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THE EFFECT OF POTASSIUM FERROCYANIDE IN ELECTROLESS COPPER BATH STABILITY

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ABSRACT
This research work investigated the effect of potassium ferrocyanide as additive in electroless copper bath. An experimental work was conducted where two electroless copper baths were set up one containing the potassium ferrocyanide, formaldehyde, copper sulphate and other additives at room temperature while in the other bath potassium ferrocyanide was removed. An insulator of polymer material was used and the copper material were successfully coated on surface of the polymer material. The result analysis using SEM and EDS showed that, the deposition of copper materials on the polymer surface was uniform and smooth due to the presence of potassium ferrocyanide which acted as stabilizer in copper electroless bath while in the other set of bath in which the potassium ferrocyanide was removed, the electroless copper plating on the polymer material surfaces were rough, broad and irregular. Generally, potassium ferrocyanide reduces the rate of deposition of copper but at the same time stabilizes the process and made the coating uniform, regular and smooth on the surface of the material. Finally,It recommended that, Potassium ferrocyanide cyanide ($K_4Fe(CN)_6$complex) should be used in copper plating bath to prevent irregular, rough coating, and it should replace potassium cyanide (KCN) to prevent hazard as potassium cyanide(KCN) alone is poisonous.There should be a collaboration between higher institutions of learning and industries in research projects and SIWESS. However further research should be conducted on other complex compounds of cyanide to investigate their effect in electroless copper bath.

Key words; potassium ferrocyanide, copper and electroless plating

1.0 INTRODUCTION
Electroless plating uses a redox reaction to deposit metal on a substrate without the passage of an electric current. Copper electroless solution contains a metal salt, a reducer, a stabilizer and a buffer system. A redox reaction occurs between metallic ions (Cu^{2+}) and a strong reducer without the aid of an external electric potential(Jiang, B. Q., Xiao, L., Hu, S. F., Peng, J., Zhang, H. and Wang, M. W.2009). Metal forms around the catalyst in the polymer and grows in the polymer nearby surface as well as on the surface via an autocatalytic electroless reaction. Almost all the metals of the Group IB and VIII of the periodic table (Au, Pt, Ni, Cu, Co, Fe, etc.) can be plated and exhibit autocatalytic behavior(Nicolas-Debarnot, D., Pascu, M., Vasile, C. and Poncin-Epaillard, F.2006).

Successful electroless plating cannot be guaranteed by simply adding a solution of the reducing agent such as Formaldehyde (HCHO) to one containing metal ions (copper

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$CuSO_4$). In actuality, local changes in pH can lead to precipitation of the metal in bulk solution. To overcome this difficulty, complex compounds are added to the plating bath to maintain the metal ion in solution. The complex compound depresses the free metal ion concentration to a value determined by the dissociation constant of the metal complex. In addition to preventing precipitation within the solution, the complex compound also allows the bath to be operated at higher pH values. Ions will be available for deposition. For instance, Ethylene diamine tetraacetic acid (EDTA), which has a high stability constant, requires very careful control if plating is to occur. Oxidation of the reducing agents employed in electroless copper plating invariably involves the formation of either hydrogen (H^+) or hydroxyl (OH^-) ions. Consequently, the pH of the plating solution changes during plating and thus affects the rate of deposition and the properties of the deposit. Therefore, buffers are added to stabilize the pH of the solution. These include carboxylic acids in acid media (which also act as complex ants) and organic amines in alkaline solutions (Eom, K., Cho, K. And Kwon, H. 2008).

Electroless plating formulations are inherently unstable and the presence of active nuclei such as dust or metallic particles can lead, over time, to homogeneous decomposition of the plating bath. The presence of the complex ant in the correct concentration does not prevent this from occurring. To circumvent this problem, stabilizers such as 2-mercaptobenzothiazole are added to the bath in small concentrations. The stabilizers competitively adsorb on the active nuclei and shield them from the reducing agent in the plating solution. However, the stabilizers are used in excess, metal deposition may be completely prevented, even on the substrate itself. The plating rate is sometimes inordinately lowered by the addition of complexants to the bath. Additives that increase the rate to an acceptable level without causing bath instability are termed exaltantsoraccelerators.Thesearegenerallyanions,suchasCN^-,whicharethoughttofunction by making the anodic oxidation process easier(Meek, R. L. 1975). In summary, typical electroless plating formulations contain (a) a source of metal ions, (b) a reducing agent, (c) a complexant, (d) a buffer, (e) exaltants and (f) stabilizers.

1.1 THE BACKGROUND OF THE RESEARCH:

Electroless copper deposition technology has advanced rapidly in recent years including widespread application in areas such as through-hole plating in printed circuit boards, decorative plating of household utensils and in the automotive industry, electromagnetic interference shielding of electronic components, conductive traces in electronic interconnection devices and integrated circuit manufacturing. In an attempt to bring more innovations and advances in electroless copper plating, this research come up to investigate and address one fundamental aspect in electroless copper plating bath which is the stability of the process that always affect the smoothness of coating on the surface of the material to be coated.

1.2 THE RESEARCH PROBLEMS:

It is generally believed that, Electroless copper planting bath produces poisonous gases during the process and in most cases the surfaces of coated materials appear to be irregular and rough with high deposition in one area while low deposition in

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another area on the surface of the material coated as a result of the instability of the bath. In view of the above this research aimed to address the stated problems by replacing potassium cyanide (KCN) which is poisonous and accelerator with potassium ferrocyanide complex [$K_4Fe(CN)_6$]as additive in the electroless copper bath which is not poisonous acting as stabilizer and accelerator so as to prevent the release of poisonous gases to the environment and stabilizes the bath to achieve regular and smooth deposition on the surface of the coated materials.

1.3 SIGNIFICANT OF THE RESEARCH:

This research will be benefited to the industries using electroless copper bath to reduce the release of exodus and in the production of quality materials with smooth surfaces. The research will be benefited to the society by removing poisonous gases from the electroless copper bath which is release to the environment. it will also benefit the chemical and technical students to understand safer and effective electroless copper plating process. it will generally address the problems of instability in copper electroless bath by introducing the potassium ferrocyanide and solve the problem of using potassium cyanide (KCN)which is poisonous and releasing poisonous gases during electroless copper plating.

1.4 THE ROLE OF POTASSIUM FERROCYANIDE

It is generally believed that, Potassium ferrocyanide act as stabilizer in copper electroless bath and as such has a levelling effect in deposition of cupper on to surface of the material.

The plating rate of an electroless copper bath at room temperature decreases in the presence of even minute amounts of potassium ferrocyanide although according to some authors the cyanide complexes of iron also act as accelerators in electroless copper bath.

2.0 EXPERIMENTAL

2.1 CHEMICAL/REAGENTS

All the chemicals used are pure and high standard in quality of Analargrades.

TABLE 1: Chemical used for the Experiments

S/N	CHEMICALS/REAGENTS		CONCENTRATIONS
1.	$CuSO_4$	Copper (II)sulphate	0.04 mol/L and 16g/L
2.	HCHO	Formaldehyde	0.20 mol/L and 5mL/L
3.	$NaKC_4H_4O_6$	Sodium potassium tartrate	30 g/L

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4.	Na_2EDTA	Salt of ethylenediaminetetraaceticAcid	0.12 mol/L and 20g/L
5.	$K_4Fe(CN)_6$	Potassium ferrous cyanide	25 mg/L
6.	Na_2SO_4	Sodium sulphate	0.14 mol/L
7.	HCOONa	Sodium formate	0.30 mol/L
8.	KCN	Potassium cyanide	$4.6x10^{-4}$ mol/L
9.	CH_3CH_2OH	Ethanol	70 Ml
10.	NaOH	Sodium hydroxide	2.5 mol/L
11.	HCl	Hydrochloric acid	8 mol/L
12.	$PdCl_2$	Palladium chloride	4.5x10 mol/L
13.	$SnCl_2$	Tin chloride	0.2 mol/L
14.	H_2SO_4	Tetraoxosulphate (vi)Acid	0.8 mol/L
15.	CH_3COOH	Acetic acid	2.5 mol/L

The laboratory work was carried out by setting two set of copper electroless bath in which one potassium ferrocyanide was added while in the other bath potassium ferrocyanide were not added. In both set of baths polymer material was placed for one hour. The polymer material was removed after immersed in to the electroless copper plating bath for one hour and allowed to dried. The most important reaction, occurring in the electroless copper plating when formaldehyde was used as reducing agent, is as follows:

$$Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu \downarrow + 2HCOO^- + 2H_2O + H2\uparrow$$

2.2 TABLE 2. The Electroless Copper Plating Bath Solutions without Potassium Ferrocyanide

S/N	**CHEMICALS**		**CONCENTRATIONS**
1.	$CuSO_4$	Copper (II)sulphate	0.04 mol/L
2.	HCHO	Formaldehyde	0.20 mol/L
S/N	**CHEMICALS**		**CONCENTRATIONS**
3.	Na_2SO_4	Sodium sulphate	0.14 mol/L
4.	HCOONa	Sodium formate	0.30 mol/L

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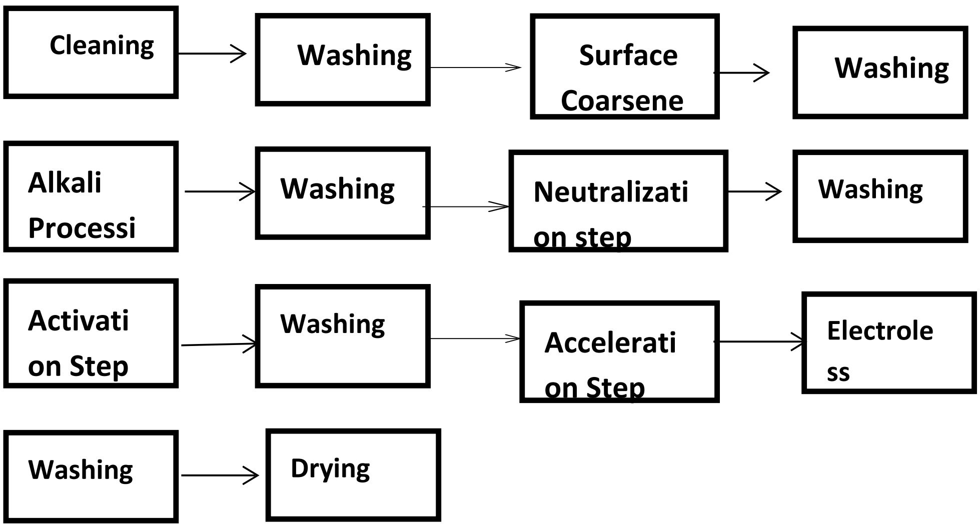
5.	KCN	Potassium cyanide	$4.6x10^{-4}$mol/L
6.	Na_2EDTA	Salt of ethylenediaminetetraaceticAcid	0.12 mol/L

2.3 TABLE 3. The Electroless Copper Plating Bath Solutions containing Potassium Ferrocyanide $K_4Fe(CN)_6$

S/N	CHEMICALS		CONCENTRATIONS
1.	$CuSO_4$	Copper (II)sulphate	16 g/L
2.	HCHO	Formaldehyde	5mL/L
3.	$NaKC_4H4O_6$	Sodium potassium tartrate	30 g/L
4.	Na2EDTA	Salt of ethylenediaminet etraaceticAcid	20 g/L
5.	$K_4Fe(CN)_6$	Potassium ferrous cyanide	25 g/L

2.4 PROCEDURE

The research was designed to use two different methods for electroless copper plating. One set of electroless copper bath containing potassium ferrocyanide $K_4Fe(CN)_6$ while in another different set of electroless copper bath the potassium ferrocyanide $K_4Fe(CN)_6$ is not added but Potassium cyanide (KCN) were used. The method for electroless copper plating was carried out in multi-step processes in each set of bath for the two methods above which includes



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Before the electroless copper plating took place the polymer material has to be treated to make the surface ready for the coating.

The first step was cleaning of the polymer material where ethanol was used the washed with distilled water. The surface of the polymer material was made to be rough by heating under reflux in acetic acid for two hours which is then removed and washed by distilled water. The polymer material was also treated with sodium hydroxide where it placed in container containing sodium hydroxide solution for five minutes then removed and washed with water. It followed by the neutralization step where the polymer material was placed in hydrochloric acid solution for ten minutes the removed and washed with distilled water. The polymer material was also activated for coating by the use of palladium chloride and tin chloride which serves as binding agent between the copper and the surface of the polymer material. The polymer material was washed and place in the electroless copper bath solution containing Copper (II) sulphate, Formaldehyde, Sodium sulphate, Sodium formate, salt of ethylene diamine-tetraacetic Acid and potassium cyanide. After one hour the polymer material was removed, washed with distilled water and dried.

The above process was repeated with different set of electroless copper bath containing potassium ferrocyanide Instead of potassium cyanide. Both polymer materials used for the two set of baths were taken to the analysis after the experiment.

3.0 RESULTS AND DISCUSSION

The polymer materials that were plated in the two set of baths were characterized using SEM and EDS,

the properties of the material were investigated as follows

3.1 FRESH POLYMER MATERIAL BEFORE COATING (SAMPLE A)

The SEM image analysis of the polymer morphology in **Fig.1** below indicates that, the surface is smooth and clear. According to the image, the surface is fresh and clear because it is untreated.

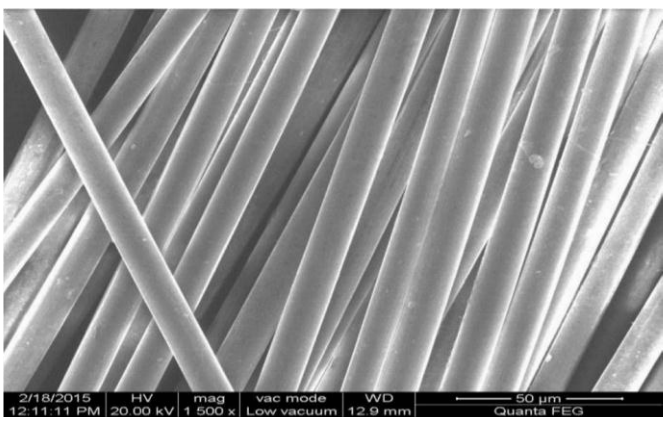

Fig.1 The SEM image for fresh polymer before coating

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3.2 POLYMER MATERIAL AFTER COATING (SAMPLE B) IN THE BATH WITHOUT K4Fe(CN)6

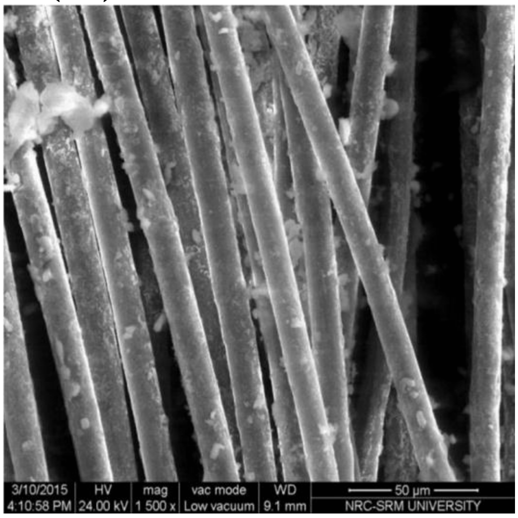

Fig.2 The SEM image for polymer after coating/plating

The image obtained and presented for polymer after the coating in **Fig. 2**indicates a high deposition of copper material around the surface of the polymer. The copper is scatted and deposited on the surfaces in which the deposition is highly dense and rough around the surface.

3.3 POLYMER MATERIAL AFTER COATING (SAMPLE C) IN THE BATH CONTAINING POTASSIUM FERROCYANIDE $K_4Fe(CN)_6$

The SEM image obtained of the polymer material after the coating in **Fig.3**below indicates smooth and regular deposition of copper throughout the surface of the polymer material. The copper is scatted at regular and same level while the deposition of copper on the surfaces is smoothly achieved.

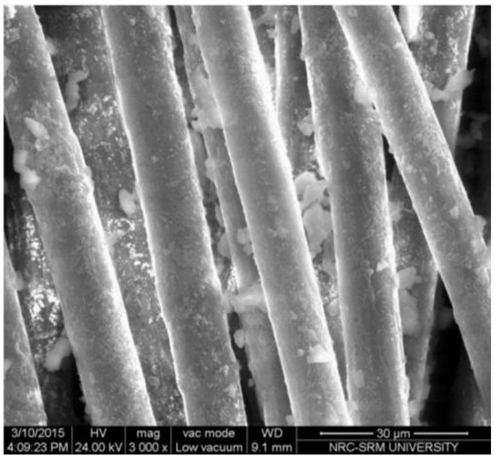

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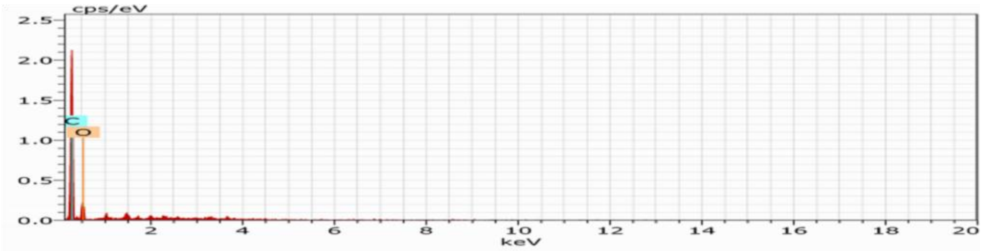
Fig.3The SEM image obtained for polymer fiber after courting. (in the bath that, contains potassium ferrocyanide)

3.4 THE EDS RESULT FOR POLYMER MATERIAL BEFORE COATING (SAMPLE A)



Spectrum: training

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	74.62	74.62	79.66	12.62
O	8	K-series	25.38	25.38	20.34	7.62
		Total:	100.00	100.00	100.00	

Fig. 4

According to the (EDS) result above in **Fig.4** obtained from fresh polymer shown that, only carbon peak and oxygen are present which are the main elements constituting the polymer fiber material, Oxygen at 25.38 % and Carbon at 74.62 % making 100%.

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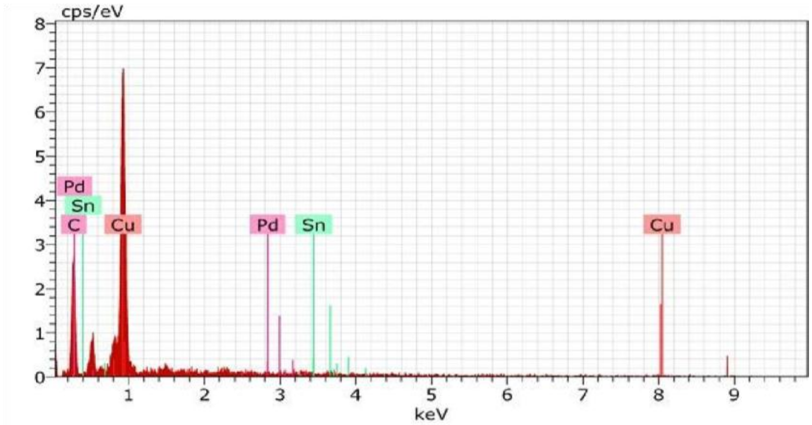
3.5 THE EDS RESULT FOR POLYMER MATERIAL AFTER COATING (SAMPLE B) IN A BATH WITHOUT POTASSIUM FERROCYANIDE(FIG.5)



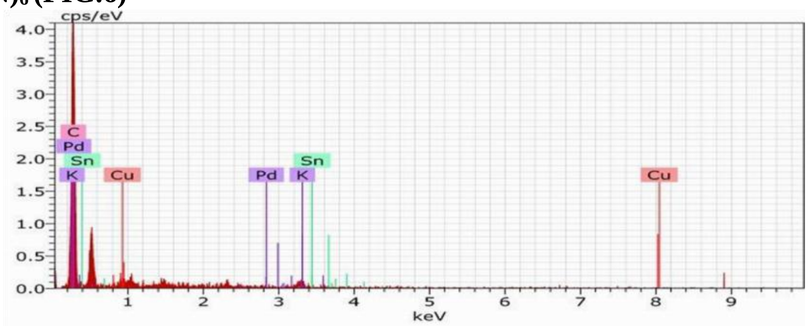
Spectrum: training

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Cu	29	L-series	66.00	66.00	27.36	10.31
C	6	K-series	33.02	33.02	72.42	6.76
Sn	50	L-series	0.74	0.74	0.16	0.15
Pd	46	L-series	0.24	0.24	0.06	0.08
		Total:	100.00	100.00	100.00	

Fig. 5

The EDS result in Fig.5 above shown the presence of the copper with high percentage of 66% which confirms high deposition of copper on to the surface of the polymer material. However, this is due the irregular and dense deposition in some areas on the surfaces of polymer.

3.6 THE EDS RESULT OF POLYMER MATERIAL AFTER COATING (SAMPLE C) IN A BATH CONTAINING POTASSIUM FERROCYANIDE $K_4Fe(CN)_6$ (FIG.6)



Spectrum: training

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	83.23	83.23	95.22	16.72
K	19	K-series	8.57	8.57	3.01	0.89
Cu	29	L-series	8.20	8.20	1.77	3.87
Sn	50	L-series	0.00	0.00	0.00	0.00
Pd	46	L-series	0.00	0.00	0.00	0.00
		Total:	100.00	100.00	100.00	

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The percentage of copper which is just 8.20% in EDS result (Fig.6) above made it clear that, the deposition of copper on to the surface of the polymer material in the presence of potassium ferrocyanide in the bath was less in amount compared with other result of sample (B). this is simply because the deposition on the sample (C) is moderate and the electroless copper bath is stabilized addition of potassium ferrocyanide.

4.0 CONCLUSIONS

The result analysis using SEM and EDS shown that, the deposition of copper materials on the polymer surface was uniform and smooth due to the presence of potassium ferrocyanide which acted as stabilizer in copper electroless bath while in the absence of potassium ferrocyanide, the electroless copper plating on the polymer material surfaces were rough, broad and irregular with higher dense deposition of copper around the surfaces. Generally, potassium ferrocyanide reduces the rate of deposition of copper but at the same time stabilizes the process and made the coating uniform, regular and smooth on the surface of the material. However, the result in the other media (electroless copper bath without Potassium Ferrocyanide) the coating appeared to be irregular, broad and there is high deposition of the copper metal on some areas on polymer surface. In summery potassium ferrocyanide $K_4Fe(CN)_6$ is not poisonous and acted as accelerator and stabilizer in the electroless copper bath because it is a complex compound containing cyanide as well as iron while potassium cyanide (KCN) is poisonous and acted only as accelerator in which the process lack control due the instability of the bath which resulted an irregular deposition of copper on the polymer surface and at the same time made the electroless copper bath solution poisonous.

5.0 RECOMMENDATIONS:

1- Potassium Ferrocyanide $K_4Fe(CN)_6$ should be used in electroless copper plating bath to prevent irregular and rough coating instability in the system.

2- Potassium Ferrocyanide $K_4Fe(CN)_6$ should be used in electroless copper bath instead of Potassium Cyanide KCN which is poisonous in nature.

3- Further research should be conducted on other complex compounds of cyanide to investigate their effect in electroless copper bath.

4- There should be a collaboration between higher institution of learning and industries in research projects and SIWESS.

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