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COATING FERROUS METALS

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ABSTRACT OF THE DISCLOSURE

Protective coatings are applied to ferrous metals by:

(A) Etching the metal first in nitric, then in hydrofluoric acid;

(B) Forming a magnetite coating on the etched metal by heating in contact with aqueous hydrazine, and

(C) Applying an organic coating to the magnetite-coated ferrous metal.

This invention relates to protective coatings on metals. More particularly, this invention relates to a process for applying a coating of hydrazine-formed magnetite on ferrous metals and then applying an organic coating to the magnetite surface. This invention relates further to a particular etching treatment of the ferrous metal surfaces prior to the treatment with hydrazine to form a protective coating of magnetite having special bonding capability for organic coatings.

It is well known that surfaces of metals normally tend to oxidize or rust when exposed to moisture and oxygen. Various methods have been suggested to promote better protection against corrosion and rust formation including the application of organic coatings.

Rigorous cleaning methods must be employed to prepare the metal surface for the application and retention of organic coatings. When oils and greases are removed from metal surfaces, the protective effect of such materials is eliminated and they must be replaced, suitably by more adherent and desirable organic coatings. For this purpose, various thermoplastic materials have been extruded, sprayed, or otherwise applied to metallic surfaces to provide corrosion-resistant surfaces. However, when the protective layer is scratched or otherwise damaged, exposing the base metal, corrosion of the metal not only takes place where exposed but usually penetrates under the coating causing eventual widespread failure. Further, it is necessary to provide an intermediate substrate on the metal to obtain adequate adhesion of the organic coating.

U.S. Pat. 3,257,159 shows pickling iron in 10 percent hydrochloric acid and then placing the iron surface at room temperature in contact with aqueous hydrazine for 14 days to form on the iron a black layer of Fe_3O_4. U.S. Pat. 3,257,160 shows pickled iron immersed in aqueous hydrazine containing 5 mg./l. of methylene blue to form a thin, stable protective layer on the iron.

Burns et al., "Protective Coatings for Metals," 2nd ed., 1955, pp. 572–3 discloses that black oxide coatings formed on steel by immersion in hot, alkaline nitrite, nitrate or chlorate solutions are suitable as a base for paints and other organic coatings.

It is one object of this invention to provide a coated ferrous metal substrate that resists and retards corrosion. It is another object to provide coated ferrous metals that are highly receptive to paints, lacquers and other organic coatings. A more specific object of this invention is to provide a ferrous metal, resistant to rust and corrosion, wherein said metal is coated with a highly adherent organic coating which is air-tight and corrosion-resistant.

Various other objects, advantages, features and variations of the invention will become apparent from the following description.

The above and other objects are accomplished by the method of:

(A) Etching the ferrous metal by immersing it first in aqueous 2 to 20 percent nitric acid, rinsing with water, immersing in aqueous 1 to 10 percent hydrofluoric acid and rinsing with water;

(B) Contacting the resulting etched ferrous metal with an aqueous solution containing hydrazine at temperatures of 50 to 250° C. to form on said ferrous metal a coating of magnetite and rising the thus coated ferrous metal with water; and

(C) Applying an organic coating on the resulting magnetite-coated ferrous metal.

The invention is thus characterized as a novel combination of steps as defined in the claims, each step being required to produce the unobvious and advantageous results obtained by the practice of this invention.

The ferrous metal is etched first with nitric acid and then with hydrofluoric acid to provide a properly cleaned metal base for further coating. Etching is suitably accomplished by dipping the metal in the acid, by spraying the acid onto the metal or by any other suitable thorough contacting of the metal with the acid. Suitably the concentration of the nitric acid is from about 2 to 20 percent and of the hydrofluoric acid from about 1 to 10 percent. The etching is ordinarily carried out at ambient temperatures and the etching is timed to stop short of substantial gassing. The time for each of said acid treatments varies according to the particular metal, acid concentrations and temperatures but is ordinarily from about 30 to 150 seconds in the nitric acid and from about 5 to 30 seconds in the hydrofluoric acid. Thorough rinsing after each of the two acid treatments is required.

The magnetite coating is applied to the resulting etched ferrous metal by heating the metal in contact with aqueous hydrazine. Conveniently the operation is carried out in the liquid phase at temperatures of about 50 to 150° C. or in the vapor phase at temperatures of 50 to 250° C. At temperatures above about 95° C., superatmospheric pressures are suitably used when it is desired to maintain a liquid aqueous phase. Alternatively, the magnetite coating is suitably formed by exposing the etched ferrous metal to vapors of hydrazine and water at atmospheric pressures. In a further suitable alternative, the etched ferrous metal is wet with aqueous hydrazine and exposed to superheated steam at atmospheric pressure and temperatures of 100 to 250° C.

The concentration of hydrazine in the aqueous solution may conveniently vary from about 100 to 2,000 p.p.m. This is not critical since negligible amounts of hydrazine are actually consumed and the treating solution has an indefinite life.

In preparing aqueous hydrazine solutions for this purpose, demineralized water is advantageously used. Water containing significant quantities of dissolved salts results in imperfect coatings. Distilled water or other purer forms of water are also suitable.

Under the conditions specified, relatively short times of contact of 1 hour or less in the aqueous hydrazine are sufficient, especially at the higher temperatures. However, longer times of contact are also suitable and frequently are more convenient. Times as long as 66 hours are not deleterious. Provided the etching was properly carried out, the hydrazine treatment produces on the ferrous metal a uniform, fine-pored protective coating of magnetite which is particularly receptive to organic coatings.

Ferrous metals, suitably iron or steel, properly etched, having a magnetite coating prepared as described are ap-

propriately covered by any of a variety of organic coatings including polyolefins, phenolic resins, natural rubber, synthetic rubber, siloxycarboranyl polymers and polyurethanes. More specific examples include polyethylene, polypropylene, phenol formaldehyde resins, phenol melamine resins, Neoprene rubber, butadiene rubber, polyisoprene rubber, styrene-butadiene rubber, polyester urethanes and polyether urethanes.

EXAMPLE I

Polyethylene-vinyl chloride coating on magnetite

(A) Magnetite coating.—Mild steel panels were dipped for 1 to 2 minutes in 10 percent nitric acid, rinsed with water, followed by a 10 to 20 second dip in 2 percent hydrofluoric acid and then a water rinse. These panels were exposed for 20 hours under pressure at 110° C. in an aqueous solution initially containing 1000 p.p.m. hydrazine in demineralized water. The panels were then air dried. The so-treated panels had a uniform coating of black iron oxide (magnetite) on the surface.

(B) Polyethylene-vinyl chloride coating.—The magnetite coated panels prepared in (A) were coated with a diluted proprietary mixture of vinyl chloride resin and polyethylene resin in the form of a clear solution containing 50 percent solids. It was diluted to 20 percent solids by adding methyl isobutylketone. The panels were dipped into the diluted coating solution and then air dried to produce a white coating which was baked for 10 minutes at 150° C. A second dip coat was similarly applied and baked. A third coat was applied and baked at 175° C. for 30 minutes to cure the composite topcoat. The resulting coating had a thickness of 5 to 6 mils. The same coating was similarly applied to panels of untreated steel, sand blasted steel, wheel ground steel and acid-etched steel wtihout the magnetite coating.

(C) Reverse impact test.—A Gardner 160 inch pound capacity impact tester was used at 160 inch pounds to compare the adhesion of the cured topcoat to the hydrazine-based magnetite substrate with the adhesion of the same cured topcoat to wheel-ground substrates. On the hydrazine-based magnetite, the coating stretched away from itself without separation from the magnetite. Where the metal was stretched, the coating turned white. On reheating in an oven at 175° C., the coating returned to a cohesive integral layer combined with the substrate. The topcoat separated from all the other substrates tested, including the untreated steel, sand blasted steel, acid-etched steel and wheel-ground steel.

(D) Mandrel test (ASTM–D552–60).—The same topcoat on various substrates was tested for adhesion using the ⅛" x 2" solid cone mandrel. A full bend in the coated coupon to 360 degrees over the ⅛" and showed no separation of the coating from the hydrazine-based magnetite. The organic coating stretched substantially without breaking. The organic coating separated from all the other substrates listed in (C) above when the panel was bent over the ⅛" end of the mandrel. The adhesion of the coating to the hydrazine-based magnetite substrate was equal to or greater than the cohesive strength of the cured coating itself.

(E) Relative humidity.—The same topcoating on three types of substrates was tested for 17 days in 100 percent relative humidity at 70° C. One substrate was hydrazine-based magnetite, the second was clean, wheel-ground mild steel, and the third was untreated cold rolled mild steel. The coating on each coupon was cross-hatched with a knife before the test and inspected after the 17 day test. On the hydrazine-based magnetite, no lifting or undercutting occured on the coupon surface in the areas of the cross-hatch. On the wheel ground panel, staining occurred under the coating and coating was lifted at the cross-hatch edges. On the untreated substrate, the whole coating was lifted and extensive rusting of the whole coupon occurred.

This high temperature, high humidity test shows that even though the organic coating is soft, it is adherent to the hydrazine-based magnetite. Water does not migrate under the coating and lift it off the substrate.

(F) Acetic acid salt spray (ASTM B287–62).—The same topcoating applied to two different substrates was exposed for 300 hours in an acetic acid-salt spray fog. The 5 to 6 mil topcoat on the wheel-ground substrate was blistered and undercut by the solution. The hydrazine-based magnetite was stained in minute pits in the stressed areas and along the edges of the panel but was not blistered or under cut. The adhesion of the organic coating on the hydrazine-based, magnetite was outstanding compared to the adhesion on other substrates.

EXAMPLE II

Phenolic resin coating on magnetite

(A) Magnetite coating.—Paint panels of cold rolled 1010 mild steel were dipped for 1 to 2 minutes in 10 percent nitric acid, rinsed with water, followed by a 10 to 20 second dip in 2 percent hydrofluoric acid and then a water rinse. The panels were then exposed for 16 hours under pressure at 110° C. in an aqueous solution containing 500 p.p.m. hydrazine in demineralized water. The panels were then air dried. The so-treated panels had a uniform coating of black iron oxide (magnetite) on the surface.

(B) Phenolic resin coating.—A proprietary phenolic resin drum lining composition was applied to the magnetite-coated panels prepared in (A) and similarly to panels of untreated cold rolled 1010 mild steel, wheel-ground cold rolled 1010 mild steel and nitric acid etched 1010 mild steel without the magnetic coating. This phenolic resin is a clear liquid phenolic varnish type resin used extensively for commercial shipping containers. It is compatible with volatile organic solvents and with water. The panels were dipped in the varnish as received and baked for 15 minutes in an oven at 175° C. A second coat of the varnish was then applied by a second dip followed by baking at 190° C. for 30 minutes. The two coats provided a topcoat of about 2 mils thickness.

(C) Reverse impact test.—A Gardner 160 inch pound capacity impact tester was used at 160 inch pounds to compare the adhesion of the phenolic resin coating to the various substrates. On the hydrazine-based magnetite, the adhesion was superior to cohesion in the phenolic resin coating itself. In addition, there was no separation of the magnetite from the steel, even where the metal was compressed by the ball impactor on one side and stretched on the opposite side. On the untreated cold rolled 1010 mild steel, the phenolic resin coating completely separated from the substrate. On the wheel-ground substrate, adhesion was better than on the smooth substrate. The acid-etched substrate showed a slight separation indicating that adhesion of the organic coating to the substrate was equal to cohesion of the phenolic resin coating to itself.

(D) Mandrel test (ASTM–D552–60).—The phenolic resin topcoats on various substrates were then tested for adhesive qualities using the mandrel test. Each of the thin metal panels with topcoating was bent a full 360° over a ⅛" x 2" solid cone. The substrates and the topcoatings were then inspected for separations and surface cracks.

On the hydrazine-based magnetite, there was no failure visible to the naked eye in the topcoating or the substrate. Under the microscope, closely packed cracks parallel to the axis of the cone appeared. These cracks in the surface of the phenolic topcoating occurred at very high frequency over the surface indicating a fine grained, evenly dispersed bonding to the magnetite substrate.

On the acid-etched substrate, there were cracks in the topcoating visible to the naked eye. Under the microscope, no separation from the substrate metal appeared but the cracks in the surface of the topcoat over the mandrel were relatively further apart. In this respect, the bond between the acid-etched metal and the phenolic resin topcoat was inferior to the bond between the same organic

coating and the hydrazine-based magnetite. The phenolic topcoat was highly discolored apparently due to contamination by the substrate.

On the wheel-ground substrate, the phenolic resin coating showed both surface cracks and separations from the substrate. The cracks were more than ⅛" apart at the small end of the mandrel. Adhesion was poorer on the rough surface of this substrate due to wheel grinding.

On the smooth cold rolled steel surface, the phenolic resin topcoat showed complete separation even over the 2" end of the mandrel. The adhesion of the phenolic resin was poor when untreated metal was subsequently deformed in any way.

(E) Relative humidity.—In a test of 17 days at 100 percent relative humidity at 70° C. each of two panels covered with three coats of the phenolic resin varnish over a substrate of hydrazine-based magnetite showed absolutely no visible change. The moisture had no effect on the phenolic coating and it is stable at the temperatures encountered with shipping containers.

EXAMPLE III

Rubber latex coatings on magnetite

(A) Magnetite coating.—Mild steel panels were dipped for 1 to 2 minutes in 10 percent nitric acid, rinsed with water, dipped for 10 to 20 seconds in 2 percent hydrofluoric acid and rinsed with water. The panels were then exposed for 16 hours under pressure at 150° C. in an aqueous solution containing 1000 p.p.m. hydrazine in demineralized water.

(B) Latex coatings.—Coating of natural rubber latex and of neoprene latex were applied to the panels prepared in (A) and also to panels of clean, untreated steel, brass (85–15 and 70–30), Phosphor bronze and copper. Both the natural rubber latex and the neoprene latex contain 50 percent solids and have a pH of 10.4.

The wet panels were dipped in the latex, slowly withdrawn and allowed to drain. Each panel was then dried approximately 30 minutes in an air oven at 60° C. Two coats of latex were applied by dipping them while still warm in the latex, drying and repeating the process. These were called "thin coats." "Heavy coats" were formed by three coats of latex, thus applied.

The dry latex-coated panels were then cured by heating in an oven at 130° C. for 1 hour. The panels were aged for several days to obtain maximum strength in the coating.

(C) The 180° peel strength tests (ASTM–D903–49).—The panels prepared as described in (B) were tested by this ASTM method with the results shown in Table I.

TABLE I.—THE 180° PEEL STRENGTH TESTS

Sample No.	Substrate and coating	Strength in pounds per inch: Natural latex	Strength in pounds per inch: Neoprene latex
	Thin coats on—		
1, 2	Steel (clean, untreated)	0.5	0.45.
3, 4	Hydrazine-based magnetite on steel.	1.5	Coating tears.
5, 6	Brass (70–30)	Coating breaks.	4.15.
	Heavy coats on—		
7	Hydrazine-based magnetite on steel.		6.8.
8	Brass (85–15)		5.8.
9	Phosphor bronze		4.9.
10	Copper		4.25.
11	Brass (70–30)		4.15.

The data of Table I show that natural rubber cures to a weak film and adhesion is poor (No. 1). Adhesion is improved *three-fold* on the magnetite (No. 3). On the magnetite substrate, the thin neoprene latex coating (No. 4) was superior to the natural rubber latex coating (No. 3) but failed by tearing.

With heavy neoprene coatings, hydrazine-based magnetite (No. 7) is superior to the more reactive substrates of brass, bronze or copper (Nos. 8, 9, 10). Adhesion was better with neoprene on the hydrazine-based magnetite than on the more reactive metals, apparently due to better penetration into the hydrazine-based magnetite.

EXAMPLE IV

Neoprene latex with primer on magnetite

(A) Magnetite coating

Mild steel panels were dipped for 1 to 2 minutes in 10 percent nitric acid, rinsed with water, followed by a 10 to 20 second dip in 5 percent hydrofluoric acid and a water rinse. The panels were then exposed for 16 hours at 150° C. to an aqueous solution containing 1000 p.p.m. hydrazine in demineralized water to form a magnetite coating on the surface. The treated panels had highly water absorbent and uniform black iron oxide coatings.

(B) Primer coating

The so-treated panels were then dipped in a resorcinol-formaldehyde latex, thoroughly penetrating the surface with the latex. The wet panels were air dried at 65° C. and then baked at 130° C. for 15 minutes to cure the primer coating. The resorcinol-formaldehyde latex is a commercial latex adhesive specifically made to give a cohesive bond between rubber and tire cord materials used in tire construction. It is prepared by combining a Solution No. 1 of alpha-vinyl-pyridine with a Solution No. 2 of reactive resorcinol-formaldehyde.

	Grams
Solution No. 1:	
Alpha-vinyl pyridine	162
Ammonia (58 percent)	6
Water	326
Solution No. 2:	
Resorcinol	10.7
Flake caustic	0.17
Formaldehyde (37 percent)	16.2

Solution No. 2 is added to Solution No. 1, mixed for 15 minutes and aged for 18 hours before using. It is stirred for 5 minutes every day. This mixture is suitably diluted with water when solutions of lower solids content are indicated. This adhesive is widely used in the tire industry to bond nylon, rayon, polyester and glass fiber to rubber latex materials. Nylon, rayon, and polyester cord are coated and individual glass fibers are coated in the construction of high strength tires.

(C) Neoprene coatings and tests

(1) Neoprene coatings.—The neoprene latex used in Example III(B) was applied to the primed magnetite coatings. Three consecutive air dried and baked neoprene topcoats were applied according to the procedure described in Example III(B). In the tear test, the neoprene layer tore without any separation at the surface of the magnetite.

(2) Neoprene and fabric coatings.—Mild steel panels coated with magnetite, prepared as described in Example IV(A) and primed as described in Example IV(B) were similarly treated with only one coat of neoprene latex. The final coat was rayon cloth, canvas and glass cloth dipped in the mixed primer, applied to the cured neoprene topcoat and baked for 1 hour at 130° C. In the tear test, the rayon cloth tore without separation at the magnetite surface. The canvas and glass cloth laminates separated in the primer layer between the cloth and the neoprene.

The glass cloth laminate was further baked at 150° C. for one hour. This heat treated coating was then subjected to the 180° peel test and gave a peel strength of

9.8 pounds per inch. The cohesive break occurred in the primer between the glass cloth and neoprene.

These experiments show that the primer is more strongly bonded to the hydrazine-based magnetite than to the glass cloth and that the neoprene is more strongly bonded by the resorcinol-formaldehyde primer to the hydrazine-based magnetite than to the glass cloth.

EXAMPLE V

Siloxycarboranyl coatings on magnetite

(A) Magnetite coating.—Mild steel panels were dipped 1 to 2 minutes in 10 percent nitric acid, rinsed with water, followed by 10 to 20 second dip in 2 percent hydrofluoric acid and a water rinse. The panels were then exposed for 16 hours under pressure at 110° C. to an aqueous solution containing 500 p.p.m. hydrazine in demineralized water, forming a magnetite coating on the surface. The panels were then air dried. The so-treated panels had a uniform coating of black magnetic iron oxide.

(B) Siloxycarboranyl coatings. — Siloxycarboranyl polymers are known and described in U.S. Pats. 3,388,-090; 3,388,091; 3,388,092 and 3,388,093. "Dexsil 202" is a liquid polymer of this type and was used as a mixture withe equal parts by weight of titanium dioxide pigment. A mixture of 50 percent Dexsil 202 and 50 percent TiO_2 was sprayed on one of the magnetite-covered panels prepared in Example V(A) and on untreated stainless steel panels. The coatings were exposed to 425° C. for 500 hours. The coatings on the stainless steel panel cracked and separated due to shrinkage during the cure. The coating on the hydrazine-based magnetite, even though under high stress due to dissimilar shrinkage, did not separate in any way. Only minute surface cracks appeared after 500 hours at 425° C.

Another magnetite panel was cut into one inch strips and coated with a mixture of:

	Parts by weight
"Dexsil" polymer	100
Benzoyl peroxide	1
Boric acid	1
Graphite powder	10

The mixture was blended on a rubber mill and a heavy coating was applied to the magnetite-coated steel strips. This coating, cured at 250° C., gave a cohesive break under shear at 1000 p.s.i.g. while the magnetite substrate remained completely integral with the Dexsil adhesive topcoat.

These tests show that the hydrazine-based magnetite is stable at high temperatures. It gives unexpectedly good results with coatings that shrink during cure and when exposed to high temperature. This magnetite substrate can be cured with flexible adhesives to yield unexpected adhesive strengths on metal. With the hydrazine-based magnetite, adhesive bonding can be outstanding with either hard or elastomeric coatings.

EXAMPLE VI

Urethane coatings on magnetite

(A) Magnetite coating.—Mild steel panels were dipped for 1 to 2 minutes in 10 percent nitric acid, rinsed with water, followed by a 10 to 20 second dip in 2 percent hydrofluoric acid and a water rinse. The panels were then exposed for 16 hours at 110° C. to an aqueous solution containing 500 p.p.m. hydrazine in demineralized water, forming a magnetite coating on the surface. The panels were then soaked for 20 minutes at ambient temperature in a water bath containing 1000 p.p.m. hydrazine. This last step increases surface wettability and promotes more uniform coverage by the organic topcoat. The panels were then air dried. The so-treated panels had a uniform coating of black iron oxide.

(B) Urethane coating and tests.—The coating applied was "Astrocoat 115 P," a polyethertolylene diisocyanate prepolymer consisting of 55 percent solids in 45 percent solvent, a mixture of xylene and Polysolv EE acetate. This prepolymer solution was mixed with an amine catalyst in a weight ratio of 50:1 immediately before applying as a coating material. After application, the solvent was removed by evaporation and the coating was cured in a moist atmosphere.

To epoxy resin panels, adhesive divinyl butyral primer was first applied and then a coating of "Astrocoat 115 P," applied as described in the preceding paragraph. The catalyzed solution was sprayed on to the magnetite-covered panels, using a standard paint sprayer, to give a film thickness of about 2 mils. Other panels were coated by repeated dipping in the prepolymer solution. The coatings were then allowed to air dry. For comparison, the same urethane coating was applied to a number of other surfaces by the same techniques. The coatings were then subjected to the 180° peel test (ASTM D–903–49) to determine adhesive strength. The results are shown in Table II.

TABLE II.—URETHANE COATINGS 180° PEEL TEST (ASTM D–903–49)

No.	Substrate	Peel strength, lbs./in.
1	Mild steel, untreated	0.20.
2	Divinyl butyral primer	6.0.
3	Alkaline oxidizing process	1.07.
4	Mild steel, HNO_3-etched, no magnetite.	2.50.
5	Mild steel, no acid etching N_2H_4-based magnetite.	0.87.
6	Mild steel, HNO_3-HF etched, N_2H_4-based magnetite.	The urethane coating could not be peeled off, it tore first.

The combination (No. 6) of ntiric acid and hydrofluoric acid etching followed by the hydrazine treatment to form magnetite provides a substrate with very high adhesion for the organic topcoat. The nitric acid etch alone (No. 4) does not provide such a substrate, nor does the hydrazine treatment alone (No. 5) without etching. The black oxide coating produced in the standard alkaline oxidizing process (No. 3) is also inferior to the magnetite coating (No. 6) formed according to this invention. The standard divinyl butyral primer (No. 2) normally recommended as a substrate for the urethane coating is superior to the black oxide surface produced by the alkaline oxidizing process (No. 3) but is also much inferior to the magnetite substrate on the etched metal (No. 6).

The alkaline oxidizing process (No. 3), used for comparison in this example, is a conventional process for applying a black magnetic iron oxide coating on steel surfaces by the following steps:

(1) Soak for 20 minutes in an alkaline cleaner at 205° F. (96° C.) to remove rust and stain.

(2) Dip four times in hot, flowing rinse water at 185° F. (74° C.) maximum.

(3) Soak for 20 minutes in sodium nitrate-nitrite-caustic Bath No. 1 at 293±3° F. (145±1.65° C.).

(4) Dip two times in flowing cold water rinse.

(5) Soak for 20 minutes in Bath No. 2 at 303±3° F. (151±1.65° C.).

(6) Dip four times in flowing cold water rinse.

(7) Soak for 10 minutes and then dip two times in 125° F. (52° C.) flowing rinse water.

(8) Soak 30 minutes in 150° F. (66° C.) hot water.

(9) Dry in warm air.

Bath No. 1 and Bath No. 2 are made up as follows:

Bath No. 1:		
Sodium hydroxide	oz.	120
Sodium nitrate	oz.	5
Sodium nitrite	oz.	40
Water	gallon	1
Bath No. 2:		
Sodium hydroxide	oz.	216
Sodium nitrate	oz.	5
Water	gallon	1

EXAMPLE VII

Effect of acid treatment and time on magnetite formation

Mild steel panels were dipped for 1 to 2 minutes in 5 percent sulfuric acid or 5 percent hydrochloric acid, all at ambient temperature. The panels were then rinsed with water and exposed for 16 hours at 90° C. to an aqueous solution containing 1000 p.p.m. hydrazine in demineralized water. The panels that had been pretreated with sulfuric acid developed an uneven coating of mixed red to black oxides, with some of the metal completely bare. The panels that had been pretreated with hydrochloric acid developed only a very thin, blue oxide coating, about 500 A. thick.

Mild steel coupons were dipped for 1 minute in 10 percent nitric acid and then rinsed with water. Some of these panels were then dipped for about 20 seconds in 2 percent hydrofluoric acid. All operations were at ambient temperature.

The coupons treated as above were then immersed in an aqueous solution containing 400 p.p.m. of hydrazine in demineralized water for 20 hours at 110° C. The panels treated with nitric acid alone developed a uniform deep black magnetite over about 75 percent of the surface, as judged by microscopic examination. The panels that had received the combination nitric acid-hydrofluoric acid treatment developed a uniform deep black magnetite coating covering 95 to 100 percent of the surface, as judged by microscopic examination.

Three-mild steel coupons were acid-treated by a 2 minute dip in 10 percent HNO_3, a water wash, a 20 second dip in 5 percent HF, and a final water wash, all at 25° C. The 3 coupons were then exposed at 150° C. to an aqueous solution containing 1430 p.p.m. N_2H_4 in demineralized water for 2, 16 and 66 hours respectively during which time a magnetite coating was formed which was uniform and completely coated the surface. The quality of the coating was excellent, as judged by the oxalic acid test (See MIL-C-13924, Black Oxide for Iron and Steel). This shows that short treatment times, of the order of 2 hours or less give an excellent coating and that prolonged exposures are not deleterious.

What is claimed is:

1. Method of bonding organic coatings to ferrous metals by the steps of:

(A) Etching the ferrous metal by immersing first in aqueous 2 to 20 percent nitric acid, rinsing with water, immersing in aqueous 1 to 10 percent hydrofluoric acid and rinsing with water;

(B) Contacting the resulting etched ferrous metal with aqueous hydrazine at temperatures of 50 to 250° C. to form on said etched ferrous metal a coating of magnetite and rinsing the thus coated ferrous metal with water; and

(C) Applying an organic coating on the resulting magnetite-coated ferrous metal.

2. Method as claimed in claim **1** in which said etching is carried out at ambient temperature.

3. Method as claimed in claim **1** in which said etching is terminated before substantial gassing occurs.

4. Method as claimed in claim **1** in which said contacting is carried out in the liquid phase at temperatures of 95 to 150° C.

5. Method as claimed in claim **1** in which said contacting is carried out in the vapor phase at temperatures of 50 to 250° C.

6. Method as claimed in claim **1** in which said aqueous hydrazine is a solution of hydrazine in demineralized water.

7. Method as claimed in claim **6** in which said solution contains 100 to 2,000 parts per million of hydrazine.

8. Method as claimed in claim **1** in which said ferrous metal is mild steel.

9. Method as claimed in claim **1** in which said organic coating is selected from the group consisting of polyolefins, phenolic resins, natural rubber, synthetic rubber, siloxycarboranyl polymers and polyurethanes.

10. A composite article prepared by the process of claim **1.**

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RALPH S. KENDALL, Primary Examiner

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117—75, 49