

Corrosion Inhibition in Paper and Pulp Industry by Some Organic Compounds.M.A. Quaraishi^{a*} B.Lal^b and Vakil Singh^b

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Abstract

Paper industries in India face serious problems due to corrosion of structural components and their high cost of replacement and maintenance. Amongst the wide spectrum of preventive measures available, addition of inhibitors is considered to be a reliable and cost effective means for dealing with corrosion problems. The present investigation aims at evaluation of a few organic compounds, namely lauric hydrazide, undecenoic hydrazide, aniline and para anisidine on corrosion behavior of mild steel in simulated corrosive environment, encountered in paper industries, using weight loss and potentiodynamic methods.

Key words: Corrosion inhibitor; potentiodynamic polarization; mild steel; paper and pulp industry; inhibitor efficiency.

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Introduction

Paper is an important material in economic development of a country and its demand is continuously increasing day by day. Corrosion poses serious problem in the paper industry especially in the digester, bleaching and paper machine sections. A variety of stainless steels are being used to control corrosion problems in these sections of the paper industry, however, they suffer from pitting and crevice corrosion. Numerous investigators have worked on control of corrosion in the different sections of the paper industry. The properties of various polymorphic materials, polyvinyl chloride, natural and synthetic rubbers, polyester, epoxides and composites, used in paper industry to handle bleach plant chemicals like chlorine, alkali, hypochlorite, have been studied by Trivedi [1]. Muller [2] pointed out the influence of chloride ion concentration on pitting and suggested that corrosion might be reduced by increasing the pH above 3 and also proposed use of alternative materials such as titanium and fiberglass for cathodic protection. Studies by Garner [3] indicate that recycling of filtrates can cumulate corrosion problems. Garner [4] evaluated a number of bleaching plant material by exposing the section of pipe in a D1 washer seal tank. While the Hastelloy G30 experienced a significant attack the Hastelloy alloys C-22, C276 and Inconel 625 did not show any localized attack. Bennet [5] has evaluated the localized corrosion behavior of 316L stainless steel in chlorine dioxide bleach stage washer environment with peroxide additions by potentiodynamic anodic polarization technique. Several investigators have shown that presence of thiosulphate ions enhances the corrosiveness of the environment and thereby causes severe damage to materials [6-8]. Among the available methods for control of corrosion, the use of inhibitors is one of the most reliable and cost effective methods of corrosion control. The present work was undertaken to study the influence of a few organic compounds, namely, lauric hydrazide, undecenoic hydrazide, and aniline and para anisidine on corrosion behavior of mild steel in simulated corrosive environments encountered in paper industry.

Experimental

The efficiency of the inhibitors was evaluated in simulated corrosive environments of different sections of the paper industry. The compositions of the simulated corrosive

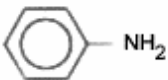
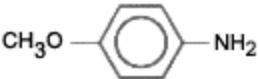
environments encountered in the different sections of the paper industries are given Table 1.

Table 1 Simulated composition of the corrosive environments in different sections.

S.N.	Section	NaCl	Na ₂ SO ₄	Na ₂ S ₂ O ₃	NaOCl	pH
1	White Water	1000 ppm	1000 ppm	50 ppm	-	3.5
2	Bleaching Water	1000 ppm	50 ppm	-	5000 ppm	8.5
3	Washer	5500 ppm	50 ppm	-	-	1.8

Weight loss experiments were carried out as per the standard method using mild steel strips of 2.5 x 2 x 0.25 cm and exposing the specimens for 3 days. The temperature of the corrosive medias was maintained at 55⁰C in all the cases. Weight of the sample following corrosion, was measured precisely using an electronic balance of high sensitivity. Mild steel strips coated with lacquer, leaving an area of exposure of 1 cm², were used for potentiodynamic polarization studies. Potentiodynamic polarization studies were carried out using EG & G PARC potentiostat (model 173), universal programmer (model 175) and x-y recorder (model RE0089). Platinum foil was used as an auxiliary electrode, and a saturated calomel was used as a reference electrode. The molecular structures of the inhibitors used in the present investigation are given in Table 2.

Table 2 Molecular structures of the different inhibitors used.

Structure	Designation and abbreviation
$\text{CH}_3(\text{CH}_2)_{10} \text{---} \overset{\text{O}}{\parallel} \text{C} \text{---} \text{NHNH}_2$	Lauric Hydrazide (LH)
$\text{CH}_2=\text{CH} \text{---} (\text{CH}_2)_8 \text{---} \overset{\text{O}}{\parallel} \text{C} \text{---} \text{NHNH}_2$	Undecenoic Hydrazide (UDH)
	Aniline (ANI)
	para-anisidine (PANI)

Results and Discussion**Weight Loss Studies**

The present study deals with the assessment of corrosion inhibition efficiencies of aniline, para anisidine, lauric hydrazide and undecenoic hydrazide for mild steel in different corrosive environments encountered in paper industries, viz., white water, bleaching section and washer section. Tables 3-5 summarize the results of weight loss studies. Figure 1 & 2 show variation of inhibitor efficiency (IE) with concentration of the four different inhibitors in bleaching water and white water, respectively. It is evident from Figure 1 that efficiency of the inhibitor LH is highest and is followed in decreasing order by those of PAN, UDH and ANI over the entire range of the concentration except at the lowest ones (≤ 300 ppm), in the bleaching water. Further, the efficiency of the inhibitors LH and PANI is much higher even at the lower concentrations of ≤ 300 ppm. The efficiency of the inhibitor PANI is 80% at 200 ppm and increases marginally with increase in concentration and reaches to 82.3 % at 500 ppm. On the other hand, the efficiency of the inhibitors is quite different in the white water. The efficiency of PANI is highest at the lowest concentration of 200 ppm and remains highest even up to the concentration of 400 ppm. This behaviour is almost opposite to that seen in the bleaching water. The efficiency of PANI increases marginally at the highest concentration of 500 ppm. The efficiency of LH is lowest at the lower concentrations (≤ 300 ppm) but increases rapidly at higher concentrations and reaches to the highest value amongst the all, at 500 ppm. Intermediate type of behavior is exhibited by the other two inhibitors (UDH & ANI). The variation of IE and PANI in white water is similar to that in the bleaching water. However, the level of its efficiency curve is higher in bleaching water than that in the white water.

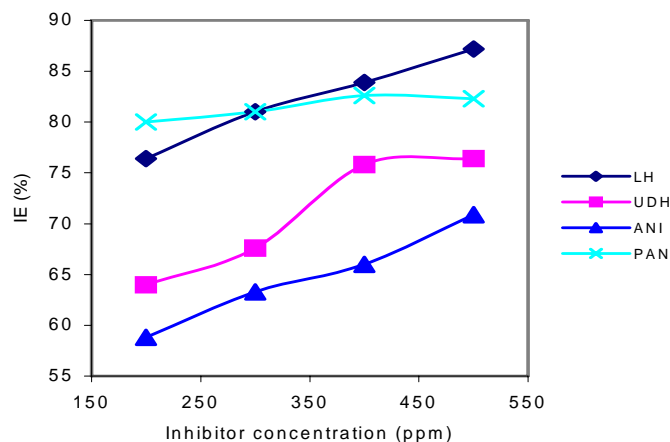


Figure 1 Variation of inhibitor efficiency with concentration of inhibitors in bleaching water.

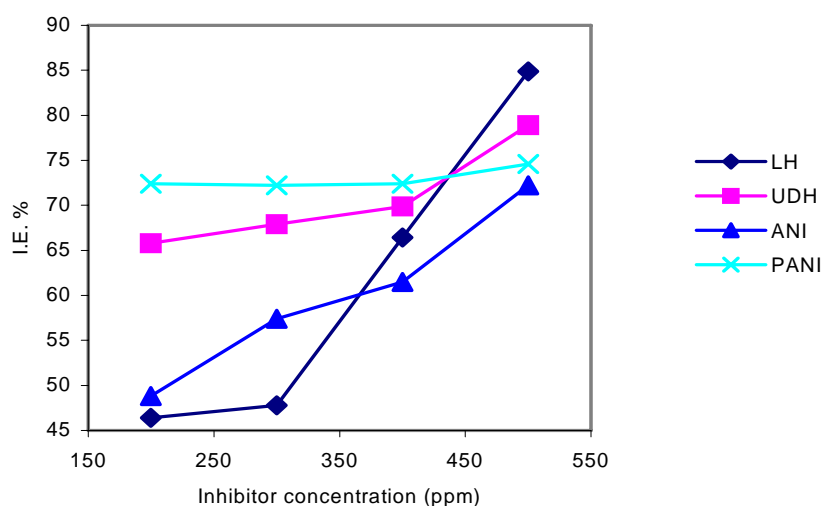


Figure 2 Variation of inhibitor efficiency with concentration of inhibitors in white water.

Table 3 Weight loss behaviour of mild steel in bleaching water

Inhibitor	Concentration (ppm)	Weight loss (mg)	I.E.(%)	Corrosion rate (mpy)
Nil	-	30.6	-	18.9
LH	200	7.2	76.4	4.4
	300	5.8	81.0	3.5
	400	4.9	83.9	3.0
	500	3.9	87.2	2.4

UDH	200	11.0	64.0	6.8
	300	9.9	67.6	6.1
	400	7.4	75.8	4.5
	500	7.2	76.4	4.4
ANI	200	12.6	58.8	7.7
	300	11.2	63.3	6.9
	400	10.4	66.0	6.4
	500	8.9	70.9	5.6
PANI	200	6.1	80.0	3.7
	300	5.8	81.0	3.5
	400	5.3	82.6	3.2
	500	5.2	82.3	3.1

Table 4 Weight loss behaviour of mild steel in white water

Inhibitor	Concentration (ppm)	Weight loss (mg)	I.E. (%)	Corrosion rate (mpy)
Nil	-	51.2	-	31.6
LH	200	27.4	46.4	19.6
	300	26.7	47.8	16.5
	400	17.2	66.4	10.6
	500	7.7	84.9	4.7
UDH	200	17.5	65.8	10.8
	300	16.4	67.9	10.1
	400	15.4	69.9	9.5
	500	10.8	78.9	6.6
ANI	200	26.2	48.8	16.2
	300	21.8	57.4	13.4
	400	19.7	61.5	12.1
	500	14.2	72.2	8.7
PANI	200	14.1	72.4	8.7
	300	14.1	72.4	8.7
	400	14.1	72.4	8.7
	500	13.3	74.6	8.27

Table 5 Weight loss behaviour of mild steel in washer stage water

Inhibitor	Concentration (ppm)	Weight loss (mg)	I.E.(%)	Corrosion rate (mpy)
Nil	-	58.4	-	36.1
LH	500	7.7	86.6	4.7
PANI	500	24.9	57.3	15.4

It may be seen from Table 5 that in the washer stage water the efficiency of the inhibitor LH at 500 ppm is almost 50% higher than that of the inhibitor.

It is seen that the corrosivity is maximum (corrosion rate 36.1) in washer stage water while the corrosion rate in white water and bleaching water section was 31.6 mpy and 18.9 mpy, respectively. The more corrosivity in washer stage water and bleaching water section is due to high salt concentration and low pH. Corrosion rate is comparatively less in bleaching environment.

Potentiodynamic Polarization Studies

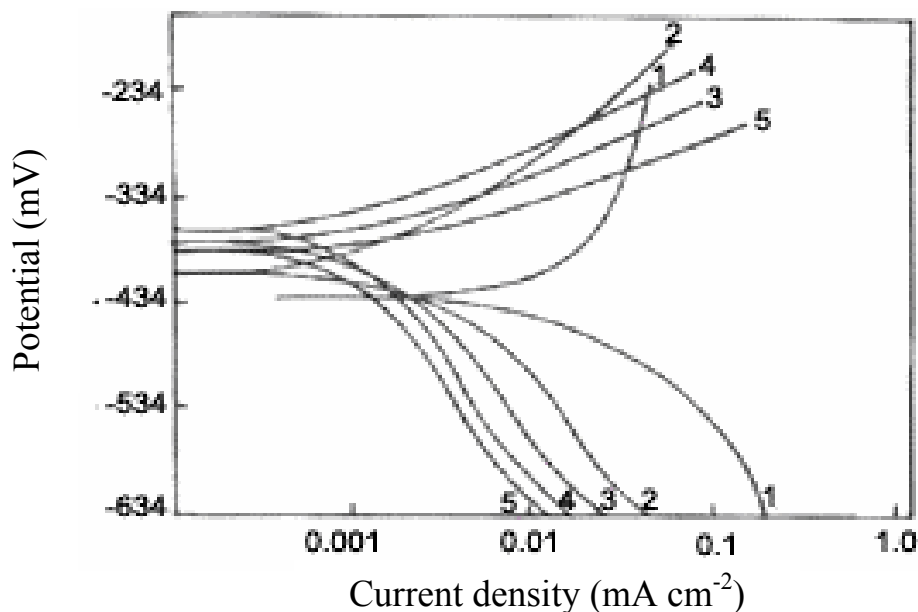


Figure 3 Potentiodynamic polarization curves for corrosion of mild steel in simulated bleaching water containing 500 ppm of inhibitors. 1. No inhibitor, 2. UDH, 3. ANI, 4. PANI, 5. LH.

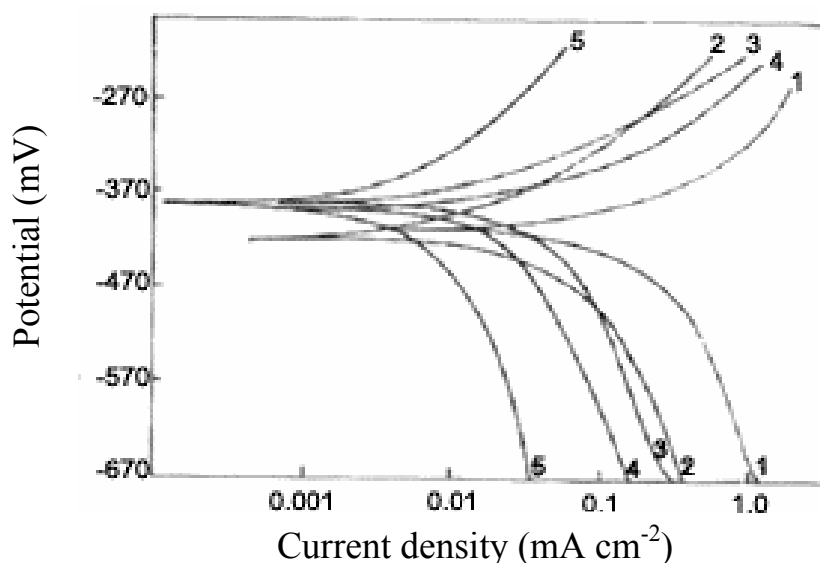


Figure 4 Potentiodynamic polarization parameter for corrosion of mild steel in simulated white water containing 500 ppm of inhibitors. 1. No inhibitor, 2. ANI, 3. PANI, 4. UDH, 5. LH.

Figure 3-4 show polarization behavior of mild steel in bleaching and white water without inhibitor and with different inhibitors. The values of the various electrochemical parameters are given in Table 6, 7 and 8.

Table 6 Potentiodynamic polarization parameters for corrosion of mild steel in simulated bleaching water containing 500 ppm of inhibitors

Inhibitor	E_{corr} (mV)	I_{corr} (μAcm^{-2})	I.E.(%)
Nil	-434	50	-
UDH	-404	4.5	91.0
ANI	-376	2.5	95.0
UDH	-390	25	83.3
LH	-384	7	95.3

Table 7 Potentiodynamic polarization parameters for corrosion of mild steel in simulated white water containing 500 ppm of inhibitors

Inhibitor	E_{corr} (mV)	I_{corr} (μAcm^{-2})	I.E.(%)
Nil	-410	150	-
ANI	-424	50	66.6
PANI	-382	40	73.3
UDH	-390	25	83.3
LH	-384	7	95.3

Table 8 Potentiodynamic polarization parameters for corrosion of mild steel in simulated washer stage water containing 500 ppm of inhibitors

Inhibitor	E_{corr} (mV)	I_{corr} (Acm^{-2})	I.E.(%)
Nil	-512	150	-
PANI	-520	20	83.6
LH	-550	10	93.3

It may be seen from Table 6 that in the bleaching water environment that all the inhibitor compounds have inhibited corrosion efficiency and all the compound have inhibited corrosion predominantly under anodic control. The corrosion inhibition efficiencies were excellent and $\geq 90\%$.

In white water environment lauric hydrazide showed maximum corrosion inhibition efficiency of 95.3% while inhibition efficiencies of other compounds were more or less in agreement with the results of weight loss studies. lauric hydrazide and para anisidine acted predominately as anodic inhibitor while aniline and undecenoic hydrazide acted as more or less as mixed inhibitor.

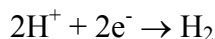
In washer stage water lauric hydrazide exhibit 93.3% corrosion inhibition efficiency while para anisidine has shown corrosion inhibition efficiency of only 46%. lauric hydrazide has acted predominately as cathodic inhibitor.

Corrosion of mild steel in acidic media such as simulated white water and washer section takes place as a result of two partial reactions while occur simultaneously at electrode surfaces.

Anodic



Cathodic



The proposed mechanism for the corrosion of mild steel in acidic media containing the inhibitors Lauric hydrazide (LH), Undecenoic acid (UDH), Aniline (ANI) and para-anisidine (PANI) can be explained on the basis of adsorption of inhibitors on electrode surfaces. In acidic media the protonated positive part of inhibitor is adsorbed on the surface of cathode and the negative part or the end having greater electron density i.e. benzene ring of the molecule of inhibitor is adsorbed on the surface of the anode and lead to decrease of cathodic and anodic reactions, respectively. Corrosion in basic media in presence of the inhibitors may also follow more or less similar mechanistic paths.

Conclusions

Following conclusions are drawn from the present investigation:

1. The corrosivity of the washer stage for mild steel was maximum followed by those of white water and bleaching section.
2. In the bleaching section the corrosion inhibition efficiency, evaluated through weight loss study, was maximum for LH (87.2) and was followed in decreasing order by those of PANI (82.3), UDH (76.4) and ANI (70.9).
3. In the white water environment the corrosion inhibition efficiency, evaluated through weight loss study, was highest for lauric hydrazide (84.9) and decreases progressively for undecenoic hydrazide (78.9), para anisidine (74.6) and aniline (72.2).
4. In washer stage lauric hydrazide exhibited corrosion inhibition efficiency of 86.9% while para anisidine showed 57.3%, at concentration of 500 ppm.
5. Overall performance of LH as corrosion inhibitor was found to be best among all the corrosive environments encountered in pulp paper industry. Further, its effectiveness is quite high even at lowest concentration of 200 ppm.

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