PERFORMANCE EVALUATION OF SOME VEGETABLE OILS AS CORROSION INHIBITORS OF STEEL REINFORCED CONCRETE IN SOME ENVIRONMENTS

By

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Abstract

An experimental study on the performance of some vegetable oils (ground nut oil, soy beans oil, and cotton seed oil) as corrosion inhibitors on mild steel rebars buried in concrete admixed with the inhibitors and exposed selected aggressive environments is reported. The Corrosion rate of the steel bars was evaluated using the linear polarization resistance and weight loss techniques. The results of the potential shift obtained indicate that all the organic inhibitors are effective in retarding reinforcement corrosion in the aggressive environment chosen. The efficiency of inhibition increased with increase in concentration of the inhibitors due to the hydrophobic property of the inhibitors chosen.

Introduction

The use of reinforcing steel to improve the physical properties of concrete has been an accepted practice for many years (De Belie *et al*, 2000). Reinforced concrete structures are usually durable in average environments, but their integrity can be compromised when exposed to carbonation or other environments such as chloride salts. These environments reduce the potential service life of the structures and increase maintenance costs(Frenay, 1993).

Premature deterioration of many structures may also be attributed to the corrosive effects of chloride-based accelerating agents added to concrete during construction (Ebiogwu, et al, 2002).

Another corrosive agent that leads to rapid deterioration of reinforced concrete structures is hydrogen sulphide (H_2S). The H_2S dissolves in moisture films on the exposed concrete surfaces where it under goes oxidation by aerobic bacteria to sulphuric acid, commonly referred to as biogenic sulphuric acid attack (De Belie et al, 2000). In addition, the H_2S attacks concrete directly by reacting

with the calcium hydroxide in a set cement to form calcium bisulphide (Frenay and Zilverberg, 1993).

Concrete provides a protective alkaline environment around steel. However, corrosion can be initiated either when the hardened cement paste carbonates to the cover depth reducing alkalinity, or when chlorides migrate through the concrete cover and build up in sufficient quantities to break down the passive oxide layer found when the steel is first cast into concrete. As the steel corrodes, the rust occupies a volume two to four times greater than the parent steel, resulting in bursting stresses that ultimately crack and spall the concrete cover (Batis et al, 2003).

Corrosion of the reinforcement is the most important cause of failure of reinforced concrete structures (Gaildis, 2001).. Given the high financial cost of repairing or replacing deteriorated structures a number of methods are being used to extend the life reinforced concrete structures. These include (i) Low permeability concrete cover (ii) Coatings for the concrete surface, (iii) Surface coatings to the reinforcements e.g epoxy coated rebar, (iv) Electrochemical methods e.g. cathodic protection, chloride removal and (v) Corrosion inhibitors (Mai *et al*, 1992).

The use of corrosion inhibitors concrete is now well established. The use of corrosion inhibiting admixture has grown over the last 25 years because they provide a level of protection and longevity that would be too difficult and expensive to achieve otherwise. The flexibility to corrosion inhibitors with regard to dosage and their compatibility with all aspects of construction and operation of structures makes them useful for protection against corrosion (Gaidis et al 2001).

Corrosion inhibitors are admixtures, which usually do more than just inhibit corrosion. They may influence initial set, later strength gain or other properties. The effects they produce in the field depend on condition there.

Of the corrosion-inhibiting admixture technologies for reinforced and prestressed concrete currently available in the market place, the two most commonly used chemistries are calcium nitrite (Rosenberg et al 1977) and a water based organic inhibitor (Nmai et al, 1992) which consist primarily of amines and fatty –acid esters.

Calcium nitrite inhibits corrosion by reacting with ferrous ions to form a protective ferric oxide film, (Berke, 1989) but the water-based organic inhibitor functions via a two fold mechanism; first, by reducing chloride ion ingress into concrete through hydrophobic

property imparted by the fatty-acid esters and second, through the formation of a synergistic protective coating on the surface of the embedded steel by the film-forming amine components as well as the fatty-acid esters. The water-based organic inhibitor also provides benefit in reducing deterioration due to the ingress of other progressive species such as sulphate, because of its permeability-reducing property (Nmai, and Krauss, 1994).

Literatures on the use of local fatty-based oils as inhibitors for the control of corrosion in structures in aggressive environments are scare. This work therefore seeks to evaluate the effectiveness and performance of their locally available fatty-based vegetable oils as corrosion inhibitors in some hostile environments thereby using local solution to combat local problems.

MATERIALS AND METHOD

Concrete cubes preparation

Two grades of concrete – 30 and 40 were used in this investigation. The materials used for the concrete cubes are granite of 19mm maximum size, sharp river sand, Portland cement, inhibitors and tap water. The thoroughly mixed concrete was cast into 150mm cube moulds and compacted mechanically giving an average required design density of 2450 kg/m^3. After the initial wet curing three cubes were randomly selected from each of the grades of concrete and crushed, using Avery Denison universal testing machine with maximum capacity of 500kN. The average crushing load of the three cubes from each of the grades was taken as the 28 day compressive strength. At intervals of 5 days, 4 blocks were removed from each medium and cracked to remove the steel reinforcements. On removal, each of the steel coupons was pickled, dried and reweighed. The losses in weight recorded were then used to as the corrosion rate of the reinforcement. In addition, the surfaces of the specimens were visually observed to identify the type of corrosion damage that may have affected the steels.

The steel rod used has the chemical composition shown below (table 1) and the reinforced concretes were made from Portland cement of composition shown below (table 2).

The results of chemical compositions of oils, and the compressive strength of grade 30 and 40 concrete in various media are different concentrations of the inhibitors are shown in table 3, 4 and 5.

Testing

At the end of the various immersion periods (7 days. 14 days and 28 days), three concrete cubes for each of the grades of concrete were removed from each of the four different concentrations. These cubes were thoroughly rinsed with tap water and air dried in the laboratory for 24 hours. They were weighed to determine their densities and later crushed. The average crushing load was taken as the compressive strength of the concrete after each immersion period.

Corrosion Testing

Ground nut oil, Soy beans oil and cotton seed oil were obtained locally from Sunseed Oil Mills Ltd., Zaria. From this stocks, different concentration of the organic inhibitors were prepared with ethanol as solvent. The procedure for weight loss, was similar to that reported previously (Yawas, 2002). The inhibition efficiency of the inhibitors was determined using the equation:

$$\%IE = 1 - \frac{W1}{W2} x\,100 \text{ ---------- (1)}$$

where W_1 and W_2 are the weight losses of the mild steel in inhibited and uninhibited solution.

The polarization resistance is a measure of the resistance of a metal to undergo corrosion in a certain environment. It is defined as the slope of the potential –current (E-i) curve at the corrosion potential, i.e.

$$R_p = (\Delta E/\Delta i)_E = E_{corr} \text{ ohm cm}^2 \text{ .....(2)}$$

Where i is the current density in A cm^{-2} and E_{corr} is the electrode potential of the corroding metal. The polarization resistance method has attracted considerable attention. It has been used in corrosion monitoring and in the determination of corrosion rates, inhibitor efficiency, corrosion mechanism and, occasionally, Tafel slopes.

The linear polarization method is used to measure the corrosion rate based on the stern-Geary equation:

$$\left(\frac{\Delta E}{\Delta i}\right)_{E_{corr}} = R_p = -\frac{b_a b_c}{2.3 i_{corr}(b_a + b_c)} \text{ .....(3)}$$

$$i_{corr} = K\left(\frac{\Delta i}{\Delta E}\right) = K\frac{1}{R_p} \text{ .....(4)}$$

where ΔE and Δi are the changes of potential and current over a small range near the open circuit potential; E_{corr} and i_{corr} are the corrosion potential and current; b_a and b_c are the Tafel slope of anodic and cathodic polarization curves; and Rp is the electrochemical polarization resistance.

According to Ebiogwu . *et al*, (2002), polarization resistance (R_p) and corrosion rate are inversely related. Hence, increasing values of R_p are indicative of decreasing corrosion rates.

Their corrosion potential readings were obtained by placing a $Cu/CuSO_4$ reference electrode firmly at the concrete surface. The $Cu/CuSO_4$ electrode was connected to a 'Beckman HD 110' Multimeter through the steel rebar of the concrete. Readings were taken at intervals of 7 days for a period of 6 weeks.

The corrosion rate of the reinforced concrete was measured using the linear polarization resistance (LPR) technique; an electrochemical evaluation based on the measurement of the anodic and cathodic corrosion current (i_c) at the corroding potential, Ec. During corrosion, the system is in equilibrium, so there is no net current flow. The LPR technique involves shifting the system from this condition and changing the anodic and cathodic reaction rates such that a net current is measured. The test thus relies on the relationships between the potential and current. A schematic representation of the LPR experimental arrangement is shown in fig. 1. The corrosion cell consisted of a reference electrode that was located on the concrete surface, a working electrode (W.E) that was the rebar embedded in the concrete specimen, and an auxiliary electrode that was placed in the salt solution around the concrete specimen. A stainless steel frame was used as the auxiliary electrode.

It is known that within 10mV more passive (noble) or more active that the corrosion potential in a corroding system, the applied current density is a linear function of the electrode potential. Similarly, the slope of this linear polarization curve is related to the kinetic parameters of the system according to the equation:

$$\frac{\Delta E}{\Delta i_a} = \frac{\beta_a \beta_c}{2.3 i_c (\beta_a + \beta_c)} \quad \text{.....(5)}$$

where β_a and β_c are the Tafel slopes of the anodic and cathodic reactions, respectively. The term $\Delta E/i_a$ is given in Ohms. For steel in aqueous media, β_a and β_c values equal to 0.12 volt are normally used, thus, equation 5 then reduces to:

$$\frac{\Delta E}{\Delta i_a} = \frac{0.026}{i_c} \quad \text{.....(6)}$$

The above expression can be converted into corrosion rate using the equation:

$$\text{Corrosion rate (mpy)} = \frac{Kai_c}{nD} \text{ -.....(7)}$$

Where a is the atomic weight of the metal, i_c is the current density; n, the number of electrons lost; D, the density; and K, a constant, usually taken as 0.129.

Open circuit potential studies

For OCP measurements, each concrete test specimen was partially immersed in H_2SO_4, HNO_3, and seawater and potential readings

were obtained by placing a $Cu/CuSO_4$ firmly on concrete specimen. One of the two terminals of a digital voltmeter was connected to the $Cu/CuSO_4$, and the other was connected to the exposed part of the reinforced steel bars to make a complete electrical circuit. OCP readings were taken of six specimens at an interval for about a month. All the experiments were performed under free corrosion potential conditions and at ambient temperature.

Immersion test

The laboratory immersion tests were carried out at ambient temperature and open atmospheric conditions. Concrete specimens were immersed vertically in H_2SO_4, HNO_3 and seawater. In these media, specimens were dipped only 75% and 25% of the area remain exposed to air. H_2SO_4, HNO_3 and seawater were regularly replenished by adding required amount of distilled water to maintain the level in the container. Three specimens from each of the environment were taken out after immersion periods of 1, 2, 3,4, 5 and 6 weeks.

Result and Discussion

The 28 days mean compressive strength for concrete grades 30 and 40 (before immersion) were recorded to be $30.95N/mm^2$ and $40.50N/mm^2$ respectively. The strength of the concrete cubes immersed in water (control cubes) after 7 days were found to be $33.45N/mm^2$ for grade 30 and $41.42\ N/mm^2$ for grade 40 concrete. Similarly, at the end of 14 days of immersion in water, compressive strength of the cubes were $34.70N/mm^2$ and $43.90N/mm^2$ while the compressive strength of the concrete after 28 days of immersion in water were found to be $35.30N/mm^2$ and $43.50N/mm^2$ for grades 30 and 40 respectively. These show that there was a steady increase in the compressive strength of the cubes immersed in water with increase in the duration of immersion for the two grades of concrete, as expected which is slightly higher than the values obtained from the studies on plant extracts reported by Yawas, (2005).

Tables 4 and 5 show the results of the compressive strength of the concrete cubes 30 and 40 after 7, 14, and 28 days of immersion in the various aggressive media. The tables indicate that the lower the concrete grades the higher the rate of strength reduction relative to the control experiment. For example, the percentage decrease in strength for grades 30 and 40 were found to be 9.63% and 6.12% respectively showing variance with the experimented results using plant extracts (Yawas, 2005).

The fall in the percentage compressive strength gain as the grade of the concrete increase can be attributed to the increase in the quantity of

alkalis (Na_2O,K_2O) in the cement with increase in the concrete grade; since both concrete grades were subjected to the same aggressive environment and immersion periods. High cement creates a strong bond between the concrete particles, thereby preventing easy ingress of water into the concrete structure. Easy ingress of chemical water into concrete causes drastic reduction in strength.

Figures 2-17 summarize the results obtained in the potential – time behaviour for the various combinations of specimens at different concentration studied in the acidic media(H_2SO_4, HNO_3 and Seawater).

Specimens admixed with inhibitor (specimens A to C) displayed passive tendencies, with both specimens measuring electrochemical potentials more positive than -350 mV after 6 weeks of exposure. The relative retardation in corrosivity observed in the last weeks was attributed to the passivation of the reinforcement bar. This result is in agreement with (Ebiogwu et al., 2002; Martinez, 2000), that inhibitors play a vital role in passivating corrosion in reinforced concrete.

Fig. 18 shows the corrosion rates for steel reinforcement in concrete as a function of concentration. The results of the control specimen show high corrosion rate which decreased with the exposure time. The corrosion rate recorded for the inhibited specimens (with cotton seed oil, soy beans oil and ground nut oil) were substantially less as the concentration of the inhibitors increased showing good inhibition efficiency.

CONCLUSIONS

The following conclusions can be drawn from the results obtained.

1. The concrete cubes immersed in water (control cubes with o % inhibitor) increased steadily in compressive strength from 30.95 N/mm^2 to 35.97 N/mm^2 at the end of 28 days of immersion for grade 30 concrete. Likewise, a steadily increase in compressive strength from 40.50 N/mm^2 to 42.65 N/mm^2 at the end of 28 days of immersion was recorded for grade 40 concrete.

2. For all the acidic media considered, the compressive strength of the cubes increased with increase in the concentration of the fatty acid based vegetable oil inhibitors.

3. The compressive strength of cubes increases with duration of immersion. The longer the immersion period, the more strength gained in the presence of the three inhibitors.

4. The corrosion rate of the rebars decreased with increase in the concentration of all the organic inhibitors. The mechanism of corrosion inhibition of the added inhibitors compounds is related to protective film formation on the metal surface which renders it passive and the hydrophobic property of the selected inhibitors.

5. The lowest potential was observed for steel sample inhibited with cotton seed oil followed by soy beans oil then groundnut oil i.e among the inhibitors studied cotton seed oil gave the best corrosion protection of steel reinforcement in the environments considered.

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Tables 1: Chemical composition of steel rod

Element	C	S_I	M_n	P	S	C_u	N_I	C_r	F_e
%Composition	0.22	0.2	0.6	0.03	0.03	0.02	0.1	0.1	Bal

Tables 2: Chemical Composition of the Portland cement

Element	SiO_2	Al_2O_4	Fe_2O_3	CaO	MgO	SO_3^{2-}	Na_2O	K_2O
%Composition	21.4	3.9	2.2	62.5	9.5	4.7	9.8	0.6

Tables 3: Chemical Composition of the vegetable oils

Fatty acid	Chain length	%in ground nut oil	% in soy bean oil	% in cotton seed oil
Myristic	14.0	-	-	0.6
Palmitic	16.0	7.5	12	22.9
Stearic	18.0	4.5	6	2.2
Caprytic	8.0	-	-	-
Capric	10.0	-	-	-
Lauric	12.0	-	-	-
Arachidic	2.0	3.0	12	-
Beharic	22.0	2.0	-	-
Lignoceric	24.0	2.0	-	-
Oleic	18.0	62.0	34	24.7
Linoleic	18.0	20.0	54	49.7

Table 4: Compressive strength of grade 30 concrete after immersion in the various media at different concentration of inhibitors

Inhibitor concentration	Strength before immersion (N/mm^2)	Strength after 7 days of immersion (N/mm^2)	Strength after 14 days of immersion (N/mm^2)	Strength after 28 days of immersion (N/mm^2)
0% (All alkalis)	30.98	32.29	33.93	35.97
5%+H_2SO_4	30.95	33.32	34.70	35.75
" HNO_3	30.95	32.64	33.83	34.60
" Sea water	30.95	33.45	34.61	35.53
10%+H_2SO_4	30.95	34.10	34.90	36.30
" HNO_3	30.95	33.18	34.02	34.95
" Sea water	30.95	33.84	34.57	36.15
15%+ H_2SO_4	30.95	34.20	35.60	36.90
" HNO_3	30.95	33.05	34.20	35.50
" Sea water	30.95	33.81	34.90	35.89
20%+ H_2SO_4	30.95	34.28	35.90	36.80
" HNO_3	30.95	33.62	34.90	35.70
" Sea water	30.95	34.32	35.00	36.10

Table 5: Compressive strength of grade 40 concrete after immersion in the various media at different concentration of inhibitors

Inhibitor concentration	Strength before immersion (N/mm^2)	Strength after 7 days of immersion (N/mm^2)	Strength after 14 days of immersion (N/mm^2)	Strength after 28 days of immersion (N/mm^2)
0% (All alkalis)	40.50	41.04	41.92	42.65
5%+H_2SO_4	40.50	41.42	42.56	43.90
" HNO_3	40.50	40.36	41.68	42.84
" Sea water	40.50	41.42	42.32	43.60
10%+H_2SO_4	40.50	41.86	43.10	43.95
" HNO_3	40.50	40.67	41.87	43.05
" Sea water	40.50	41.77	42.34	43.86
15%+ H_2SO_4	40.50	42.48	43.70	44.00
" HNO_3	40.50	41.03	42.25	43.90
" Sea water	40.50	42.12	42.68	43.94
20%+ H_2SO_4	40.50	42.66	43.86	44.12
" HNO_3	40.50	41.27	42.33	43.32
" Sea water	40.50	42.24	42.82	43.78

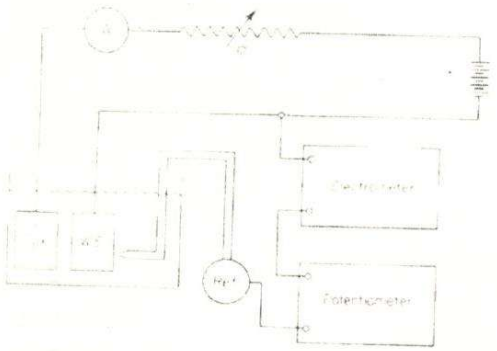

Fig. 1: Circuit Diagram

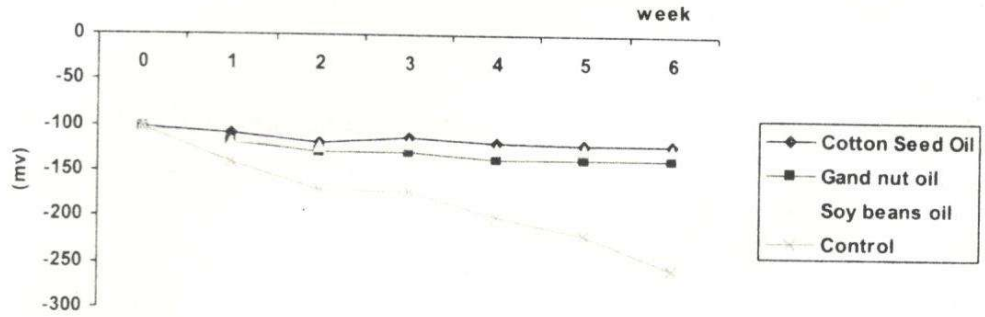

Fig. 2 Inhibition of Reinforcement at 5% concentration inhibitors (Sea water)

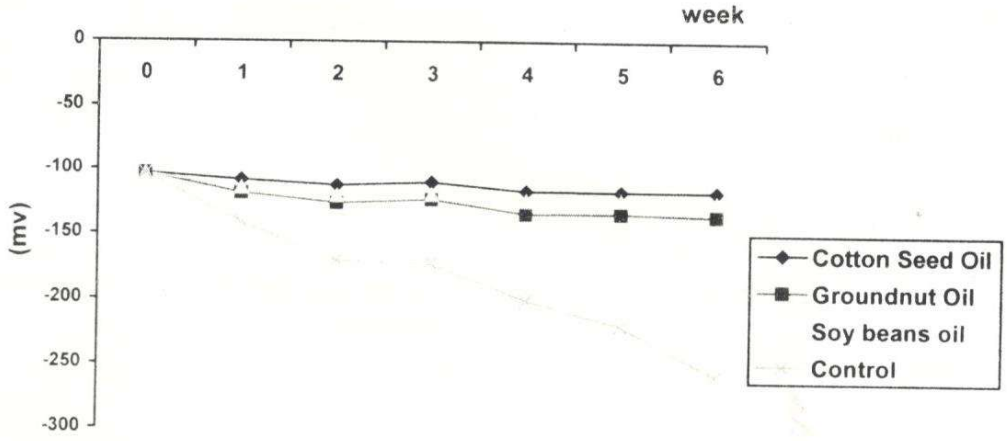

Fig. 3 Inhibition of Reinforcement at 10% concentration of the inhibitors in sea water

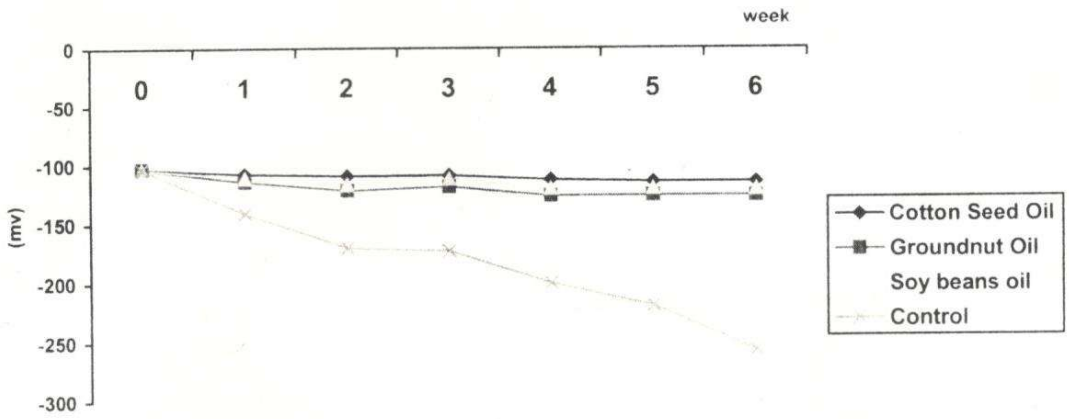

Fig. 4 Inhibition of reinforcement at 15% concentration of the inhibitors in sea water

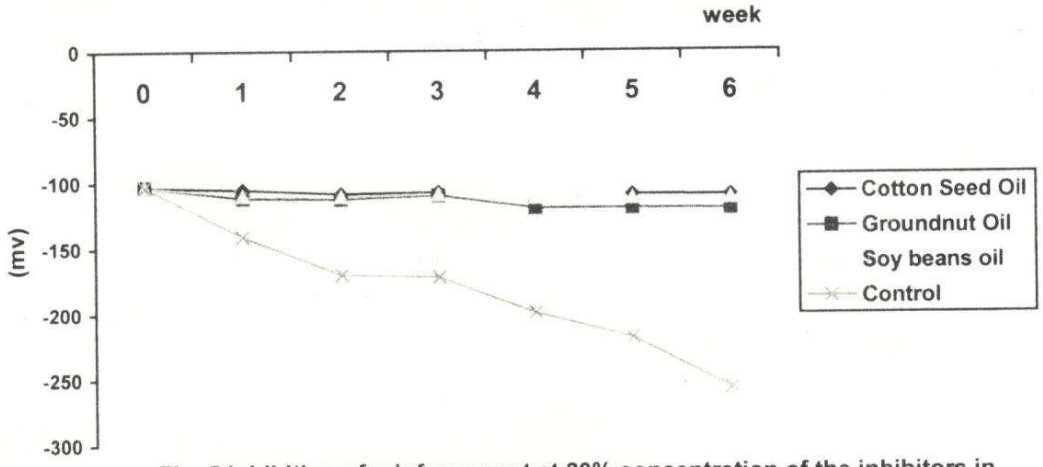

Fig. 5 Inhibition of reinforcement at 20% concentration of the inhibitors in sea water

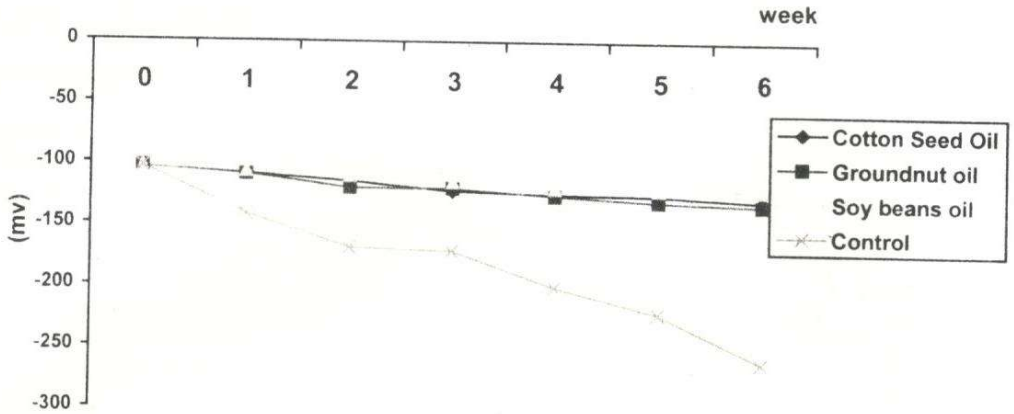

Fig. 6 Inhibition of reinforcement at 5% concentration of the inhibitors in water

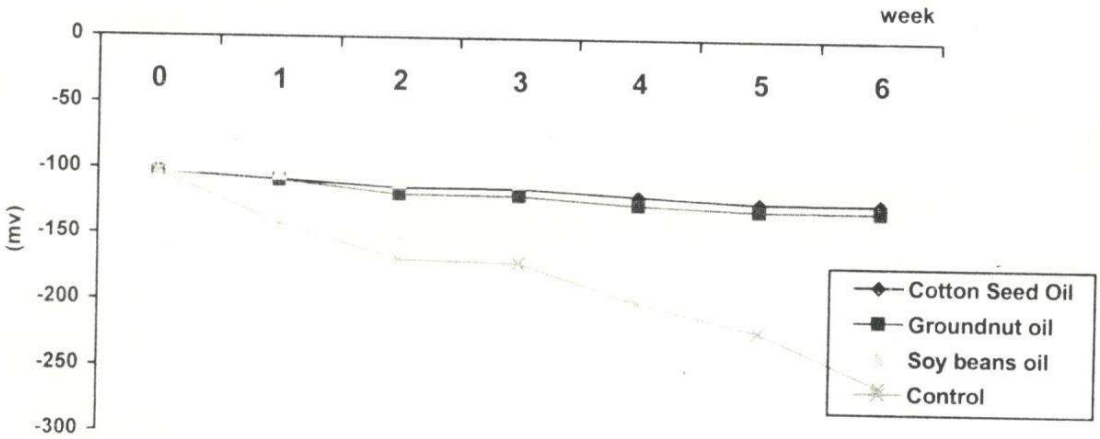

Fig. 7 Inhibition of reinforcement at 10% concentration of the inhibitors in sulphuric acid

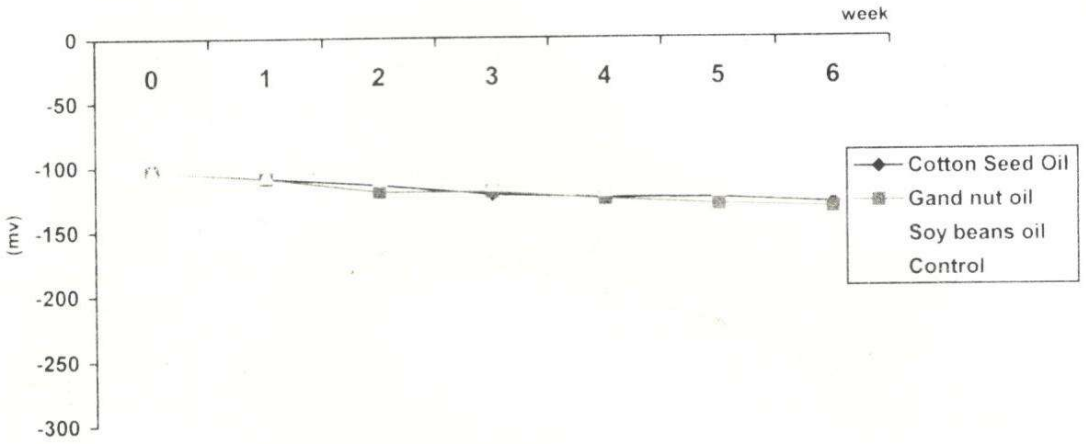

Fig. 8 Inhibition of reinforcement at 15% concentration of the inhibitors in sulphuric acid

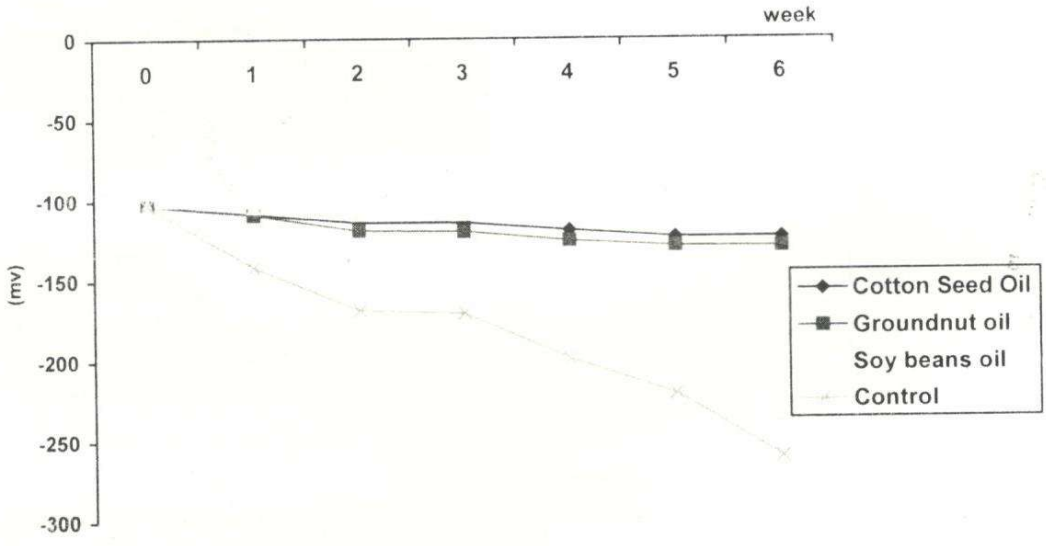

Fig. 9 Inhibition of reinforcement at 20% concentration of the inhibitors in sulphuric acid

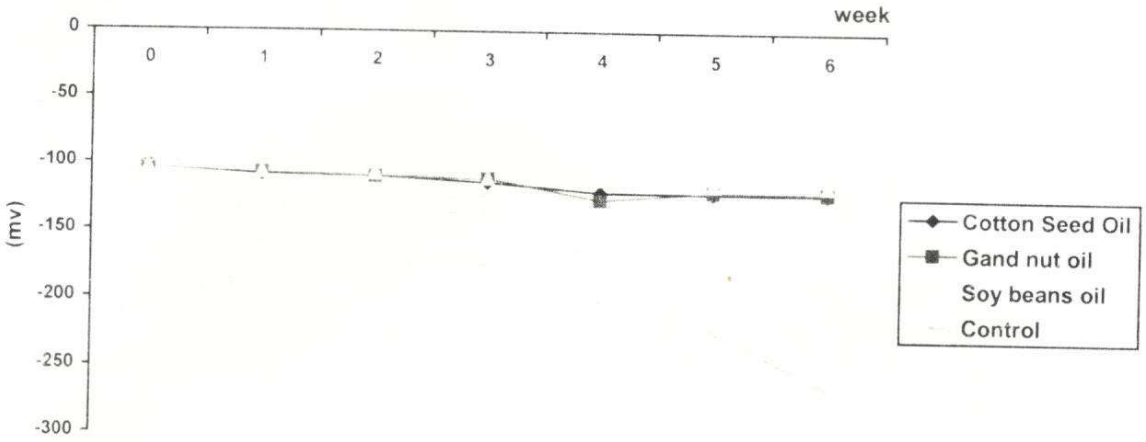

Fig. 10 Inhibition of reinforcement at 5% concentration of the inhibitors in nitric acid

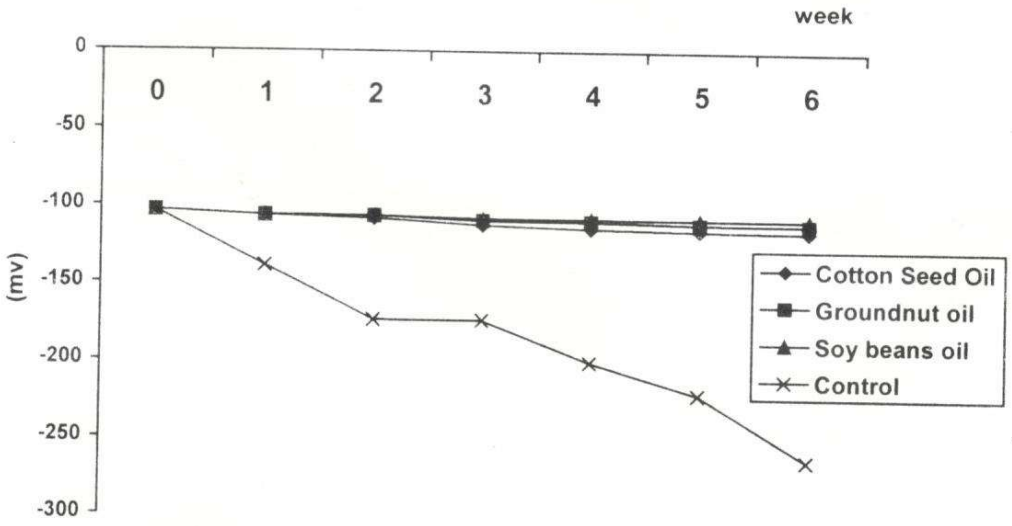

Fig. 11 Inhibition of reinforcement at 10% concentration of the inhibitors in nitric acid

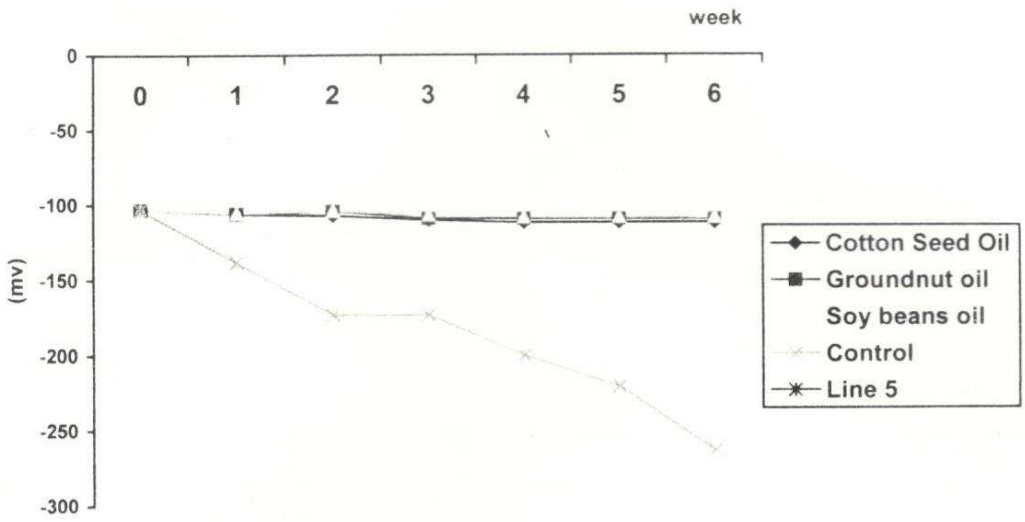

Fig. 12 Inhibiton of reinforcement at 15% concentration of the inhibitors in nitric acid

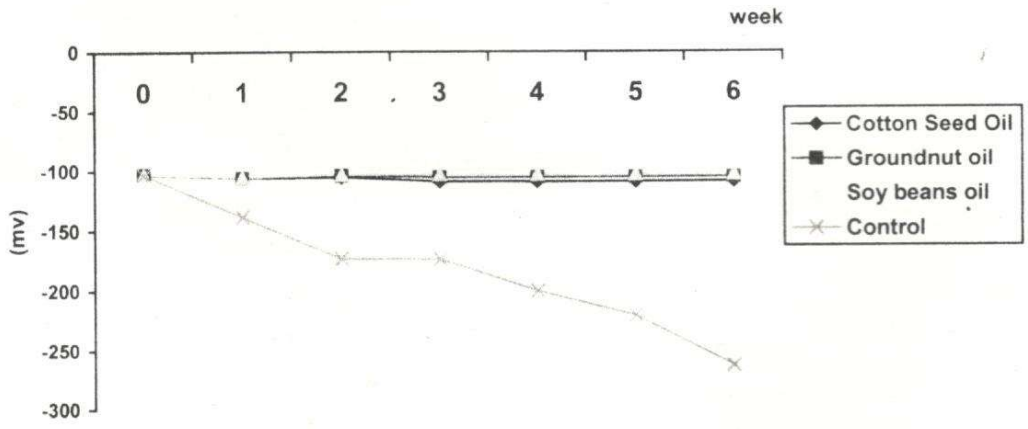

Fig. 13 Inhibition of reinforcement at 20% concentration of the inhibitors in nitric acid

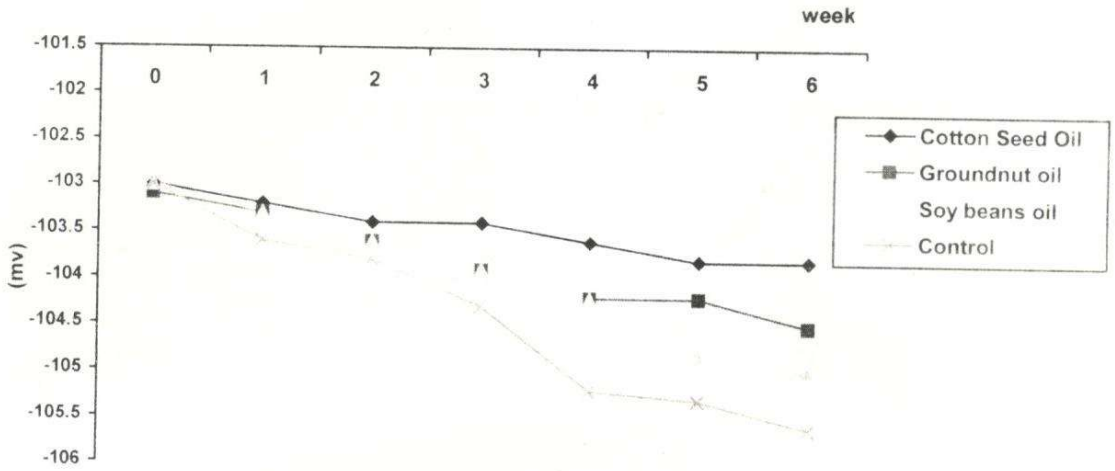

Fig. 14 Inhibition of reinforcement at 5% concentration of the inhibitors in atmospheric environment

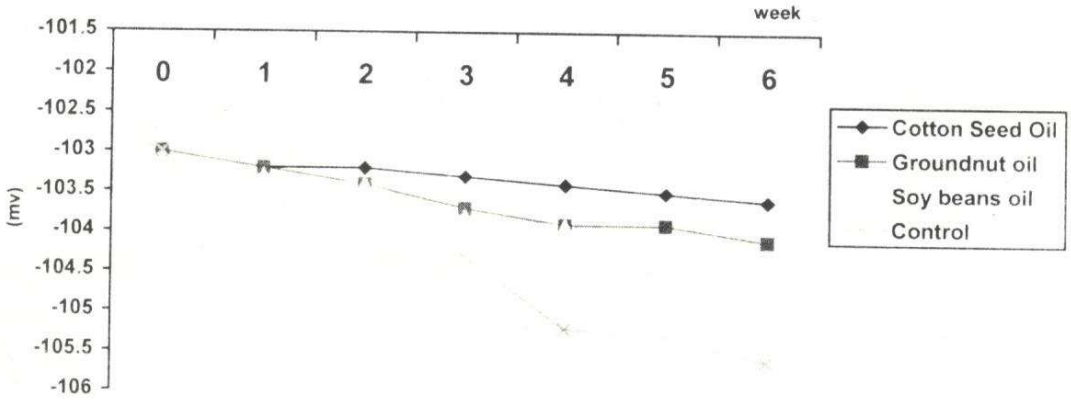

Fig. 15 Inhibition of reinforcement at 10% concenration of the inhibitors in atmospheric environment

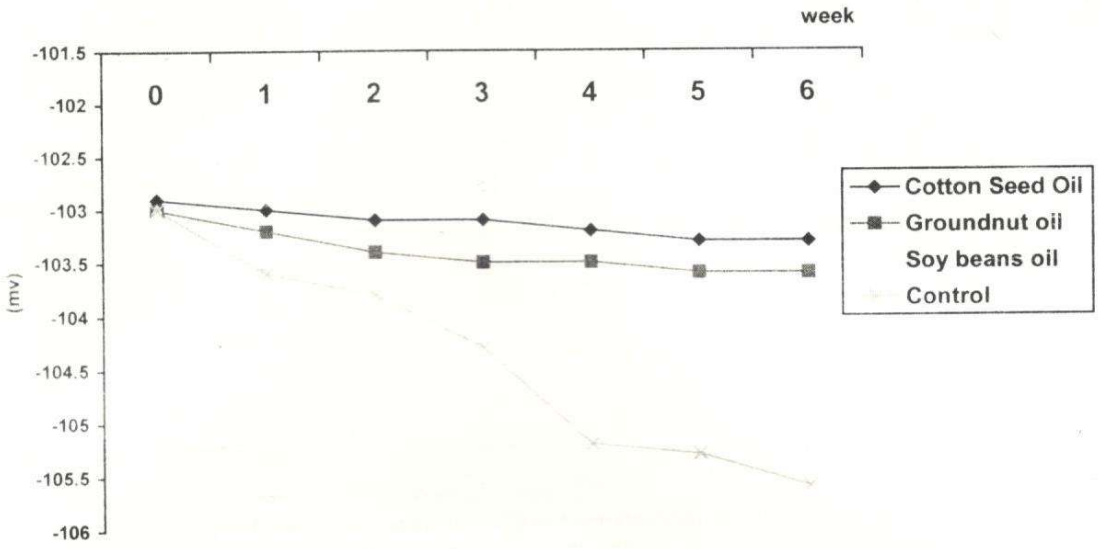

Fig. 16 Inhibition of reinforcement at 15% concentration of the inhibitors in atmospheric environment

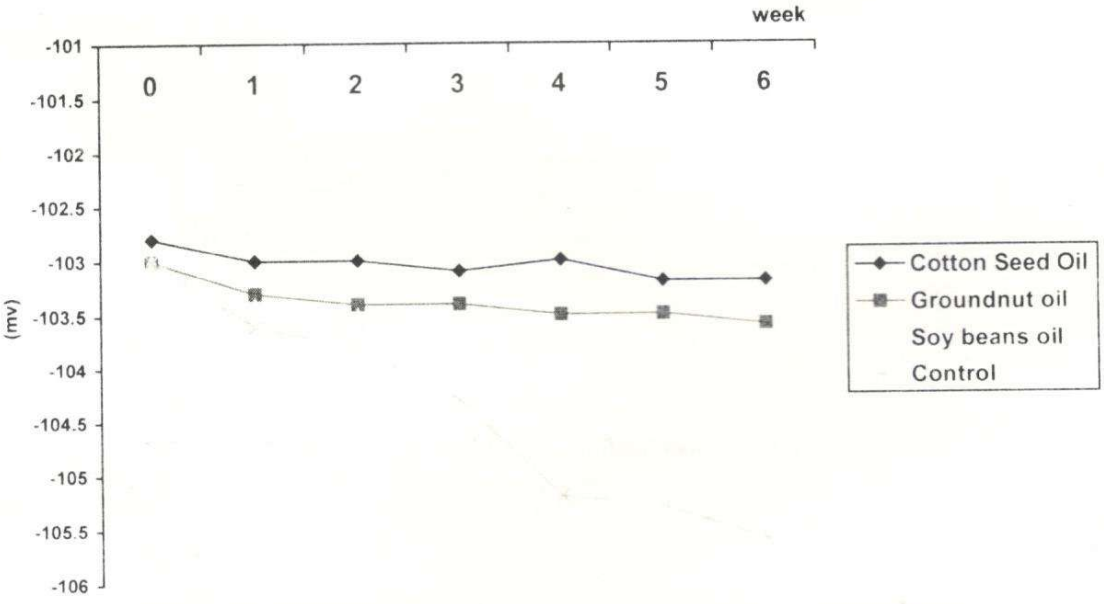

Fig. 17 Inhibition of reinforcement at 20% concentration of the inhibitors in atmospheric environment

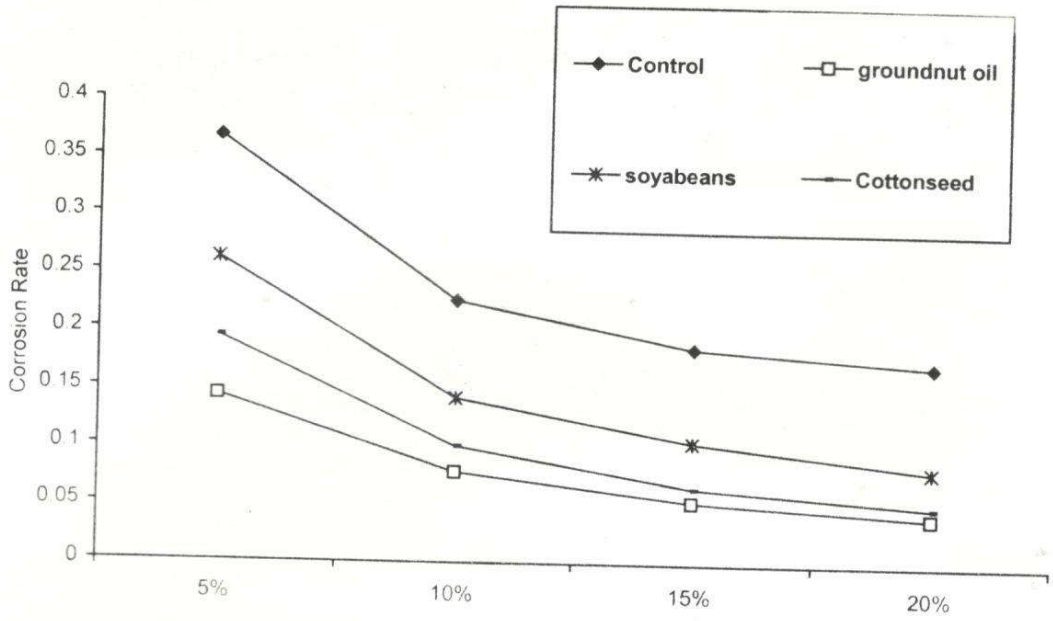

Figure 18: Corrosion rate against concentration inhibitors