion inhibition on each of the mechanical properties is highest because its asphaltenes content is highest among the bitumen samples as can be observed from Table 4.1b, while that of Ondo S-A is least because its asphaltenes content is lowest. It can also be seen that the proportion of naphtalene aromatics and resins in Ondo S-A are appreciable but its overall inhibition performance on a given mechanical property of the steel is least. From Figures 4.5a and 4.5b, it is also clear that corrosion inhibition of a bitumen sample increases dramatically with its asphaltenes content as compared to the other chemical fractions. It is however noteworthy that, bitumen generally contains traces of water, mineral accessories, sands, and some other less important chemical

compounds. It is the interaction and association of all these, asphaltenes, naphthalene aromatics, saturates, and resins, that produce the overall inhibition performance of a whole bitumen sample on a metal. According to Srivastava and Roijen (1988), "one of the technologies to upgrade bitumen without need for expensive facilities is to restore and/or improve the balance between its chemical fractions, particularly between asphaltenes and resins. This is achievable by adding special additives to the bitumen. To assure that these additives are fully incorporated in the bitumen, they need to be compatible with the bitumen. Bitumen upgraded in this way is stiffer, less temperature-susceptible, and more resistant to ageing than the original bitumen". From this statement, it can also be inferred that the asphaltenes and resins have more important role in technological applications of bitumens than the other chemical fractions.

4.2.7 Comparative assessment of the bitumen coatings and sodium benzoate as a standard corrosion inhibitor

From Tables 4.13 to 4.16, it is demonstrable that the inhibition efficiencies increase with the quantity of sodium benzoate treatment of the medium likewise with the coating thickness of the bitumen. The highest inhibition performance (27%) of the benzoate at its 250ppm concentration treatment of the medium is much lower than the least value of 53.36% from the least bitumen coating thickness of 0.81mm. In the atmosphere, corrosion of steel increases with chloride and moisture contents of the air depending on the distance from the natural source, prevailing temperature and humidity and other conditions. At a very high chloride content of 11.1% and 50 yards from the tropical surf beach and high humidity in Lagos, Nigeria; the corrosion rate for ingot iron is 0.95mm/yr as obtained by Ambler and Bain (*Sodium Benzoate,* 2011). By continuous aeration and circulation of the corrosive admixture (30% NaCl, 5% H_2SO_4 and 65% water), the corrosive medium simulates the specimen's exposure to the

atmospheric tropical surf beach environment of 100% relative humidity and acidic nature. By the aeration and circulation of the medium more of the benzoate inhibitor, the dissolved sodium chloride and oxygen are supplied in contact with the specimen. This enhances the effectiveness of the inhibitor, whilst by the continuous contact supplies of oxygen and the sodium chloride the corrosion agents are invigorated. In aerated distilled water, as little as 0.007% of sodium benzoate concentration effectively inhibits steel corrosion, but inhibition is not observed in deaerated distilled water. The increase in corrosion with sodium chloride concentrations in all aqueous environments is due to enhanced solution conductivity. However, in aqueous medium that is not continuously aerated and circulated increase in sodium chloride concentration leads to higher dissolved salts and this leads to decrease in solubility of dissolved oxygen and corrosion rate decrease steadily beyond 3% by weight of the sodium chloride (Alwan, 2010). High inhibition performances with 100ppm treatment concentrations of 3% by weight sodium chloride solution prepared separately at different pH levels of 3, 5, 7, 9, and corresponding temperatures of 25, 30, and 40^{o}C; have also been obtained by Alwan (2010). He found that the inhibitor effect decreased with temperature of the solution but increased with pH values. The highest inhibition performance value (88%) was obtained at the solution condition of 25^{0}C and pH = 9, while the lowest (74%) at 25^{o}C and pH = 3. The comparatively poor performance of the sodium benzoate treatment concentrations of the test corrosive medium in inhibiting the corrosion deterioration of the steel properties is because it is negatively affected by sodium chloride even in small concentrations as low as 0.1% in any environment (INTERNET, 2011b) but the prepared corrosive medium contains as much as 30% of sodium chloride, though its acidity is low at 11.2. Moreover, it is due to the continuous aeration and circulation of the medium.

4.2.8 X-ray diffraction analysis

Results for KPB coating No. 1 show the presence of sucrose, sucrose octaacetate, nickel iodide triethylamine n-oxide, codeine phosphate dihydrate and barium neodymium titanium oxide mineral phases total 4.374% by weight within the scanned area. The identified principal mineral phases in KPB coating no. 2 are HCL, zirconium oxide, codeine phosphate dihydrate, nickel iodide triethylamine n-oxide, sucrose octaacetate and sodium aluminium silicates totalling 4.847% by weight within the scanned area. Ondo S-A coating is constituted of five different mineral phases which are principally; lead oxide, magnesium silicate hydroxide, chromium nitride and calcium silicate hydroxide hydrate totalling 3.75% by weight. From results in Tables 4.17 to 4.19 it can also be observed that most of the chemical elements carbon, hydrogen, oxygen, sulphur, aluminium, nitrogen, vanadium, titanium, manganese that constitute the distinct mineral phases by the XRD analyses are also found in the entire structure of the bitumen as shown in Table 4.1 by results from the neutron activation analysis and the chromatographic methods.

The difference between the as-produced KPB coatings (Nos. 1 and 2) is in the presence or absence of the sucrose, iron chromium oxide, sodium aluminum silicate, hydrochloric acid, barium neodymium oxide in one or the other. This means that, there are some microstructural variations in the as-produced coatings even with bitumen from the same source. This by implication indicates that even a very small quantity of bitumen is not regularly chemically structured within itself. This agrees with UNEP and ILO (2004) of the complexity of chemical composition and structure of bitumen which scientists and engineers are yet to completely analyze.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results and discussions of the study, the following conclusions can be drawn;

i. The natural bitumen around the region of Agbabu village in Ondo state, and a KRPC-manufactured bitumen with the blend of Basara and Nigerian crudes in Nigeria are of high and acceptable qualities in comparison to reputable bitumens of high qualities from other locations in the world as per international standards-IS 73:1992 and 2006, and UNEP and ILO for 60/70 and 80/100 penetration grade bitumens.

ii. Coat-treating the steel specimen in the range of 0.81 to 2.1mm coating thicknesses with the bitumen manifested in appreciable inhibition of corrosion deterioration of mechanical properties of the steel to the tune of 63.0 to 100% tensile strength, 53.5 to 100% fatigue strength, 69.53 to 100% hardness, and 57.26 to 100% impact strength in an aerated high sodium chloride acidic test medium.

iii. Corrosion coat-inhibition of the test bitumen samples depends mainly on and increases with their asphaltenes contents. This information is useful when sourcing for bitumen of optimal corrosion inhibition capabilities from resource sites.

iv. In comparison with the coatings, sodium benzoate treatment concentrations in the range of 50 to 250 ppm provided the highest inhibition of 27.4% at the 250 ppm concentration in the same medium.

v. About 3.75 to 4.84% by weight of the coatings consist of distinct mineral phases that vary in type and amounts with even bitumen from the same location.

5.2 Recommendations

The following recommendations are made from the study:

i. Bitumens of comparable quality to clear natural bitumens around the region of Agbabu village and the KRPC-synthesized bitumen with the blend of Nigerian and Basara crudes from Nigerian resources are recommended to be produced in large quantities and used for corrosion coat-protection with consideration of coating thicknesses from 2.1mm.

ii. The study and results from it should serve as basic and technical information for design coating-treatments; and by extension formulation of corrosion-resistant coatings such as paints, bituminous wrappings, admixtures in concrete encasements etc; and modifications of the bitumens to economically reduce the cost and effects of structural steel corrosion in pipelines, surface and underground tanks in water, petroleum and other chemical industries in the country.

iii. The bitumen coatings must be oxidized to dry-harden them to prevent them from changing properties with temperature change before service use.

iv. Notwithstanding the good corrosion inhibition performance by the bitumen coatings, field and service tests should be additionally conducted on similar coatings of the same bitumens on the same steel to crosscheck and optimize the inhibition data.

v. Researches on optimal modifications of bitumens from the sample sources to mitigate poor characteristics such as temperature-dependence of properties

which are generally associated with all bitumens should be conducted using locally available materials in Nigeria.

vi. Similar tests with coating treatments of bitumens from other locations in Nigeria should be conducted to complement results from this work.

vii. The Nigerian Standards Organization should understudy the coat-inhibition information from this study vis-à-vis other further parallel and relevant information in conjunction with existing standards worldwide on coating usage of bitumens and issue a code of practice for bitumen.

viii. Researches on development of a facility for automated mass coating of metals with bitumen by the bath dipping method should also be undertaken.

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APPENDIX

LITERATURE REVIEW INFORMATION

Table 2.1: Approximate constitution of the atmosphere at 38^{o}C and 100KN/m^{2} excluding impurities (Meetham, 1968)

Constituent	Weight [g/m^{3}]	Weight [%]
Air	1172	100
Nitrogen	879	75
Argon	15	1.26
Water Vapour	8	0.70
Carbon Dioxide	0.5	0.04

Table 2.2: Effects of sea salt on the rate of rusting (Shreir, 1979a)

Distance from the surf (Yards)	Salt content of air (%)	Rate of rusting (mm/year)
50	11.1	0.95
200	3.1	3.80
400	0.8	0.055
1300	0.2	0.040
25 miles	-	0.048

Table 2.3: Effect of month of exposure on the corrosion rate of steel (Chandler and Stanners, 1963)

Month test begun	Rate of rusting [mm/year]
January	0.081
March	0.064
May	0.076
July	0.070
September	0.94
November	0.89

Table 2.4: Effect of plate thickness on corrosion of steel (Shreir, 1979a)

Plate thickness (mm)	55	28	12.5	5
Average general penetration (mm)	0.038	0.033	0.031	0,030

Table 2.5: Effect of the surface condition at the time of exposure on the atmospheric corrosion of mild steel as conducted by (Shreir, 1979a)

Surface condition	Average penetration [mm]
As-rolled	0.545
Picked	0.545
Sandblasted	0.532
Machined	0.534
Polished	0.532

Table 2.6: Rates of rusting of mild steels in sea water as reported by Shreir (1979a) for a 2003–day Total immersion at Plymouth, Britain.

S/N	Types of Steel	Analysis %				Average General Penetration (mm/y)
		C	Mn	P	S	
1.	Basic Bassemer, Rimming Ordinary	0.05	0.64	0.60	0.02	0.143
	High Phosphorus	0.03	0.31	0.14	0.143	0.143
	High Phosphorus and sulphur	0.03	0.30	0.10	0.07	0.148
2.	Open-hearth, rimming	0.13	0.33	0.03	0.03	0.143
	Ordinary from haematite pig	0.03	0.32	0.01	0.03	0.140
3.	Open – hearth, killed Ordinary	0.10	0.35	0.03	0.02	0.0140
	From haematite pig	0.11	0.34	0.01	0.03	0.136
4.	Open – hearth, killed Ordinary	0.22	0.71	0.03	0.03	0.143
	From haematite pig	0.21	058	0.02	0.03	0.158

C = carbon, P = phosphorus, MM = manganese, and S = sulphur contents of the steel.

Table 2.7: Effect of exposure period on corrosion rate of mild steel in sea water (Shreir, 1979a)

Exposure time (months)	Average corrosion rate (mm/year)
1	0.33
2	0.25
3	0.19
6	0.15
12	0.13
24	0.11
48	0.11

Table 2.8: Effect of depth of burial on the rusting of mild steel fiats as obtained by Shreir (1979a) for a test duration of 5 years

Site	Type of soil	Average general penetration (mm/year)	
		1.37m Depth	0.61m Depth
Benfleet	London clay	0.0185	0.0361
Gothan	Keuper mart	0.0132	0.0094
Pitsea	Alluvium	0.0353	0.0284
Rothmsted	Clay with flints	0.0201	0.0213