# EXPERIMENTAL ACCOUNT FOR VARIATION IN LEVELS OF CORROSION COAT-INHIBITION PERFORMANCES AMONG BITUMENS

By

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**Abstract**

*Corrosion of carbon steel as a prime structural material is a much more serious and costly problem in the oil and gas industries where corrosion is preponderant. Bitumen exists naturally or is manufactured in different locations and qualities around the world. Previous studies have shown that, Nigeria has abundant bitumen resources for sustained exploitation as common and economical coat-inhibitors of corrosion in the key sectors of her economy, and the inhibition protection of a metal such as low carbon steel by a given coating thickness of each bitumen obtained from different sources can vary widely depending on the* *quality of the bitumen. To account for such variation, three bitumen samples were procured at three different critical locations of Nigerian bitumen resource sites and each was separated into its principal chemical fractions. The capability level of each fraction per se to inhibit corrosion deterioration of impact fracture strength and then hardness of a low carbon steel were test-determined. Analyses of the obtained results indicated that the inhibition depends mainly on a sample's asphaltenes content and will increase with the content. The paper contributes to applicable information for optimal quality harvesting of bitumen from Nigerian and other sources for corrosion protection of structural steel works.*

The key economic sector of Nigeria is oil and gas. The oil and gas sector generates up to 85% of her total revenue. Petroleum products are transported from one state to the other through pipelines which pass through the sea, rivers, underground or on the surface of the soil in urban and rural areas to their respective destinations. The deterioration of these pipelines and other aspects of plants in the sector as a result of corrosion is a huge cost to the country in terms of subsequent oil leakage and spillage, product contamination, reduction of efficiency of operating plants, loss of production, over design, protection and maintenance, replacement of parts, fire and other general losses. Moreover, the increasing stringent environment and safety laws make almost any kind of fluid leak to the environment unacceptable (Shreir, 1979; Ali, 1998; Wami, 1998; Yawas, 2006; Guma and Oguchi, 2011). About 80% of refinery equipment and transmission pipelines are made up of carbon steel particularly of the low carbon class (Yawas, 2006). The amount of steel which is allowed to rust away for lack of adequate protection amounts to about 1000 tonnes every single day (Higgins, 1993). It is therefore important that these pipelines should be properly protected at economical costs.

There are many methods of protecting steel from corrosion, however the most economical, versatile, and commonly used method is by paints or organic coatings. It is estimated that about 90% of all steel surface are protected with paints or organic coatings (Laque, 1975; Pludek, 1977).

Bitumen is a cheap, common and important organic material in today's technological world. It has been used in various forms such as; bituminous wrappings, bituminous tapes, bituminous paints, admixtures in concrete encasements, coatings or coating supplements to other protective methods, etc; for protecting steel used in pipelines and other aspects of plants in the petroleum or other chemical and water industries from corrosion, based on its excellent resistance to industrial pollution (Jackson and Ravindra, 1996). In Nigeria, natural bitumen has been found in Ondo, Lagos, Ogun, Edo and Enugu States with a proven reserve of over 14.6 billion barrels. Ondo State is however the most important source area and Kaduna Refining and Petrochemical Company (KRPC) the most important synthetic bitumen outfit in Nigeria with an installed capacity for manufacturing up to 4,000 barrels of bitumen in a day (Oshinowo, Ademodi and Adediran, 1982; Fed. Min. Sol. Mine. Dev. 2006; Olalere, 1991; Field Surveys, 2009; INTERNET, 2012). The bitumen content or quality of the Nigerian tarsand is not the same but varies from location to location and from topsoil downwards. Very rich natural bitumen deposits are found in Ondo State around Idiobilayo, Foriku, Agbabu, Okitipupa and Aiyibi (Oshinowo et al, 1982; Sheikh, 2003; Fed. Min. of Sol. Mine. Dev, 2006).

Experimental assessment of capability levels of each of three whole bitumen samples-Ondo S-A, Ondo S-B; collected from clear natural bitumen deposits in a waterlogged area and underground through a standard extraction hole at Agbabu village in Ondo State; and KPB from bitumen synthesized at KRPC with Nigerian crude blended with Basra crude from Iran as feedstock; to coat-inhibit corrosion deterioration of mechanical properties of a low carbon steel had been undertaken by Guma, Madakson, Yawas and Aku (2010, 2011a-b; 2012). Analyses of the obtained results showed different but appreciable inhibition performances by various coating thicknesses for each case of the bitumen samples. Comparatively, the samples generally performed in close range but KPB exhibited the highest inhibition performance and Ondo S-A the least

Bitumen can generally be divided into two broad chemical groups asphaltenes and maltenes. The maltenes can further be divided into three main chemical fractions- naphtalene aromatics, resins, and saturates. Asphaltenes are considered as highly polar, complex aromatic materials with a tendency to interact and associate. They have fairly high molecular weights ranging from about 1000 to 100,000. The asphaltenes content has a large effect on the rheological characteristics of a bitumen. Increasing the content produces harder bitumen with lower penetration, higher softening point and consequently higher viscosity. Generally most bitumen contain between 10 to 20% asphaltenes. Aromatics (naphtalene aromatics) are weakly polar. They serve as the dispersion medium for the peptised asphaaltenes and constitute 55 to 75% of a whole bitumen. Their average molecular weight ranges from 300 to 2000. Resins (polar aromatics) are very polar in nature and are dispersing agents for the asphaltenes. Resins have molecular weights ranging from 500 to 50,000. Generally bitumen contains 10 to 25% resins. Saturates (aliphatic) are non-polar viscous oils with a similar molecular weight range to aromatics. The components include both waxy and non-waxy saturates. Saturates contain from 5 to15% of the bitumen. All these bitumen chemical fractions are soluble in carbon disulphide (Srivastava and Roijen, 1988; Mumah and Muktar, 2001; INTERNET, 2011). . The prime objectives in this paper are as follows.

i. To separate each of Ondo S-A, Ondo S-B and KPB into its principal chemical fractions.
ii. To determine the level of corrosion inhibition of treatments on the low carbon steel used by Guma et al (2010, 2011a-b, 2012) involving each fraction per se through its resistance to impact fracture strength and hardness deteriorations of the steel using appropriately, properly prepared specimens of the steel.
iii. To analyze the collected results to account for the variation in the inhibition performances among the different sourced whole bitumen samples.

## Materials and Methodology

### Materials

The materials used for the test were:

a. The remaining and same procured low carbon steel rods of ascertained consistent similar chemical composition and microstructure used by Guma et al (2010, 2011a-b, 2012)
b. Portions of the remaining three different bitumen samples Ondo S-A, Ondo S-B, and KPB; used by Guma et al (2010, 2011a-b, 2012).

### Methodology

A portion (420g) of each as-collected bitumen sample was separated into its main chemical fractions; saturates naphthalene aromatics, resins and asphaltenes. The asphaltenes was first separated as the insoluble phase by adding 300ml of n-heptane to a portion of Ondo S-A in a glass beaker followed by properly stirring it for two hours and then allowing the portion solution to settle overnight. The insoluble asphaltenes were obtained by filtering the solution through filtering paper using Schleider and Schull No. 50 prepleated filters. This was done in accordance with the method used by Srivatava and Roijen (1988) and Huang (1997). The remaining maltene material was separated chromatographically by heating it in the temperature range of 300 to over 400$^{o}$C in a closed steel container with a control opening of a liquid-gas chromatography separating unit and injecting it into a special separation column of the unit that was made to absorb and elute out; the saturates, naphthalene aromatics, and resins with alkane, aromatics and polar solvents respectively. This was similarly repeated with a portion of Ondo S-B, and then KPB, all in principle to the methods used by Pavia, Lapman and Kriz (1982), Huang (1997) and, Fan and Buckley (2002). The type and percentage amount of each chemical fraction in the bitumen samples as separated and extracted are presented in Table 1.

**Table1: Mass Percentages of Some Chemical Fractions Separated and Extracted From the Bitumen Samples**

| Bitumen Sample | Chemical Fractions by Mass % | | | |
|---|---|---|---|---|
| | | Maltenes Materials | | |
| | Asphaltenes | Naphtalene aromatics | Resins | Saturates |
| Ondo S-A | 18.1 | 59.0 | 10.9 | 5.2 |
| Ondo S-A | 18.6 | 58.3 | 11.1 | 6.1 |
| KPB | 19.8 | 58.1 | 11.5 | 7.8 |

Meanwhile the procured low carbon steel rods each of whose consistent as-analyzed average composition by percentage elemental weight by Guma et al (2010; 2011a-b, 2012) is shown in Table 2; were used to machine-produce 25 hardness test specimens each of diameter 25mm and thickness 8mm; and 25 ASTM impact fracture test specimens.

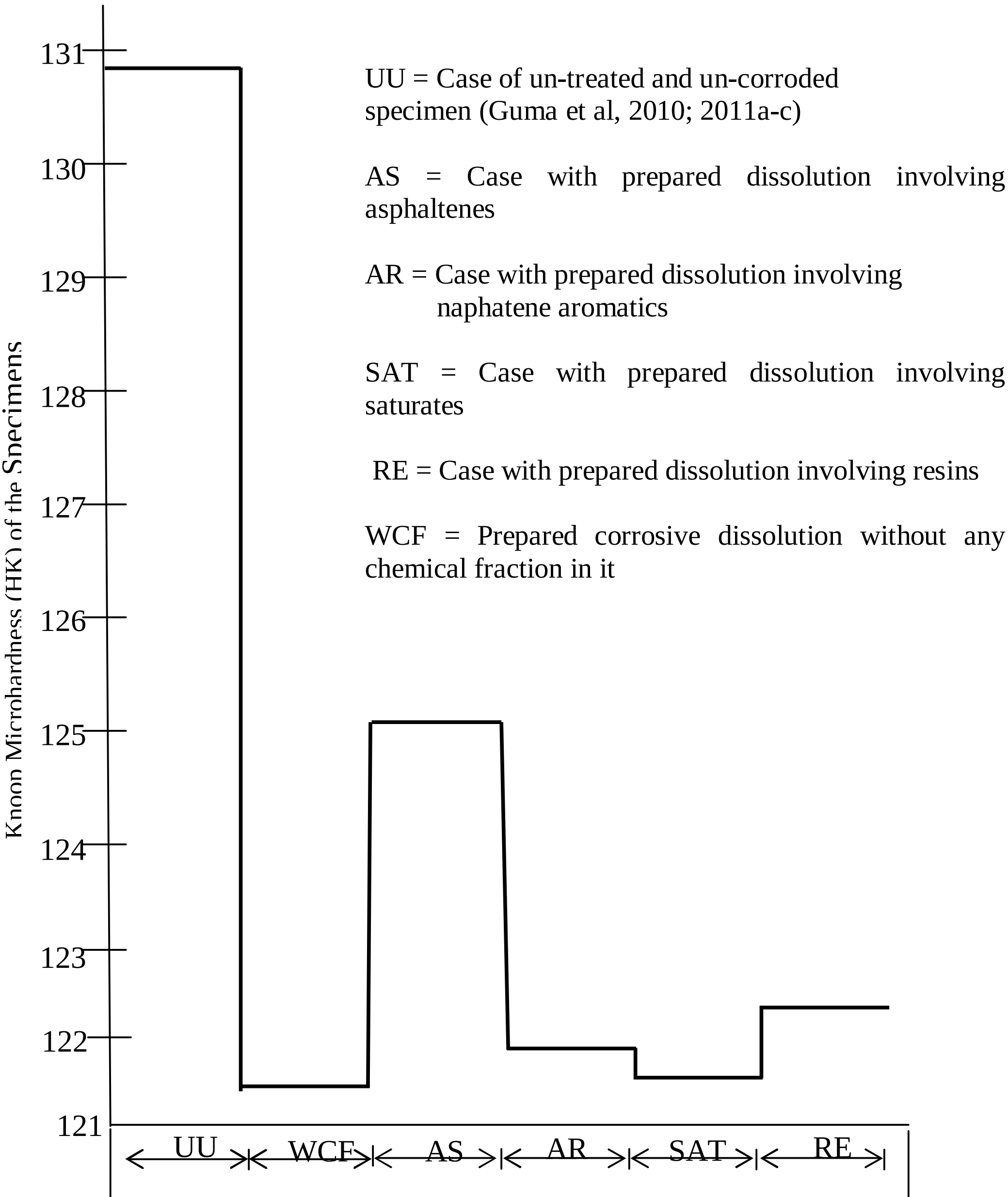
Table 2: **Ascertained Overall Consistent and Similar Chemical Composition of Each of All the Low Carbon Steel Rods Used For the Tests (Guma Et Al, 2010; 2011a-B, 2012)**

| Element | Ca | Mn | Mo | Eu | Fe | Ag | C | Si | S | Re | Cu | Ni | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [%] by weight | 0.095 | 0.29 | 0.20 | 0.05 | 95.21 | 0.50 | 0.26 | 0.60 | 0.83 | 0.20 | 0.14 | 0.30 | 0.29 |

Each produced specimen was then similarly machine-polished with various grades of polishing paper starting with the 250-grade and finishing with the 400, followed by etching it in nital. This produced a consistent average surface finish of 25 microns on each specimen as was ascertained using a profilometer. Each polished specimen was then relieved of any possible machining stresses in it to its as-received steel status by properly normalizing it by heating it in a furnace to a temperature of about $850^0$C, holding it there for enough time of about two hours, removing and cooling it in air at room temperature. These were all in accordance with the procedures used by Laque (1975), Pludek (1977), Barton(1976), Shreir (1979), Rajan; Sharma and Sharma (1977), and Guma et al (2010, 2011a-b, 2012). The prepared specimens were thence used to investigate corrosion inhibition of the steel by each extracted chemical fraction from each bitumen sample through the fraction's effects on corrosion deterioration of the steel specimen's hardness and impact fracture properties. This was achieved by dissolving 50g of each chemical fraction separately in 30ml of carbon disulphide in a 100-ml test tube followed by adding 20ml of con. $H_2SO_4$ to each tube content to obtain a corrosive dissolution involving a specified fraction from each sample. In this way, corrosive dissolutions were prepared in 12 separate test tubes. Also a corrosive dissolution was similarly prepared in another test tube but without any of the samples' chemical fraction in it (WCF). The dissolutions were each properly mixed, and one hardness and one impact test specimens were then soaked in each dissolution and exposed to the atmosphere in the laboratory and allowed to continuously undergo any possible corrosion for 20 days. This was done in principle to the procedures used by Anafi and Obi (2004), and Yawas (2005). At the end of the time, each specimen including those soaked in WCF was appropriately removed from the test tubes using a crucible tong, properly cleaned using a clean rag, and appropriately tested of its Knoop micro-hardness or impact fracture strength. This was repeated similarly for the other 12 hardness and 12 impact specimens but with the mass of each chemical fraction in each of the dissolutions raised to 70g and the same added quantity of $H_2SO_4$ content. In this way results were collected in each case.

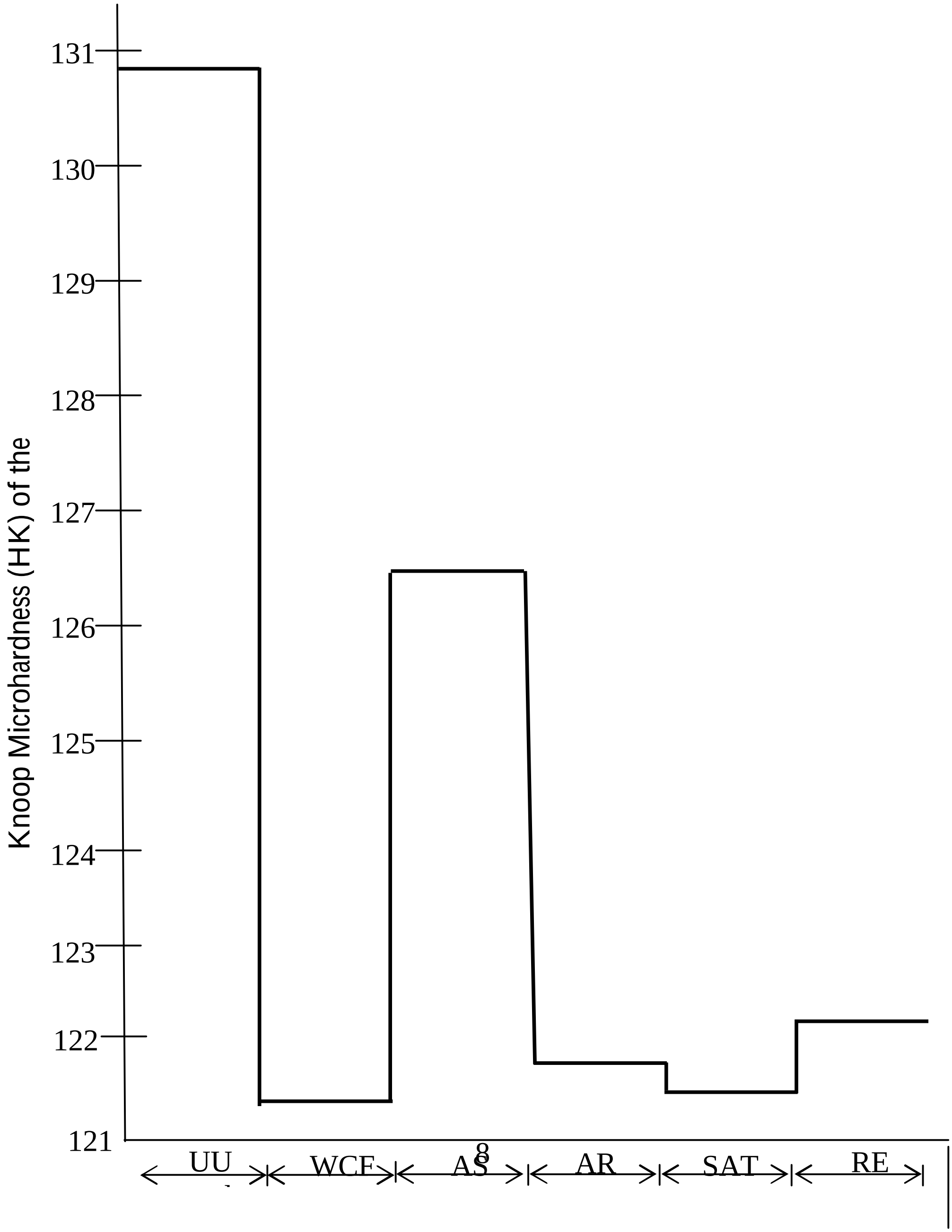
## Results and Discussion

The test-obtained results for each case of impact fracture strength and hardness of the low carbon steel specimens are presented in Figures 1 and 2 respectively



Status of specimen treatment in the prepared dissolutions involving each specified chemical fraction

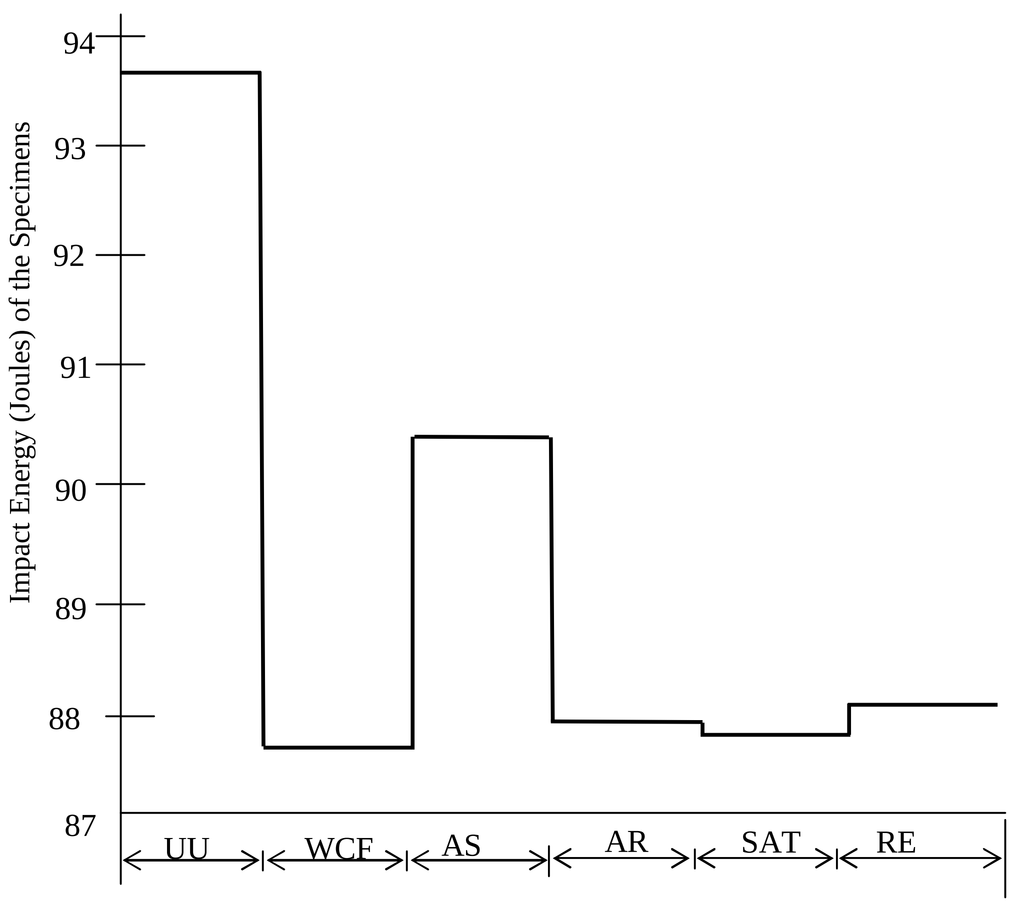
(a) Case involving 50g of the specified chemical fraction from a bitumen sample in a prepared dissolution.



Status of specimen treatment in the prepared dissolutions involving each specified chemical fraction

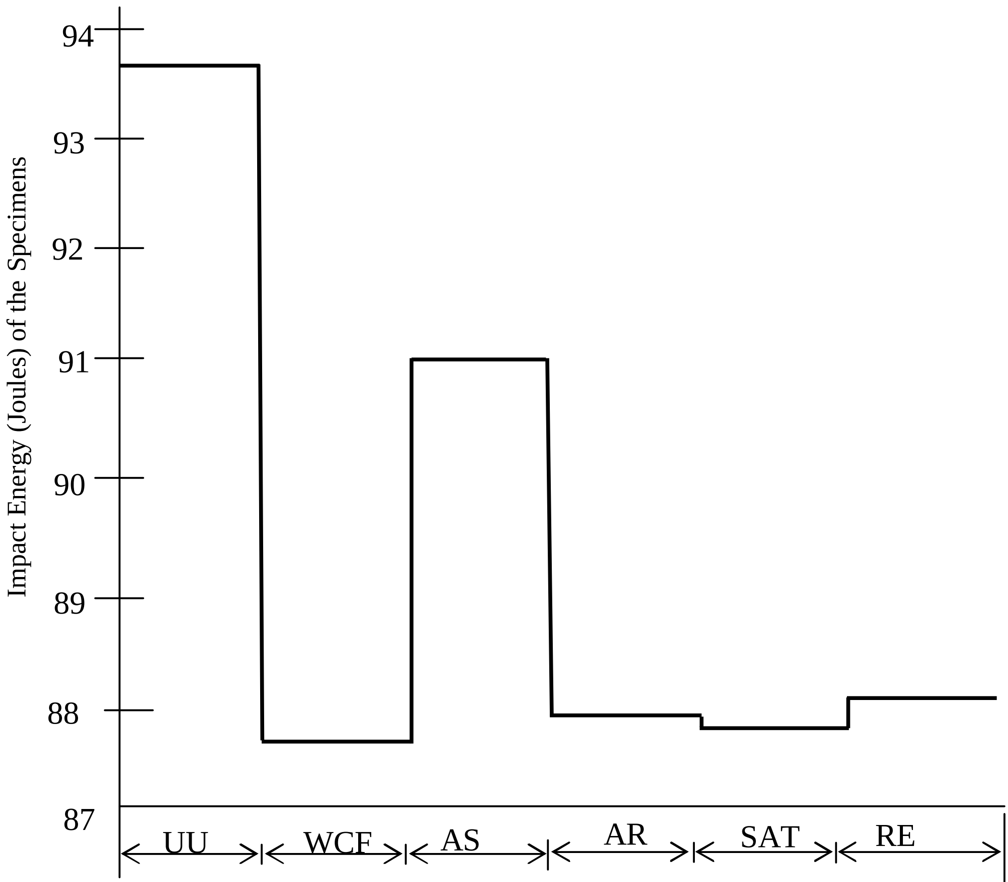
(b) Case involving 70g of the specified chemical fraction from a bitumen sample in a prepared dissolution

**Fig. 1:** Knoop Microhardness of Specimens of the Specified Status of Treatment Involving
Chemical Fractions Extracted From each of Ondo S-A, Ondo S-B and KPB



Status of specimen treatment in the prepared dissolutions involving each specified chemical fraction

(a) Case involving 50g of the specified chemical fraction from a bitumen sample in a prepared dissolution




Status of specimen treatment in the prepared dissolutions involving each specified chemical fraction

(b) Case involving 70g of the specified chemical fraction from a bitumen sample in a prepared dissolution

**Fig. 2:** Impact Strength of Specimens of the Specified Status of Treatment Involving Chemical Fractions Extracted From each of Ondo S-A, Ondo S-B and KPB

The presented results show that the asphaltenes chemical fraction which has the highest molecular weight 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 contributes minimally to the overall inhibition performance of a bitumen sample as can be observed from Figures 1 and 2. One would have expected naphthalene aromatics which constitutes the largest fraction in each bitumen sample as can be seen from Table 1, to contribute most to the inhibition but it is only third to the highest in the contribution, while saturates are the least. From this and other earlier provided facts, it can be inferred that the inhibition performance by a chemical fraction is more or less proportional to its molecular weight. 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 1, 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 of corrosion deterioration of a given mechanical property of the steel is the least. From Figure1 (a & b), it is clear as can be observed that corrosion inhibition of a bitumen sample increases outstandingly 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 content, naphthalene aromatics, saturates, and resins, that can 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.

## Conclusion and Recommendation

Bitumen resources exist in abundant quantities in Nigeria and some other countries of the world where they can be exploited as common and economical corrosion inhibitors. This experimental study has clearly indicated that corrosion coat-inhibition of low carbon steel to avert deterioration of its mechanical properties by any harvested bitumen from Nigerian resources or elsewhere for a given coating thickness will depend principally on the asphaltenes content of the bitumen and will be higher with increase in the content. Each of the other chemical fractions in a bitumen contribute minimally to the inhibition performance. Other inferences drawn from the study shows that the performance is proportional to the molecular weight of a chemical fraction. The presented information is therefore recommended to be used as a guide for optimal quality harvesting of bitumens from Nigerian resources or elsewhere for corrosion protection of structural steel works.

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