

ROLE OF PHOSPHATING SYSTEMS IN ELECTRODEPOSITION PRIMING AND LATEST TRENDS IN SURFACE COATING IN AUTOMOBILE INDUSTRY

S.S. Jangbahadur, Rajneesh Garg and Chirag Agarwal
Quality Assurance, Telco, Jamshedpur

1.0 INTRODUCTION :

Iron and steel are so very widely used in Engineering Industry that any Country's progress can be judged from the consumption of this. Iron is mostly found as oxide minerals in the nature from which by metallurgical processes we convert these oxides of iron into metallic iron and by alloying we make steel. Unfortunately natural process is such that this iron and steel due to atmospheric action again tries to go back to oxide state which we call corrosion.

It is therefore necessary that we have to prevent this and protect iron and steel from corrosion. Various types of corrosion phenomenon takes place while using this metal.

Corrosion is an electro-chemical phenomenon. The attack starts on the surface and then penetrates through the body in an aggressive medium.

By making the surface non-conducting, we can improve corrosion protection. Surface can be made non-conductive by the process of conversion coating i.e., phosphating. This process chemically converts the surface of base metal into suitable metal phosphate Zn, Mn, Fe (Di-cationic, and tricationic) under proper condition of solution composition, temperature, concentration and process time. The surface being generally non-conductive and crystalline, helps in corrosion resistance and holds subsequent film firmly.

2.0 PHOSPHATING :

2.1 DEVELOPMENT OF PHOSPHATING :

- 2.1.1. Phosphating was first invented and patented in 1869 in U.K by William Alexander Ross.
- 2.1.2. However it was Mr. T.W. Coslett who gets the honour of introducing phosphating for Industrial use in 1906.
- 2.1.3. The next development took place by Parker rust proof company in USA using Zn and Mn salts and also accelerator to hasten the process to be successfully used on production line from 1908.
- 2.1.4. In 1927, Parker Rust Proof Company sold the rights in U.K. to Pyrene Company and a number of companies started using this process.

- 2.1.5. In 1930, phosphating process was developed to cut down the process time from 30 mts to 5 mts.

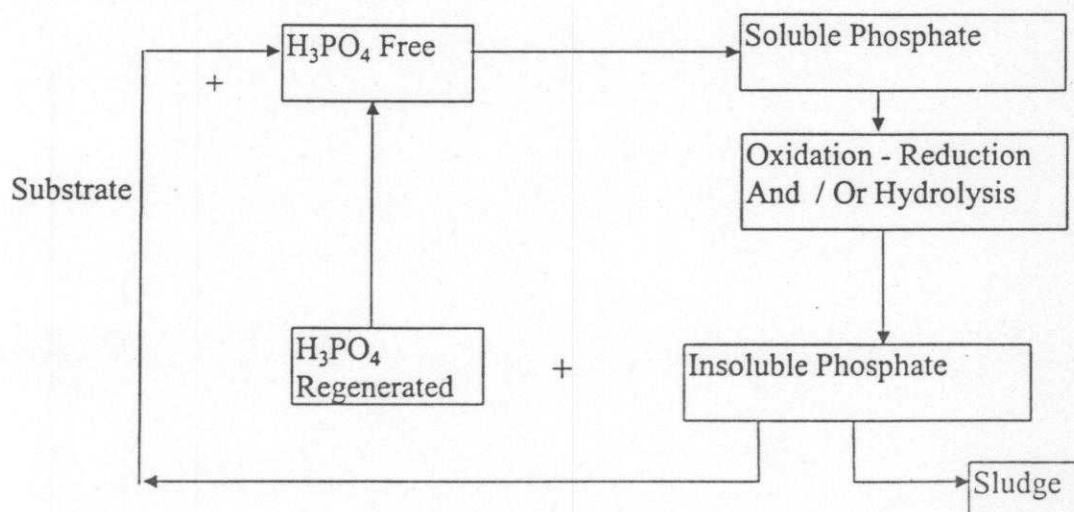
The development then progressed steadily in U.K., France and Germany and spray phosphating plants installed in 1931.

- 2.1.6. The application areas in different fields such as cold forming, wire drawing expanded rapidly and low temperature phosphating developed in U.K and Germany.
- 2.1.7. In India, Pyrene Rai started marketing the phosphating chemical from Dec 1968 in collaboration with Pyrene U.K.
- 2.1.8. In recent years, Nihon Parkerising in collaboration with Goodlass Nerolac, Nippon with Asian PPG, ICI UK with ICI India, Henkel Germany with Chembond and Chemetall Germany with Chemetall Rai (earlier Pyrene Rai) are marketing phosphating chemicals in India.

2.2 MECHANISM OF PHOSPHATING :

The chemical mechanism is of complex nature and is still a controversial topic. This is mainly due to the fact that various reacting species take part in the reaction and are not always well defined.

The phosphate bath generally consist of a primary soluble metal phosphate - normally Zn, Fe, Mn, Ni, certain amount of free phosphoric acid and a suitable accelerator or oxidant. However for the formation of necessary phosphate coating, the energy state of the surface is important. The micro cathodes and micro anodes are involved in the formation of an oxide underlayer and most important thing is that the process of even distribution of active centers i.e., nuclei around which phosphate coating builds up depends on initial cleaning treatment of the surface. The basic reactions involved in this type of phosphating conversion coatings can be summarized as follows :



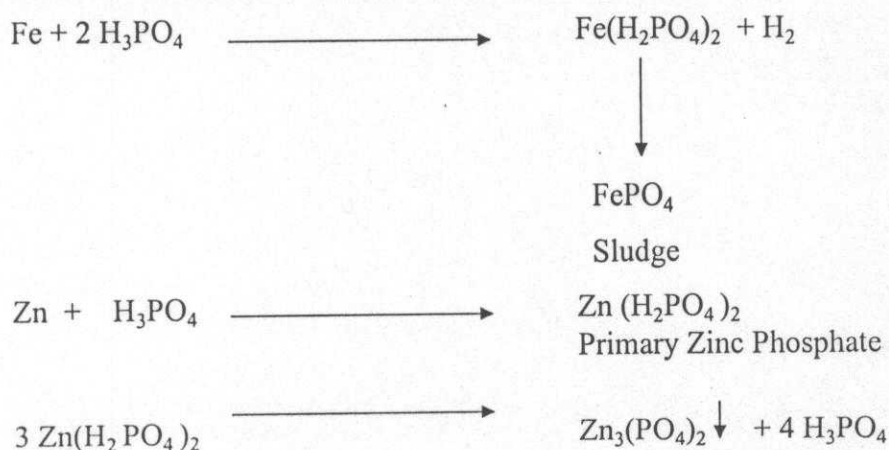
To explain in brief, we can say that when a clean metal sheet is immersed in a phosphating bath which is generally composed of soluble primary metal phosphate (Zn, Fe, Mn, Ni) with certain amount of free phosphoric acid and an accelerator, the free acid attacks the metal surface solid-liquid interface causes anodic dissolution of the metal while releasing hydrogen ion. This being ionic reaction results in lowering of acidity at the interface resulting in hydrolytic precipitation of phosphates. Lowering of free acidity at the interface cause the deposition of insoluble phosphate on bare metal. The crystal growth takes place at the active centers or nuclei on the metal surface and oxidising agent helps in removal of hydrogen ion formed during the reaction and throwing of soluble iron phosphate as sludge.

Phosphate bath pH is 2.5 -2.8. During reaction of metal to phosphate bath, pH increases at the metal solution interface. When pH goes to 4.5 and above, that pH is called point of inceptient precipitaion (PIP) and at that pH, coating formation takes place.

Phosphate coating because of its non-conductive nature and being integral part of the substrate metal and fine crystalline form helps in giving following advantage for protection against corrosion. The properties are :

- i) The coating is firmly attached to the substrate.
- ii) The porous crystalline structure provides an extended surface for paint bonding.
- iii) The Zn-phosphate coating is compatible with almost all paints.
- iv) The coating provides non-conducting layer and when sealed, avoids under-paint corrosion.
- v) In case of break in the paint film, the phosphate film prevent under-cuttings of organic finish due to corrosion of metal.
- vi) The corrosion resistant of phosphate coating depends upon coating weight and coating texture i.e., free pore area of the crystal structure.

2.3 THE CHEMICAL REACTION TAKING PLACE :



In phosphate bath different forms of Zinc phosphate present are :

$\text{Zn}(\text{H}_2\text{PO}_4)_2$	Primary Zinc phosphate : Soluble at bath pH 2.5 - 2.8
$\text{Zn}_2(\text{HPO}_4)_2$	Secondary Zinc phosphate : Sparingly Soluble - Intermediate
$\text{Zn}_3(\text{PO}_4)_2$	Tertiary Zinc phosphate : Insoluble coating

Hence Zinc phosphate coating on iron substrate has following types of crystalline phases i.e.,

$\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	Phosphophyllite structure
$\text{Zn}_2\text{Mn}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	Heuralite structure
$\text{Zn}_2\text{Ni}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	Phosphonicolite structure
$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	Hopeite structure

The modern trend is to get more than 96% P-ratio.

$$\text{P-ratio} = \frac{\text{P}}{\text{P}+\text{H}} \times 100$$

Where, P = Phosphophyllite
H = Hopeite

2.4 TYPES OF PHOSPHATE COATING :

Type	Process Temp.	Use	Classification as per coating weight
1. Zinc Phosphate			
Light coating	65-75 ° C	Paint bonding	Class III 100-430 mg/ft ²
Medium coating	65-75 ° C	Paint finishing, improved corrosion resistance and deep drawing	Class II 430-750 mg/ft ²
Heavy coating	65-75 ° C	Cold forming, Extrusion and corrosion resistance	Class I 750-3000 mg/ft ²
2. Manganese Phosphate			
Heavy coating	90-95 ° C	Corrosion and wear resistance	Class I 1000-2000 mg/ft ²
3. Iron Phosphate			
Light coating	50-60 ° C	Cleaning cum phosphating for painting	Class III Below 100 mg/ft ²
Heavy Coating	50-60 ° C	Corrosion resistance, special applications	Class I Above 750 mg/ft ²

In the recent year, new type of phosphate chemical has been developed in the Indian market and is called tricationic phosphate system consisting of Zn, Mn, & Ni and they can be used in multi-metal cab and cowl.

Further, only tricationic system is suitable for anodic or cathodic Electrophoretic priming system because dissolution of the phosphate coating is very low.

Due to increase in environmental awareness, the modern Zn-phosphating chemicals have :

- Nitrite free accelerators
- Nickel is reduced or eliminated
- Chromium free final rinse
- Recycling of final rinse water through ion exchange columns.

2.5 SELECTION OF PRETREATMENT PROCESS :

The choice of sequence and number of operational steps for a Pretreatment / Phosphating plant depends upon job contour, surface contamination, purpose of phosphating and end use of component. There are normally three types of processes :

- Dip Process
- Spray Process
- Dip cum Spray Process

The selection of the process is mainly decided on the requirement of the quality. In the automobile industry, presently three types of material handling systems are used :

- Continuous chain conveyor
- Reciprocating type conveyor
- Power and free conveyor —————> Most popular in India
- Roll-over-Dip system

The latest system "Roll-over-Dip" is used in the Volvo Truck Corp Plant in New River Dublin, Va, the second in Curitiba, Brazil and the third in Umen, Sweden. The technology is based on conventional floor conveyor on which the cabs are conveyed and stopped over the dip process tank, and automatically fixed to a tilting device and turn into the tank by rotating 180° along the horizontal axis perpendicular to the conveyor direction. The cab remains in the tank until the required residence time for that process is reached and is then rotated up to the upward position with an intermediate stop to allow the liquid in the interior cab to drip back into the process tank. This reduces the carry over from one stage to another and reduces chemical consumption. After being rotated back to the upward position, the cab is released from the tilting device and conveyed to the next process stage.

Continuous conveyor has a single continuous chain and all tackles are fixed on it at a pitch equal to that of consecutive stations. In each cycle, conveyor is indexed by one pitch taking each tackle to next station. From there independent hoists take over the tackle, dip in the tank and again put it back on the conveyor hook. In this system cycle time at all stations are same. Drawback of continuous conveyor is that any breakdown in conveyor system or at any station, interrupts activity at all stations.

Reciprocating type conveyor has special trolley arrangement which pushes the trolley forward during forward motion of conveyor while backward motion of conveyor does not result in any movement of trolley. Trolleys can easily be engaged or disengaged with the conveyor. In this system, cycle time at different station can be varied as per requirement.

Power and free conveyor has a continuous moving chain on which tackles can be engaged or disengaged with easy and simple mechanism. Cycle time at different stations can be varied in this system and jobs can be stacked if some station goes under breakdown or at the end of the shift.

3.0 THE PRETREATMENT :

For phosphating, following sequence are required in an automobile industry :

With On-line derusting

- i) Knock-Off degrease
- ii) Degreasing
- iii) Rinse I
- iv) Rinse II
- v) Derusting
- vi) Rinse I
- vii) Rinse II
- viii) Activation
- ix) Phosphating
- x) Rinse
- xi) Passivation

Without on-line derusting

(International practice)

- i) Knock-Off degrease
- ii) Degreasing
- iii) Rinse I
- iv) Rinse II
- v) Activation
- vi) Phosphating
- vii) Rinse
- viii) Passivation

3.1 DEGREASING :

During the degreasing process, following action takes place :

- Dissolution of oil, dust

- Saponification of oil by alkali
- Emulsification of mineral oil present on the body.

The chemical composition is based on low cost, the chemical should be serviceable at lower temperature, the chemical should not have foaming tendency during spraying and should have a property to separate oil and the oil should float on the surface which can be removed easily by skimming or by suitable oil separator.

The present trend is to use low alkali or the composition of degreasing chemical should be free from caustic. Usage of strong alkali chemical for degreasing operation will spoil the active centers required for uniform phosphate coating. This will result in coarser and thick phosphate coating.

The Rinsing after degreasing is very essential in order to remove all the alkali rest from the surface before it is going to derusting tank. Two rinses are required after degreasing in order to get a cleaner surface as well as to reduce the water requirement. Overflow from second rinsing tank should come to first rinsing tank and that from first rinsing tank should be discarded. In second rinsing tank, fresh water should be added. This is called **cascading**. Contamination level in Rinse-I should be max. 1.5 and that in Rinse II should be max. 1.0. Rate of overflow should be adjusted to maintain these contamination levels.

3.2 DERUSTING :

Derusting is an operation to remove rust from the metal surface. It removes inorganic compounds like oxides, hydroxides and dirt from the metal surface. The chemical composition is based on phosphoric acid, surface active agents and corrosion inhibitors.

DERUSTING IS NOT DESIRED IN MODERN PRETREATMENT LINE BECAUSE DUE TO DERUSTING SHEET METAL ACTIVE CENTERS ARE DESTROYED AND UNIFORM PHOSPHATE COATING WILL NOT TAKE PLACE. IN EUROPEAN COUNTRIES ELECTRO ZINC COATED SHEETS ARE USED IN AUTOMOBILE INDUSTRY, SO NO DERUSTING OPERATION IS REQUIRED IN THE PRETREATMENT LINE.

But in Indian Automobile Industry (Heavy and Medium vehicles Manufacturers) are still using ordinary steel of quality D513 where rust forms during fabrication and derusting is required in order to remove rust from the surface. Indian manufacturers of cars and luxury vehicles are using Electro Zinc coated sheets and therefore in their plants derusting operation is not existing.

After derusting, again two rinses are required with cascading arrangement and contamination level max. 1.5 in Rinse I and max. 1.0 in Rinse II.

3.3 SURFACE ACTIVATION :

Because of degreasing and derusting, where Alkali and Acid has been used, which destroys the active centers, surface activation becomes a necessity. The chemical composition is Ti-phosphate with certain additives to maintain pH of the bath solution 9.8 -10.5. These surface active agents creates active centers of Ti-salt, which acts as a nucleus for crystal growth on which a uniform phosphate coating takes place. The system should be under continuous circulation in order to maintain the uniform Ti-concentration throughout the bath.

3.4 PHOSPHATING :

Present trend of phosphating is tricationic phosphate which contain Zn, Ni, Mn - salts, phosphoric acid, combination of Sodium Nitrate/ Nitride as accelerator with the system. The phosphate bath should have continuous circulation with the external heat exchangers and continuous sludge removal system. After dipping the job, the free acid reacts with the surface, and pH at the interface changes, then the phosphate which becomes insoluble in the bath gets precipitated on the job.

After phosphating, job is rinsed in tank with continuous overflow system. Contamination level in the Rinse tank should be max. 1.0.

3.5 PASSIVATION :

A crystalline phosphate coating is not homogenous consisting of phosphate crystals of varying composition and sizes separated by intercrystalline zones and there exposed areas of the metal substrate may act as possible weak spots on the surface in case of contact with corrosion agents.

Passivation seals these exposed areas or voids by reaction with exposed area as well as phosphate crystals surrounding the exposed area. Passivation is normally carried out with composition of Hexavalent Chromium and Trivalent Chromium but now Chrome-free passivation chemicals are also available in the Indian Market.

3.6 DEMINERALISED RINSES I, II AND III :

For Electrodeposition priming process, jobs should be free from any water soluble salts or contaminants. After passivation, jobs are rinsed with demineralised water in two or three stages to remove all the water soluble salts. Drip water conductivity before Electrodeposition should not be more than 30 micro Siemens.

3.7 OPERATING PARAMETERS OF PRETREATMENT LINE :

(FOR AUTOMATIC PLANT WITH INDEXING TYPE CONVEYOR)

<u>Stage</u>	<u>Parameter</u>	<u>Working range</u>
Spray degrease	Concentration	2%
	Temperature	50-55 °C
	Spray time	5 mts
Dip degrease	Concentration	4-5 %
	Temperature	60-65 °C
	Spray time	4 mts
Dip Rinsing	Contamination	1.0-1.5 pointage max.
	Dip time	4 mts
Dip Derusting	Concentration	30-35 %
	Dip time	4 mts
Dip Rinsing	Contamination	1.0-1.5 pointage max.
	Dip time	4 mts

<u>Stage</u>	<u>Parameter</u>	<u>Working range</u>
Preactivation Spray	Concentration	0.15 %
	Spray time	5 mts.
Dip Activation	Concentration	0.15 %
	Dip time	4 mts
Dip Phosphating	Concentration	4-5 %
	Temperature	48-52 °C
	Dip time	4 mts
Dip Rinse	Contamination	1.0 pointage max.
Spray Rinse	Contamination	0.5 pointage max.
DM water Rinse	Conductivity	30 mS max.
Fresh DM water Rinse	Conductivity	10 mS max.

4.0 PRIMERS :

In an Automobile Industry, following types of Primers are used :

- a) Solvent based Dip primer
- b) Water based Dip primer
- c) Spray type primer based on solvent
- d) Electrophoretic dip primer

Now a days in Automobile Industry only Electrophoretic primer is used for Automobile body.

4.1 TYPES OF ELECTROPHORETIC PRIMER :

- a) Anodic
- b) Cathodic :
 - i) Regular build
 - ii) Medium build
 - iii) High build

4.2 WHY ELECTRODEPOSITON PRIMER :

Because of the following benefits :

- a) Better material usage 95%
- b) Protection of box section area : Which is not possible in spray system
- c) Less pollution : Water based
- d) No fire hazard
- e) Uniform coating of edges, corners, crevices, box-section. Not possible by any other method.
- f) High degree of corrosion resistance.
- g) No sagging or solvent back wash
- h) High Production rate
- i) Less labour
- j) No rework
- k) Reduced volatile or fume emission through oven.

4.3 PRINCIPLES OF ELECTRODEPOSITION :

ANODIC ELECTRODEPOSITION	CATHODIC ELECTRODEPOSITION
Type of Resin a) Malenised oil b) Epoxy Ester c) Poly Butadiene Anodic system is used only in few places in India but nobody is using this system abroad . Polymers with Carboxy group  COOH Salt formation with Amines  COO⁻ N⁺ R₃H (For Polybutadiene system) Salt formation with Potassium Hydroxide  COO⁻ K⁺ (For Epoxyester system) pH is controlled by adding Tri-ethylamine / Ammonia in case of Polybutadiene and KOH in case of Epoxy Ester system	Type of Resin a) Epoxy Ester This system is being used all over the World and new Automobile units coming in India are having this system Polymers with Amino group  NR₂ Salt formation with Acids  N⁺R₂H OOCR⁻ pH is controlled by adding Formic Acid / Acetic acid

ANODIC ELECTRODEPOSITION	CATHODIC ELECTRODEPOSITION
pH Range Polybutadiene : 7.0 - 8.0 Polyester : 8.0 - 8.4 Painted object $\longrightarrow$ Anode Reaction at Anode a) Oxidation of Water : $2\text{H}_2\text{O} - 4\text{e} \longrightarrow 4\text{H}^+ + \text{O}_2 \uparrow$ (Acidic reaction) b) Electro coagulation of soluble binder : $\sim \text{COO}^- + \text{H}^+ \longrightarrow \sim \text{COOH} \downarrow$ (Insoluble deposited film) Reaction at Cathode : Reduction of water : $2\text{H}_2\text{O} + 2\text{e} \longrightarrow 2\text{OH}^- + \text{H}_2 \uparrow$ (Alkaline Reaction) Excess Alkali removed by Electrodialysis	pH Range : 6.0 - 6.8 Painted object $\longrightarrow$ Cathode Reaction at Anode a) Oxidation of Water : $2\text{H}_2\text{O} - 4\text{e} \longrightarrow 4\text{H}^+ + \text{O}_2 \uparrow$ (Acidic reaction) Excess H^+ removed by Electrodialysis Reaction at Cathode : a) Reduction of water : $2\text{H}_2\text{O} + 2\text{e} \longrightarrow 2\text{OH}^- + \text{H}_2 \uparrow$ (Alkaline Reaction) b) Electrocoagulation of soluble binder : $\sim \text{NR}_2\text{H}^+ + \text{OH}^- \longrightarrow \sim \text{NR}_2 \downarrow + \text{H}_2\text{O}$ (Insoluble Deposited film)

4.4 THE ADVANTAGES OF CATHODIC ELECTRODEPOSITION :

- Better wet adhesion
- No disruption of Phosphate coating
- Higher film resistance
- Higher application voltage
- Better coating in box section area because of better throwing power
- Freedom from cosmetic corrosion
- Better bath stability

- h) Can be used even at low production level
- i) High Coulomb yield : Consumes less electricity
- j) No bacterial contamination
- k) Low emission of fumes in the oven (max. 5% against 10-15% in AED)

4.5 OPERATING PARAMETERS OF ELECTRODEPOSITION PRIMER :

<u>PARAMETER</u>	<u>ANODIC</u>	<u>CATHODIC</u>
• Non Volatile content (by wt %)	10-12 %	20-25 %
• Bath temperature	27-29 °C	22-28 °C
• Applied Voltage	180-200 V	250-300 V
• Deposition time	3-4 mts	2-2.5 mts
• pH at 27 °C	8.0-8.4	6.0-6.8
• Specific conductivity	4000-6000 mS	1000-2000 mS
• Film Thickness	15-20 microns	18-35 microns
• Curing temperature	160-165 °C / 30 mts	160-165 °C / 20 mts

4.6 PROPERTIES OF DRY FILM AT 20-25 MICRONS DRY FILM THICKNESS OVER TRICATIONIC ZINC PHOSPHATING COATING :

<u>PARAMETER</u>	<u>ANODIC</u>	<u>CATHODIC</u>
• Appearance	Smooth & uniform, Free from bits, craters etc.	Smooth & uniform, Free from bits, craters etc.
• Pencil Hardness	> 2H	3H
• Pendulum Hardness (Konig 6° - 3° oscillation)	90 - 100	140 - 150
• Cupping Value	> 6mm	> 6mm
• Cross cut adhesion	0/100	0/100
• Salt Spray resistance (ASTM B117)	Passes 600 hrs with creepage below 2 mm	Passes 1000 hrs with creepage below 2 mm
• Water immersion	More than 240 hrs	More than 240 hrs

5.0 TOP COATS :

5.1 TRENDS IN TOP COAT :

Latest developments in Top coat formulations are taking place for :

- Upgradation of appearance and performance
- Convenient and efficient application (Both by conventional system and Automatic applicator)
- Lower emission : Less pollution
- Lower energy for curing.
- Cost reduction by using appropriate application system.

Upgradation of appearance and performance of Top coats can be achieved by :

- i) Newer types of pigments resistant to Weathering and Ultraviolet light : This will provide a better DOI and Gloss retention.
- ii) Improved variety of resin eg. from Alkyd to Polyester and Polyurethane which provides better cross linking and better weathering resistance. And also better chip resistance and higher flexibility.

- iii) Use of sag control agents (microgels) in order to have better flow and rheological property so that orange peel can be eliminated.

5.2 DEVELOPMENT OF TOP COAT APPLICATION :

Objectives :

- Better material utilization from 50% to 80%
- Faster rate of Production
- More automation - less dependence on operators skill.

Trends :

- Conventional spray to Electrostatic spray
- Electrostatic Air-assisted to Electrostatic High speed bell
- Manual to Automatic (Robotics)

5.3 QUALITY PARAMETERS :

Quality requirements for Polyester top coat for Automobile Industry:

- i) Resin type: Synthetic oil modified polyester.
- ii) Oil length : 30
- iii) Gloss : 90 units at 20 deg.
- iv) Weathering: 300 hrs with UVB 313 lamp in weatherometer. Loss of gloss should not be more than 10% of the original gloss.
- v) DOI (Distinctness of Image clarity) : By PGD meter
 - 0.7 Vertical
 - 0.8 Horizontal
- vi) Salt spray life (with CED primer underneath) : 1200 hrs.
- vii) Humidity test (as per IS-101) : Should pass at least 300 hrs.
- viii) Cupping value : Before & after aging not less than 6 mm.

Operating Parameter in the Spray Booth:

Paint viscosity	:	21-23 sec Cup B4
Humidity	:	65 ± 5 RH
Temperature	:	30 deg. C
Air Velocity	:	0.3 - 0.5 m/sec
Spray Pressure:		40 - 60 psi