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Green Inhibitors for Petroleum Product Pipelines

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Impact of corrosion inhibitors on environment has received increased attention in recent years. The new generation of environmental regulations requires the replacement of toxic chemicals with so-called "Green chemicals". In the present study neem oil, castor oil and punga oil were used for corrosion inhibition evaluation in petroleum product (diesel) along with 2% water containing 120ppm chloride. Weight loss and polarization studies were employed to find out the corrosion inhibition efficiency (IE). Weight loss study revealed that castor oil gave higher efficiency (89%) when compared to other neem oil and punga oil. The mechanism of corrosion inhibition was investigated by using surface techniques viz., Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM).

Key Words : Diesel Transporting Pipeline, Green Corrosion Inhibitors, FTIR, SEM

1 Introduction

Internal corrosion control programmes for petroleum product pipelines usually involve chemical treatment with corrosion inhibitors. Corrosion inhibitors are marked in several basic types, such as oil soluble, water-dispersible, water soluble, limited solubility and volatile etc., and each performs uniquely in different pipeline conditions. Organic film forming inhibitors are used in oil and gas production, transportation and storage systems.[1-4] Many of these formulations contain chemicals, which are considered as "priority pollutants" at present by various countries. The new generations of environmental regulations require the replacement of such chemicals with so-called "green" chemicals. In this paper, the authors discuss the result of some of the "green" inhibitors identified by them and comment on the direction of future research.

Amine based inhibitors are used in petroleum product pipelines.[5] But due to the water contamination in petroleum product pipeline, these inhibitors face biodegradation. Hence, identification of non-degradable and eco-friendly inhibitor is needed for petroleum product pipelines.[6,7]

In the past two decades, the research in the field of "green" corrosion inhibitors has been addressed towards the goal of using cheap, effective molecules at low or "zero" environmental impact. These compounds include certain amino acids and derivatives, which have been tested for various metals, such as Ni,[8] Co,[9] iron and mild steel[10-12] corrosion in acid and neutral system.[13]

2 Experimental Methods

2. 1 Corrosion study

API 5LX steel specimens (C-0.29 max, S-0.05 max, P-0.04 max, Mn-1.25 max) of size 2.5 cm^2 were polished to mirror finish mechanically and degreased using trichloro ethylene. Evaluations of inhibitors have been carried out in 500 ml of oil with 2% of water (120 ppm of chloride) as control system, 500 ml oil with 2% of water (120 ppm of chloride) and 500ppm of green chemicals (Caster oil, punga oil and neem oil) were used as experimental system. After the immersion period of 7 days, the coupons were removed and pickled in pickling solution, washed in water and dried by using air drier. Final weights of the coupons were taken and the corrosion rate has been calculated. The average weight loss values of six coupons are presented. The main compositions of the used green inhibitors have been presented in Table 1. The inhibition efficiency was calculated using the following equation,

$$\text{I.E (\%)} = 100\ [1 - W_2/W_1]$$

where, W_1= weight loss in the absence of inhibitor
W_2 = weight loss in the presence of inhibitor

2. 2 Electrochemical study

Polarization measurements were carried out potentiodynamically using model PGP201 potentiostat employing the volta master-1-software. The system was allowed to attain a steady potential value for 10 minutes. Steady state polarization was carried out from the open circuit potential level to -200 and to +200 mV vs. saturated calomel electrode (SCE) using separate electrodes at a scan rate of 0.5 mV/s.

A mixture of diesel oil and water (containing 120 ppm chloride ion) in the ratio of 2:1 was made.[14] Four different systems were made. In each system two electrodes (mild steel) were immersed and the solution was stirred vigorously for a period of 7 days. At the end of the immersion period, anodic and cathodic polarization experiments were carried out using separate electrodes.

2. 3 Surface examinations

The mild steel (API 5LX) specimens were immersed in various test solutions for a period of 7 days, taken out and dried. The nature of the film formed on the surface was analysed by using Fourier Transform Infrared

Table 1 Physical and chemical characteristics of refined Punga oil, caster oil and Neem oil.

Characteristics	Punga oil (Pangamia glabra)	Castor oil (Ricinus Communis)	Neem oil (Azadirachta indica)
Percent free fatty acid [% w/w]	0.18		
Iodine value [g/100 g]	89.6	82 -90	84 - 94
Saponification value [mg/g]	187.8		
Unsaponification fraction [% w/w]	2.1	< 1 %	
Density at 20℃		0.950 - 0.970	0.920 - 0.940
Refractive index at 20℃		1.4750 - 1.4850	1.4750 - 1.4810
Acid value		< 5.0	< 20.0
Fatty acid compositions [% w/w]			
Ricinoleic acid	-	90 %	
Palmitic acid	8.9		18 %
Stearic acid	8.1		15 %
Oleic acid	52.3	3 to 4 %	50 %
Linoleic acid	21.8	3 to 4 %	13 %
Arachidic acid	3.0		2 %
Behenic acid	3.1		
Lignoceric acid	2.8		
Eicosenoic acid	9.5-12.4%		
Odour	Perfectly bland	Specific	Specific
Peroxide value [meq/kg]	1.3	< 5.0	
Colour	Yellow	Pale yellowish colour	Opaque dark brown

Spectroscopy (FTIR). The surface morphological characteristics of the control and experimental mild steel were observed under scanning electron microscope (SEM) Hitachi model S-3000H at magnification ranging from 50X to 200X operated at an accelerating voltage of 25 kV.

3 Results and Discussions

3. 1 Weight loss and electrochemical study

Corrosion inhibition efficiency of green inhibitors is presented in Table 2. The highest efficiency is observed in caster oil compound (89%) when compared to the other oils. This is the first time that these three oils were found to show corrosion inhibition property in oil pipeline environment.

Polarization study was carried out to examine the electrochemical behavior of the compound on corrosion process. From the polarization curves, corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (b_a) and cathodic Tafel slope (b_c) were determined and presented in Table 3.

Table 2 Corrosion inhibition efficiency data for green inhibitors at 30℃.

Sl. No.	System	Wt. Loss (mg)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	Control: 500ml Diesel + 2% water (120ppm chloride)	27.8	0.1425	---
2	Test1: 500ml Diesel + 2% water (120ppm chloride) + 500 ppm Caster oil	3.0	0.0153	89
3	Test2: 500ml Diesel + 2% water (120ppm chloride) + 500 ppm Neem oil	5.3	0.0272	81
4	Test3: 500ml Diesel + 2% water (120ppm chloride) + 500 ppm Punga oil	4.6	0.0235	83

The corrosion current (I_{corr}) for control sample is 1.46×10^{-6} A/cm^2, while in the presence of 500 ppm of caster oil the current decreased to 3.76×10^{-9} A/cm^2 (Fig. 1). However, in presence of neem oil and punga oil the corrosion currents are 3.77×10^{-7} A/cm^2 and 1.49×10^{-8} A/cm^2 respectively. The anodic Tafel constant value is in the range between 38 and 95 mV/decade, where in the cathodic Tafel slope is in the range between 153 and 298 mV/decade. The nature of polarization curves indicate that the reduction of both anodic and cathodic currents in presence of inhibitors when compared to control. Electrochemical polarization study reveals that the green inhibitors act as "mixed inhibitor". It is probably due to the adsorption of amines and fatty acids of green inhibitors.

3. 2 FTIR spectral analysis

The FTIR spectrum of the film formed on the surface of the metal surface after immersion in the control system (without inhibitor) containing 120ppm chloride is shown in Fig. 2. It can be seen that the C-H aliphatic stretching frequency of the alkane and alkyl group at 2923 cm^{-1} and 2855cm^{-1}, which was present in diesel oil. Other peak at 1459 cm^{-1}, indicates the presence of C-H deformation of methyl (CH_3) group and the aromatic substituted peak occurs at 882 cm^{-1}. The Fe-O stretching peak is noticed at 470 cm^{-1}.

The FTIR spectrum of the film formed on the surface of the metal surface after immersions of inhibitor system

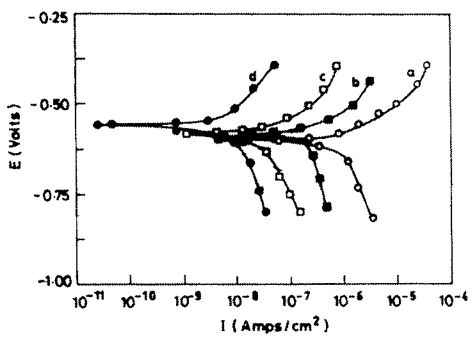

Fig. 1 Polarization curve for API 5LX in presence of green inhibitors at 30℃. a: Control, b: Neem oil, c: Punga oil, d: Caster oil.

Table 3 Polarization data for the three green inhibitors at 30℃.

Sl. No	System	E_{corr} mV Vs SCE	I_{corr} A/cm^2	b_a mV/ decade	b_c mV/decade
1	Control -1: 150ml Diesel + 75 ml water	-602	1.46×10^{-6}	67	228
2	Test 2: 150ml Diesel + 75 ml water + 500 ppm Caster oil	-554	3.76×10^{-9}	95	163
3	Test 2: 150ml Diesel + 75 ml water + 500 ppm Neem oil	-573	3.77×10^{-7}	38	298
4	Test 2: 150ml oil + 75 ml water + 500 ppm Punga oil	-581	1.49×10^{-8}	55	153

(Caster oil, Punga oil and Neem oil) are shown in Fig. 2. The new peak noticed at 3449 cm^{-1}, indicates presence of N-H stretching frequency for amine group. It indicates that all the three green inhibitors contain amines and fatty acids. Nitrogen atom of the amino group has coordinated with Fe^{++} and formed as green compound complex on metal surface. The other new peaks at 1592 cm^{-1} and 1155 cm^{-1} are due to the C = O stretching frequency of the carboxyl group. This is due to the fatty acids, which are present in green inhibitors (Neem oil, punga oil and caster oil). It reveals that the oxygen atom of the carboxyl group has coordinated with Fe^{++} - green complex and formed as organo metallic complex.[15-17] Binding of a green inhibitor (amino acids and fatty acids) on metal surface can lead to the formation of protective layer.

3. 3 SEM analysis

SEM picture of the metal surface was recorded before and after the treatment with inhibitor. Pitting type of corrosion was observed in the absence of inhibitor (Fig. 3) whereas in the presence of inhibitors uniform corrosion (Fig. 4-6) was noticed.

3. 4 Mechanism of inhibition

All green inhibitors offered good inhibition for the corrosion of carbon steel (API 5LX) in diesel/water mixture. The main components of green inhibitors are fatty acids (oleic acid, stearic acid, palmitic acid) and amino acids (Tyrosine, phenylalanine, Histidine). The inhibitive of action of fatty acids were attributed to the formation of passive layer of fatty acids on the metal surface.[18]

At the corroding surface, these acids (fatty acids and aminoacids) may perform the following functions. a) Chemisorbing on the surface, b) forming a more or less stable complex with a corrosion intermediate from the dissolution sequence, c) forming of a complex with a

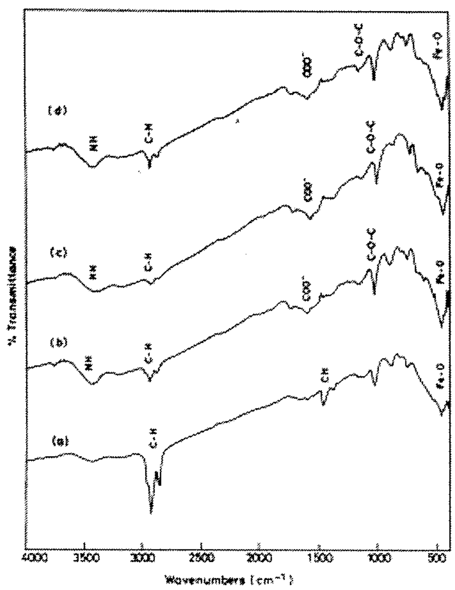

Fig. 2 FTIR spectrum for surface film of API 5LX in presence and absence of green inhibitors. a: Control, b: Neem oil, c: Punga oil, d: Caster oil.

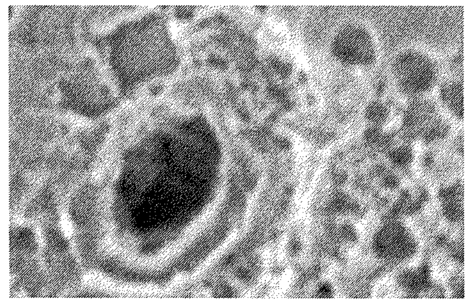

Fig. 3 SEM picture of API 5LX in control system at 500X.

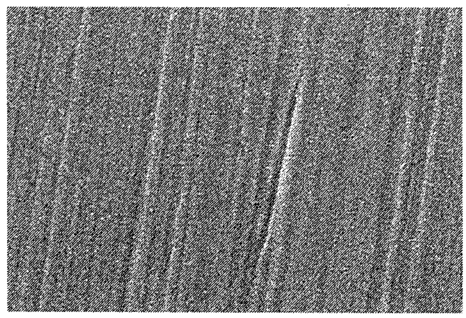

Fig. 4 SEM picture of API 5LX in Neem oil system at 500X.

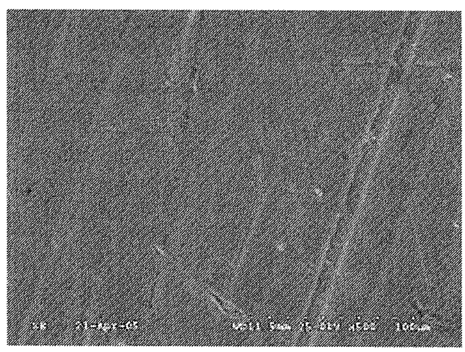

Fig. 5 SEM picture of API 5LX in Punga oil system at 500X.

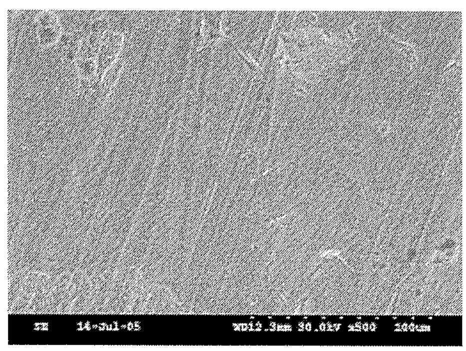

Fig. 6 SEM picture of API 5LX in Caster oil system at 500X.

final oxidative propensity. The electron distribution through out the molecule will have some effect in the above three functions.

At anodic areas iron dissolves as Fe^{2+} . This reaction is rapid in most media.[19]

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (1)$$

In deaerated solutions the cathodic reaction is given as

$$2H_2O + 2e \rightarrow H_2 + 2OH^{-} \qquad (2)$$

The cathodic reaction is accelerated by dissolved oxygen (3).

$$O_2 + 2H_2O + 4e \rightarrow 4\ OH^{-} \qquad (3)$$

Depending upon the conditions, various iron-containing products may form which may be ferrous hydroxide $[Fe(OH)_2]$ or hydrated ferrous hydroxide ($FeO.nH_2O$) which may be converted to hydrous ferric oxide or ferrous hydroxide.[20]

Therefore, the over all reaction can be expressed by

$$Fe^{2+} + 2\ [R_1R_2\ COO^{-}] \rightarrow Fe\ (COOR_1R_2)_2^{2-}$$

$$\downarrow e^{-} \qquad e-$$

$$Fe\ (COO^{-}R_1R_2) + COO^{-}R_1R_2 \rightarrow Fe + COO^{-}R_1R_2$$

4 Conclusion

1. Punga oil, Caster oil and Neem oils can be used as corrosion inhibitors in petroleum product pipeline. They act as mixed inhibitors.
2. The new class green inhibitors are cheap, readily available and non-toxic.
3. Among the three compounds caster oil showed higher corrosion inhibition efficiency.

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