EFFECTS OF SOME BITUMEN COATING TREATMENTS ON THE CORROSION FATIGUE STRENGTH OF LOW CARBON STEEL

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Abstract

Fatigue strength is a basic mechanical property of a structural material and must be maintained in the application of the material for its continuous satisfactory service. In this paper, results of proper laboratory corrosion tests conducted to investigate effects of coating treatments with each of three clear bitumen samples got from important Nigerian bitumen sources on corrosion fatigue strength of the steel is presented. 165 ASTM fatigue specimens were produced from the steel and used for the tests. 15 were not coated while each bitumen sample was used separately to coat a set of 10 specimens eac to the same coating thickness. This was repeated four times using the remaining 120 specimens but to four different coating thicknesses. Five un-coated specimens and a set of five coated specimens with each bitumen sample for each coating thickness were corroded continuously for 50 days in an environment in which the corrosive factors of one of the worst natural corrosive environments-the tropical surf beach, were simulated with reasonable higher aggressiveness. Overall analysis of effect of the corrosion through appropriately determined fatigue strength values of each of all corroded specimens and, the others for control; indicates that any bitumen as-obtained from the sources will inhibit the corrosion to over 82.45% for a coating thickness of over 1.46mm in any natural environment. The availability of the bitumen resources in the country for the protective purpose is substantial and dependable for several years.

Keywords: Nigerian economy, petroleum dependence, pipelines, fatigue strength, rusting corrosion, economically available and dependable protective resources and methods, organic coating and painting method of protection.

Nomenclature of Specimen Treatment and Corrosion Status

UU = Un-treated and un-corroded

UC = Un-treated but corroded

TU = Treated and un-corroded

TC = Treated and corroded

Introduction

Of all metallurgical problems which confront the engineer few can be more economically important than the prevention of metallic corrosion. Several millions of American dollars are spent worldwide annually on researches on the science and methods of preventing corrosion. Corrosion is preponderant in the oil and gas industries, and should be seen as an economic and engineering problem.

The cost of corrosion to the industry worldwide is staggering. A figure of 300 billion US dollars was mentioned in the United State 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 be huge. For example corrosion and its related effects cost United States of America transmission pipeline companies as much as $8.6 billion dollars per year. In developing countries, the general level of corrosion consciousness and counteractions are however minimal and the deleterious phenomenon is more or less silently taking its toll directly or indirectly on their economies and people's lives. Nigeria is a developing nation that is frantically groping for ways of catapulting herself to the status of an industrialized nation without necessarily preparing the ground for it. No Government yet in Nigeria has come to grips with the reality of the devastating effect of corrosion on the economy. Nigeria is endowed with an abundance of critical and strategic material resources that could help her to easily attain the industrial status if managed properly. So far, the utilization of these resources is dependent wholly on the industrialized economies. It is amazing that the emphasis in this country today is still on exportation of raw materials. Awareness of the technological and economic consequences of the wastage by corrosion is very low both in the public and private sectors. As a result one would therefore put the cost of corrosion in this country to be higher per capita than the average value for industrialized nations. The contribution of social costs, some of which are peculiar to Nigeria would significantly increase the cost of corrosion in the country. The current situation in Nigeria remains unsatisfactory and therefore demands the attention of all (Wami, 1998; Callister, 2000; Yawas, 2006; INTERNET, 2008; Guma et al, 2010; 2011a&b).

The key economic sector of Nigeria is oil and gas. The oil and gas sector amounts to 85% of her total revenue. A lot of wastage occurs through corrosion process in this country. Yet all the metallic materials of construction in this industry are imported. An enormous amount of foreign exchange is lost to corrosion in the industry and indeed all her other chemical industries. The 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 important 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 an environment unacceptable (Yawas, 2006; Shreir, 1979; Ali, 1998; Wami, 1998).

Because of the critical role played by the steel industry in infrastructural and overall economic development, the industry is considered to be an indication of economic and technological prowess of any country. Steel is by far the most important engineering alloy, and low carbon steel is the most used-about 90% on the tonnage basis. Possibly the most serious fault of steel is that it rust-corrodes and considerable amounts of money are spent in protecting it from corrosion (Raghaven, 1989 & 1990; Higgins, 1993). Corrosion of steel increases with decrease in its carbon content and, or amounts of alloy elements to it. Low carbon steel is the most important material in terms of fabrication properties and structural usage, but is the most susceptible type to corrosion failures and suffers the greatest rusting ravage per tonne every year due to lack of adequate protection. No wonder Cottrell (1985) stated, "as regards the world economy by far the most important corrosion problem is the rusting of structural steel works". Rusting is a uniform or nearly uniform form of corrosion. The symptoms of final rust form on steel are pitted oxidized surface showing flakes or scales reddish-brown in colour. The rust generally is poorly bonded to the steel surface and flakes off easily resulting in wastage of the steel material and reduction of the area of the section, and correspondingly reduced load bearing capacity of the steel member. Its desirable mechanical properties such as strength are impaired with the degree and time of corrosion. If corrosion continues unchecked at an unacceptable rate, the member may snap or buckle, or even collapse (Johnson, 1965; Guma et al, 2010). Guma et al (2011a&b) have shown that any clear natural bitumen got around Agbabu village in Ondo State of Nigeria or a manufactured type at Kaduna Refining and Petrochemical Company (KRPC) in the country using Nigerian crude feedstock blended with Basra crude from Iran will coat-inhibit tensile and impact fracture strengths corrosion deteriorations of low carbon steel to the tune of at least 91% and 84.31% respectively in any natural environment when coated on low carbon steel with a thickness of at least 1.46mm. However in actual service many of the structural steels are subjected to fatigue loading, and fatigue is estimated to be responsible for 90% of all metallic failures. Furthermore, it is catastrophic ordinarily coming without warning (ASM, 1975; Khanna, 1999; Choudary, 2003). Design principle will therefore also demand information on fatigue strength of the steel in respect to resistance to corrosion deterioration when used in some particular applications and coat-protected with the bitumens.

About 80% of refinery equipment and transmission pipelines are made of carbon steel, essentially of the low carbon type (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). Although the most important natural steel-corrosive environments include acidic soils, highly saline soils, and sea water; of noteworthy the material rusts at almost incredible rates on surf beaches in the tropics where it is exposed to a continuous spray of moisture and sea salts on surf beaches. Corrosion rates on the surf increase with the salt content of the prevailing atmosphere. At a very high salt content of 11.1% and a distance of 50 yards from the surf the rate is 0.95mm/year for ingot iron (Shreir, 1979).

The prime consideration of a method for corrosion protection is cost and effectiveness of the method. Organic coating and painting is the most versatile, economical, important, and widely used method of corrosion protection. It is estimated that about 90% of steel surfaces are protected with organic coating and painting systems. The protectiveness depends mainly on their quality and adhesion to the surface of the steel, type of steel or its composition, surface conditions and preparation of the steel, exposure environmental conditions, exposure time, method of coating, coating thickness, and heat treatment status of the steel (Shreir, 1979; Laque, 1975; Barton, 1976).

Bitumen is a highly viscous black, sticky mixture of organic liquids that has been in use since ancient times for many purposes with general satisfactory performance. It has been used for protecting steel and other materials from corrosion through coatings, based on its excellent resistance to industrial pollution. Natural bitumen from different or even the same regional sources, or manufactured from petroleum of even the same source using different manufacturing processes; can however have extremes of variation in chemical composition and other physico-chemical characteristics; and different levels of service performances (Brady and Clauster, 1977; Hornbastel, !978; Jackson and Ravindra, 1996; Usmani, 1979; UNEP and ILO, 2004). Design reliability and standards therefore demands that specific cases with a bitumen should be consulted and applied instead of average information on bitumens.

In Nigeria, natural bitumen has been found with a proven reserve of over 14.86 billion barrels. The most important sources of natural bitumen in the country are from Ondo State, while KRPC is the country's most important synthetic bitumen outfit. Tarsands with 5-10% bitumen content are designated as good or medium grade. The average bitumen content of Nigerian tarsand is 20%. Generally the bitumen content of the tarsand varies from topsoil downwards and from location to location. 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 Solid Mine.Dev.2006; INTERNET, 2012). On the other hand KRPC has an installed capacity for manufacturing up to 4000 barrels of bitumen per day. Despite Nigeria's potentials for sustained production of natural and manufactured bitumens in large available quantities at economical rates for uses in the country, surveys show that her bitumen resources are not yet being harvested for corrosion protection of steelworks and there is no public engineering-applicable research information in place on levels of suitability of bitumens from her resources for protecting steel corrosion (Fed.Min.of Solid Mine.Dev.2006; Guma et al, 2010 & 2011a-b). The prime objectives in this paper are therefore;

i. To highlight the problem of cosrrosion of low carbon steel as a prime structural material in relation to the Nigerian economy.

ii. To provide some information on bitumen resources from Ondo State and KRPC in coating usage as common inhibitors.

METHODOLOGY

The study was carried out using corrosion test procedures recommended by Shreir 1979, Laque 1975, Barton 1976, Pludek 1977 and Rajan et al 1997. Low carbon steel rods were procured from the same supplier in Lagos, Nigeria, in suitable sizes. The rods were properly analysed to determine their chemical composition, and metallography. The chemical composition of the rods was achieved by grinding out fine powder samples from each of the rods and analyzing it by the method of energy dispersive X–ray fluorescence spectrometric analysis. The carbon contents of the samples which were not detectable by the method were determined by a proper chromatographic method. The test confirmed that the rods were similar. Their consistent similar composition is presented in table 1 and micro-structure shown in plate 1. The rods were used to machine-produce 165 ASTM fatigue specimens. Each produced specimen was then machine-polished with various grades of polishing paper to a finishing grade of 400, followed by etching it in nital. This produced a similar surface finish of 25 microns on each specimen as ascertained using a profilometer.

Two natural bitumen samples were procured from more or less richest bitumen spots at Agbabu village in Ondo State. One sample was from underground through a standard extraction hole drilled by early explorers of bitumen in the village and the other from clear outcrop deposits in waterlogged areas on the outskirt of the village. The two samples were assigned identification names as Ondo S-B and Ondo S-A respectively. Also, a sample of manufactured bitumen using Basra crude from Iran blended with the Nigerian crude feedstock, with identification name KPB; was collected from KRPC. Using the bitumen samples, the number of fatigue specimens prepared for tests with each was as shown in table 2.

The bitumen coating was carried out by a dipping process in accordance to a temperature range of 150-246^{o}C recommended by Illston et al (1979), and Painting and Decorating Contractors (1995) for heating and applying most bitumens. Ondo S-A was heated in a steel bath to a temperature of 170^{o}C using a 10-kilogramme gas-fired heating unit. Two specimens each handled by an assistant were then dipped at the same time in the bitumen and held at that temperature for 30 seconds and then withdrawn. A suitable thin-lipped crucible tong was used for handling a specimen on its head. For the same temperature, the coating was repeated for another set of eight fatigue specimens. The bitumen temperature in the container as monitored by a thermometer was raised in more or less four equal steps up to a temperature of 230^{o}C through increments in the duration of heating or adjustments of gas flow rates to burn more gas. In each step the same procedure of dipping and withdrawing two specimens and repeating for another set of eight was conducted. This produced coatings of good adherence to the specimens in five 10-sets of different coating thicknesses with the bitumen sample. The overall as-described procedure was similarly repeated using Ondo S-B, and then KPB. Thus the number of specimens and their coatings with each bitumen sample, at various coating temperatures, for the indicated status of corrosion were as shown in table 3.

The thickness of each bitumen coating was carefully determined by measuring the diameter of an un-coated specimen at 10 different sections along its length using a micrometer and finding the average value, and repeating this procedure over the coating at the same sections after coating the specimen at a given temperature and the coating had cooled to room temperature. The overall average coating thickness was then taken as the difference between the two values for each with the three bitumen samples. The more or less average coating thicknesses achieved at various coating temperatures with each bitumen sample is as shown in table 4.

Appreciable corrosion loss from the natural environments do occur only after a long period of time such as a year but a laboratory corrosion test is usually conducted in a much shorter time using an appropriate corrosive environment of reasonable higher aggressiveness to obtain results that are comparable to those from field tests and hence of practical applications (Shreir, 1979; Doyle, 1969). Accordingly, the corrosive factors of the tropical surf beach environment were simulated to produce such corrosive environment (30% NaCl + 5% Con. H_2SO_4 + 65% air of 100% relative humidity). Using an electronic digital weighing scale, 461.5385g of NaCl and 76.923g of concentrated H_2SO_4 were determined and mixed thoroughly in 1000cm^3 of water to get the percentage compositions. Each specimen for the UC and TC status was then placed vertically in the mixture. Air from a compressor at a pressure of slightly above atmospheric one was released and allowed to flow through thin hoses into the mixture. This made the mixture to circulate gently in an up and down fashion over the specimens. In this way, the specimens were allowed to rust continuously for 50 days at the prevailing room temperature of more or less 38^{o}C. This was achieved using Armfield corrosion studies kit. The specimens were then removed for the fatigue tests using a dynamic fatigue testing machine. During tests each specimen of a given status of coating with a given bitumen sample and corrosion was subjected at room temperature to repeated application of a chosen small cyclic stress load which was individually incapable of producing detectable plastic deformation, until the load caused the specimen to fracture. Such a 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. The number of cycles to failure in each case of the tests at a minimum chosen stress load of 250N/mm^2 was recorded automatically on the machine. The procedure was repeated at progressively increasing stress loads up to 350N/mm^2 appropriately on each of the remaining five-set of fatigue specimens. The resulting data was presented as a plot of stress (S) versus semi-logarithm of the number of cycles to failure (N) of each specimen appropriately for each given five-set specimens. This was also done appropriately for each case with a bitumen sample used and coating thickness. The TU specimens are control specimens. The fatigue strengths of half their number for each bitumen case were determined 55 days earlier at the commencement of the experiment together with the UU specimens and other half after testing the strengths of the corroded ones.

The average inhibition performance (IP) for each case of coating thickness with the bitumen sample used was then determined appropriately as;

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

where ΔT_i is the difference in corresponding values of number of cycles to failure between the UC curve and TC curve, for the case of a given coating thickness and an applied stress value of S_i, and ΔC_i is that between the UU and the UC curve values for the same S_i; with due consideration to any ageing effects in the UU or others in the TU specimens; and 'n' is the number of stress loads considered.

Results and Discussion

The levels and patterns of experimentally determined fatigue strength of specimens of given status of coating with Ondo S-A, Ondo S-B, and KPB and or corrosion; at specified coating thicknesses are shown in figures 1-5 while the obtained average values of IP for, and in comparison with each bitumen sample used is shown in table 5. Each figure shows clearly the comparative performance for the case with each bitumen sample used. In each figure, there are five endurance curves. The uppermost curve is the behaviour of each of the two UU, and each of the entire TU specimens irrespective of bitumen sample used. This implies that no ageing had occurred in the specimen during the 55-day duration of the tests, and the bitumen themselves or method of coating them on the specimens has no effect on the specimen material. The next curve to the uppermost in each figure is for specimen coated with KPB. This is followed by the one for specimen coated with Ondo S-B and then Ondo S-A. The lowest of the five curves is the one for the set of specimens that corroded most-the UC. It can be observed that as the coating thickness decreases, the TC curves shift closer to the UC curve. This implies that corrosion inhibition capability increases with bitumen coating thickness. With the coating thicknesses used for the tests, it has not been possible to completely inhibit the corrosion of the specimen. This may be so because according to Shreir (1979), '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 thickness which can be economically applied with good adherence to inhibit the corrosion completely or nearly completely is acceptable. From table 5, it is very clear that the inhibition performances of all the bitumen samples are in close range, however; KPB has an edge over the other samples followed by Ondo S-B and then Ondo S-A. One reason that may be attributed to this is in the degree of associated mineral accessories, sand, water, and other organic matter contents in the samples, since the quality of a bitumen increase with its freedom from most of these.

Conclusion

Nigeria has potentials for sustained production of large available quantities of bitumen for technological uses. In this paper, it has been shown through a proper accelerated corrosion test that any clear natural bitumen around the region of Agbabu in Ondo State and the as-manufactured type by KRPC per-se can coat-inhibit corrosion fatigue strength of low carbon steel from 53.36% to over 82.45% for a coating treatment thickness of from 0.81 to over 1.46mm respectively in any natural environment. Results also indicate that the as-manufactured bitumen will give the best protection performance followed by natural bitumen extracted underground to the least by surface bitumen at Agbabu. The corrosive environment used for the tests was prepared with a much higher factor of aggressiveness compared to the worst corrosive natural environmental conditions, while the corrosion time of 50 days for the specimens is appreciable. The entire specimens used were indeed of consistent low-carbon steel material. The corresponding average specimen coating thicknesses obtained using each bitumen sample were found to have minimal variations. The method of coating with each bitumen sample for a given overall specimen coating thickness was similar. The results obtained are therefore meaningful and basic for reliable effective results in practical applications. The information presented in this paper and in conjunction with further relevant researches and standardization can be useful in utilizing Nigerian bitumen resources for economical corrosion protection of transmission pipelines, underground and surface tanks, etc; either directly in oxidized form for coating or in the forms of bituminous wrappings, bituminous paints, admixtures in concrete encasements, coating supplements to other coating or protective methods, etc; in the petroleum and water industries particularly in Nigeria. Bitumens are used in oxidized forms and modified forms for such coat-protections because of some undesirable characteristics associated with them.

Recommendation

The results presented in this paper are recommended to the supplemented by those of parallel researches such as field and actual service tests for a better overall one, and to establish the time durability of protection with different coating thicknesses of the bitumen. Natural bitumen around Agbabu Village and as-manufactured bitumen from KRPC should be producing in large available quantities and exploiting for corrosion protection. Bitumen generally are known to be associated with some poor characteristics such as temperature-dependant properties, poor resistance to organic solvents, and not being mechanically tough enough to withstand much wear and stress, etc (Usmani, 1979). Further researches to improve on the characteristics; need to be done on the bitumens

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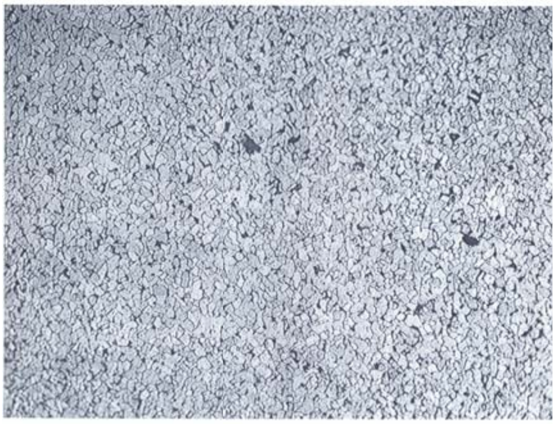


Plate I: Consistent microstructure of each of all low carbon steel rods used for the tests

Table 1: Ascertained overall consistent and similar chemical composition of each of all the low-carbon steel rods used

Element	Ca	Mn	Mo	Eu	Fe	Ag	C	Si	S	Re	Cu	Ni	P
Percentage Content	0.095	0.29	0.20	0.05	95.23	1.50	0.26	0.60	0.83	0.20	0.14	0.30	0.29

Table 2 Number of prepared specimen for the tests

Bitumen sample	**UU (NO)**	**UC (NO)**	**TU (NO)**	**TC (NO)**
Ondo S-A	10	5	25	25
Ondo S-B			25	25
KPB			25	25

Table 3: Number of specimen coated with each bitumen sample at specified temperatures for the indicated status of corrosion

Temperature (^{O}C)		**170**	**180**	**200**	**220**	**230**
Ondo S-A	TU (NO)	5	5	5	5	5
	TC (NO)	5	5	5	5	5
Ondo S-B	TU (NO)	5	5	5	5	5
	TC (NO)	5	5	5	5	5
KPB	TU (NO)	5	5	5	5	5
	TC (NO)	5	5	5	5	5

Table 4: Overall average bitumen coating thicknesses achieved on specimens at different temperatures

Coating temperature (^{o}C)	170	180	200	220	230
Coasting thickness (mm)	1.46	1.29	1.13	0.93	0.81

Table 5: Inhibition performance (IP) of coating thicknesses on the corrosion fatigue strength of low-carbon steel using the bitumen samples

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

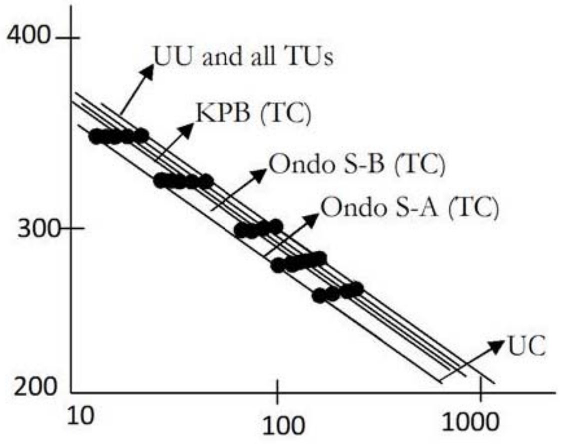


Fig. 1: Applied stress Vs cycles to failure showing TC specimen of 1.46mm coating thickness

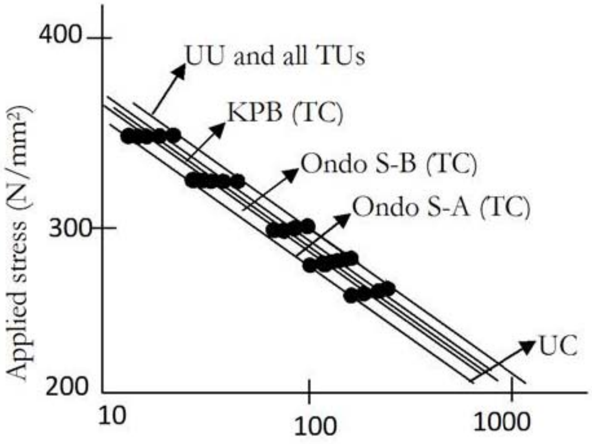
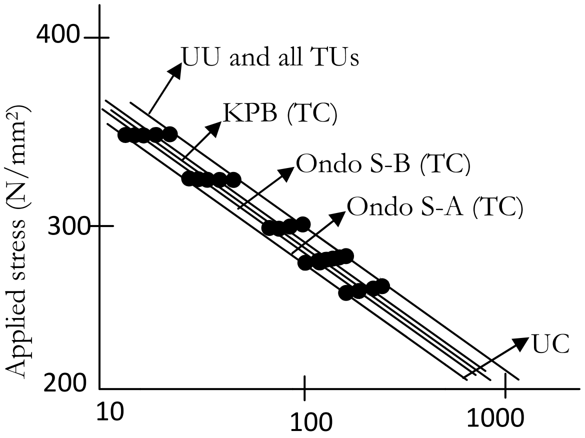
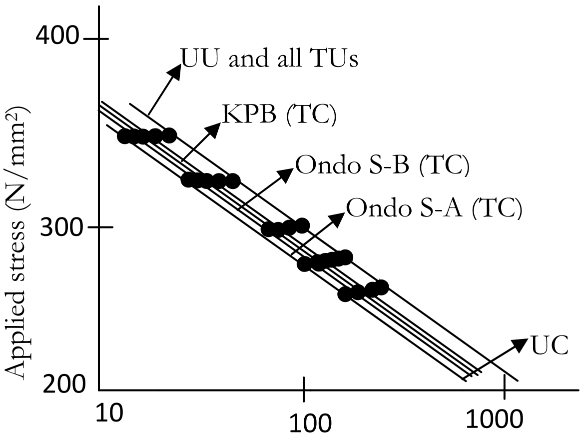


Fig. 2: Applied stress Vs cycles to failure showing TC specimen of 1.29mm coating thickness



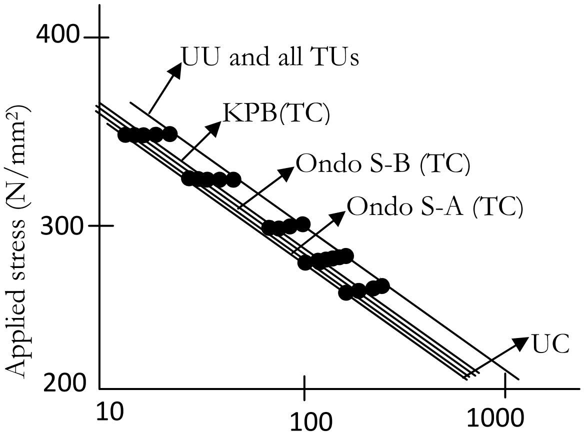
Stress cycles (thousands) to failure on semi-log scale

Fig. 3: Applied stress Vs cycles to failure showing TC specimen of 1.13mm coating thickness



Stress cycles (thousands) to failure on semi-log scale

Fig. 4: Applied stress Vs cycles to failure showing TC specimen of 0.93mm coating thickness



Stress cycles (thousands) to failure on semi-log scale

Fig. 5: Applied stress Vs cycles to failure showing TC specimen of 0.81mm coating thickness