(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 057 334**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **81400514.6**

(51) Int. Cl.³: **B 05 D 3/00**

(22) Date of filing: **31.03.81**

(30) Priority: **29.12.80 US 221176**

(43) Date of publication of application: **11.08.82 Bulletin 82/32**

(84) Designated Contracting States: **AT BE CH DE FR GB IT LI LU NL SE**

(71) Applicant: **BALTIMORE AIRCOIL COMPANY, INC., Montevideo Road, Jessup, Maryland 20 794 (US)**

(72) Inventor: **Geary, David F., 323 Tunstall Court, Severna Park Maryland 21146 (US)**
Inventor: **Honchar, Dennis R., 4017 High Point Road, Ellicott City Maryland 21043 (US)**

(74) Representative: **Corre, Jacques et al, Cabinet Regimbeau 26, Avenue Kléber, F-75116 Paris (FR)**

(54) Pretreatment process for galvanized metal prior to its coating with organic powder.

(57) This invention relates to a pretreatment process for galvanized metal which, unlike existing processes, was specifically developed for galvanized metal. Because of the natural corrosion protection properties of the zinc cladding of galvanized metal, no additional passivation is necessary as is required with existing processes. Also, the invention relates to the galvanized metal which has been pretreated by the process of this invention prior to application of an organic powder coating. Galvanized metal treated by this pretreatment process prior to coating leads to a uniform coating which is impervious to acid, base and salt solutions, and which will not scratch or flake off on impact.

EP 0 057 334 A2

TITLE OF THE INVENTION

PRETREATMENT PROCESS FOR GALVANIZED METAL PRIOR TO ITS COATING WITH ORGANIC POWDER

BACKGROUND OF THE INVENTION

As background to the invention, a general discussion of metal preparation for powder coating will be presented. This will lead into a comparison of conventional metal preparaton systems and the system of the present invention.

One skilled in the art would recognize that achieving a goal of providing the ultimate corrosion protection of steel with a powder coating requires that several steps be satisfied. First, the surface must be thoroughly cleaned of all dirt, oil, oxidation products and any other foreign matter. Second, sites to which the powder can bond must be available on the surface. These are generally provided by depositing certain crystals on the surface during the preparation operations. Third, the coating must be a functional type, which, unlike decorative coatings, is especially formulated to impart corrosion resistant properties to the steel when applied in thicknesses generally less than 0.010 inches (0.25 mm).

Those expert in the area of powder coatings recommend that functional coatings be applied over mild or "black" steel. Exotic surface preparation systems for mild steel have been developed. These systems first clean the steel, then rinse it with a solution which deposits a microscopic layer of crystalline material, such as zinc phosphate. The purpose of this microscopic layer is to passivate the surface against corrosion and to provide bonding sites for the functional powder. Galvanized steel is not normally recommended as the substrate, despite its superior resistance to corrosion, resulting from the zinc

cladding, because experience has indicated that the functional powder does not bond as well to the zinc cladding as to the properly prepared mild steel.

It has been determined that this incorrect conclusion was reached because previous investigations have applied to galvanized steel, surface preparation systems developed for mild steel and then when the resulting adhesion of the functional powder coating was inferior, it was concluded that the galvanized steel was an undesirable substrate.

An investigation leading to the subject invention concluded that it was possible to prepare the zinc surface in such a manner that the adhesion of the functional powder coating to the zinc cladding is equivalent to the adhesion achieved to properly prepared mild steel. This means that it is possible to utilize galvanized steel as the substrate and benefit from the superior corrosion resistance of the zinc cladding and still achieve the desired outstanding adhesion of the functional powder coating to the substrate.

A major advantage of the use of galvanized steel over mild steel as the substrate is realized where the powder coating becomes physically damaged, as can occur, for example, in shipping, rigging, or installing of industrial equipment. In this situation, the corrosion resistance is determined only by the substrate material and the zinc cladding of the galvanized steel provides significantly greater corrosion protection than is possible through the use of a passivating rinse, as typically used on mild steel.

As further background to the invention, the presently used eight-stage or eight-step pretreatment

process of galvanized metal prior to its organic powder coating will be described. The present invention which is an improved four-step pretreatment process will then be described. The eight-stage or eight-step pretreatment process is as follows:

Step 1 - The first step cleans the galvanized metal zinc substrate surface of any grease or dirt that is present. The grease and/or dirt is removed using an alkaline-type cleaning solution with its pH maintained so that it will not attack the zinc.

Step 2 - A water rinse is applied to remove the alkaline cleaner from the substrate. Due to carry-over of the alkaline cleaner from step 1, this rinse is a mild alkaline rinse.

Step 3 - A second water rinse is utilized to remove any of the mild alkaline residues remaining on the surface following step 2. Thorough removal of all alkaline residues is important because the fourth step requires a delicate acid balance for the zinc phosphate solution. If any alkalinity is left on the substrate, it will affect the acid balance of the zinc phosphate solution.

Step 4 - Substrate passivation, through the spraying of a zinc phosphate solution on the substrate, is accomplished in this step, which is the key to the eight-step system. Reaction of this acidic solution with the zinc substrate results in the formation and deposition of water insoluble zinc phosphate crystals on the surface. It is important that this zinc phosphate solution be maintained at a pH near 3 or a powdery precipitate will be deposited on the substrate. This precipitate is undesirable, as it will significantly

reduce coating adhesion.

The purpose of the zinc phosphate crystals is to passivate the substrate and give irregular molecular sites to which the powder coating can mechanically bond.

Step 5 - The fifth step is a water rinse which is necessary to remove excess zinc phosphate and any water soluble salts (chlorides, sulfates, or nitrates) that may be on the surface of the substrate. These water soluble salts have to be removed from the surface or they will reduce adhesion of the coating.

Step 6 - The sixth step is an acidified rinse using chromium compounds such as chronic acid. The purpose of this rinse is to remove the less soluble salts remaining from the water rinse in step 5. The chromium compound is used to deposit an additional barrier coat and to give the substrate some added corrosion protection. The chrome also fills some of the pores which exist in the zinc phosphate crystal film, thereby enhancing the passivation of the metal while providing additional molecular bonding sites for the powder coating.

Step 7 - The seventh step of the pretreatment process is a water rinse whose purpose is to remove any foreign salts or minerals.

Step 8 - The last step involves thoroughly drying the galvanized metal by the application of heat.

It should also be mentioned that in the prior art and in previous pretreatment processes for galvanized metal there is a so-called six-stage or six-step system. This system is similar to the eight-step system except that steps 3 and 7, which are respectively the two water rinse steps, are eliminated.

DESCRIPTION OF THE INVENTION

This invention comprises a pretreatment process, particularly a four-step pretreatment process for galvanized metal prior to its coating with an organic powder. This pretreatment process was specifically developed for application with a galvanized metal substrate, which does not require passivation to assure protection of the steel from corrosion.

It is an object of this invention to provide a pretreatment process for galvanized metal so that when coated with a functional organic powder, the adhesion of said coating will be superior to that possible with conventional pretreatment systems.

It is another object of this invention to provide a powder coating system for galvanized metal whereby the metallic zinc layer on the steel is utilized directly to provide sacrificial corrosion protection for the metal rather than utilize less effective chemical rinses, such as a zinc phosphate rinse, to deposit a corrosion protective layer on the surface.

It is another object of this invention to provide a four-step process for pretreating galvanized metal prior to organic powder coating of said metal which process results in savings in material, time, and labor when compared to the prior art pretreatment processes.

It is another object of this invention to provide a pretreatment process for galvanized metal prior to the organic powder coating of said metal which uses no chrome compounds and which thus eliminates the problems of hazardous wastes.

It is a further object of this invention to provide a pretreatment system for galvanized metal which

deposits minimal zinc phosphate on the metal (unlike other systems which deposit significant amounts of zinc phosphate on the metal) thus insuring better powder coating adhesion to the metal. It has been found that adhesion of the organic powder coating on galvanized metal with a minimum of zinc phosphate thereon is superior to that achieved with the prior pretreatment systems. It has been concluded that by immediately organic powder coating the metal, the passivating effect of the zinc phosphate crystals is not required.

The four-step system of applicants' invention follows:

Step 1 - The first step in the four-step pretreatment system of this invention is a cleaning and phosphoric acid etching. Grease and dirt are removed herein while at the same time the galvanized metal is etched by the phosphoric acid, resulting in small amounts of zinc phosphate crystals randomly distributed over the substrate surface.

Step 2 - The second step is a water rinse, which is applied to remove excess cleaning and etching solution from step 1, plus any salts (chlorides, nitrates, sulfates, and the like) that may be on the surface of the substrate. Due to acid carry-over from step 1, this rinse is a mild acid rinse.

Step 3 - The third step is a water rinse which is utilized to fully remove any of the mild acid, salt, or mineral residues which remain on the surface following step 2. This step requires less time or equipment if the water is heated.

Step 4 - The last step involves thoroughly drying the galvanized metal by the application of heat.

The following is a more detailed description of each of the above steps, including a detailed description of the methods for carrying out the steps.

The first step in the preparation of the galvanized metal for coating involves cleaning and acid etching to assure a clean and oxide-free surface. This is accomplished through the use of a typical biodegradable solution (liquid acid solution) containing phosphoric acid, solvents and surfactants and which is obtainable commercially in various formulations from, for example, Oakite Products, Inc., in Berkeley Heights, New Jersey. It is formulated for removing light grease, shop dirt, welding fluxes, oxides, and mill scale from the galvanized metal and in general microscopically etches the metal prior to organic powder coating. Since the cleansing and etching agent contains phosphoric acid, a small amount of zinc phosphate crystals, resulting from the chemical reaction of the phosphoric acid with the zinc, are randomly distributed over the surface substrate of the metal. Typically a 3-20% solution by volume of this acid compound at 110-150^{o} is used. The exact temperature and concentration must be adjusted to achieve thorough cleaning with minimal attack of the zinc. The solution is usually contained in a vat which is large enough so that the entire piece of galvanized metal can be dipped therein. It has been found that the minimum dipping time in this solution is 1 1/2 to 3 1/2 minutes with more time needed if the galvanized metal is heavily

contaminated with dirt or oil or has been treated with special rinses by the metal vendor. Sometimes, instead of dipping, the cleaning and etching solution is sprayed onto the galvanized metal.

The second step involves a water rinse which is required to remove excess cleaning agent from step 1 plus any salts, such as chlorides, nitrates or sulfates which may be on the surface of the substrate. Typically, tap water is used, but in areas where it contains high mineral levels, deionized water may be more suitable. Water used in this step becomes slightly contaminated with the acidic cleansing agent used in step 3 as a result of carry-over of the cleansing agent on the surface of the galvanized steel.

Step 3 also involves a water rinse. As stated previously, this water rinse is required to assure that all of the dilute cleaning agent, plus any salts and minerals remaining on the surface following step 2, are removed.

In step 4, the treated galvanized metal must be dried prior to its coating with the organic powder. This drying is usually done by inserting the pretreated and rinsed galvanized metal into an oven at 130°-400°F for approximately 2 to 10 minutes so that it thoroughly dries. A preferred typical condition would be inserting the pretreated and galvanized metal in the oven at 250°F for approximately 5 minutes.

Upon completion of the four-step pretreatment process, the galvanized metal must be powder coated within a short period of time or at least before any amount of zinc oxide develops on the galvanized metal as a result of exposure to the atmosphere of other oxidizing agents.

This is so because unlike conventional pretreatment systems, no passivation coating is deposited in the instant invention. Ideally, then the galvanized metal should be powder coated immediately after it has been dried. As a practical matter, however, due to equipment limitations and location, manpower requirements, moving needs, and the like, it has been found that the time lag between drying (step 4) and powder coating of the galvanized metal can range from about 5 minutes to 6 hours with an average time lag of about 10 minutes. Although 6 hours has been stated as an upper limit, this is an approximation, since it has been determined that if 2 or 3 days elapse between dry-off (step 4 of this invention) and powder coating, the adhesion of the coating will not be as good as if the time lag were 5 minutes to 6 hours. Impact of lag time on coating adhesion will vary with exposure of the galvanized metal to temperature and humidity conditions (i.e. inside a building storage or outside storage and the like).

The coating to be used is a typical organic powder such as, for example, epoxy, polyester, acrylics, or hybrids which are mixtures of polyester and epoxy powders. Such products which have been used with great success in the instant invention are epoxy coating powders such as Pulvalure ^{R}, Scotchkote ^{R}, Corvel ^{R}, or Vedoc ^{R}, which are manufactured by and available from various suppliers. These typical epoxy coating powders are hemogenous, melt-mixed, 100% solids designed for application to metals.

The organic powder coating is applied typically by electrostatic spray although it can also be applied by dipping the treated, rinsed, and dried galvanized metal

into a fluidized bed of this powder. When applied by an electrostatic spray, the powder issues from a gun which imparts it with an electrically positive charge. Since the galvanized metal is negatively charged, the powder is attracted and caused to adhere to the metal. The particular thickness of the coating is not critical, although a typical thickness which has been found to be ideal is .004 inches (0.1) millimeters $\pm$ .001 inches (.0254 millimeters). This is the approximate thickness which is deposited on the pretreated, rinsed, and dried galvanized metal before putting it in an oven for curing. Proper curing involves baking the powder coated metal in an oven at approximately 300°-550°F for about 1-20 minutes. Temperatures and curing times are usually given by the manufacturer of the organic powder used.

Having thus described the invention with particular reference to the preferred forms thereof, it will be obvious to those skilled in the art to which the invention pertains, after understanding the invention, that various changes and modifications may be therein without departing from the spirit and scope of the invention and defined by the claims appended hereto.

WHAT IS CLAIMED IS :

1. A process for coating galvanized metal, characterized in that it comprises :

- cleaning and acid etching the galvanized metal ;
- thoroughly rinsing said metal ;
- drying said metal ; and
- applying an organic powder coating before any substantial amount of zinc oxide forms on the galvanized metal.

2. The process of claim 1, characterized in that the powder coating is performed within 6 hours after drying of the galvanized metal in step 4.

3. The process of claim 1, characterized in that the cleaning and acid etching material is a solution containing phosphoric acid, solvents and surfactants.

4. The process of claim 1, characterized in that the organic powder coating is an epoxy powder coating.

5. The process of claim 1, characterized in that the rinsing of said metal consists of two water rinses.

6. The process of claim 1, characterized in that the metal is zinc.

7. Powder coated galvanized metal, characterized in that the powder coating is applied on galvanized metal pretreated according to the process of one of claims 1 to 5.

8. The product of claim 7, characterized in that the metal is zinc.