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(54) Process for optimizing corrosion protection of coated substrates.

(57) The life of protective and/or wear resistant coatings which are applied to substrates, particularly metallic surfaces which are subject to corrosion, are extended by the deposition of poly(p-xyxylene) which penetrates and plugs microscopic pores as small as 500 angstroms in the coating. Even if the coating surface is polished or subject to wear through abrasion, the parylene has penetrated sufficiently deep into the pores forming an undisturbed protective barrier between the substrate and corrosive fluids.

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BACKGROUND OF THE INVENTION

(1) FIELD OF THE INVENTION

This invention relates in general to a process for optimizing or enhancing the corrosion protection of coated substrates. In one aspect, this invention is directed to a process for protecting coated substrates, particularly metal substrates, from corrosion due to microscopic pores, voids, holes or cracks in a corrosion protective or wear resistant coating which has been applied to the substrate. In a further aspect, the invention relates to a process for enhancing the corrosion protection of a wide variety of articles, such as tool parts, engine components, sheet metal, automotive parts, rollers, decorative articles and the like.

(2) DESCRIPTION OF THE RELATED ART

A variety of methods have been reported in the literature for providing protective or wear resistant coatings to substrates. In many instances, the substrate is comprised of a metal or metal alloy which easily corrodes upon exposure to the atmosphere or corrosive fluids. By coating the substrate with a protective coating which is inert to corrosive fluids and the atmosphere, corrosion of the underlying substrate is eliminated or at least retarded.

In many instances, the protective coating may also impart decorative or aesthetic effects to the substrate such as chrome plated articles, for example, automotive parts and the like. Likewise, the protective coating may be deposited on the substrate to impart a wear resistant coating as well as to protect from corrosion. In most instances, a single protective coating of a corrosion resistant material is all that is applied to the substrate to prevent or retard corrosion.

In view of economic considerations it is, of course, desirable to limit the thickness of the protective coating to that thickness just sufficient to protect the substrate. In most instances the cost of the protective coating per unit weight is much higher than the cost of the substrate material.

It is well known that substrates such as iron and steel can be protected by deposition of metal or metal alloy coatings which protect the substrate. Additionally, other materials including metal compounds such as metal nitrides and plastics can also be protected by the deposition thereon of a protective coating. Several methods are known in the literature for depositing protective coatings and include, but are not limited to, electrodeposition from solutions, cathodic deposition, plasma deposition, sputtering, "D" gun deposition, and the like.

Thus, prior to the present invention, a variety of coatings both inorganic and organic have been applied directly to substrates to provide protection. For instance, the use of organic protective coatings such as silane coatings has been disclosed as corrosion inhibitors for iron and steel.

In U. S. Patent 3,890,269 methods are disclosed for the prepartion of aminofunctional organopolysiloxanes which are indicated to be useful as sizing agents and as corrosion inhibitors. U. S. Patent 3,759,751 discloses a primer comprised of an epoxy resin, an inorganic chromate and an aminosilane for use on aircraft surfaces. Trimethylsilylacetamide has also been disclosed in U.S. Patent 4,310,575 as a corrosion inhibitor for steel. More recently, novel silane compounds have been disclosed in U. S. Patent 4,645,846 as having utility as corrosion inhibitors for metal surfaces.

While organic coating can be useful in providing corrosion protection to substrate material, they are of course, not useful where the material will be subject to abrasion or strong corrosive conditions. In such instances, metal or metal-containing protective coatings are employed. The patent literature contains numerous methods for the application of such protective coatings many of which also serve as wear resistant coatings as well.

While the aforementioned compositions are useful for protecting metal and other surfaces from corrosion, they are not entirely effective if the protecting surface itself is characterized by microscopic voids. Such compositions can contain small crevices, pores and other openings in the protective coating which eventually allow corrosive fluids to penetrate to the substrate material. However, if it were possible to seal or plug such microscopic voids in the protective coating, the corrosion resistance of the coating could be extended.

Accordingly, one or more of the following objects will be achieved by the practice of the present invention. It is an object of the present invention to provide a process for optimizing the corrosion protection of a variety of materials. Another object of the invention is to provide a process for the protection of coated substrates which are easily corroded and have been coated with a wear resistant and/or decorative coating. A further object of this invention is to provide a process for imparting a corrosion barrier to coated substrate materials thereby extending the useful life of such materials. A still further object of the invention is to

provide a "micro pore filler" that protects coated substrates form corrosion even though the outer surface of the "filler" may be abraded away. Another object is to provide a process for providing corrosion protection by applying to a coated substrate material a thin layer of parylene. These and other objects will readily become apparent to those skilled in the art in the light of the teachings herein set forth.

SUMMARY OF THE INVENTION

In its broad aspect, the present invention relates to a process for optimizing corrosion protection of a variety of articles having a protective coating and to the corrosion protected articles themselves.

The process optimizes corrosion protection of substrates having a protective or wear-resistant coating wherein the coating itself exhibits microscopic pores, at least some of which provide a continuous path from the substrate to the outer surface of the protective coating. The process comprises applying to the protective coating a thin coating of at least one poly(p-xylylene) in an amount sufficient to at least partially fill or plug the microscopic voids and prevent exposure of the substrate material to fluids, including atmospheric elements capable of corroding the substrate.

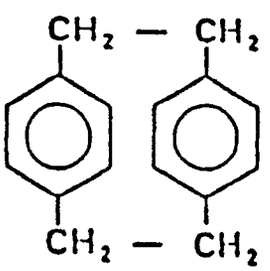
DESCRIPTION OF THE PREFERRED EMBODIMENT

As indicated above, the process of the present invention provides a convenient method for retarding or preventing corrosion or degradation of metallic and other substrates which have been coated with a protective or decorative coating. During application, or deposition, such coatings may be characterized by microscopic pores, holes or cracks, etc., which eventually allow penetration of atmospheric elements or fluids to the substrate itself. alternatively, such voids may occur some time after the initial coating was applied to the substrate. In both instances, treating the coated substrate with parylene in accordance with the teachings of the present invention retards or prevents corrosion and/or degradation and thereby extends the useful life of the article.

The term "corrosion" as employed throughout the specification and appended claims is meant to include not only the usual oxidation of substrate material, such as metals, by normal oxidation, but degradation of the substrate material by exposure to a wide variety of gases, liquids and the like. The term is also intended to include destruction of the bond which binds the protective coating to the substrate, such as protective coatings which are applied to plastic and other non-metallic surfaces.

Normally one would not see any reason to apply an organic coating over a substrate which has already been coated with a protective or wear resistant coating. If the coated article is a hand tool for example, the organic coating would quickly abrade off. However, parylene has the unique ability to penetrate even the smallest microscopic pores, holes or cracks and hence can fill voids which are well below the surface of the protective coating and can even penetrate to the underlying substrate. Thus, while the metallic coating itself may be only a few millimeters in thickness, parylene has the ability to penetrate even the finest microscopic cracks, crevices and holes in the metallic coatings and thereby provide portection against corrosion of the substrate due to failure of the principal protective coating. Even if the parylene closest to the surface wears off through abrasion or the like, the parylene in the pores which extend to the substrate provides a barrier and ample protection against air, liquids and the like from contacting the substrate surface. Hence, although parylene itself is an organic polymer and can be abraded, the parylene in contact with the substrate is protected from abrasion by the stronger walls of the coating material which surround the voids or pores.

Parylene is a generic term applied to a class of poly-p-xylylenes which are derived from a dimer of the structure:



Parylene is an inert, transparent, conformal coating which has excellent barrier properties and can be

used at relatively high temperatures. Due to its ability to provide thin films and conform to substrates of varied geometric shapes, it is ideally suited for use as a conformal coating in a wide variety of fields, particularly in the electronics industry.

The dimer itself, from which the parylene coating is prepared, is made via the pyrolysis of p-xylene or Hofmann elimination reaction of p-methylbenzyltrimethylammonium hydroxide, and is usually obtained in relatively low yields. Accordingly, the overall process for the application of parylene as a conformal coating is expensive and severely restricts its application where it might otherwise be used.

The preparation of p-xylylene polymers by various routes has been reported in the patent literature. For example, U.S. Patent 2,719,131 which issued in September 27, 1955 to E.I. DuPont de Nemours and Company disclosed a process for preparing poly-p-xylene wherein the vapors of p-xylene were pyrolyzed in the presence of chlorine gas.

Also in British patent number 650,947 which was granted March 7, 1951, polymer formation was detected on the walls of a cooling chamber after p-xylene was vaporized and pyrolyzed.

In U. S. Patent 3,149,175 which issued September 15, 1964 a process was reported for the preparation of di-para-xylylenes in yields of 10 percent and higher. The process involved pyrolyzing a mixture of steam and p-xylene at a temperature between about 800°C and 1000°C to generate a free radical and condensing the reactive diradical in a fluid medium.

More recently, U. S. Patent 4,532,369 issued on July 30, 1985 to Hartmut Hartner of the Federal Republic of Germany and discloses and claims a process for the preparation of 2,2-paracyclophane from p-methylbenzyltrimethylammonium hydroxide. It is indicated in the patent that known processes which existed prior to the invention disclosed gave only low yields or the starting materials were not readily accessible. By contacting aqueous p-methylbenzyltrimethylammonium hydroxide with sodium or potassium hydroxide in the presence of dimethylsulfoxide (DMSO) the patentee indicated that yields as high as 70 percent were obtained, It was also indicated at column 1, lines 55-58, that the resulting high yields were surprising since the addition of other comparable aprotic solvents such as dimethyl-formamide, N-methyl-pyrollidone or sulfolane had no effect.

Although the literature contains several references to the use of parylene as a conformal coating and even as a direct coating on metal surfaces to prevent corrosion, there is no disclosure of using parylene as an adjunct to protective coatings contained on substrates to serve as "micro pore fillers" for microscopic crevices and voids in such coatings. The use of parylene applied directly to substrate surfaces, is limited due to the fact that it is an organic compound and easily abraded. Hence, it is not useful, for example, in the direct coating of hand tools or other articles subject to abrasion. However, by utilizing parylene as a micro filler in conjunction with a less abradable or even a wear resistant protective coating, the corrosion protection of the underlying substrate material is optimized or enhanced.

Thus, while the literature such as U. S. Patent 2,785,090 may disclose and claim fabrics coated with poly-p-xylylene which are then useful as filters or in the production of corrosion resistant industrial garments, there is no primary protective coating since the parylene is in direct contact with the fibers and the parylene itself serves as the corrosion protective layer.

In U. S. Patent 3,246,627 which issued April 19, 1966 to W. E. Loeb and is assigned to the same assignee as the present invention, The basic apparatus for the vapor deposition of films of parylene or derivatives thereof is disclosed and claimed. It is indicated in the patent that the apparatus is useful for coating the surfaces of containers, electrical components, wire, plastics and metallic films, sheets and the like with a uniform coating of the linear thermoplastic film.

The apparatus is comprised of a pyrolysis chamber having two temperature zones, a first zone provided with heating means sufficient to vaporize the dimer thereby prventing local overheating and degradation of the dimer which could occur with direct pyrolysis, and a second zone communicating with the first zone and provided with heating means sufficient to pyrolyze the vaporous dimer to reactive diradicals. A nozzled portion of tubing terminates the anterior end of the pyrolysis chamber and penetrates one face of a coating chamber, the coating chamber and a portion of the nozzled tubing being enclosed in a vacuum chamber, thus providing a continuous linear passage for the reactive dimer diradicals from the pyrolysis chamber to the coating chamber wherein condensation and polymerization occur.

While many improvements and variations have been made on the basic apparatus the essential concept remains. Accordingly, one skilled in the art to which this invention pertains can utilize the apparatus of the aforementioned patent or modifications thereof for depositing a parylene coating on protective coatings having the microscopic voids.

As indicated, the process of the present invention takes advantage of the unique physical and chemical properties of parylene. Parylene forms a continuous and conformal coating over any surface on which it is deposited. Since polymerization is effect at essentially the same time as the vaporized dimer is deposited,

it is possible for the dimer to penetrate extremely small openings in the range down to about 500 angstroms, and even smaller. Accordingly, only a very small amount of parylene is needed to coat very large surface areas.

Although there are several types of parylene products commercially available, it has been found that optimum corrosion protection is achieved by using parylene N or parylene C. These products are known and procedures available for depositing the coating on a variety of coated substrates.

The following examples are illustrative of the present invention.

Examples 1-6

In the following examples, six 1" x 2" metal bars coated and uncoated were tested for salt spray in accordance with with ASTM B117-64 (100 hours) and examined for corrosion/degradation every 24 hours over the 100 hour period.

The test chamber (TL-207 Industrial Filter & Pump Type 411.3C) at a temperature of 95oC ± 3 and a nozzle pressure of 10 psi. 2 pounds of NaCl were used in 39 pounds of demineralized water to provide a salt solution concentration of 5.13%.

The following information was noted relative to the chamber performance:

1.	Initial salt solution pH	6.52 @ 35.5oC
2.	Initial salt solution specific gravity	1.034 @ 24oC
3.	Volume of condensate collected in a near nozzle collection dish having 80 square cm of horizontal collecting area, during a 16 hour exposure period	30.5ml
4.	Specific gravity of condensate collected in 3 above	1.038
5.	Volume of condensate collected in a far nozzle collection dish having 80 square cm of horizontal collecting area, during a 16 hour exposure period	17.5ml
6.	Specific gravity of condensate in 5 above	1.038
7.	Temperature of condensate when measurements 4 and 6 above were made	35oC

The parameters listed in 1-7 above, comply with the requiremenutlined in ASTM B117-64.

The six metal bars employed in the test were identified as follows:

Sample	Coating
1	parylene over base steel
2	1 micron titanium nitride coating plus parylene coating
3	2 micron titanium nitride coating plus parylene coating
4	3 micron titanium nitride coating plus parylene coating
5 & 6	control

A scribe line was also made across the surface parallel to the narrow edge and after the coatings were completed.

The sample metal bars were thereafter subjected to the salt spray test as indicated above and examined after 24, 48, 72 and 100 hours of exposure.

Inspection of the bars after 24 hours revealed some corrosion of the control samples 5 and 6. After 48 hours minimal corrosion was noted in samples 1-4 along the scribe lines which separted the different coatings. The control samples exhibited further corrosion.

Inspection after 72 hours revealed that for samples 1 and 2 the minimal corrosion noted after 48 hours along and around the scribe lines, began to develop in the coated areas. Samples 3 and 4 showed minimal corrosion around the scribe lines only.

After 100 hours, corrosion around the scribe lines and coated areas of sample 1 had propogated. Inspection of sample 2 showed additional minimal corrosion near the edges of the coated areas. Sample 3 only exhibited minimal corrosion near the edges of the coated area. Finally, sample 4 showed corrosion around the scribe line only. Each of control samples 5 and 6 exhibited further corrosion over the entire surface.

While the process of the present invention is particularly well suited for the corrosion protection of coated metal surfaces, it can also be employed on surfaces comprised of materials both organic and inorganic, which are susceptible to the presence of microscopic pores, voids and crevices in their initial surface or even after a period of use. Thus, for example, it might be desirable to treat some surfaces in accordance with the process of the present invention not only at the time the protective coating is first applied, but at a later date after the coated surface may have undergone physical or chemical changes which produce voids or cracks. For example, the process of the present invention has been successfully employed to enhance the life of rollers used in industrial operations which have a plastic coating and which over periods of use develop microscopic cracks in the coating and subsequent penetration of fluids to the underlying substrate material.

Although the invention is illustrated by the preceding examples, it is not to be construed as being limited to the materials employed therein, but rather, the invention relates to the generic area as hereinbefore disclosed. Various modifications can be made without departing from the spirit or scope thereof.

Claims

1. A process for optimizing corrosion protection of substrates having a protective or wear resistant coating and wherein said coating exhibits microscopic pores, at least some of which provide a continuous conduit from said substrate to the outer surface of said coating, said process comprising depositing on said coating at least one poly(p-xylylene) in an amount sufficient to at least partially fill said microscopic pores and thereby prevent exposure of said substrate to fluids capable of corroding said substrate.

2. The process of claim 1 wherein said parylene is N parylene.

3. The process of claim 1 wherein said parylene is C parylene.

4. The process of claim 1 wherein said substrate is a metal.

5. The process of claim 1 wherein said metal is iron.

6. The process of claim 1 wherein said metal is steel.

7. The process of claim 1 wherein said substrate is a metal alloy.

8. The process of claim 1 wherein said coating is a metal.

9. The process of claim 1 wherein said coating is a metal alloy.

10. The process of claim 1 wherein said coating is a wear resistant coating.

11. The process of claim 1 wherein said substrate is non-metallic.

12. The process of claim 1 wherein said coating contains chromium.

13. The process of claim 1 wherein said coating contains titanium.

14. The process of claim 1 wherein said coating is titanium nitride.

15. An article comprised of a substrate, a protective coating on at least some of its surfaces and containing parylene within the microscopic voids of said coating in an amount sufficient to prevent corrosive fluids from penetrating said coating and reaching said substrate.

16. The article of claim 14 which is a hand tool.

17. The article of claim 14 which is an automotive part.

18. The article of claim 14 which is an engine part.

19. The article of claim 14 wherein the coating is a decorative coating.

20. The article of claim 14 wherein the coating is a wear resistant coating.

21. The article of claim 14 wherein the coating a transparent coating.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 4159

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 225 647 (R.A. PARENT) * Column 5, lines 21-28; column 8, lines 36-?; examples; claims *	1-3,11, 15,19	B 05 D 7/24 B 05 D 5/08 B 05 D 5/02
Y		4-10,20	
Y	FR-A-1 331 796 (WESTINGHOUSE ELECTRIC CORP.) * Page 5 *	4-10,20	
A	DE-U-8 518 198 (W. HEINZEL) * Claims *	12,13	
P,X	EP-A-0 412 242 (AEG KABEL AG) * Examples; claims; drawings *	1-3,11, 15,21	
A	US-A-4 178 509 (K.A. MORE et al.) * Column 3, lines 1-16 *	1,15	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B 05 D

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	17 June 91	BROTHIER J-A.L.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

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The Hague	17 June 91	BROTHIER J-A.L.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

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