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Inhibitory Effect of 1 – Phenyl – 3 – Methylpyrazol – 5 – One on the Mechanical Properties of Copper in Aqueous Media

KEYWORDS: Copper; Weight loss; Mechanical Properties; Kinetic parameters.

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ABSTRACT *Inhibitory effect of 1 – Phenyl -3 – Methylpyrazol -5- One (HPMP) on the mechanical properties of copper in acid environments was studied using weight loss method. Results obtained showed that HPMP inhibited the corrosion of copper in Hydrochloric and Nitric acids, but didn't in Perchloric acid environment. Calculated values of rate constants and half –life confirmed the inhibition of the metals by HPMP. HPMP is therefore a good and effective inhibitor for copper, as it caused a remarkable decrease in the hardness and tensile strength of the coated coupons, rendering them more ductile compared to the uncoated coupons.*

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1.0 Introduction
Pure metals and alloys react chemically/ electrochemically with corrosive medium to form a stable compound, in which the loss of metal occurs. The compound so formed is called corrosion product and metal surface becomes corroded (Adetunji and Adewoye, 2010, Pandian and Mathur, 2008). Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular (Sulaiman et al., 2012 and Fayomi and Popoola, 2012). Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media.

The inhibition of copper corrosion in various media using several organic and inorganic compounds has been studied. Results showed that organic compounds, especially those containing nitrogen or Sulphur, gave a very good inhibition for copper corrosion in different media (Osarolube, 2007 and Oforka et al. 2005). Copper and Copper alloys are widely used in many environments and applications because of their excellent corrosion resistance, which is coupled with combinations of other desirable properties, such as superior electrical and thermal conductivity, ease of fabricating and joining, wide range of attainable mechanical properties.

The usefulness of a metal for an engineering project is determined by its mechanical properties. Such properties are also used to specify and identify metals during design stages and structures. Commonly determined mechanical properties are tensile strength, hardness and modulus of elasticity. HPMP and its derivatives have received increasing interest from researchers due to their commercial importance as analgesics, antifungal and photochemical agents (Osarolube and James, 2014). It is synthesized and used for anticorrosion of copper in this research.

The present work is undertaken to evaluate the inhibition efficiency of HPMP in controlling the corrosion of copper in different acidic solutions and its effects on the hardness and tensile strength of the metal.

2.0 Material and methods
2.1 Preparation of HPMP Inhibitor
The HPMP inhibitor was synthesised using the method by Vogel (2002). It is insoluble in water, but soluble in a mixture of ethanol and water.

2.2 Preparation of specimen
Pure copper sheet was mechanically pressed cut into different coupons of dimension 4cm x 4cm x 1cm. Each coupon was thoroughly cleaned with a hole drilled at one end to allow for easy passage of thread. Thereafter, they were degreased in ethanol, dried in acetone and stored in a desiccator for further use after the initial weight had been taken. Solutions were prepared using analar reagents and distilled water.

2.3 Coating of the specimens with HPMP
The coupons were coated with HPMP as discussed in previous work (Osarolube, 2014).

2.4 Weight loss measurements
The precleaned coated and uncoated copper coupons were completely immersed in 250ml beakers containing 200ml of test solutions at ambient temperature. The weight loss was determined by retrieving the coupons at 24 hour interval progressively for 168 hours (7days), washed with rubber cork in distilled water, degreased in ethanol, dried in acetone and reweighed. The weight loss was taken to be the difference between the weight at a given time and the original weight of the coupons. The Inhibition efficiency (%) of HPMP was evaluated using the following equation:

$$I\% = (1 - W_1/W_2) \times 100 \qquad (1)$$

Where W_1 and W_2 are weight losses for copper in the presence and absence of the inhibitor respectively in the acid solutions.

2.5 Hardness Test
The indentation was performed with the frank Rockwell hardness testing machine. A pre – load (minor load) of 10kgF was applied on the coupons and then a major load of 100 KgF, giving a total of 110KgF. Thereafter, the hardness value was read directly from the scale. This test was carried out for both the coated and uncoated coupons.

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2.6 Tensile Strength Test

The tensile strength tests were carried out with the Tinus Olsen Tensile testing machine. Gauge lengths of 50mm were marked off on the samples and were firmly gripped at both ends within the tension mode. The load and extension were recorded continually until fracture occurred.

3. Results and Discussion

3.1 Analysis of Results from weight loss experiment

Whenever an effective inhibitor is used, corrosion process is retarded. Table 1 shows the weight loss of the metal, uncoated and coated with the inhibitor, and it can be seen that HPMP Inhibited the corrosion of copper in the HCl and HNO_3 environments, as lower values of weight loss were recorded for the coated samples. Inhibition efficiency was found to be related to the quantity of metal lost during exposure to the media .This was deduced from the magnitude of weight loss of the copper coupons. The coated samples in the $HClO_4$ had higher values of weight loss than the uncoated samples. This signifies that the inhibitor coating on these

TABLE 1: Weight loss (g) of coated and uncoated copper samples in various acidic medium.

Time (Days)	Weight loss (g)					
	HCl	HNO$_3$		HCLO$_4$		
	Uncoated sample	Coated sample	Uncoated sample	Coated sample	Un-coated sample	Coated sample
1	0.0439	0.0360	0.8320	0.0521	0.0112	0.0130
2	0.2577	0.2137	1.0104	0.0700	0.0179	0.0215
3	0.7801	0.6914	1.2262	0.2230	0.0284	0.0389
4	1.2261	1.1142	1.4028	0.5577	0.0378	0.0523
5	1.7208	1.6196	1.4403	0.7749	0.0498	0.0709
6	2.2758	2.1617	1.6039	0.9175	0.0601	0.0930
7	2.8342	2.7352	1.6480	1.2195	0.0697	0.1133

samples dissolved, thereby aiding the corrosion of the metal.It was also observed that the weight loss increasedwith increase in exposure time for both uncoated and coated samples.

3.2 Kinetic Analysis of the Weight Loss Result

The rate constants (K) at room temperature were used to calculate the half-life ($t_{1/2}$) of the system by making use of the first order reaction equation.

$t_{1/2} = 0.693/K$ (2)

Where K is the rate constant calculated using equation (3).

$K = 1/t \ln W_i/W_f$ (3)

Where W_i is the initial weight of the sample, W_f is the final weight of the sample and t is the immersion time (days). Calculated values of rate constants (K) and half –life ($t_{1/2}$) are presented on table 2. The results further confirm the inhibition of the metals by HPMP as higher values of half-life were obtained for the coated samples. HPMP retarded corrosion by adsorption onto the metal, to form a thin invisible film only a few micrometres thick. As for the uncoated samples in $HClO_4$ solution, it will take about 1386 days for it to decay by half, while the coated samples will decay by half in 990 days.

TABLE 2: kinetic data from weight loss measurements for uncoated and coated copper in acid solutions.

Nature of coupon	Acid	Rate Constant K (day^{-1})	Half-life, $t_{1/2}$ (days)
Uncoated	0.05M HCl	0.0184	37.7
Coated	0.05M HCl	0.0172	40.3
Uncoated	0.05M HNO_3	0.0106	65.4
Coated	0.05M HNO_3	0.0097	71.4
Uncoated	0.05M $HClO_4$	0.0005	1386
Coated	0.05M $HClO_4$	0.0007	990

The lower value of half-life obtained for the coated copper sample is a further proof that HPMP did not inhibit the corrosion of copper metal in the perchloric acid environment.

3.3 Inhibitory Action of HPMP

The result of inhibition efficiency as shown in figure 1 is evaluated using the equation as shown below:

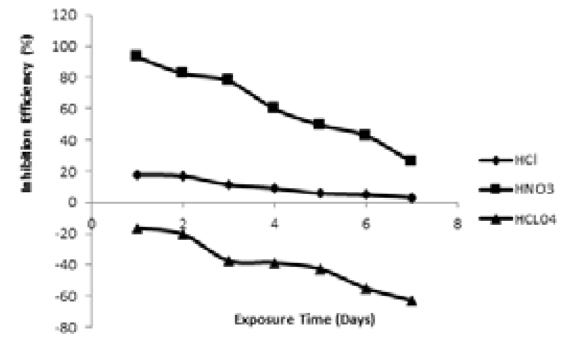

Fig.1 Variation of inhibition efficiency (%) with time (days) of copper in HCL, HNO_3 and $HCLO_4$ solutions.

Inhibition Efficiency (IE %) = $(1 - W_c/W_u) \times 100$ (4)

Where W_c and W_u are weight loss of the coupons for coated and uncoated conditions respectively. A maximum inhibition efficiency of 93.29% was obtained in the HNO_3 environment. Negative values of inhibition efficiency obtained in the perchloric acid environment are a further proof that there was no inhibition of copper in $HClO_4$. This behaviour is attributed to the fact that $HClO_4$ is one of the strongest acids known and thus caused fast dissolution of the metal.

The plot also reveals a downward trend in inhibition efficiency with time. This observation could be attributed to direct attack on the HPMP coating on the surface of the metals, which is washed away with time during the corrosion process, thereby exposing the metal to attack by the acid. The inhibition of the corrosion process by HPMP can be attributed to adsorption of its molecules on the metal surface through an unshared pair of electrons belonging to the nitrogen atom, thereby blocking its active sites. This is usually observed by the decrease in corrosion loss as measured by weight loss (Shah et al., 2011).

3.4 Effect of HPMP Coating and Acid Concentration on the Mechanical Properties of Copper

3.4.1 Hardness

The values obtained from the Rockwell hardness test as presented on table 3, show that the uncoated samples generally had higher hardness values than the as – received and coated samples. This implies that the HPMP coating actually inhibited the metal. The observed increase in hardness of the metals with time is due to the corrosion process. The higher the hardness values of the material,

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the more brittle it becomes. This result is in agreement with that of Amula et al. (2005) and Abiola et al. (2008), who observed from their work that for metals generally, as the hardness values increase, so do the shear, tensile and compressive strength but ductility and malleability of the material reduces.

Results on table 3 also show that the coated metals are more ductile than the uncoated ones. In terms of use, brittle materials are generally not adequate for engineering applications as their failure in service is usually very catastrophic. Unlike the ductile materials, they give no warning before failure.

TABLE 3 Hardness Values of As-Received, Uncoated and Coated Samples of Copper in acidic media.

	ACID					
	HCl		HNO3		HClO4	
Time(days)	As-Received sample (37.00)		As-Received sample (37.00)		As-Received sample (37.00)	
	Uncoated Samples	Coated Samples	Uncoated Samples	Coated Samples	Uncoated Samples	Coated Samples
1	43.70	40.67	60.20	50.50	62.80	44.00
4	44.20	43.05	62.00	51.17	64.50	47.47
7	51.10	50.00	63.75	51.33	64.90	53.30

Table 4 shows the effect of concentration on the hardness of the metal in the various acidic media. Hardness is seen to increase with concentration. This can be explained by the fact that at higher concentration, there is increased collision of the active species in the corrosion reaction. Thus, the more the attack on the metals as a result of increased concentration, the more brittle the metal becomes. This in turn increases the hardness of

TABLE 4 Hardness values of Uncoated Copper Samples on the 4th Day at various Acid Concentrations.

Concentration (M)	Hardness		
	HCl	HNO_3	$HClO_4$
0.5	44.20	58.00	64.50
1.5	50.50	60.20	65.00
3.0	53.00	64.20	66.00

the metal. $HClO_4$ environment recorded the highest hardness value of 66.00 followed by HNO_3 with 64.20, and lastly, HCl with 53.00.

3.4.2 Tensile Strength

Results on table 5 reveal a general decrease in the tensile strength of the copper samples, when compared with that of the as – received samples.The corrosion process had a negative

TABLE 5: Tensile Strength of As-Received, Uncoated and Coated Samples of Copper in acidic media.

	ACID					
	HCl		HNO3		HClO4	
	As-Received sample (567)		**As-Received sample** (567)		**As-Received sample** (567)	
Time (days)	Uncoated Samples	Coated Samples	Uncoated Samples	Coated Samples	Uncoated Samples	Coated Samples
1	337.0	241.0	241.0	224.3	337.8	243.5
4	349.3	243.8	243.7	237.5	349.6	261.8
7	349.7	275.6	275.7	281.8	349.8	343.9

effect on the tensile strength of the metal. Lower values of tensile strength were obtained for the coated samples, compared with that of the uncoated samples, indicating that the inhibitor actually protected the metal. Perchloric acid had the most negative effect on the tensile strength of copper. This could be attributed to the high oxidizing power of the acid. Tensile strength is also seen to increase with time and concentration.

Conclusion

The effects of corrosive media on the mechanical properties of copper were drastic as deduced from the results of the experiments carried out. HPMP is an effective inhibitor for copper, as it caused a remarkable decrease in the hardness and tensile strength of the coated coupons, rendering them more ductile compared to the uncoated coupons. The hardness and tensile strength also increased with concentration and time. Therefore, adequate considerations should be given to mechanical properties and corrosion resistance of materials while selecting them for service conditions.

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