EFFECT OF BATH COMPOSITION ON MICROHARDNESS AND TRIBOLOGICAL PROPERTIES OF ELECTROLESS NI-P COATINGS

Abstract

The exceptional tribological, physical, and mechanical properties of Sodium hypophosphite reduced electroless coatings make them frequently employed. The bhavieors of the coating depend on its composition. In order to comprehend the significance of phosphorus concentration in the tribo-mechanical behavior of coatings, electroless Ni–P coatings are created on an AISI 1040 steel substrate. As-deposited coatings SEM data show a nodular type surface morphology that is helpful in lowering friction and coating wear. The EDX elemental analysis results indicate that the phosphorus concentration reduced from 11.4 to 8.9%. This decline in bath level concentration is accompanied by increases in surface hardness measured by micro-indentation technique. The microhardness is also observed to reduce with nickel sulfate and nickel chloride, Sodium hypophosphite, and sodium succinate concentration in the coating bath solution.

Keywords: Electroless Deposition, Surface Engineering, Phosphorus Content. Microhardness, Coefficient of friction, Wear Behaviour

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I. INTRODUCTION

Coating deposition is the popular method for the process of laying down a material onto a surface. This process is used to protect the surface. This can be done through various methods, including physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, and, electroless deposition like Ni-P coating. Deposition can create extremely thin layers (atomic or molecular) or thicker films depending on the technique and application. Coating, on the other hand, specifically refers to the resulting layer applied to the surface [1]. It emphasizes the function of providing a cover or altering the surface properties of the underlying material [2]. Coatings can be applied through deposition techniques, but also through simpler methods like painting, dipping, or brushing. The thickness of a coating can range from micrometers to millimeters. Electroless Ni-P (ENP) plating is a widely used technique for depositing a thin layer of nickel-phosphorus alloy onto a variety of substrates [3-5]. Unlike electroplating, which requires an electrical current, electroless deposition is a chemical process. This allows for uniform coating on even complex shapes, making it a valuable tool in various industries. The uniformity of EN coatings is a crucial characteristic that guarantees a uniform deposition of the solution on even holes or sharp edges that come into contact with it [6]. Three types of EN coatings are commonly identified: alloy coatings, composites, and pure nickel. The dangers of using hydrazine as the reduction agent have led to the discontinuation of pure electroless nickel coatings. Sodium borohydride or sodium hypophosphite-based electroless baths are used to generate nickel alloy plating, which has grown in popularity. Even in harsh conditions, Ni-P deposits display exceptional mechanical and tribological properties [7]. The coating's remarkable hardness is attributed to the crystalline nickel phosphide phases that are formed after heat treatment [8–9]. High temperatures are an ideal temperature range for Ni-P plating's wear resistance. The primary elements are nickel (Ni) and phosphorus (P), with the P content playing a crucial role in determining the final properties of the coating [10]. The coating improves the substrate's ability to withstand friction and wear, extending its lifespan and reducing maintenance needs [11]. This is crucial for parts subjected to constant friction or abrasive environments. Ni-P coatings can provide a more uniform and aesthetically pleasing finish compared to the raw substrate material. Compared to replacing or using more expensive materials, Ni-P coating offers a cost-efficient way to upgrade the performance of existing substrates. Ni-P acts as a barrier, protecting the substrate from environmental factors that cause degradation, like moisture, salt, or chemicals.

Extensive literature analysis reveals that the microstructure of Ni-P coatings significantly affects their microhardness and tribological performance. The novelty of this research lies in its comprehensive investigation of electroless Ni-P coatings with varying bath compositions, focusing on the relationship between coating composition and properties like microhardness, coefficient of friction, and wear behavior. While previous studies have explored these aspects in other electroless coatings (Ni-B, Ni-W-B, and Ni-Mo-B), a thorough evaluation of these parameters in Ni-P systems is relatively underexplored, making this researches a valuable contribution to the field. This investigation also aims to explore the comparative behavior of the mechanical and tribological performance of electroless Ni-P coatings in various bath compositions. The coatings are heat treated at 450°C, with heating durations 1hour. Metallurgical properties are evaluated with the help of scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). The study focuses on evaluating the tribological responses, viz. friction and wear of the coatings in a dry environment and employs a Vickers microhardness tester to measure microhardness.

II. EXPERIMENTAL DETAILS

1. Coating Deposition

In the present study four bath combinations of electroless Ni-P coatings have been developed. These coatings are denoted as, ENP2, ENP3 and ENP4, corresponding to the electroless Ni-P coating level1, Ni-P coating level2, Ni-P coating level3 and Ni-P coating level4, respectively. The experimental setup for the electroless nickel deposition is shown in Figure 1. These coatings are developed by following a series of steps as outlined in Figure 2. Bath composition and deposition conditions are selected based on available literature [9, 12]. To maintain consistency in thickness, the deposition time and bath load is kept constant at 2 h and 30cm2/L respectively. The bath composition and deposition conditions are shown in Table 1.

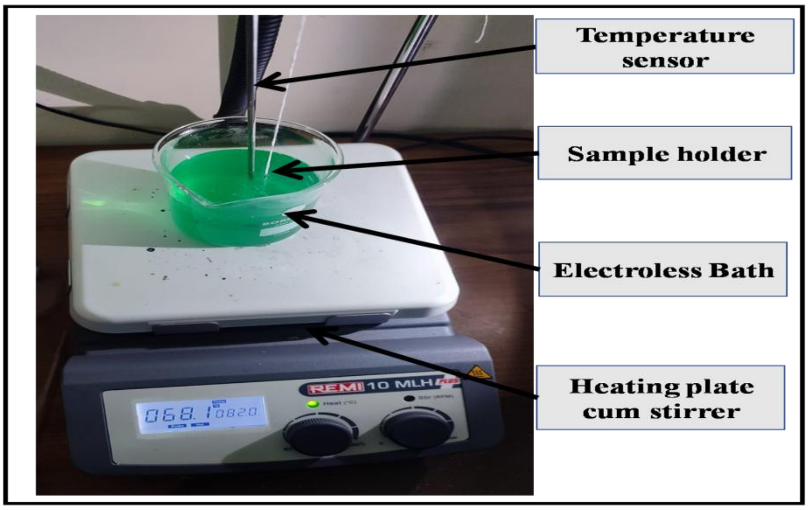
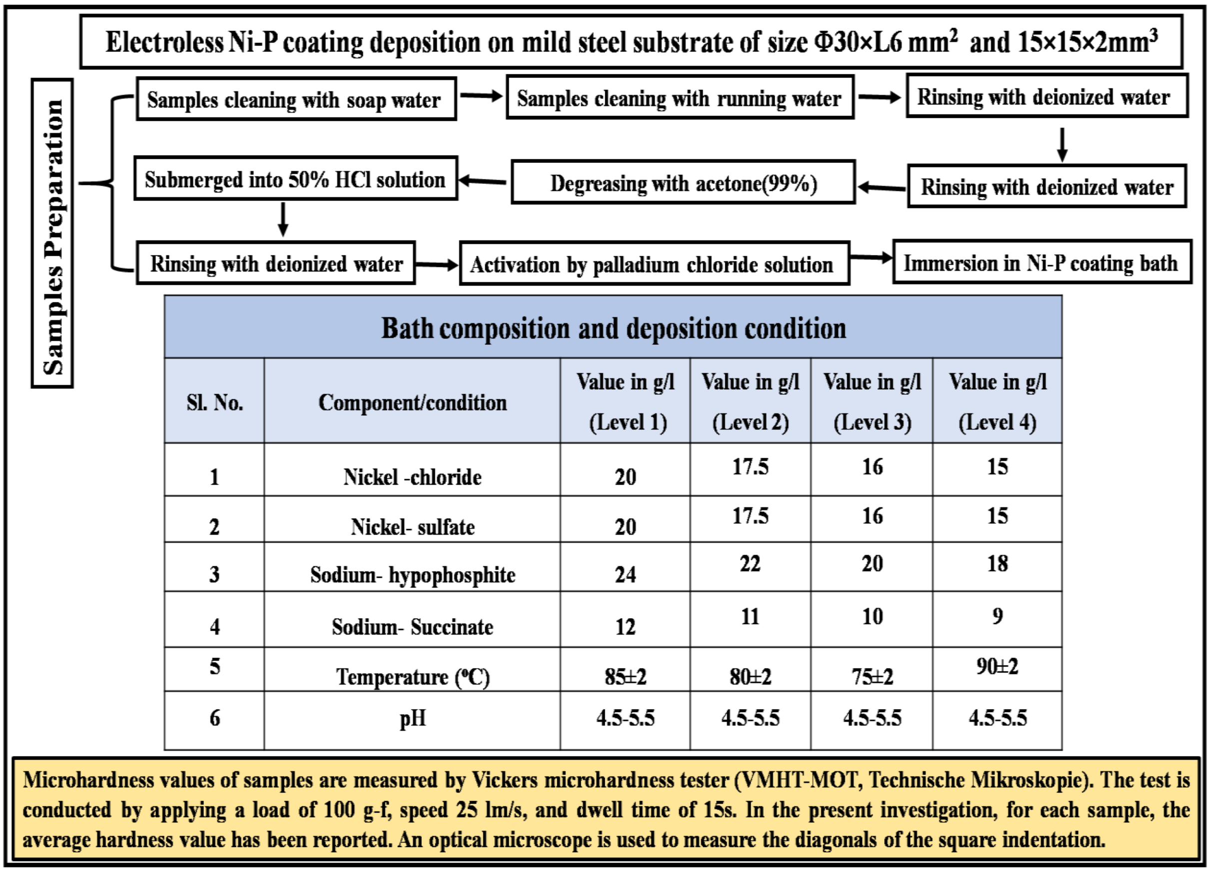


Figure 1: Experimental set-up

Table 1: Bath composition and deposition conditions of electroless Ni-P coatings

SL No	Component/ condition	Various types of Ni-P Coating composition			
		Value in g/l Level 1	Value in g/l Level 2	Value in g/l Level 3	Value in g/l Level 4
1	Nickel Chloride	20	17.5	16	15
2	Nickel Sulfate	20	17.5	16	15
3	Sodium hypophosphite	24	22	20	18
4	Sodium Succinate	12	11	10	9
5	Temperature	85±2	80±2	75±2	90±2
6	pH	4.5-5.5	4.5-5.5	4.5-5.5	4.5-5.5



Sl. No.	Component/condition	Value in g/l (Level 1)	Value in g/l (Level 2)	Value in g/l (Level 3)	Value in g/l (Level 4)
1	Nickel -chloride	20	17.5	16	15
2	Nickel- sulfate	20	17.5	16	15
3	Sodium- hypophosphite	24	22	20	18
4	Sodium- Succinate	12	11	10	9
5	Temperature (°C)	85±2	80±2	75±2	90±2
6	pH	4.5-5.5	4.5-5.5	4.5-5.5	4.5-5.5

Figure 2: Flow diagram of the Ni-P coating deposition process

2. Heat treatment

The coated samples were heat-treated at 450°C for 1 hour in a muffle furnace.

3. Microhardness Measurement

The microhardness test is conducted on the coating's upper surface. Figure 2 shows the specifics of the microhardness measuring process [4].

4. Microstructural Observation

The microstructure of the coatings is analyzed using a scanning electron microscope (SEM; FEI, QUANTA FEG 250, Germany) to examine the surface morphology of the coatings at different temperatures both before and after heat treatment. The composition of the EN coatings is investigated in terms of the percentages of nickel and phosphorous using EDX analysis in conjunction with SEM [12-18].

5. Tribological test

The tribological tests are carried out using a multi-tribo-tester instrument (TR-25, DUCOM, India). Samples are held still by the specimen holder throughout the test and are permitted to slide up against the counter face disk. The disc speed and test duration are controlled by a computer that is connected to the tribometer. Measuring the actual load being applied to the samples is made easy by the normal load sensor, which is located near the loading lever [4]. Table 1 presents the test parameters that were used along with their respective values. The mass loss of the samples is used to quantify wear. Because the counter-face material is harder than the coating, it bears mentioning that it wears down far less than the specimen.

Table 2: Tribology test parameters

SL No	Parameters	Value
1	Track diameter (mm)	80
2	Applied normal load (N)	20
3	Sliding speed (rpm)	50
4	Sliding duration (min)	10

III. RESULTS AND DISCUSSION

1. Microstructural Characterisation of ENP Coating

The surface morphology of as-deposited electroless Ni-P coating is shown in Figure 3 in various bath compositions. As seen in Figure 3, the electroless Ni-P coating's surface morphology reveals a nodular shape. There are no contaminants present in the coating sample. The deposited sample's apparent nodule size has a radius ranging from 10 to 15 μm. The substrate surface seems to be porous-free and uniform in appearance. A smooth, featureless surface suggests high phosphorus content and potentially an amorphous structure. Amorphous Ni-P coatings offer superior corrosion resistance but may have lower hardness. In contrast, a faceted or bumpy surface with distinct features indicates a more microcrystalline structure, likely with higher nickel content. Heat treatment at 450°C for 1 hour significantly impacts coating microstructure and properties as shown in Figure 4. Decreasing porosity leads to increased compactness and density. Reduced porosity and improved microstructure contribute to better wear resistance. By reducing porosity, heat treatment can significantly impact coating performance and lifespan. The heat treatment provides the energy for hydrogen atoms to diffuse out of the coating, reducing internal pressure and pore formation Heat treatment can induce amorphous structures can transform into crystalline phases. Existing crystalline structures can grow, influencing properties. Higher heat treatment temperatures and longer durations facilitate atom diffusion and rearrangement as shown in Figure 4a-4d. Grain growth can enhance mechanical and tribological properties, such as strength, durability, and wear resistance [19].

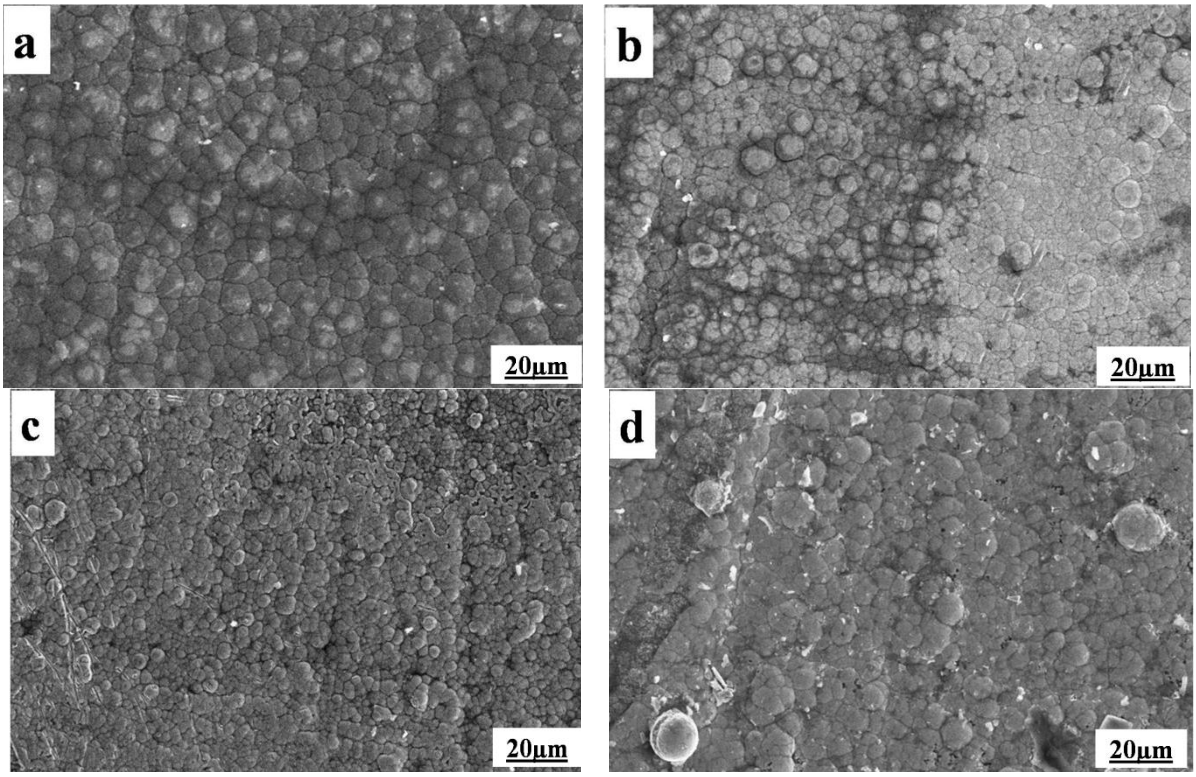


Figure 3: As-deposited coating (a) ENP1, (b) ENP2, (c) ENP3 and (d) ENP4

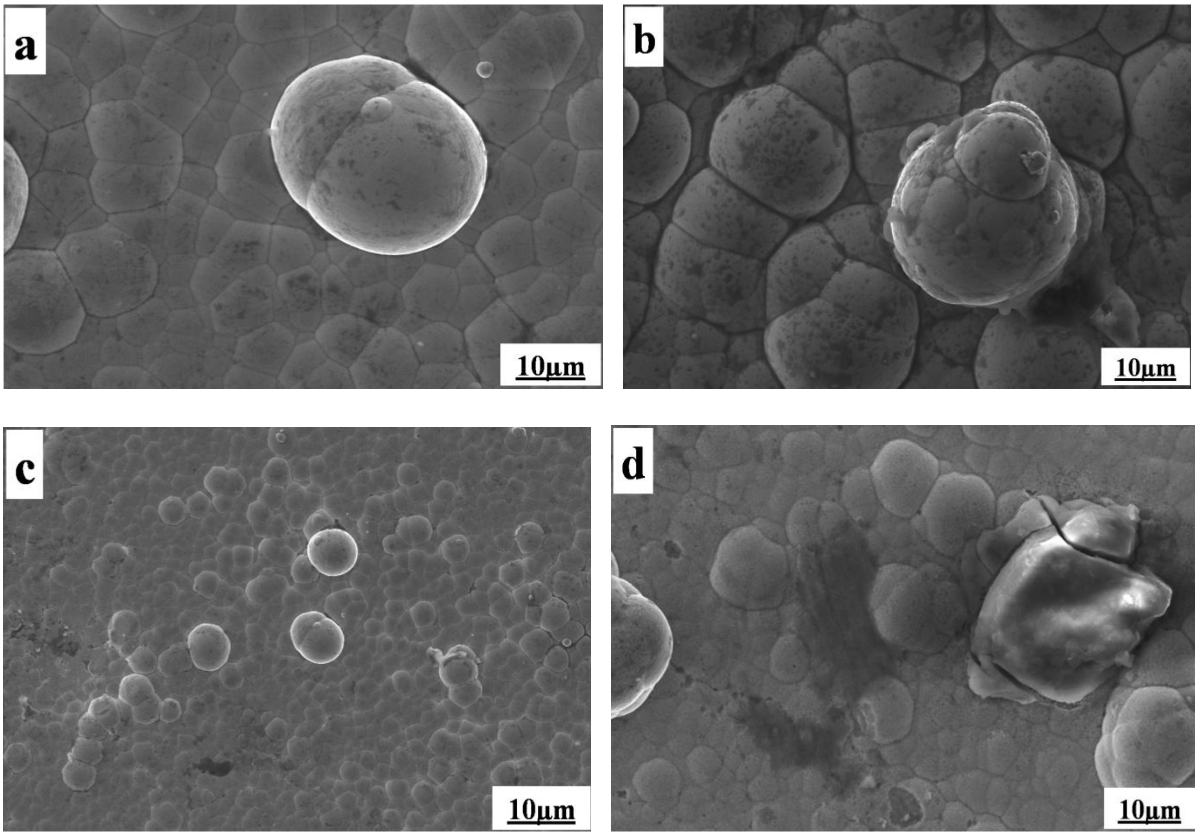


Figure 4: heat treated coating (a) ENP1, (b) ENP2, (c) ENP3 and (d) ENP4

The elemental content of the coatings are assessed using the EDX analyzer. EDX confirms the presence of Nickel (Ni) and Phosphorus (P) in the coating, along with the weight percentage of each element as shown in Table 2. The phosphorus content may vary depending on the electroless plating process parameters but plays a crucial role in the coating's properties. Each coating is classified as having a high phosphorus content based on the amount of phosphorous it contains. Higher phosphorus content is directly correlated with the coating's amorphous character, as documented in the literature [13].

Table 2: EDX data of the as-deposited samples

Coatings	**Element in wt.%**	
	Ni	P
ENP1	88.6	11.4
ENP2	88.3	10.5
ENP3	90.4	9.6
ENP4	91.1	8.9

2. Microhardness

The microhardness measurements for the various electroless Ni-P coatings for as-deposited state are shown in Figure 4. The microhardness of electroless Ni-P coatings depends on several factors, like phosphorus content, bath composition and deposition condition. Low-phosphorus ENP coatings are crystalline, medium-phosphorus ENP coatings are microcrystalline, and high-phosphorus ENP coatings are amorphous, according to the literature [2]. The characteristics of deposited ENP coatings are solely determined by their microstructure [14]. The microhardness often diminishes as the P content rises. It is possible to infer from the microhardness measurement findings that the ENP coating with the lowest P had the highest microhardness value. According to Figure 5, the microhardness of as-

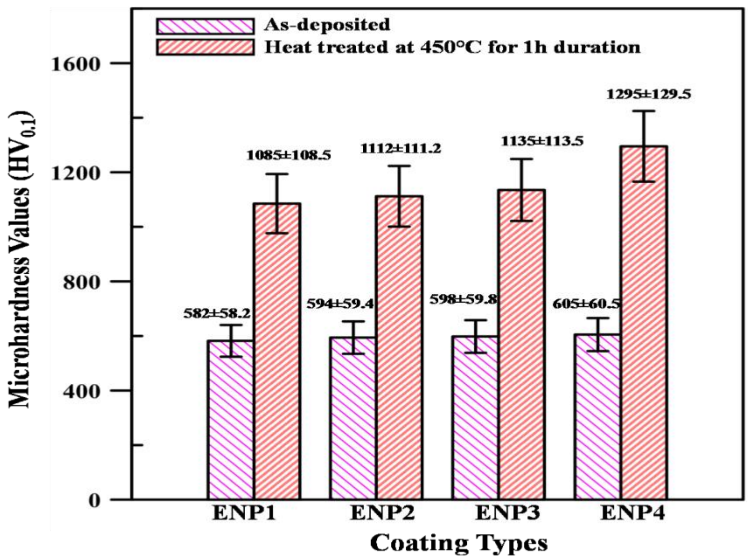


Figure 5: Microhardness results for various ENP coatings

Deposited coatings reduced as the P concentration increased (Figure 5) , in line with previous research [15]. The percentages of P content are already described in Table 2. Electroless Ni-P coatings typically exhibit a significant increase in microhardness after heat treatment at 450°C for 1 hour due to the precipitation of Ni_3P phases. The microhardness can increase from approximately 582-605 $HV_{0.1}$ in the as-plated state to around 1085-1295 $HV_{0.1}$ after heat treatment as shown in Figure 4. This enhancement is attributed to the transformation of the amorphous Ni-P structure into a crystalline structure with the formation of Ni_3P[9]. Both as-deposited and after heat treatment, a lower phosphorus percentage in electroless nickel-phosphorus (Ni-P) coatings typically results in a greater microhardness value. Higher phosphorus content typically results in an amorphous or mixed amorphous/crystalline structure, whereas low phosphorus coatings have a more crystalline structure, which is responsible for their higher hardness.

3. Co-efficient of Friction

The average coefficient of friction (COF) for the present coatings under as-deposited conditions is shown in Figure 6. The coefficient of friction (COF) of ENP coatings depends on a complex interplay between several factors. The surface topography of the coating plays a crucial role. Rougher surfaces tend to have a higher COF due to increased interlocking and real contact area between sliding surfaces. The material the Ni-P coating slides against significantly affects COF. Softer materials tend to conform better to the coating surface, potentially reducing friction. Surface roughness, phosphorus content, and coating thickness are some of the factors that affect the coating's COF. High phosphorus coatings have a greater friction coefficient than medium or low phosphorus electroless coatings, according to the results of a friction study conducted on EN coatings [16, 17]. Also, a lower COF is the result of a harder coating's decreased contact area (refer to Figure 5 and 6). When electroless Ni-P coatings undergo heat treatment, their coefficient of friction often decreases compared to their as-deposited state. This reduction is attributed to the precipitation of Ni_3P phases and crystallization of the Ni matrix, which enhance the coating's hardness. The specific friction coefficient value is influenced by factors such as heat treatment temperature, phosphorus content, and the presence of additional materials in composite coatings. The coefficient of friction (COF) is reduced by approximately: 43% for ENP1, 46% for ENP2, 45.83% for ENP3 and 50% for ENP4 compared to their as-deposited conditions.

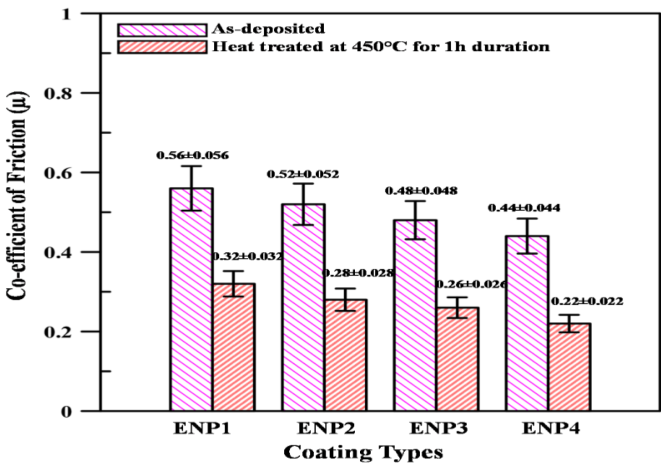


Figure 6: COF results for various ENP coatings

4. Wear Behavior

The wear rate of the current ENP coatings in as-deposited stages is shown in Figure 7. In the as-deposited condition, the lowest wear rate for ENP4 is noted due to higher hardness (refer to Figure 4). There exists a theoretical relationship between a surface's hardness and resistance to wear. But there are a lot of other factors that also affect a surface's wear qualities, like the type of stress applied and the surface morphology [16, 18]. The wear resistance of ENP coating depends on phosphorus content. While increased hardness is beneficial, excessive phosphorus can make the coating brittle, potentially leading to wear through cracking and chipping. Heat treatment has been shown to dramatically reduce the wear rate of electroless Ni-P coatings, as evidenced by present studies. The heat-treated Ni-P coatings' improved hardness leads to improved resistance to wear. This is because, when sliding or rubbing against a surface, the harder coating is more resilient to plastic deformation and material loss. The wear rate is reduced by approximately 38.32% for ENP1, 39.17% for ENP2, 40.35% for ENP3, and 41.66% for ENP4 compared to their as-deposited conditions.

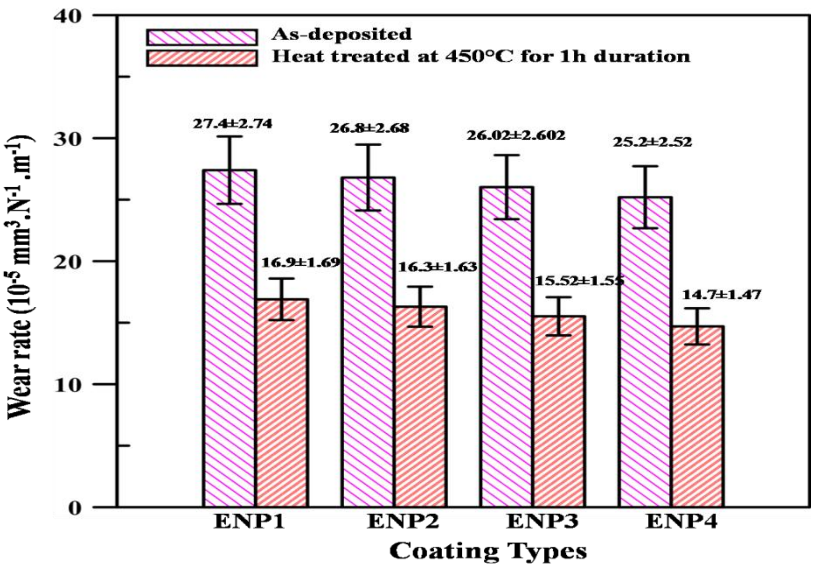


Figure 7: Wear rate for various ENP coatings

IV. CONCLUSION

This study investigated the tribological behavior of electroless Ni-P coatings with varying bath compositions. These are the conclusions that are listed below:

- **Microstructure and Hardness:** Heat treatment at 450°C for 1 hour significantly improved microhardness (up to 1085-1295 $HV_{0.1}$.) due to Ni_3P phase precipitation.
- **Coefficient of Friction (COF):** Heat-treated coatings showed reduced COF, with reductions ranging from 43% to 50% compared to as-deposited conditions.
- **Wear Behavior:** Heat treatment dramatically reduced wear rates, with reductions between 38.32% and 41.66%.

The results demonstrate the importance of bath composition and heat treatment in optimizing the tribological properties of electroless Ni-P coatings. These findings can be applied to enhance the performance and lifespan of components in various industrial applications.

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