3.1 INTRODUCTION

The present investigation is on the development of black coatings is carried out in three aspects:

(i) Development of non-toxic trivalent black chrome coatings with improved mechanical properties for automobile components.

(ii) Development of high speed black coatings based on nickel alloys with superior mechanical properties for industrial applications.

(iii) Formulation and characterization of modified black phosphating coatings for achieving enhanced mechanical properties.

The mechanical properties of the coatings have been evaluated by weight gain studies, Vicker’s micro hardness measurements (ASTM E-384), Taber abrasion resistance (ASTM D-4060) and corrosion resistance [potentiodynamic polarization measurements, impedance studies and salt spray test (ASTM B-117A)] were made to evaluate the mechanical properties of the coatings. X-ray diffraction (XRD) using ASTM F-2024, Scanning electron microscope (SEM) using ASTM E-986 and X-ray photo electron spectra (XPS) studies under ASTM E-2735 were also performed to understand the surface morphologies of deposits.
3.2 MATERIALS AND CHEMICALS USED

3.2.1 Selection of metallic components

For trial studies, mild steel specimens of 99.52% purity of size 2 x 5 x 0.2 cm$^3$ were polished with fine grit paper and degreased with trichloro ethylene. They were rinsed in double distilled water. The composition of the mild steel used in the present study is given below:

- Carbon = 0.16%;
- Manganese = 0.3%;
- Silicon, Sulphur, Phosphorus = 0.005%;
- Aluminium = 0.02% and
- Iron = 99.52%

For electrochemical studies such as polarization measurements and impedance studies,

1 cm$^2$ area mild steel specimen were used as working electrode, platinum (4 cm$^2$) as counter electrode and calomel electrode as reference electrode.

All glasswares were of Borosil make used in electrochemical cells and electrode were of imported from Sinsil instruments, USA.

A single pan with 1mg accuracy digital balance was used for mass gain measurements to determine rate of deposition through weight gain method. A digital pH meter (Elico, India) was used to measure the pH of the various plating baths and electrolytes.

The above experimental setup was adopted for developing black coatings on radiator pin plug, automotive vehicle brake tubing and lock nuts. The schematic representations of black coated components used in these studies are given in figures 3.1-3.3.
Figure 3.1 Black electrodeposited automobile components
Figure 3.2 Black Ni-Zn-Co coated on copper plate

Figure 3.3 Black coated trivalent Cr on mild steel
The reason for selecting the automotive components is based on its performance in vehicles. Steel tube is widely used in vehicle brake tubing system due to its excellent initial pressure bearing characteristics. However, the present steel tubes are vulnerable to the fluid flowing through it and undergoes corrosion from road mud and salt (particularly chloride ions) and cause damage on the surface of steel tubes. The alternate candidate for the protection of steel tube involved was copper-nickel alloy C70600, an alloy of copper (90%) and nickel (10%) which is having anti-corrosion characteristics. However, the mass production of copper-nickel alloy based vehicle tube brakes is highly expensive. An inherent corrosion resistant coating in tubing materials is the only way to enhance the life time of vehicle tube braking.

Another component chosen for the study is radiator drain plug, made of mild steel. This component is fitted with radiator which contained the mixture of anti-freeze and water. The mixture cools the engine to prevent the possibility of blown engine. However, the drain plug is more susceptible to corrosion and form rust that leads to leakage in radiator. In order to avoid the deterioration of radiator drain plug when exposed to water inside the radiator, black coatings with improved mechanical properties have to be applied.

Hence, the present research focuses on the development of black coatings to achieve improved mechanical properties that lead to enhanced life time of automotive components in the following aspects:

1) Thickness of coatings above 30 μm which is an industrial requirement in short period of time, probably in seconds.

2) Improvement in hardness, abrasion resistance and corrosion resistant in addition to its optical properties.
### 3.2.2 Choice of chemicals to form black coatings

All the chemicals used were of analytical or guaranteed reagent grades. Names of the chemicals with their make are given below:

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Make</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chromium Chloride purified</td>
<td>Merk (1)</td>
</tr>
<tr>
<td>2. Cobalt Chloride</td>
<td>S.d. fine chem. Limited</td>
</tr>
<tr>
<td>3. Sodium dihydrogen phosphate</td>
<td>Merk-schuchardt</td>
</tr>
<tr>
<td>4. Sodium fluride</td>
<td>Fisher</td>
</tr>
<tr>
<td>5. Nickel sulfate heptahydrate</td>
<td>Ranboxy</td>
</tr>
<tr>
<td>6. Copper sulphate pentahydrate</td>
<td>Fisher</td>
</tr>
<tr>
<td>7. Cobalt sulphate hexahydrate</td>
<td>Fisher</td>
</tr>
<tr>
<td>8. EDTA di sodium salt</td>
<td>Qualigens</td>
</tr>
<tr>
<td>9. Boric acid</td>
<td>Fischer</td>
</tr>
<tr>
<td>10. Zinc sulphate pentahydrate</td>
<td>Fischer</td>
</tr>
<tr>
<td>11. Ammonium thiocyanate</td>
<td>Ranboxy</td>
</tr>
<tr>
<td>12. Cobalt chloride hexahydrate</td>
<td>Fischer</td>
</tr>
<tr>
<td>13. Nitric acid</td>
<td>Qualigens</td>
</tr>
<tr>
<td>14. Phosphoric acid</td>
<td>Qualigens</td>
</tr>
<tr>
<td>15. Zinc oxide</td>
<td>Ranboxy</td>
</tr>
<tr>
<td>16. Sodium molybdate</td>
<td>S.D fine chemicals</td>
</tr>
<tr>
<td>17. Manganese sulphate</td>
<td>S.D fine chemicals</td>
</tr>
</tbody>
</table>
3.2.3 Preparation and purification of black coating solutions

For any electro plating, proper method of preparation and preconditioning of bath to remove impurities are essential to get good deposits of required mechanical properties. The bath preparation is as follows:

3.2.3.1 Preparation of trivalent chrome bath solution

About six plating formulations have been developed by adopting standard plating procedure. The formulations are given in the table 3.1.
Table 3.1 Formulation of various trivalent chromium baths

<table>
<thead>
<tr>
<th>S.No</th>
<th>Trial baths</th>
<th>Optimized bath</th>
</tr>
</thead>
</table>
| 1.   | CrCl₃ = 22 g/l  
H₂SO₄ = 22 g/l  
H₂O₂ = 53 g/l  
FAS = 0.25 g/l  
CoSO₄ = 2.1 g/l  
NH₄HF₂ = 1.8 g/l  
pH = 2-2.5  
Current density= 200-450 mA/cm²  
Plating time = 4-5 min. | Cr metal(Trivalent) = 54.45 g/l= 270 g CrCl₃  
Co metal = 6.75 g/l= 20 g CoCl₂  
NaH₂PO₄ = 6 g/l  
NaF = 21 g/l  
pH = 4.6  
Current density= 200-450 mA/cm²  
Plating time = 7 min. |
| 2.   | CrCl₃ = 263 g/l  
CoSO₄ = 15 g/l  
NaH₂PO₄ = 4 g/l  
NaF = 21 g/l  
pH = 3-3.5  
Current density= 200-450 mA/cm²  
Plating time = 4-5 min. |  |
| 3.   | CrCl₃ = 263 g/l  
CoSO₄ = 15 g/l  
Co(NO₃)₂ = 12 g/l  
NaH₂PO₄ = 2 g/l  
NaF = 21 g/l  
pH = 3.5-4  
Current density= 200-450 mA/cm²  
Plating time = 4-5 min. |  |
| 4.   | CrCl₃ = 40 g/l  
CoSO₄ = 10 g/l  
Co(NO₃)₂ = 10 g/l  
NaH₂PO₄ = 8 g/l  
NaF = 8 g/l  
pH = 3.5-4  
Current density= 200-450 mA/cm²  
Plating time = 4-5 min. |  |
| 5.   | CrCl₃ = 240 g/l  
CoSO₄ = 15 g/l  
Co(NO₃)₂ = 12 g/l  
NaH₂PO₄ = 6 g/l  
NaF = 21 g/l  
pH = 4-4.5  
Current density= 200-450 mA/cm²  
Plating time = 4-5 min. |  |
Exactly 54.45g of chromium chloride was weighed and transferred in 1000 ml clean beaker and treated with minimum quantity of double distilled water. To this cobalt chloride(6.75%), sodium dihydrogen phosphate(6%) and sodium fluride(21%) are added. The solution was made up to 1000ml using standard measuring flask with double distilled water. The oils and suspended impurities present in the solution were removed by filtration. The solution was stored in a clean closed container. The stock solution was analyzed for the Cr\(^{3+}\) and cobalt by Atomic absorption spectra (AAS), PinAAcle 900 AA spectrometer made of Perkin Elmer, USA.

Figure 3.4 PinAAcle 900 AA spectrometer for compositional analysis of coatings
The optimized bath for obtaining black Ni-Cu-Co, Ni-Zn-Co and black phosphate coatings on metallic components are given below:

**Black Ni-Cu-Co coatings**

NiSO$_4$.6H$_2$O = 40 g/l  
CuSO$_4$.6H$_2$O = 8 g/l  
CoSO$_4$.5H$_2$O = 15 g/l  
Ammonium thiocyanate = 25 g/l  
Boric acid = 30 g/l  
EDTA = 3 g/l  
pH = 4.7  
Current density = 400 mA/cm$^2$  
Plating time = 180 seconds

**Black Ni-Zn-Co coatings**

NiSO$_4$.6H$_2$O = 100 g/l  
ZnSO$_4$.5H$_2$O = 8 g/l  
CoSO$_4$.5H$_2$O = 8 g/l  
Ammonium thiocyanate = 25 g/l  
Nitric acid = 16 ml/l  
pH = 5.7  
Current density = 4 mA/cm$^2$  
Plating time = 120 seconds
Black Phosphate coatings

Phosphoric acid = 12 g/l (87%)
ZnO = 5 g/l
Sodium molybdate = 4 g/l
MnSO$_4$ = 2.3 g/l
Nitric acid = 2 ml/l (4%)
pH = 3.7
Temperature = 65°C
Plating time = 240 seconds
3.3 EVALUATION OF BLACK COATINGS THROUGH DIFFERENT TECHNIQUES

3.3.1 Weight-gain method

Mild steel specimens of 99.52% purity of size 20 x 50 x 2 mm$^3$ were used in the plating bath. They were polished with fine grit paper and degreased using trichloroethylene to remove oil and greases. Mild steel panels were pretreated in acid bath followed by alkali bath and washed with tap water. They were rinsed in double distilled water and dried. The initial weight of panel was recorded using digital weighing balance machine. The same operating conditions were used for coating on radiator drain plug, lock nut and vehicle brake tube made of mild steel. Then, both metallic components and mild steel test specimens were introduced into the plating solution under optimized conditions of the bath. The rate of deposition was calculated using the following formula:

$$\text{The rate of deposition (\mu m/h)} = \frac{W \times 10^4}{D \times A \times T}$$

Where,

$W$ – Weight of the deposit (g)

$D$ – density of the deposit (g/cm$^3$)

$T$ – plating duration (h)

$A$ – Surface area of the specimen (cm$^2$)

The experimental setups were shown in the figure 3.5 & figure 3.6. The above experiments were conducted for developing black coatings on metallic components. The following factors were analyzed with the above experiments.
Figure 3.5 High speed electroplating setup for black coatings for lock nut and brake tubes

Figure 3.6 Modified black phosphate coatings for radiator drain plug
3.3.2 Micro hardness measurements

Micro hardness measurements for all the as plated specimens (20 x 50 x 2 mm$^3$) and also for the annealed samples at 300°C were made by Vicker’s harness tester as per ASTM E-384 with a load of 100 g. A diamond shaped indentation was made on each sample at eight different places and the average value of hardness was measured from the diagonal of indendation on Vicker’s scale using the formula.

\[ V.H.N = \frac{1854 \times \text{load}}{d^2} \]

where \(d\) = diagonal of the indentor

However, the instrument displayed V.H.N directly using digital read out.

3.3.3 Taber abrasion resistance measurement

The abrasion resistances of the black coated specimens of size 100 x 100 x 4 mm$^3$ were measured as per ASTM D-4060 through Taber abraser both in as plated and annealed conditions. The abrading wheels were allowed to rotate on the coatings at a load of 100 g. Before the start of the experiment the specimen were accurately weighed. Then, the wheels are allowed to rotate against the deposit for 1000 cycles with the above load. After that the specimens were removed and weighed again. The experiment was repeated for another 1000 cycles on the specimens. The average weight loss was taken as the Taber wear index or Abrasion resistance.

Taber wear index = Average weight loss (in mg) for 1000 cycles
3.3.4 Corrosion resistance measurements

The electrochemical polarization measurement and impedance studies were made with the black coated steel surface of 10 mm\(^2\) area (working electrode), 40 mm of platinum electrode (counter electrode) and saturated calomel as reference electrode in three electrode cell assembly.

3.3.4.1 Potentiodynamic polarization method

A constant quantity of 200 ml of 3.5% NaCl solution was taken in a 250 ml beaker. The working electrode, reference electrode and the counter electrode were assembled in position and the connections were made. Initially, the potential is noted which is recorded as open circuit potential (OCP). From OCP, polarization studies were performed using Sinsil Model 604E Electrochemical Analyzer imported from USA. The readings were obtained by ranging the potential values from OCP ± 1000 mV with scan rate 10 mV per second for both as plated and annealed black coated steel surfaces.

The corrosion kinetic parameters such as \(E_{\text{corr}}\), \(I_{\text{corr}}\), anodic and cathodic Tafel slopes (\(b_a\) and \(b_c\)) were measured.

The reduction in potential values of Tafel slopes gave an idea that whether the black coatings have reduced the oxidation of metal from surface or involved in reducing chlororine gas evolution.
Figure 3.7 Block diagram of potentiodynamic polarization setup

U  = Universal programmer
P  = Potentiostat
R  = X-Y Recorder
WE = Working electrode
RE = Reference electrode
CE = Counter electrode
Figure 3.8 SINSIL Model 604E electrochemical analyzer
3.3.4.2 Impedance measurement

The SINSIL Model 604E electrochemical analyzer was used for this measurement in the frequency range of 100 kHz to 0.01 Hz under potentiostatic conditions using 3.5% NaCl as corrosive medium. The impedance measurements were carried out both as plated and annealed black coated steel surface at room temperature.

A semi-circular plots correspond to Nyquist plot was recorded for all black coated steel specimens. From the Nyquist plot, the charge transfer resistance \( R_t \) and double layer capacitance \( C_{dl} \) values were calculated. The block diagram used for the impedance analyzer is shown in figure 3.6.

The electrical equivalent circuit for the corroding system is given below:

\[
\begin{align*}
\text{R}_S & \quad - \quad \text{Solution resistance} \\
\text{R}_t & \quad - \quad \text{Charge transfer resistance} \\
\text{W} & \quad - \quad \text{Warburg impedance} \\
\text{C}_{dl} & \quad - \quad \text{Double layer capacitance}
\end{align*}
\]

Figure 3.9 Electrical equivalent circuit for impedance analyzer
The cell impedance consists of real part \((Z')\) Vs imaginary part \((Z'')\).

A plot of real part \((Z')\) Vs imaginary part \((Z'')\) gives a semicircle which cuts the real axis at higher and at low frequency \(Z\) corresponds to \((R_s + R_i)\). The difference between the two values gives \(R_t\). The double layer capacitance can be determined from the frequency at which \(Z''\) is maximum from the relation

\[
Z''_{(\text{max})} = \frac{1}{2\pi C_{dl} R_t}
\]

Figure 3.10 Block diagram of AC impedance system

- **F.R.A** - Frequency response analyzer
- **WE, RE_2** - Working electrodes
- **CE** - Counter electrodes
- **RE_1** - Reference electrodes
- **E.I** - Electrochemical interface
3.3.5 Surface morphological studies of black coatings

3.3.5.1 X-ray diffraction (XRD) studies

The X-ray diffraction patterns for the black electrodeposited mild steel specimens were made using X’ pert pro XRD,(make- Panalytical, USA) both as plated as well as annealed conditions. These measurements help to explain the intermetallic phases formed in the coatings. The X-ray diffraction patterns were obtained with Cu Kα radiation in the above instrument (Figure 3.11) with the step of 0.02°. XRD patterns were recorded for different depth profiles employing grazing incidents X-ray technique.

3.3.5.2 Scanning electron microscopic studies (SEM)

The morphology of the black electrodeposits were examined under high magnification to assess the grain size, deposit nature, heterogeneities and pores present in the deposits using a scanning electron microscope. The scanning electron microscope, which makes use of reflected primary electrons and secondary electrons, enable one to obtain information from regions that cannot be examined by others.

The deposited specimens of various black coatings were cut into 10 x 10 mm² size and mounted suitably and examined under the microscope. The SEM photographs were taken by using S-3000 model with an acceleration voltage range of 20,000 V and with the magnification range of 1000. (Figure 3.12).
Figure 3.11 Instrument for XRD measurement

Figure 3.12 Instrument for SEM measurement
3.3.5.3 Surface Characterization (XPS or ESCA analysis)

The surface characterization measurements were carried out on black coated samples under annealed conditions having surface area of $10 \times 10 \text{ mm}^2$ using X-ray photoelectron spectra (XPS) also known as Electron Spectroscopy for Chemical Analysis (ESCA) in a physical electronics PHI 5600 ESCA system (Figure 3.13) with Al K$_\alpha$ monochromatic source was used to obtain oxidation states of species along with chemical composition of surfaces. The binding energy values were calculated with a precision of ±0.2 eV. For these measurements, the samples were mounted in to an ultra high vacuum chamber at $10^{-9}$ Torr housing the analyzer. Prior to mounting, the black coated samples were placed in the preparation chamber for 6 hours in order to remove any volatile species exist on the surface.

![Figure 3.13 Block diagram for XPS analysis](image)
3.3.6 Optical properties of black coatings
Optical properties, namely the solar absorptance or solar reflectance is one of the characteristic properties of the black coatings were measured with UV visible spectra in the region of wave length from 200 to 400 nm and IR visible were obtained from 750 to 1000 nm regions and low absorptance in the visible region(>400-700 nm) were measured using ASTM E-307. The absorptance values of the black coatings layers were calculated using Kirchhoff’s law.

\[ A + R + T = 1 \]

where A is absorptance, T is transmittance, and R is reflectance of surface. In the opaque surfaces, their transmittance is zero, it can be expressed as:

\[ A + R = 1; \]
\[ A = 1 – R. \]

3.3.7 Salt spray analysis for corrosion resistance of black coated samples
The salt spray rest of the black coated steel panels were conducted in SF 850 salt spray cabinet as per ASTM B-117 in 3.5% NaCl to understand the corrosion resistance of the coatings in aggressive environment i.e. sea water medium. The corrosion degree of the samples was evaluated by average weight loss which was visibly noted by the appearance of formation of red rust spots on the coated samples used under annealed conditions. This test has established that the corrosion resistance of the coatings is higher in sea water medium as a validated result for potentiodynamic polarization and A/C impedance test.

SUMMARY
A full spectrum with regard to assessing the performance of black coatings with improved mechanical properties on automobile mild steel components has been carried out using chemical and electrochemical techniques. The results will be presented and discussed in Chapter 4.