INHIBITIVE STRENGTH OF SOME ORGANIC COMPOUNDS ON THE CORROSION BEHAVIOUR OF MILD STEEL IN CASSAVA FLUID

By

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ABSTRACT

The result of investigation into the corrosion behaviour of mild steel in cassava fluid in the presence of some organic inhibitors in regulated amounts is presented. 20ml of different concentrations – 500ppm, 600ppm and 700ppm – of sodium benzoate, diethylamine and triethylamine were introduced into 200ml cassava fluid into which mild steel was dipped and corrosion behavior evaluated using gravimetric analysis. The corrosion rate of mild steel exposed to uninhibited cassava fluid averages 0.70mmpy. Mild steel in sodium benzoate, diethylamine and triethylamine inhibited cassava fluid range 0.0629mmpy – 0.2581mmpy, 0.0297mmpy – 0.0900mmpy and 0.0568mmpy corrosion rate respectively.

Of all the three organic inhibitors diethylene amine produced the lowest values of corrosion rate range across the three concentrations. Sodium benzoate and triethylene amine were only effective in high concentrations.

Keywords: Inhibitive strength, corrosion behaviour, cassava fluid environment, organic compounds.

1.0 INTRODUCTION

Mild steel accounts for a great deal of metallic construction in the building of machines/equipment for process and allied industries[1-3]. When such metals are in contact with their environment they tend to convert to their pre-extraction state. The conversion process is faster and complex if the environment is very aggressive and contains some radicals such as sulphide radicals. Thus, machine/process equipment made of ferrous material often deteriorate and ultimately strive to produce hydrated oxide known as rust.

Corrosion in "local" perspective represents a loss in production time due to plant/equipment failure, resultant likely fatal accident to the person involved and man hour loss. In a global perspective, it represents a tremendous economic loss and much has to be done to

reduce it though it is inevitable. It is more critical in food and chemical industries as it relates to product contamination in pigments, foods and drugs. In certain situations, a very small incidence of corrosion that introduces some items into a system may cause catalytic decomposition and may make the product toxic. If the system is food based, the product may lead to fatal body injury if consumed.

Recently the Federal Government of Nigeria as part of the National Economic Empowerment and Development Scheme enunciated an ambitious policy thrust of generating about five billion dollars ($5 billion) from cassava plantation yearly. The potentials of the massive cassava plantation is not in the raw tuber but in the ancilliary products from the processed cassava. For instance, cassava is a major source of ethanol a major materials input for bio-fuel. As a matter of fact, local flour millers have been directed to blend their flour production with 10 percent cassava flour input. The implication of this policy thrust is that there will be upsurge in cassava processing industries deploying massive machineries that are ferrous material constructed. The major fluid element in the cassava plant is the glucoside cyanide which through enzyme action and hydrolysis breakdown to hydrogen cyanide a very corrosive and toxic compound. The hydrogen cyanide compound attack seriously materials of construction of agro-processing equipment. It is therefore imperative that corrosion in this medium is prevented for high productivity, health reasons and cost saving.

Jekayinfa et al[4] had studied the behaviour of mild steel on virgin cassava fluid. They inferred that mild steel that is not heat-treated corrode much more readily than heat treated steel. The implication of their work is that non-heat treated as-received mild steel must be corrosion treated before it can be used in such environment.

Materials are corrosion treated through one of appropriate material selection at the design stage, coatings, cathodic protection, sacrificial anodes, alteration of environment and the use of inhibitors. Besides primary coatings, corrosion prevention in the process and allied industry centres on the use of inhibitors. Inhibitors are called retarding catalyst. They are grouped either as organic or inorganic. They are specific in terms of metal, environment temperature and concentration range. However, they gradually lose their effectiveness as the temperature and concentration increases. The concentration range of application of inhibitors are between 1 x 10^{-3} and 1 x 10^{-6} mol/dm^3. They are adopted as constituent of organic or inorganic based coatings. The efficacy of some organic and inorganic compounds as inhibitors has been investigated by several authors. For instance, Attar and Scantlebury[11], Boris[12], Larabi and Harek and Afolabi[14] had at different times

studied some organic compounds while Shulter and Luo[15] and Bartis et al[16] had studied some inorganic compounds. Comparative analysis of these previous works revealed that the inorganic inhibitor group performed better than the organic; however, the organic is more environment friendly as they are non toxic.

In this work, the effect of three classes of organic inhibitors in reducing corrosion of mild steel in cassava fluid is investigated.

2.0 METHODOLOGY

2.1 Materials Sourcing and Preparation

Specimen Sourcing and Preparation

The mild steel specimen used for the study was obtained from Galvanizing Industries Limited, Ikeja, Lagos, Nigeria, in the form of a plate (1m x 1m x 0.01m thick). The mild steel sheet was cut into test specimen size of 2.5cm x 5.0cm.

The cut samples sheared edges were machined and ground with emery papers of increasing order of fineness to 500 grit. The surface was subsequently pickled in dilute hydrochloric acid (Hcl). Specimens were thereafter degreased by washing in acetone solvent, dried in an oven, weighed on a sensitive analytical balance and placed in a dessicator to prevent atmospheric corrosion before experimentation.

Corrodant and Inhibitor Preparation

The cassava fluid having a pH of 6.1 was prepared from freshly harvested cassava tubers and kept in the refrigerator to prevent fermentation from taking place. The organic inhibitors used for the study – triethylamine, diethylamine and sodium benzoate – were commercially procured. The triethylamine and diethylamine were in liquid form whilst sodium benzoate was in solid form. A solution of the sodium benzoate was made.

Different quantities of the substances were weighed out on a weighing balance in the laboratory to prepare the three different concentrations of 500, 600 and 700ppm that were used.

Apparatus Set up

The apparatus used for the experiment were set up as indicated in Figure 1. The containers were washed with detergent, rinsed in distilled water and dried in a warm oven. Cassava solutions of known pH were introduced into the containers and specimens immersed in such a way that they were completely covered by the solution.

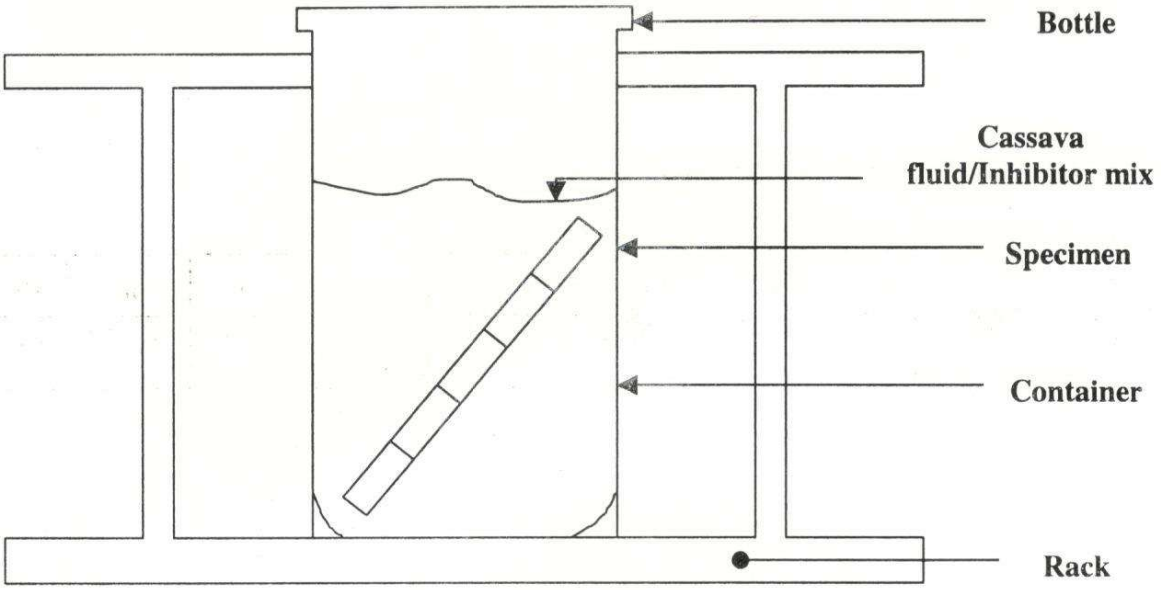

Fig. 1: Experimental Set-up

2.2 Experimental Detail

The compositional analysis of the mild steel specimen was determined by Atomic Absorption Spectroscopy (AAS). The composition is shown in Table 1.

The initial weight of the prepared 2.5cm x 5.0cm specimen were taken before being immersed in the cassava fluid solutions containing different concentrations of inhibitors. Prepared specimens were equally dipped in uninhibited cassava solution to serve as control test.

A ratio of 1 to 10ml inhibitor to corrodant was used for all the samples. Weighing for weight loss was done every 3 days for 20 days. Specimens were removed from container, rinsed thoroughly in distilled water and alcohol to remove the rust formed. Each specimen was thereafter weighed using a weighing balance for weight loss.

The corrosion rate is evaluated using the formula proposed by Fontana[17]

$$\text{Corrosion rate (mm/yr)} = \frac{87.6W}{DAT} \quad \text{I}$$

where W = Weight loss in milligrams

D = Density of specimen in g/cm^3

A = Total exposed area in cm^2

T = Exposure time in hrs.

The weight loss ratio is expressed as:

$$\text{Weight loss ratio (R)} = \frac{\text{Weight loss of specimen immersed inhibited solution}}{\text{Weight loss of specimen immersed in uninhibited solution}} \quad \text{II}$$

RESULTS

Table 1: Chemical Composition of Mild Steel Specimen

Element	C	Mn	Si	Ni	Cr	P	S	Cu	Sn	*Fe*
% Composition	*0.0922*	*0.302*	*0.276*	*0.0194*	*0.0227*	*0.0101*	*0.0125*	*0.0717*	*0.0124*	*99.181*

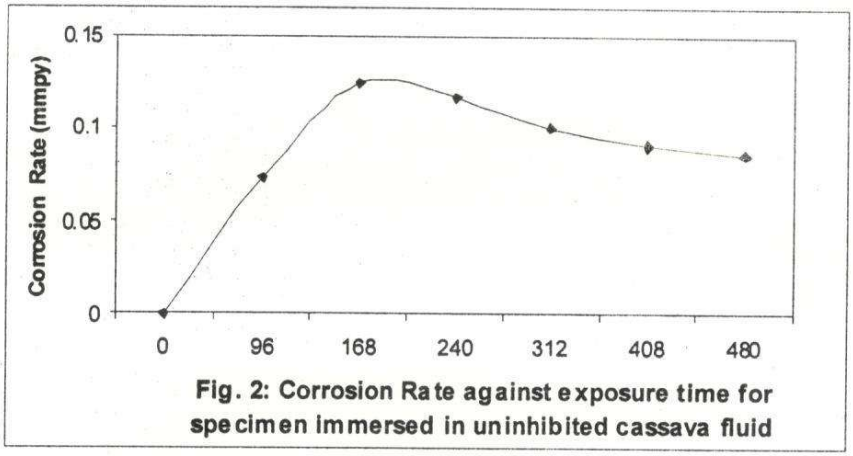

Fig. 2: Corrosion Rate against exposure time for specimen immersed in uninhibited cassava fluid

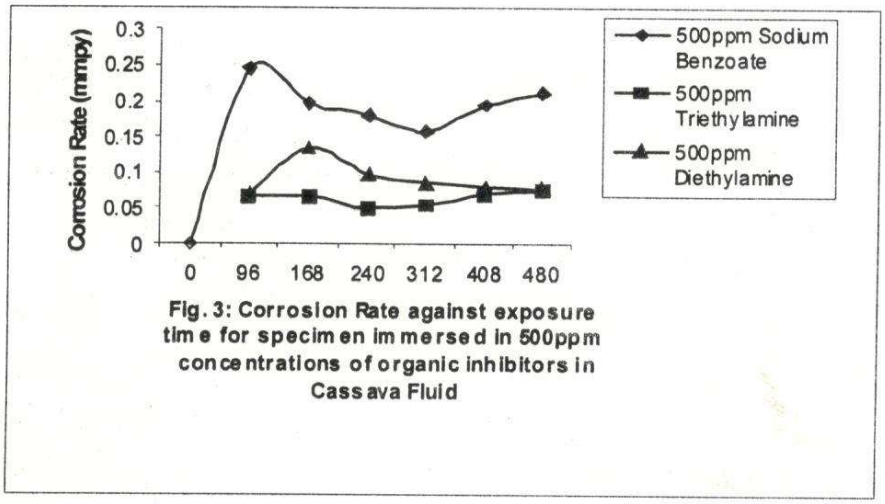

Fig. 3: Corrosion Rate against exposure time for specimen immersed in 500ppm concentrations of organic inhibitors in Cassava Fluid

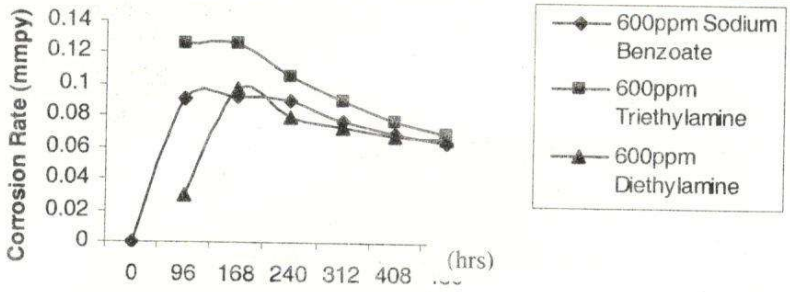

Fig. 4: Corrosion Rate against exposure time for specimen immersed in 600ppm concentrations of organic inhibitors in Cassava Fluid

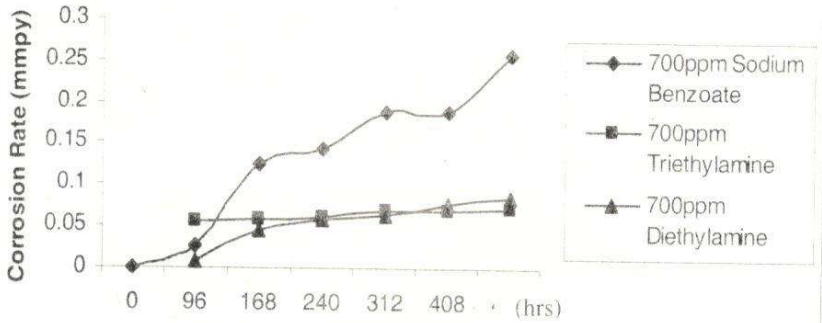

Fig. 5: Corrosion Rate against exposure time for specimen immersed in 700ppm concentrations of organic inhibitors in Cassava Fluid

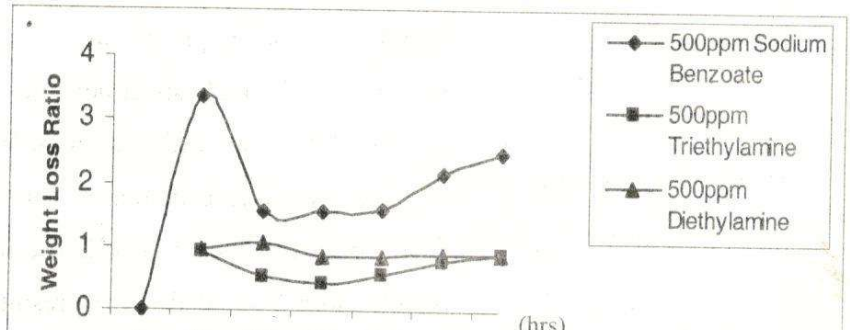

Fig. 6: Weight Loss Ratio against exposure time for specimen immersed in Cassava Fluid inhibited with 500ppm organic inhibitors

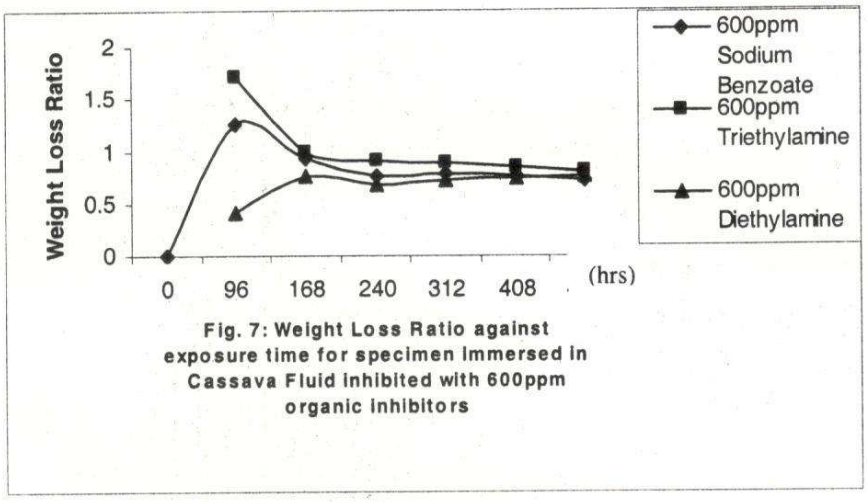

Fig. 7: Weight Loss Ratio against exposure time for specimen immersed in Cassava Fluid inhibited with 600ppm organic inhibitors

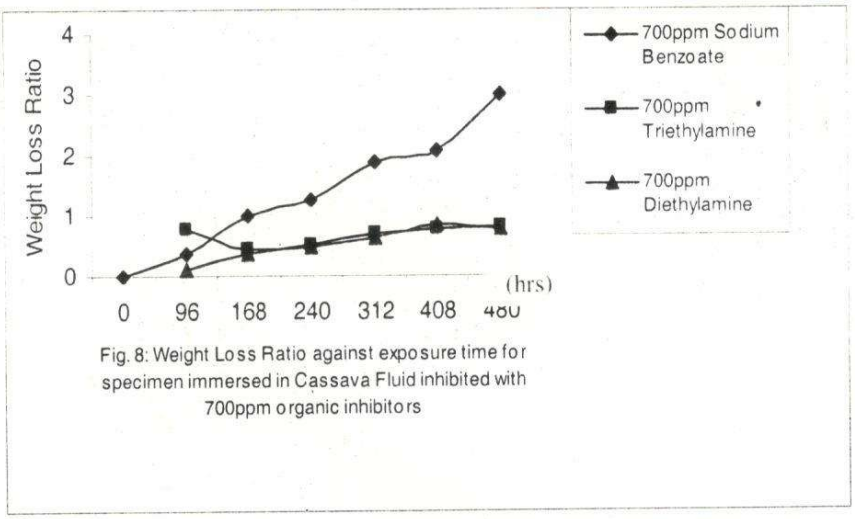

Fig. 8: Weight Loss Ratio against exposure time for specimen immersed in Cassava Fluid inhibited with 700ppm organic inhibitors

DISCUSSION OF RESULTS

The spectrometric analysis of the ferrous specimen given in Table 1 revealed that the sample is a dead mild steel 0.0926C weight percent with other trace element residued probably from metal extraction process. The levels of these residual elements are insignificant to influence the chemistry of the behaviour of the steel sample in the test media.

Figure 2 is the graphical display of corrosion rate of mild steel specimen in uninhibited cassava fluid. The mild steel in the uninhibited cassava experienced increased corrosion in the first 168 hours. This is manifested in the heavy weight loss recorded as a result of metal dissolution in the first 168 hours. The rate peaked at 168 hours and subsequently reduced afterward to a plateau. The figure indicates that the corrosion rate in the uninhibited cassava

averaged 0.1051mmpy in the first 168 hours. The apparent high intensity of corrosion during the initial 168 hours of exposure is probably due to the chemistry of the active glucoside cyanide ions. The cyanide ions in the first few days of immersion of the ferrous sample is very reactive and combines readily with the dissolved iron ions to form a thin scale of iron cyanide thereby depleting the iron concentration in the neighbourhood within the cassava fluid medium. This is the major driving force for the corrosion in the first 168 hours of immersion. The reduction in the corrosion rate after this period is premised on the dilution and reduction in concentration of the cyanide ions by its being converted to a very weak hydrogen cyanide. Besides, due to the non-turbulent nature of the medium, the thin iron cyanide scale formed earlier is not broken. This, therefore prevents the exposure of unattacked metal surface to the corroding medium. Hence, further metal dissolution is prevented. Though, the corrosion retards after 168 hours, the metal dissolution and loss was massive in the initial hours recording a total weight loss of 47mg for the 480 hours of immersion.

Figure 3 is the corrosion curve obtained for specimen immersed in 500ppm individual solutions of sodium benzoate, triethylamine and diethylamine respectively. The curve gives comparative analysis of the influence of the three different inhibitors.

The 500ppm sodium benzoate inhibitor/cassava fluid medium recorded a very sharp increase in corrosion in the first 96 hours and subsequently reduces progressively till 312 hours of immersion. Beyond 312 hours, however, there was sudden increase in corrosion rate. The 500ppm triethylamine and diethylamine both however behave a bit rather differently. In the two inhibitors, corrosion rate in the first 96 hours was somewhat marginal. However, while the 500ppm triethylamine had a sharp increase between 96 and 168 hours and later reduces, the 500ppm diethylamine inhibitor progressively had a reduced corrosion rate.

The corrosion rate averaged 0.062mmpy in sodium benzoate, 0.0568mmpy in triethylamine and 0.0297mmpy in diethylamine respectively. The average weight loss in the sodium benzoate was 44.9mg, 38mg in triethylamine and 36.6mg in diethylamine compared with the 47mg recorded in uninhibited cassava fluid over a total period of 480 hours.

Figure 4 gives the corrosion rate against exposure time for specimen immersed in cassava fluid inhibited with 600ppm concentration of organic inhibitors. The corrosion rate of the steel specimen improved relative to the rate recorded when the concentration of the three organic inhibitors was 500ppm.

The corrosion rate in the 600ppm concentration sodium benzoate inhibited cassava fluid followed the pattern observed in the 500ppm sodium benzoate though the rate is much lower. The situation in the 600ppm concentration triethylamine followed a reducing pattern right from the 96 hours of immersion. The behaviour in the 600ppm concentration diethylamine inhibitor was rather curious in relation to what was observed in the 500ppm concentration.

The general behaviour in the 600ppm concentration was that the rate increased in the first 96 hours and later reduces. The reduction in the rate of corrosion in the later hours of immersion was more noticeable in the diethylamine inhibitor than the other two.

The behaviour of the mild steel specimen in cassava fluid inhibited with 700ppm concentration of organic inhibitors is illustrated in Figure 5. The corrosion rate in sodium benzoate averaged 0.2581mmpy, 0.1253mmpy in triethylamine and 0.0676mmpy in diethylamine respectively for the total immersion period of 480 hours. The implication of this scenario is that diethylamine apparently gives the best corrosion mitigation effect among the three organic inhibitors. Besides, the various figurative illustrations revealed that increasing concentration of inhibitors contributes to lowering corrosion rate of the sample in the cassava fluid medium.

This is better confirmed in term of the weight loss ratio which probably measures the efficiency of the inhibitors.

The weight loss ratio is a term used to describe the ratio of the weight loss in inhibited solution to the weight loss in uninhibited solution.

Figure 6, 7 and 8 are the weight loss ratios for the ferrous sample in 500ppm, 600ppm and 700ppm concentrations of the three different organic inhibitors respectively.

Figure 6 is the weight loss ratio curve at 500ppm concentration of the organic inhibitors. The weight loss ratio for the 500ppm sodium benzoate was rather high in the first 96 hours. It drastically reduced at 168 hours and marginally fluctuates within the 1.5 mark beyond 168 hours. The weight loss ratios for the 500ppm triethylamine and diethylamine on the other hand were less than unit. However, the 500ppm diethyl had the least weight loss ratio. Therefore, the diethylamine at 500ppm concentration is the most effective in reducing corrosion of mild steel in cassava fluid.

The weight loss ratio curve at 600ppm concentration of organic inhibitors is given in Figure 7. As it was in Figure 6, the ratio was very high in the initial 96 hours, afterwhich, it progressively reduces and maintain a relatively constant value at 168 hours of immersion and beyond. At 600ppm concentration, diethylamine has the least weight loss ratio. This apparently implies that diethylamine is the

best inhibitor at 600ppm concentration. The weight loss ratio at this concentration for diethyl was very much less than unit while the other two were greater than unit.

In comparison to Figure 6, it is clear that increasing the concentration of organic inhibitors results in a better weight loss character. This indicates probably that a higher concentration improves the efficacy of inhibitor in reducing material loss through corrosion.

The effect of higher concentration of inhibitor on corrosion reduction is illustrated in Figure 8. The weight loss ratio resulting from 700ppm concentration of organic inhibitors was much lower compared to the ratio obtained either on 500ppm concentration or 600ppm concentration. However, there was a curious observation in the 700ppm sodium benzoate. While the weight loss ratio in the two other organic inhibitors progressively reduces, the sodium benzoate was increasing. This probably indicates that exceeding a particular concentration of inhibitor may in itself accelerate the corrosion process.

The mechanism of the gravimetric observation in the behaviour of the three organic inhibitors is better explained in terms of the reaction kinetics of the organic inhibitors in glucoside cyanide cassava fluid medium.

CONCLUSION

It is established that cassava solution has a corrosive attack on mild steel at room temperature. Mild steel exposed to cassava solution averages 0.1mmpy. This implies that an average amount of 0.1mm is corroded away from the surface of the metal every year in contact with cassava fluid. That is, a mild steel specimen of original thickness 1mm exposed to cassava solution will have a thickness of 0.9mm at the end of a year cycle, and eventually after 10 years, total depletion of the metal may occur.

The work has investigated the effects of three organic inhibitors on the corrosion behavior of mild steel in cassava fluid. The study has shown that inhibitors added in regulated amounts are effective in reducing the rate of corrosion and that if a critical concentration is exceeded, the inhibitor may in itself increase the corrosion process.

Diethylamine of the three inhibitors displayed the lowest value of corrosion rate of 0.0297mmpy average across the three concentrations. Sodium benzoate and triethylamine were only effective in high concentrations.

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APPENDIX

Table 2: Gravimetric Data of Mild Steel Immersed in Cassava Fluid Uninhibited

Time (HRS)	Initial Weight (g)	Final Weight (g)	Weight Loss (mg)	C.R. (mmpy)	*W.L. Ratio*
0	10.3901				
96		10.382	8.1	0.073	-
168		10.3655	24.6	0.1241	-
240		10.3579	32.2	0.1161	-
312		10.3540	36.1	0.1000	-
408		10.3474	42.7	0.0905	-
480		*10.3423*	*47.8*	*0.0861*	-

Table 3: Galvimetric Data of Mild Steel in Cassava Fluid Inhibited with Sodium Benzoate

Molar concentration	500ppm					600ppm					*700ppm*				
Time (Hrs)	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	W.L.R	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	W.L.R	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	*W.L.R.*
0	10.2945	-	-	-	-	10.4605	-	-	-	-	10.4025	-	-	-	-
96	-	10.2672	27.3	0.246	3.3704	-	10.4503	10.2	0.0917	1.2593	-	10.3966	2.9	0.0261	*0.358*
168	-	10.256	38.5	0.1982	1.565	-	10.4426	17.9	0.0922	0.9276	-	10.3782	24.3	0.1251	*0.9878*
240	-	10.2446	49.9	0.1799	1.5497	-	10.4358	24.7	0.0890	0.7671	-	10.3625	40	0.1442	*1.2422*
312	-	10.2375	57	0.158	1.5789	-	10.4320	28.5	0.0770	0.7895	-	10.3344	68.1	0.1881	*1.8864*
408	-	10.2031	97.4	0.1938	2.1659	-	10.4283	32.2	0.0683	0.7541	-	10.3133	89.2	0.1891	*2.089*
480	-	*10.1767*	*117.8*	*0.2123*	*2.4644*	-	*10.4256*	*34.9*	*0.0629*	*0.7301*	-	*10.2593*	*143.2*	*0.2581*	*2.9958*

Table 4: Gravimetric Data of Mild Steel in Cassava Fluid Inhibited with Triethylamine

Molar concentration	500ppm					600ppm					*700ppm*				
Time (Hrs)	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	W.L.R	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	W.L.R	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	*W.L.R.*
0	10.2965	-	-	-	-	10.4535	-	-	-	-	10.4345	-	-	-	-
96	-	10.2891	7.4	0.0667	0.9136	-	10.4396	3.9	0.1253	1.716	-	10.4382	6.3	0.0568	*0.7778*
168	-	10.2835	13	0.0669	0.5285	-	10.4291	24.4	0.1256	0.9919	-	10.423	11.5	0.0592	*0.4625*
240	-	10.2826	3.9	0.0501	0.4317	-	10.4245	29	0.1045	0.9006	-	10.4273	17.2	0.0620	*0.5342*
312	-	10.2764	20.1	0.0557	0.5567	-	10.4212	32.3	0.0896	0.8947	-	10.4097	24.8	0.0688	*0.6870*
408	-	10.2639	32.6	0.0691	0.7635	-	10.4172	36.3	0.077	0.8501	-	10.4018	32.7	0.0693	*0.7658*
480	-	*10.2542*	*42.3*	*0.0762*	*0.8849*	-	*10.4155*	*38*	*0.0685*	*0.795*	-	*10.3951*	*39.4*	*0.0710*	*0.8243*

Table 5: Gravimetric Data of Mild Steel in Cassava Fluid Inhibited with Diethylamine

Molar concentration	500ppm					600ppm					*700ppm*				
Time (Hrs)	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	W.L.R	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	W.L.R	Initial weight (g)	Final weight (g)	Weight loss (mg)	C. R. (mmpy)	*W.L.R.*
0	10.296	-	-	-	-	10.2215	-	-	-	-	10.4215	-	-	-	-
96	-	10.2882	7.8	0.0703	0.963	-	10.2182	3.300	0.0297	0.4024	-	10.4205	1.000	0.009	*0.1235*
168	-	10.2697	26.3	0.1354	1.0691	-	10.2026	18.90	0.0973	0.7682	-	10.4126	8.900	0.0458	*0.3618*
240	-	10.2688	27.2	0.098	0.8447	-	10.1994	22.1	0.0797	0.6863	-	10.4054	16.100	0.0580	*0.500*
312	-	10.2655	30.5	0.0846	0.8449	-	10.1952	26.3	0.0729	0.7285	-	10.3983	23.200	0.0643	*0.6427*
408	-	10.2580	38	0.0806	0.8899	-	10.1898	31.7	0.0672	0.7424	-	10.3854	36.100	0.0765	*0.8454*
480	-	*10.2534*	*42.6*	*0.0768*	*0.8912*	-	*10.1849*	*36.6*	*0.0660*	*0.7657*	-	*10.3745*	*47.000*	*0.0847*	*0.7833*