

ADHESION IN POWDER COATINGS

BY: Chuck Danick
Industry Manager
RUCO Polymer Corporation

At: "ADHESION IN COATINGS:
TECHNOLOGY AND CHARACTERIZATION"

May 12-13, 1994

ABSTRACT⁽³⁾

Powder coatings have long been recognized for their superior adhesion and corrosion resistance. Many factors contribute to this extraordinary performance.

In the case of powder coatings, most of the coating properties are determined by the binder, which is comprised of powder coating resin and curing agent.

To make matters worse, many of the coating properties desired are rather contradictory.

Adhesion properties of powder coatings are dependent upon the substrate as well as the binder portion of the coating.

Environmental concerns have curtailed the use of chrome seal rinse for metal pretreatment. This leaves us with pretreatment techniques that do not provide as good adhesion and corrosion resistance for powder coatings.

It is the purpose of this paper to provide information that will help maximize adhesion and corrosion resistance of powder coatings.

INTRODUCTION

For powder coatings to have good corrosion resistance, the powder coating must have good adhesion to the substrate. Without good powder coating adhesion, the coating disbonds from the substrate leaving the substrate unprotected from corrosion.

It was thought that most thin film decorative thermosetting powder coatings in the market place today would pass 1000 hours SALT FOG exposure in accordance with ASTM B-117. This is common knowledge. Unfortunately, this commonly held belief of excellent salt fog performance is dependent upon the polymer characteristics and the pretreatment process.

This paper is based upon the hypothesis that chrome-free pretreatment process and/or unfavorable polymer characteristics do not provide as good adhesion properties as a process utilizing chrome seal rinse.

ADHESION

Adhesion is as much a necessity for paint as it is for adhesives.(4)

The powder coating and substrate form a system of three phases. The substrate can be considered the adherend; and the powder coating can be considered the adhesive. The third phase is the atmosphere, mostly air, on which the layer of powder coating (adhesive) borders.

When considering the total force necessary to pull the powder coating from the substrate, it is safe to assume that the adhesion value is the sum of all the components which provide part of the total adhesion.

An adhesion model can be based on the sum of individual forces derived from:

- mechanical bonding
- polar - polar bond attractions
- chemical bonds between the polymer and substrate

The characteristics of the powder resin are essential for overall powder coating performance. This may seem odd since a powder coating formulation does not seem to be a very complex system at first sight. This seems to be true if one compares the number of components in a powder coating formulation with that of a conventional solvent based coating. The solvent used in conventional coatings is a great help to the paint formulator even though it is an environmental nuisance.(7)

In the case of thermosetting powder coatings, most of the coating properties are determined by the binder which is comprised of the powder coating resin and the curing agent. There is probably no other type of coating where the resin and coating chemists are forced to make so many compromises.

Modifying resin characteristics to improve flow by reducing polymer melt viscosity is one way to improve wetting thus improving mechanical bonding. This is a balancing act to achieve lower viscosity while not sacrificing other properties is important.

Residual carboxyl functionality can help improve polar - polar bond attractions. This functionality could also contribute to moisture sensitivity; conflicting properties again.

Research to find a means to induce chemical bonds between the polymer and substrate would be a worthy project.

No one adhesion model can adequately describe all of the interactions and various causes of failure. Additional models to describe adhesion under various forms of powder coatings "stress" may be necessary.(6)

While a wealth of data on the critical surface energy is available, little is known about the surface tension of molten polymers. This is a topic for continued research.

Powder Coating's adhesion depends upon:

Wetting

Viscosity

Pigment/binder

Flow

Molecular weight of the binder resin

EFFECT OF RESIN CHARACTERISTICS:

High Tg and High Melt Viscosity

Most recently, a case was observed where a typical thin film decorative PU (Polyurethane) powder coating was modified by utilizing an alternative polyester resin.

The purpose for using this resin was to improve edge coverage, package stability and reduce impact fusion. This polyester resin had an ICI melt viscosity @200 C of 60-90 poise. This resin had a glass transition temperature, Tg, of 65-70 C.

A multistage chrome-free pretreatment system was used on the substrate.

The above system showed obvious signs of adhesion failure evidenced by disbondment from a scribed panel within the first 100 hours of salt-fog testing.

A control utilizing a polyester resin with an ICI melt viscosity of 35-45 poise @ 200 C with a Tg of 55-58 C passed 500 hours of salt fog testing with considerably less disbondment.

It is known that both of the above polyester resin systems will pass 1000 hours salt fog testing with less than one millimeter creepage from a scribe when a pretreatment utilizing chrome seal rinse is used.

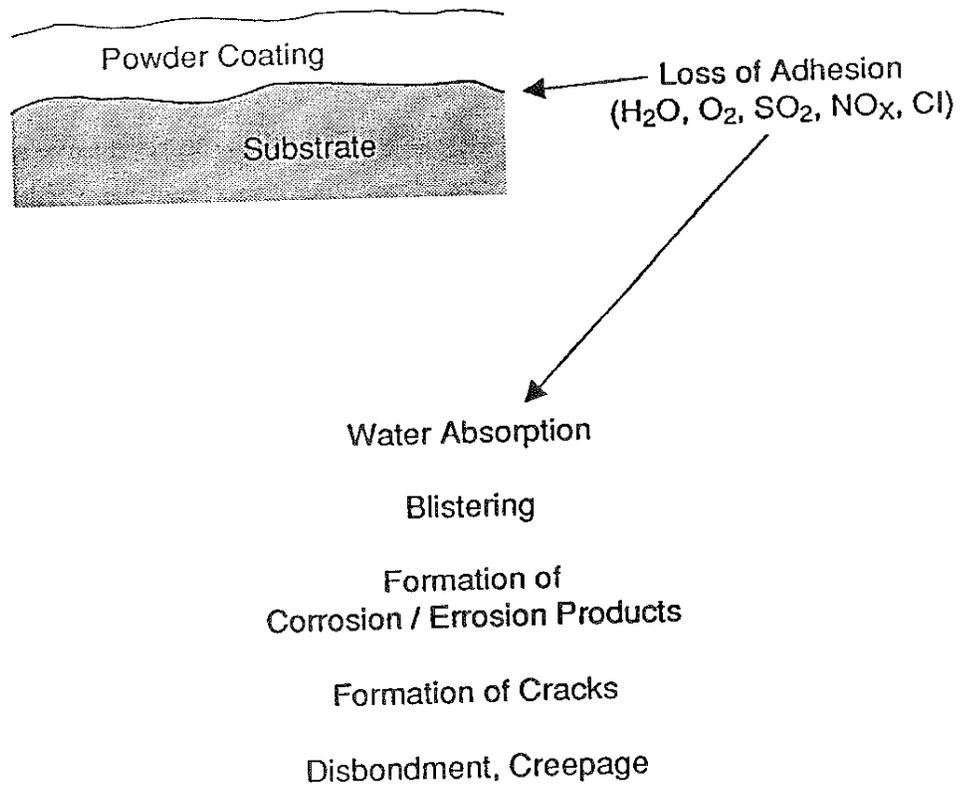
A means to get the best of both worlds was needed. The powder coating manufacturer did not want to give up the improved edge coverage, package stability and reduced impact fusion associated with the higher viscosity high Tg resin.

The end-user would not change the pretreatment to incorporate a chrome seal rinse to dramatically improve salt-fog resistance.

Wetting and adhesion additives were evaluated in an attempt to regain the adhesion associated with the lower viscosity resin. (12)

In this case, an additive was found to achieve SALT-FOG resistance essentially equal to the lower viscosity system.

POWDER COATING FAILURE



Good adhesion requires that the coating material be brought into intimate contact with the surface itself or a firmly bonded chemical pretreatment layer⁽⁴⁾.

POWDER COATING FAILURE VIA MOISTURE TRANSPORT (1,2)

The destructive effects of moisture transport in coatings has been documented at length in the literature. It is believed that deterioration of a coating immersed in an aqueous electrolyte such as a salt solution is probably due to one or more of the following phenomena:

- 1) The absorption by the coating of the electrolyte in which it is immersed.
- 2) The physical break-down of the coating through the development of pores or small physical faults that allow the electrolyte to reach the substrate.
- 3) The under film penetration of moisture between coating and substrate, traveling from a coating defect that allows the electrolyte to reach the substrate.
- 4) Permeation of the electrolyte through the coating leading to electrolyte accumulation at points where the coating is not tightly bonded to the substrate.

A direct measurement of the effect of moisture absorption into the coating can be obtained by measurement of the capacitance between the coated metallic sample and the electrolyte environment. Moisture absorption will radically lower the effective thickness of the coating to the depth of moisture absorption. The reduced thickness of high dielectric increases the capacitance between the coated panel and the electrolyte. The increased capacitance can be used as a basis for calculation of moisture absorption.

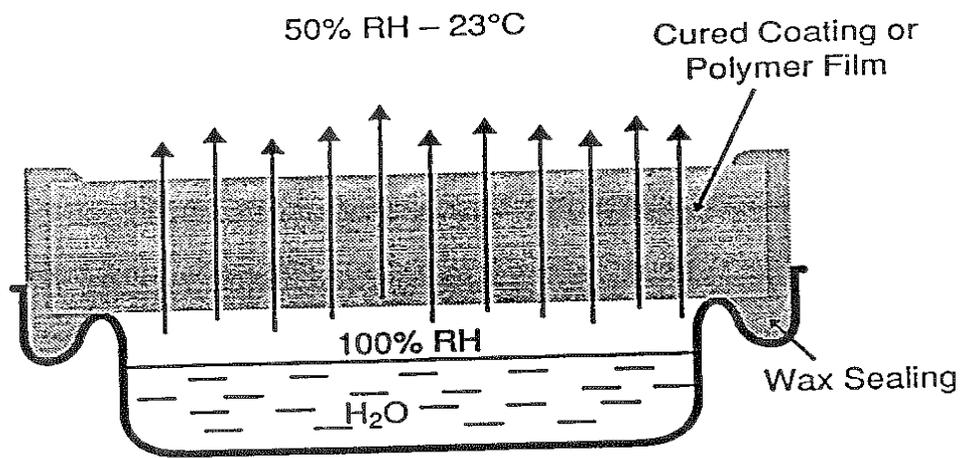
WATER VAPOR PERMEABILITY (WVP) AND PIGMENTATION (11)

Pigments play a role in the permeability of powder coatings to water. In most cases, pigmentation will reduce permeability of water.

Lamellar pigments form a barrier against the introduction of water molecules by virtue of their flaky or plate-like structure. These pigments lengthen the diffusion path of water molecules to help improve long-term corrosion protection.

MEASURING DEVICE FOR WVP-DETERMINATION

DIN 52615:1971 OR BS 3177



Examples of these lamellar pigments include:

Aluminum Powder

Micaceous Iron Oxide (MIO)

Glass Flakes

Aluminum powder is reported to be the best lamellar barrier pigment of the examples from above.

Various forms of micaceous fillers are used in powder coating formulations to help improve corrosion resistance.

WATER VAPOR PERMEABILITY (WVP) AND BINDER MOLECULES

Water molecules are likely to be absorbed in greater numbers and more strongly in coatings having polar groups. Hydroxyl and carboxyl functionality of the binder or coating that remains after crosslinking (curing) can contribute to water absorption. The idea is to formulate powder coatings so that few functional coatings groups are left after the coating is cured. Additives, surfactants, etc. that have polar groups can also contribute to WVP. Film thickness of the binder can influence WVP. It seems clear that thin films, 25 microns (1-mil) will have more fine pores and will have a higher WVP. Thick films 100-500 microns (4-20 mils) show very low WVP values. This is why under water coatings on steel utilize coatings 300-500 microns in thickness.

Cost has been driving the thickness of powder coatings to thinner films for the last 20 years or so.

Maybe somewhat thicker powder coatings, 1.5 - 2.5 mils, (38-63 microns) would help improve corrosion resistance.

THE MECHANISM OF BLISTERING

Blistering could be regarded as another step in the loss of adhesion. The size of blisters usually depends on the degree of adhesion of the coating to the substrate. When the internal pressure of liquid or gas stretches the film of the coating to the point where the internal pressure is in equilibrium with coatings adhesion, blisters form.

According to various literature, the process of osmosis is one of the most important causes of blister.

To have osmosis, two conditions must exist:

- a water permeable membrane (powder coating)
 - presence of water soluble salts or other products on the surface of the substrate

Osmosis is the passage of water through the semipermeable membrane (powder coating) from a solution of lower concentration to one of greater concentration. In all cases, the outer layer of the coating forms the area of lower concentration. The salt solution formed at the interface is the concentrated area.

Substrate contamination that will contribute to blistering includes:

sulfate salts on steel, zinc etc.

hard water deposits on steel, zinc etc.

UNDERCUTTING (CREEP) AND FLAKING BY CORROSIVE PRODUCTS

Undercutting of coatings on metallic surfaces is one sign of the obstruction of the adhesion of the coating to the substrate. Undercutting will appear in different forms. Undercutting usually begins at weak spots in the coating. The weak spots could be:

- pores
- thin areas of the coating
- cracks
- scribed/scratched areas

"Pretreatment for successful powder coating really means consistently providing a totally clean and dry, thoroughly rinsed, conversion-coated substrate to the powder booth. Sound pretreatment is the first step to satisfying your customers' needs. This can only be accomplished when you communicate your needs and allow your supplier to become an extension of your engineering or production department early on in the decision making."⁽¹³⁾

CLEANING OF IRON AND STEEL SURFACES⁽¹⁰⁾

- Solvent cleaning
- Wiping dipping/spraying
- Vapor degreasing
- Steam cleaning
- Emulsion cleaning
- Alkali cleaning
- Acid cleaning or pickling
- Blast cleaning
- Flame cleaning

Alkaline and acid cleaning are incorporated into modern spray pretreatment systems.

Alkali cleaners clean organic soils more efficiently than the inorganic soils.

Acidic cleaners clean inorganic soils more efficiently than the organic soils.

The critical difference between three and five stage pretreatment systems, is the type of cleaning detergent(s) used.

A three stage pretreatment process utilizes an acidic detergent system because cleaning and phosphating are combined in stage one. Acidic detergent systems are not as effective as alkaline cleaning products. This requires the manufacturer to have very tight control over the type of soil and the quantity of soil on incoming metal.

A five stage process allows the use of alkaline cleaners, since the cleaning step is separate from the phosphating step. Typically, alkaline cleaning produces a metal surface free of organic and inorganic soils.

The cleaning chemistries generated with alkaline systems provide considerably more latitude than acidic cleaners especially when looking at removal of heavier loads of soil.

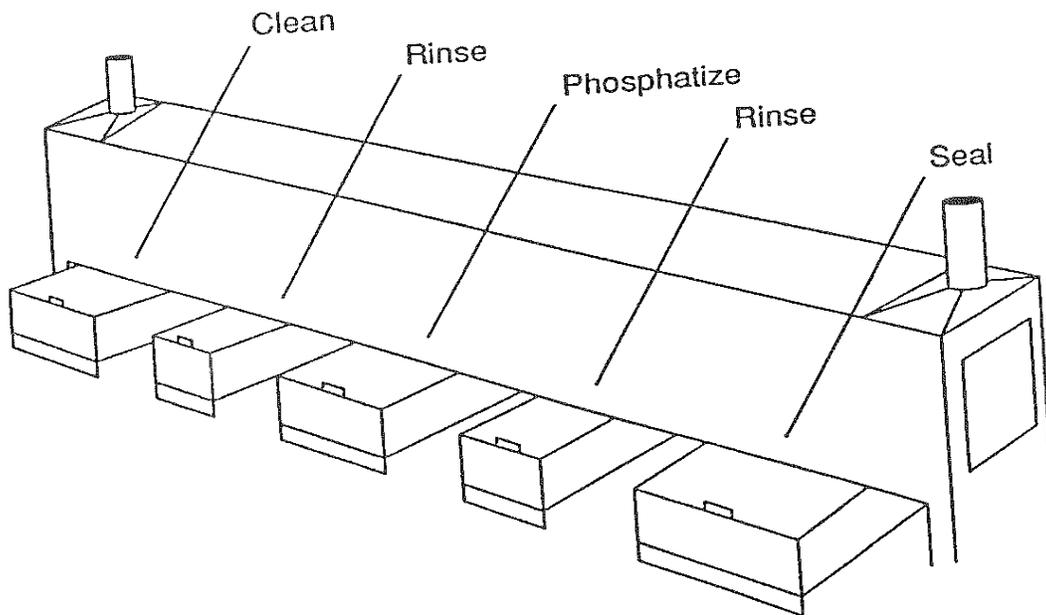
Without proper surface preparation, the best powder coating, applied with the greatest skill,

will fall short of its maximum performance capabilities. Surface preparation is the foundation upon which all else depends.

CLEANING AND PRETREATMENT PROCESSES(8)

The basic principle of pretreatment for steel is chemical reaction of the metal surface to produce a compound which is more resistant to corrosion than the metal itself and prevents "creep" of corrosion under the paint film in the event of damage. At the same time it provides a good base for the adhesion of the paint. These "chemical conversion" pretreatments are not weather-resistant in themselves but require protection of the paint before exposure to weather.

5-STAGE PHOSPHATIZING



AN EXAMPLE OF A GOOD PRETREATMENT PROCESS:⁽⁹⁾

STAGES	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
PROCESS	CLEAN	RINSE	PHOSPHATE	RINSE	SEAL RINSE
TIME	90 sec.	30 sec.	60 sec.	30 sec.	30 sec.
TEMP.	90-140°F	Ambient	90-140°F	Ambient	70-140°F
CONC.	2-4%	N/A	2-4%	N/A	0.1-0.25%
pH	ALKALINE	NEUTRAL	ACIDIC	NEUTRAL	ACIDIC NEUTRAL

FIVE OR MORE STAGES

Additional stages may include additional cleaning, rinsing, and deionized water rinse stages.

SEAL RINSES

Seal rinses represent the last pretreatment step prior to powder coating. Its purpose is to promote good powder coating adhesion, increase corrosion resistance, remove harmful residues and prevent rusting prior to the application of the powder coating.

Chrome containing seal rinses have been industry standards for years. Unfortunately, sludges produced during waste treatment are hazardous materials. The cost associated with the disposal and/or treatment of chrome containing wastes, has prompted the use of non-chrome rinses.

At least one supplier of pretreatment chemicals offers a self-contained recycling system for the chrome containing seal rinse. (13)

THE CHEMICAL THEORY OF PRETREATMENT FILM FORMATION

Phosphate coatings consist of crystalline salts of the metal which is being treated and/or crystalline salts of metal ions added to the phosphatizing solution. When the metal comes in contact with the phosphatizing solution, some pickling occurs which results in a reduction of acid concentration at the liquid-metal interface.

At this point iron is dissolved, hydrogen is evolved, and phosphate coating is deposited. Should the solution contain additional metal ions such as zinc or manganese, phosphate coatings of these ions will also be deposited.

The iron phosphate crystals are stacked vertically and closely packed horizontally. If this conversion coating is heavy enough and packed tightly enough, a micro surface with thousands of tiny canals or capillaries is formed. Powder coating melts and flows into these spaces and when cured, is mechanically locked into the crystalline structure. The mechanical lock provides adhesion.

The iron phosphate conversion coating is non-conductive. Corrosion, on the other hand, is an electrochemical process. To form rust, a flow of electrons must occur between sites with different charges. The iron phosphate crystals act as barriers to the flow of electrons.

Accelerators such as molybdate nitrite, nitrate, chlorate, peroxide or special organic chemicals may be added to increase the rate of coating deposition.

In general, iron phosphate coating weights of 25-70 mg/ft. are typically achieved.

One of the more popular pretreatment processes in use today is the molybdate accelerated system.

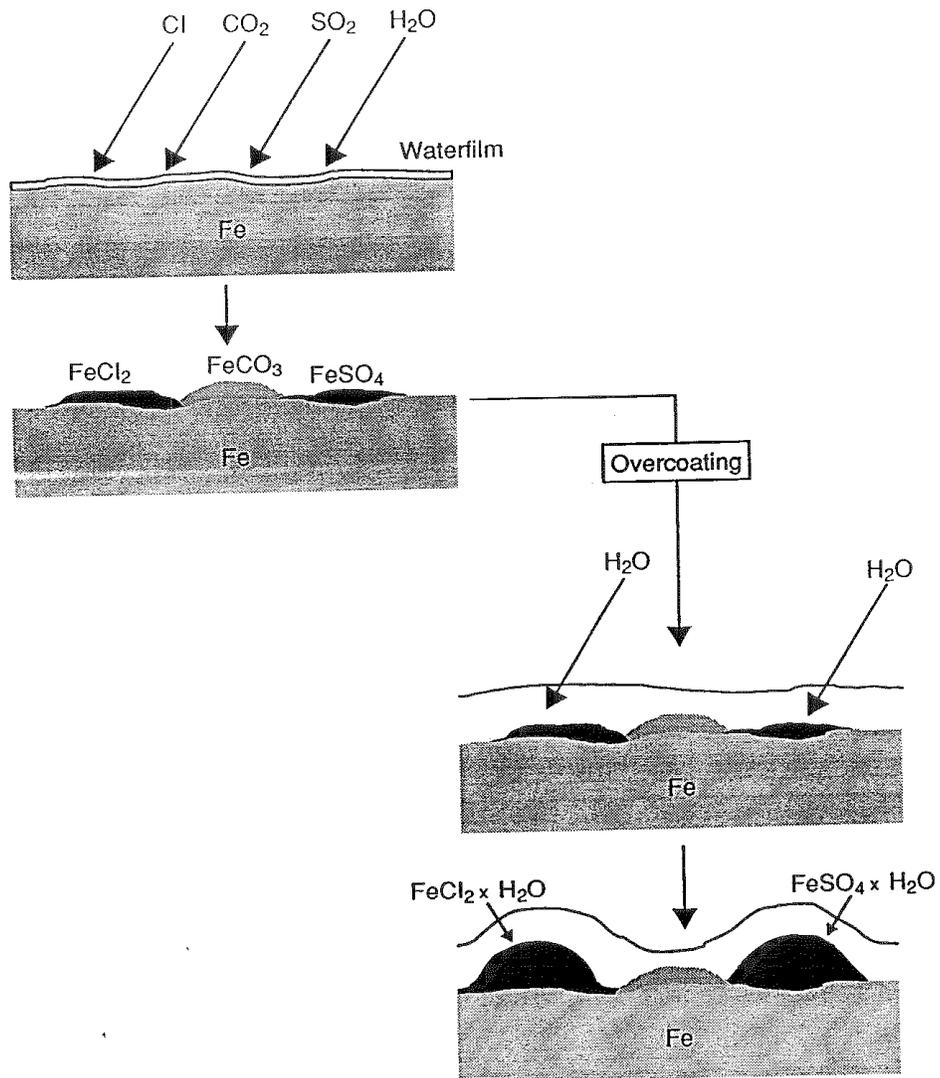
A proprietary seal rinse supplied by a small chemical manufacturer has dramatically increased adhesion properties of a chrome-free pretreatment system.⁽¹⁴⁾

The supplier states that his chrome free seal-rinse usually achieves performance no better than a 5-stage iron phosphate system with a good DI rinse.

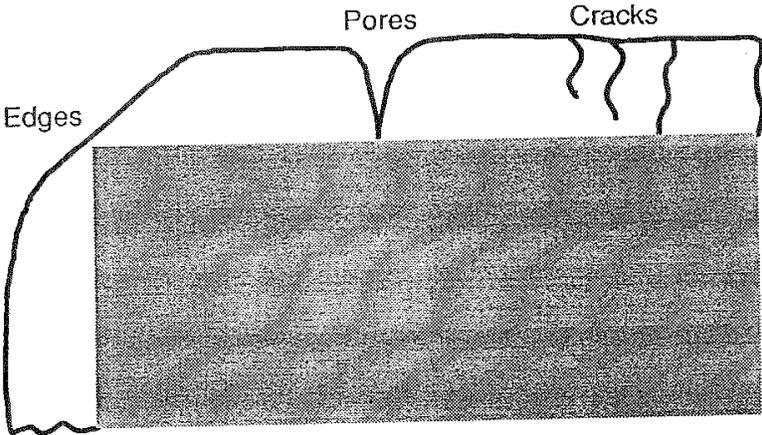
Some powder coatings seem to form a much stronger bond to this pretreatment system. One polyurethane powder coating exhibited such behavior. Panels achieving 1000 hours salt-fog resistance were observed.

A project to determine which powder coating chemistries consistently exhibit dramatically improved salt-fog resistance needs to be initiated.

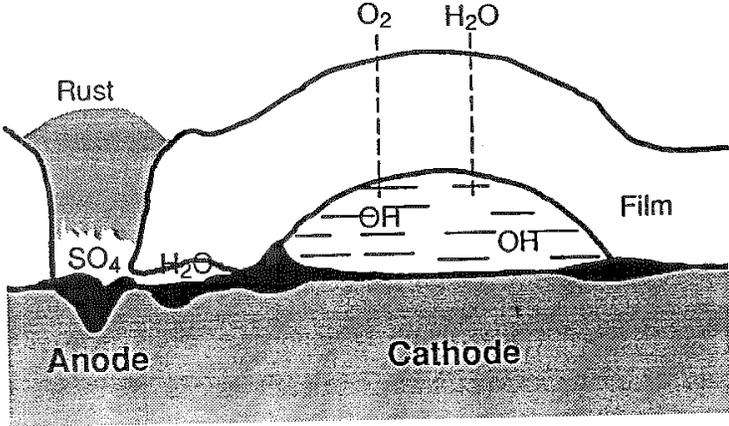
BLISTERING BY OSMOSIS AT COATED IRON (C.R.S.) SURFACES



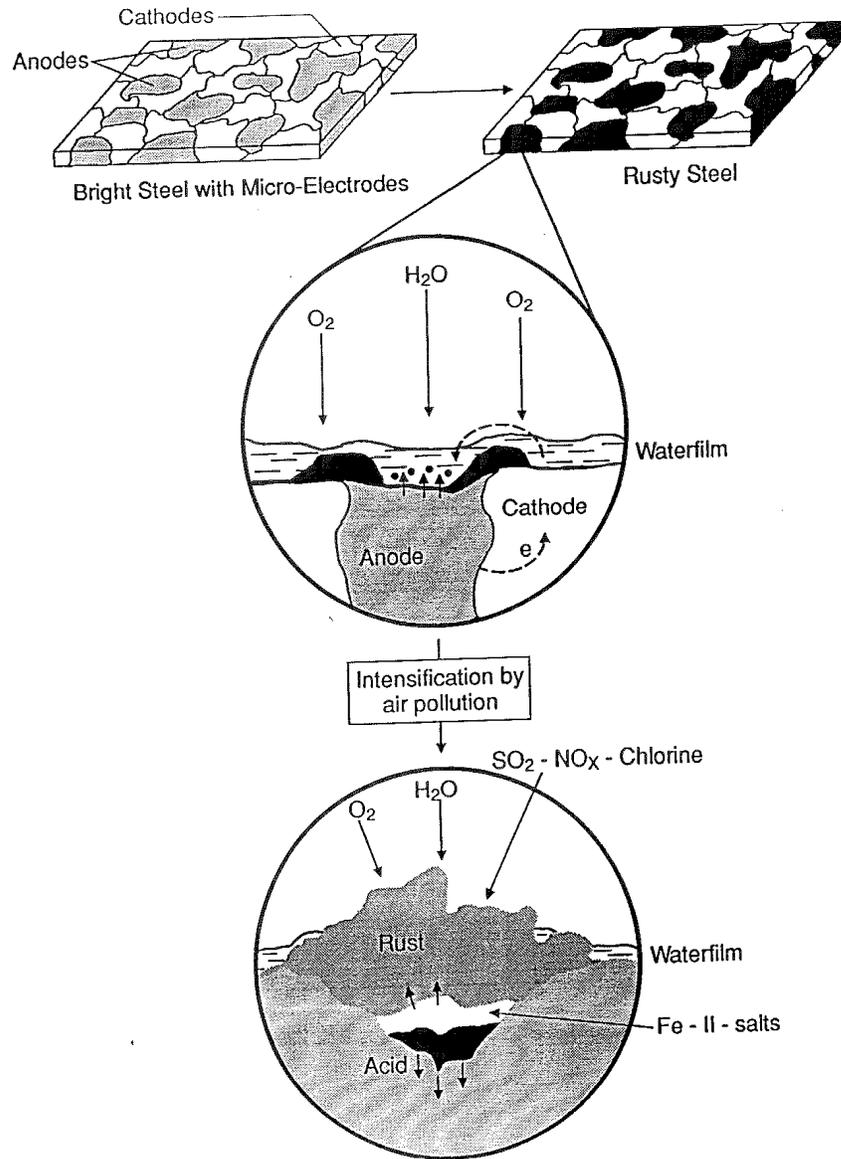
UNDERCUTTING OF POWDER COATED SUBSTRATES



Weak Spots of Paint Films.



STEEL CORROSION



CONCLUSIONS:

Now that we recognize that the optimum pretreatment process for corrosion and adhesion is no longer in common use, what can a formulator or end-user do?

FORMULATOR/POWDER COATINGS MANUFACTURER

- Select resin noted for exceptional wetting.
- Select additives noted to improve wetting.
- Select resin noted for high flow.
- Select resin chemistry system that promotes the above properties.
- Utilize corrosion inhibitive fillers such as zinc phosphate(s) etc.
- Formulate with resins that provide increased cross-link density when increased chemical resistance and corrosion resistance is required.
- Use lamellar pigments/fillers to reduce water vapor permeability (WVP).
- Test powder coatings on the same substrate as the proposed end-user.
- Report corrosion resistance data utilizing environmentally friendly pretreatment processes.
- Stop reporting corrosion resistance data utilizing chrome seal rinse as part of the pretreatment process, unless the end-user will be using that pretreatment.
- Stop talking about 1000 hour salt-fog data, unless it represents results achievable using today's cleaning/pretreatment processes.
- Don't expect to get something for nothing. As resin systems are pushed towards lower and lower functionality (lower cost), less chemical resistance will be the result.

END-USER

- Request corrosion resistance data on the substrate you will be using with the same pretreatment process.
- Optimize your cleaning/pretreatment process.
- Maintain your cleaning/pretreatment process.
- Test actual corrosion/adhesion properties on parts from your coating system regularly.
- Work with the powder coating supplier to obtain the powder coating that will meet your requirements.
- Rethink your cleaning, pretreatment needs.
- Consider utilizing a chrome seal rinse system that can be recycled, thus preventing hazardous waste and pollution.
- Utilize greater film thickness to decrease water vapor transmission.
- Maximize adhesion by using the dry-off oven to provide more heat to parts to improve wetting of the substrate. (Note: Film thickness will be more difficult to control.)

REFERENCES

1. Braches, E. and Potente, H., Electrostatic Powder Coating: Process Parameters and Protective Properties Institut für Kunststoff-Offverarbeitung an der Rheinisch-Westfälischen Technischen
2. Burkhart, Robert W., Improved Hi-Performance Coatings For Corrosion Control In a Harsh Shipboard Environment Corrosion/76, Paper No. 81
3. Danick, Charles, How To Maximize Powder Coating Adhesion and Corrosion Resistance, Presented at Pretreat '93
4. Houwink, R. and Salomon, G. Adhesion in Paint Technology pp 441-471, Adhesion and Adhesives, Vol. 2, Applications
5. Kurosawa, K. and Fukushima, T. The Effects of Oxidizing Agents on the Formation of Chemical Conversion Coatings on Mild Steels In an Na₂ MoO₄-H₃ PO₄ Type Aqueous Solution Corrosion Science, Vol. 32, No. 8 pp 893-902, 1991
6. Mills, George, The Challenges Before US- AN END-USER'S VIEW of Heavy Duty Industrial Powder Coating, Polymers Paint and Colour Journal, Aug. 23, 1989, Vol. 179, No. 4243
7. Misev, T. and Belder, E. Polyesters for Powder Coatings: Resin Parameters Correlated with Coating Properties, JOCCA, 1989 pp 363-368
8. Morgans, W.M., Finished Products, pp 48-52, Outlines of Paint Technology, Vol. 2
9. Phillips, Dick, Practical Application of the Principles Governing the Iron Phosphate Process, Plating and Surface Finishing, March, 1980
10. Roberts, A.G., ORGANIC COATINGS, Properties, Selection and Use, U.S. Dept. of Commerce, National Bureau of Standards, Feb., 1968
11. Schmid, Eric V. EXTERIOR DURABILITY OF ORGANIC COATINGS, FMJ International Publications Ltd., 1988

ACKNOWLEDGEMENTS:

12. Dr. Stan Skora, Estron Chemical Inc.
1130 Rt. 46 West
Parsippany, NJ 07054
(201) 263-2205
Wetting Additive, Oxymelt A-2

13. Brad Gruss, Fremont Industries, Inc.
Shakopee, MN 55379
(612) 445-4121
How to Minimize Pretreatment Problems to Maximize Powder Performance
Quality Phosphating Guide
Pretreatment Trouble Shooting for Powder

14. Gerald Watson, Custom Chemicals of Texas
(817) 483-7184
Chrome-free Seal-Rinse 90517