

# Investigation of Wear Behaviour Properties of Electroless Ni-Co-P Ternary Alloy Coating

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## ABSTRACT

Electroless coatings have been used in many industries now days due to their good properties, such as corrosion and wear resistance, hardness and uniform thickness. In this paper, co-deposition of Co with Nickel-Phosphorus electroless coatings on low carbon steel AISI 1026 substrates was investigated. Surface morphology and composition of coatings were studied thorough SEM and EDX. XRD analyse showed that these coatings had amorphous structure with Co-P crystalline particles. Co-P particles increased the micro hardness of the coatings. A tribometer is an instrument that measures tribological quantities, such as coefficient of friction, friction force, and wear volume, between two surfaces in contact with each other. Result showed that Co-P electroless composite coatings increased wear resistance of the substrates.

**Keywords:** Electroless Nickel, Coating, Wear, Corrosion, Micro hardness

## I. INTRODUCTION

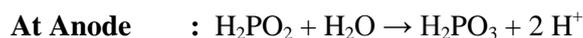
**Surface Engineering** :Surface engineering include the total field of research and technical activity used for design, manufacturing, investigation and utilization of surface layers for properties better than the core. Almost all types of materials include metals, ceramics, polymers, and composites can be coated on similar or dissimilar materials. Surface treatments that cause microstructure changes in the bulk material include heating and cooling/quenching through induction, flame, laser, and electron beam techniques, or mechanical treatments (one example is cold working). Surface treatments that alter the chemistry of a surface include Carburizing, Nitriding, Nitro carburizing, Carbonitriding, Boronizing, Siliconizing, Chromizing and Aluminizing. Hard facing is another form of surface treatment, where the bulk materials surface is given a protective layer of another material having more superior properties than those of the bulk material.

## II. METHODS AND MATERIAL

### A. Coating

**Electroless Nickel Plating:** Electroless nickel plating is self-catalysing process. In contrast with electroplating, electroless nickel (EN) plating does not require rectifiers, electrical current or anodes. Deposition occurs in an aqueous solution containing metal ions, a reducing agent, complexing and buffering agents and stabilizers. Chemical reactions on the surface of the part being plated cause deposition of a nickel alloy. An electroless nickel coating is a dense alloy of nickel and phosphorus. The amount of phosphorus co-deposited can range from less than 2% to more than 12%, depending upon bath formulation, operating pH and bath age. The deposition process is autocatalytic; i.e., once a primary layer of nickel has formed on the substrate, that layer and each subsequent layer becomes the catalyst that causes the above reaction to continue. Thus, very thick coatings can be applied, if the ingredients in the plating bath are replenished in an orderly manner.

The chemical reaction for nickel plating is



Since all surfaces wetted by the electroless nickel solution have the same plating rate, the deposit thickness is uniform. This unique property of Electroless nickel makes it possible to coat internal surfaces of pipes, valves and other parts. Such uniformity of deposit thickness is difficult, if not impossible, to achieve by any other metal finishing method table 1 respectively.

The selection of a specific grade of EN-plating is done in accordance with the nature of application, where a high hardness and low coefficient of friction is desired, low phosphorous EN is preferred (1-3%P).

**Table 1:** Electroless Nickel Coating

COMPONENT	FUNCTION	EXAMPLE
Nickel ions	Source of metal	Nickel chloride Nickel sulphate
Hypophosphite ions	Reducing agent	Sodium hypophosphite Sodium borohydride
Complexants	Form nickel complexes, prevent excess free Ni ion concentration so stabilizing solution and preventing Ni precipitation.	Monocarboxylic acids Dicarboxylic acids Ammonia
Accelerators	Activate hypophosphite ions and accelerate deposition. Mode of action opposes stabilizers and complexants	Anions of some mono and di-carboxylic acids, Fluorides, Borates
Stabilizers	Prevent solution breakdown by shielding catalytically active nuclei	Lead, Tin, Arsenic, Molybdenum, Cadmium or Thallium ions etc.
pH regulators	For subsequent pH adjustment	Sulphuric and Hydrochloric Acids, Caustic soda, Ammonia

## B. Experimental Details

### 1. Sample Preparation

For the deposition of Ni-Co-P ternary alloy coatings, mild steel was selected as substrate. The substrates were collected from long metal rod by cutting into it averagely 25mm×25mm size pieces. The approximate dimensions of the substrates were 20mm×20mm×5mm and standard specimen (pin-cylindrical shape) Ø8mm×50mm. The chemical composition and material properties of the alloy is given in table 4.1 & 4.2 respectively. The dimension chosen for the substrate is in accordance where the coated samples are to be fitted for the SEM, hardness and wear test. The substrate are meticulously prepared so that after coating the samples could be fitted precisely with its counterpart.

Ultra sonication of the substrates was done for 10 minutes by using deionized water and acetone for the removal of fine particles, which adsorbed on the sample surface during the polishing. In this way, the mirror polished substrates were prepared for deposition. Water rinse for 3-5 min to be done intermediate for each steps. Sample specimen weight been noted before coating.

### 2. Plating Bath Solution Preparation

The bath compositions and parameters used for Ni-Co-P ternary alloy coatings are reported in the below table 2 respectively.

The chemicals are weighed on electronic balance of resolution 10-5g so that no compromise is made on the accuracy of the bath composition. Before deposition, the solution was allowed for Ultra-sonication for 25minutes and magnetic stirring for 30minutes for homogenous dispersion of the metal powder in the solution. Magnetic stirring was also allowed for stirring of the bath during entire deposition so that the sedimentation of powder particles in the solution is prevented and they can be homogeneously dispersed during deposition. Temperature is maintained at 90°C while the rotation of stirrer is 130rpm constantly and at 8.5 pH value. Keeping the chemical composition of others as constant volume and varying the source of metal (cobalt chloride) as in the range 10g, 20g, 30g & 40g for different deposition. Pure nickel deposits were also done by using the parameters, which have used for

Co-P deposition for comparison of the results obtained, with the results obtained by using particle incorporation.

**Table 2: Plating Bath Solution Preparation**

Components	Values
Cobalt Chloride, Hexahydrate	10, 20, 30 & 40 g/l
Nickel Chloride, Hexahydrate	30 g/l
Sodium Hypophosphite	20 g/l
Ammonium Chloride	50 g/l
Sodium Citrate	100 g/l
Anionic Surfactant	20 mg/l
Ph	8.5
Temperature	90°C



**Figure 1. Plating Bath Solution Preparation**

After deposition, the samples were washed with distilled water, kept in the paper and preserved for Characterizations.

### III. RESULTS AND DISCUSSION

#### A. Formation of Electroless Ni-Co-P Deposits

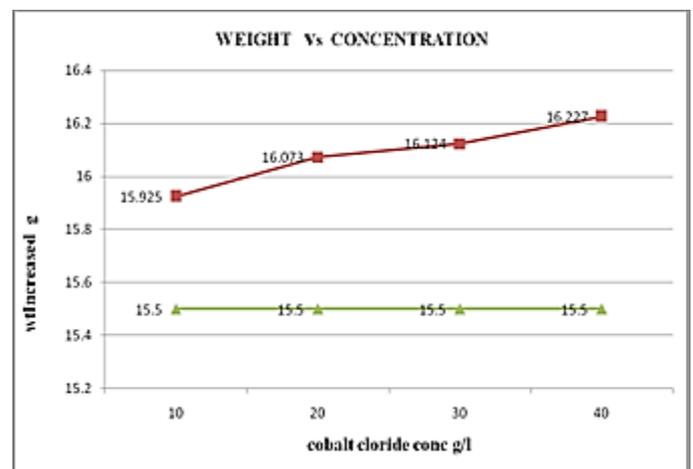
The formulation of Ni-Co-P coatings requires an alkaline plating bath since ammonium chloride readily hydrolyzes in acidic or neutral condition, preferably the pH should be higher than 7.5. This warrants the addition of higher concentration of alkali, which in turn necessitates the presence of an effective complexing agent in the bath. Since Sodium, citrate is the most preferred complexing agent for electroless nickel-plating bath. Citrate- and tartrate based completing agents have also been reported in many electroless

plating baths. The selection of stabilizer for electroless plating bath containing anionic surfactant is very critical since this bath is highly susceptible for decomposition in the absence of a suitable stabilizer.

The effectiveness of lead nitrate in anionic surfactant reduced electroless plating bath and suggested that, although these stabilizers are good in stabilizing the bath, the plating rate is low in these baths (about 10-12  $\mu\text{m/h}$ ). The use of anionic surfactant as stabilizer offers better stability and higher deposition rate. This is due to the ability of lead ions, which not only stabilizes the plating bath but also increases the reduction efficiency of stabilizer. The coatings obtained in this specimen were whitish silvery in colour with a matte glassy appearance.

#### B. Plating Weight

Plating weight of the deposits was found by means of electronic weight measurement. Weight gain after overall time been noted. All the coatings were deposited keeping time constant (one hour). Fig 2 shows that the plating weight was found to increase with increase in source of metal concentration since cobalt chloride with the presence of sodium citrate acts as good reducing agent and hence it enhanced the rate of the reaction.



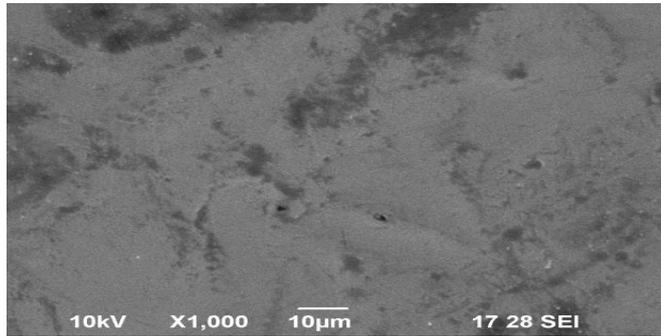
**Graph 1: Weight Vs Concentration**

#### 1. Microstructural Characterization

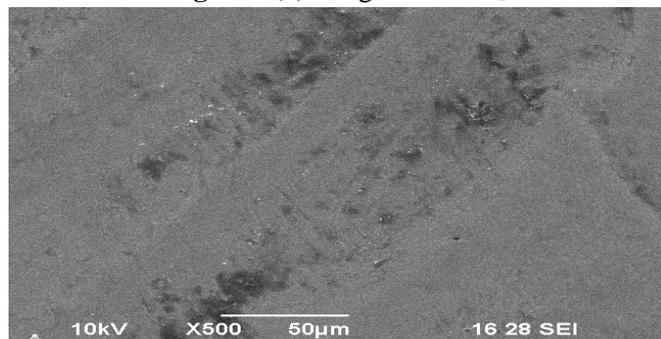
#### C. Scanning Electron Microscope (SEM) Studies

The surface morphology and particle distribution of the electroless deposited ternary alloy coatings were performed by using SEM. The below Figure 2 (a-d)

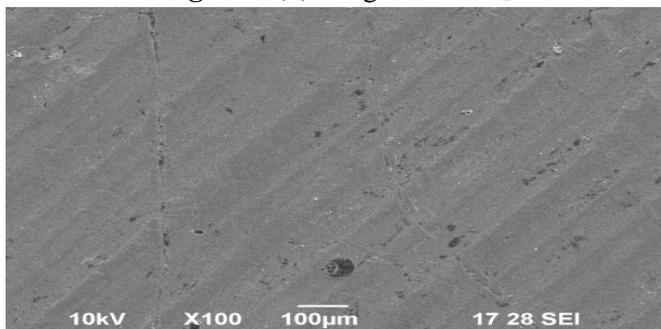
shows SEM Surface micrographs of the electroless deposited Ni-Co-P ternary alloy coatings prepared at 10 g/l, 30 g/l & 40 g/l Co in the bath, temperature of 85°C and at 8.5 pH for 1 hour.



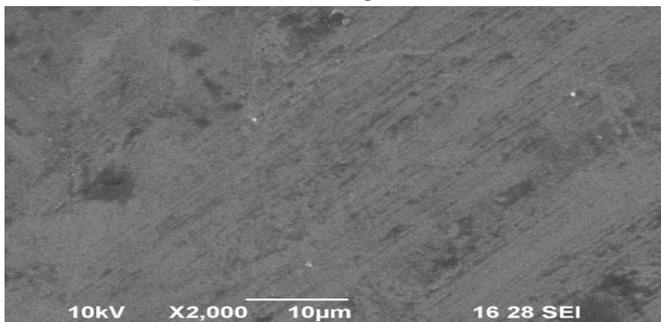
**Figure 2(a).** 10 gm of  $\text{CoCl}_2$



**Figure 2 (b).** 20 gm of  $\text{CoCl}_2$



**Figure 2 (c).** 30 gm of  $\text{CoCl}_2$



**Figure 2 (d).** 40 gm of  $\text{CoCl}_2$

**Figure 2.** SEM Images of Various Compositions of Ni-Co-P Coating

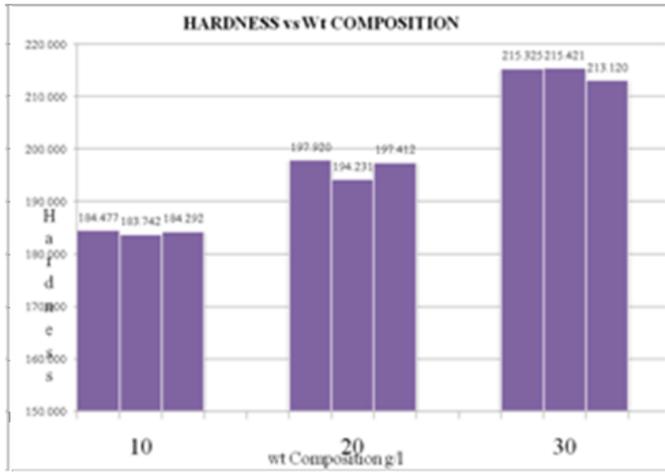
The electroless Ni-Co-P coatings are uniform and consist of agglomerates of nickel, which are randomly distributed. From the above Figure 3 it can be observed

that smooth coating surfaces at all deposition conditions and absence of nodules, cracks and dendrites like structure was observed on the coating surfaces. However, large agglomeration of the particles was observed 20 g/l & 30 g/l (Figure 2 (b & c)). However, small micro pits were observed this is attributed to evolution of hydrogen. A comparison of the morphological features of the Ni-Co-P coatings (figure 2 (a)-(d)) reveals that the size of the nodules increases with increase in concentration of cobalt chloride These nodules combined to form a granular type structure, The granular structure may make the electroless Ni-Co-P coatings naturally lubricious and enable it to achieve a higher wear resistance by reducing the surface contact similar to Ni-P coatings.

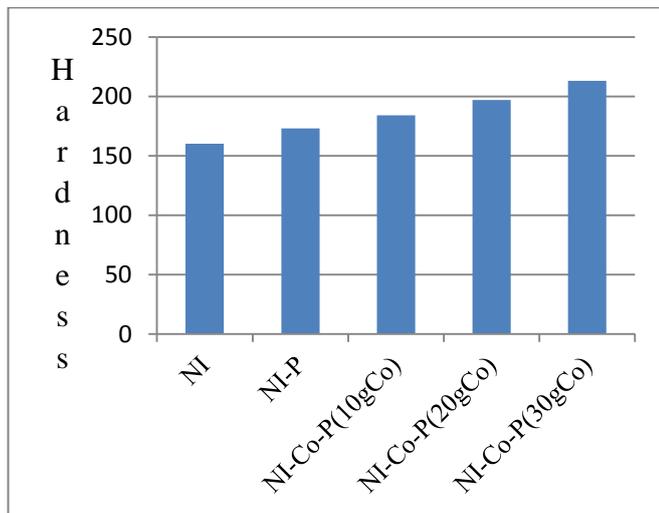
## 2. Surface Mechanical Properties

### D. Microhardness Study

A major fact contributing to increased resistance to mechanical abrasion of electroless coatings is hardness. Most of the investigators agree that electroless coatings become crystalline due to precipitation of second phase. This precipitation leads to hardness in coatings. Increased hardness in as plated electroless nickel is due to the presence of residual stresses and due to the reduced grain size in the coatings. There is higher level of strain in nickel matrix of electroless nickel deposits due to super saturation of phosphorous and cobalt. When the electroless coatings were heat treated to suitable temperatures, precipitation of second phase occurs, which act as barriers for dislocation movement thereby increasing hardness further. This unique property of electroless alloy coatings led to the widest exploitation of the coatings for applications requiring wear and abrasion resistance. The hardness profile of coatings in as-plated conditions is shown in Fig.3.



**Figure 3.** Bar chart plotted between hardness and Co composition

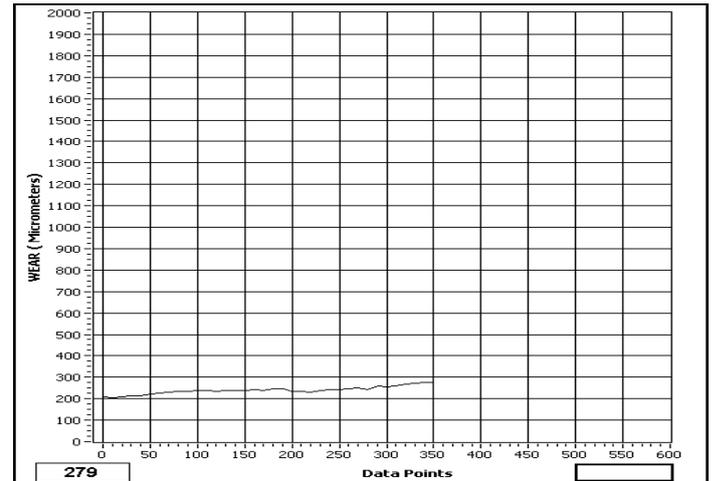


**Figure 4.** Comparison of Micro Hardness Test

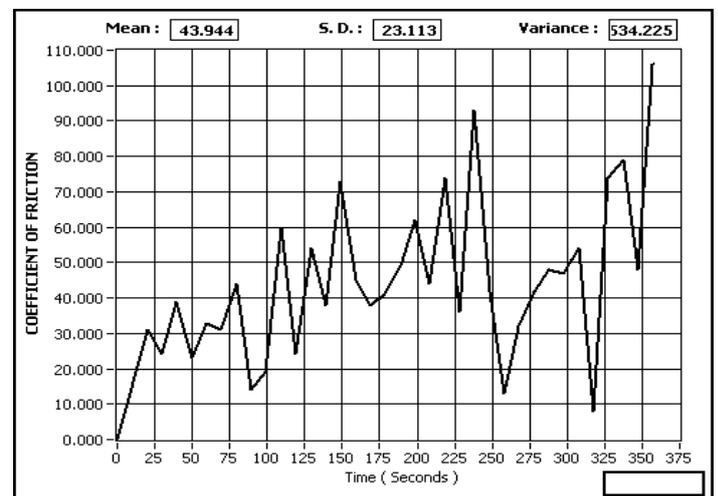
The behaviour of all the four Ni-Co-P coatings were found to be almost similar. The hardness of the coatings varies as a function for different weight percentage of source of metal (cobalt chloride). The hardness increases up to a certain range percentage, which varies for different coatings and then begins to decrease. This decrease can be attributed to the phenomena of over aging of rate of reaction where the precipitated second phase particles become coarse and inefficient in impeding the dislocations. The average hardness for MS10, MS20 and MS30 coatings it is found as 184HV, 195HV and 215HV respectively. This variation in hardness can be attributed to the formation of Ni<sub>2</sub>Co phase coating. It is also observed a similar behaviour of change in hardness with different weight compositions of source of metal in reduced electroless Ni-P coatings.

### i. Wear Study

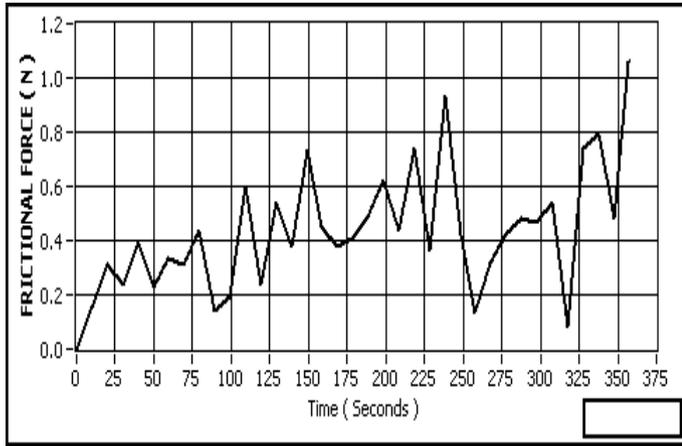
The wear test on the surfaces of the ternary alloy coatings were carried out by using DUCOM TR-208-M1 ball on plate wear tester by applying without any load for 6 minutes with 1000 rpm sliding speed on a 45mm diameter track. The below Figures shows the comparable wear lose, coefficient of friction and frictional force graphs (in terms of vertical penetration of the indenter or wear depth) as a function of sliding distance for different compositions of cobalt chloride.



**Figure 5 (a).** Wear Rate Vs Time



**Figure 5 (b).** Coefficient of Friction Vs Time



**Figure 5 (C).** Frictional Force Vs Time

The wear performance of electroless coated films is known to be mainly dependent on the microstructure of the metal matrix as well as on the amount and distribution of incorporated particles. That is the wear behavior is co related to the hardness of the surface. According to the above statement, the wear loss or extent should be high for pure mild steel and for lower wt% Co embedded samples. From the Figure it can also be observed that the wear loss of 20g of cobalt chloride is higher than the 10g which can be attributed to the coating thickness and also the loss is high for the coating developed at 20g which is due to the higher hardness of coating deposited. Frictional force and coefficient of friction are linearly dependent attains a value of 1.5 & 105 respectively. Whereas the wear rate is 279 at end of time.

The wear rate increases with increasing source of metal composition. Graph shown in above Fig 5 (c) indicates that the sample coated with 30g of cobalt chloride has more wear rate of 319 when compared to others. Frictional force and coefficient of friction are linearly dependent. Initially the cylindrical pin is weighted before wear test and after there is average loss 0.1g-0.3g weight for each substrate.

#### IV. CONCLUSION

Ternary Ni-Co-P alloy coatings have been successfully deposited on mild steel substrates from alkaline baths containing sodium citrate as complexing agents. From the detailed investigation of the results obtained, the following conclusions can be drawn:

1. The alloy phosphorus content decreased and the alloy cobalt content increased with increasing cobalt sulphate concentration in the plating bath and the composition of deposited alloy on mild steel substrates are similar to Ni – P.
2. Deposition of layer over the substrate was found by weight measurement 0.4g-0.7g of weight been increased for different percentage of source of metal for coatings.
3. From the Scanning Electron Microscope (SEM) surface morphologies obtained the coating surfaces observed at all deposition parameters were smooth, no dendrites, cracks and nodule like the one structures were observed on the surfaces. Anionic surfactant is added to the bath, agglomeration of the particles was observed in the metal matrix. Randomly oriented crystallites with loose packing were observed.
4. The micro hardness values obtained for all these substrate coated are higher than the pure mild steel hardness, the improvement is attributed to dispersion strengthening caused by the embedded second phase particles, texture and modified microstructure of metal matrix. For 10g & 20g sample, there is micro hardness of 184HV & 197HV respectively and for 30g substrate there was maximum of 213HV after addition of source of metal dispersion with respect to substrate were higher hardness values were observed while comparing the results with Ni and Ni-P coatings, these ternary alloy coatings (Ni-Co-P) have showed improved micro hardness .
5. The wear resistance of the ternary alloy coatings was higher than the substrate. The wear resistance improved with increased weight % of dispersed second phase particles in the bath compared to unreinforced metal coatings. The increase in wear resistance is due to the dispersed second phase particles and improved hardness, which decreases friction between the steel ball and the coating surface. The addition of cobalt chloride particles marginally transforms the wear from adhesive to abrasive type.

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