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3,449,176

COATING OF SOLID SUBSTRATES

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6 Claims

ABSTRACT OF THE DISCLOSURE

When metallic substrates are abraded with a low density abrasive product and thereafter promptly provided with any of a wide variety of protective decorative coats, results are superior to those achieved with other chemical or mechanical methods of surface preparation.

This application is a continuation-in-part of our co-pending U.S. patent application Ser. No. 163,885, filed Jan. 2, 1962, now abandoned.

This invention relates to the application of protective or decorative coatings to a wide variety of surfaces. Primarily, however, this invention is concerned with the application of one or more coatings to a metallic substrate.

Where a metal surface is to receive a coating, industry relies almost entirely on chemical methods of pretreating the surface. For example, in applying a phosphate coating to a mild steel surface it is traditional to follow the steps of (1) degreasing with trichloroethylene, (2) washing for varying lengths of time in dilute acid or alkali cleaners, (3) rinsing, and (4) submerging in a bath of phosphate solution. This overall process is very difficult to control satisfactorily, the inevitable small variations in the cleaning compositions, coating process, phosphate solution and/or metal surface often leading to substantial changes in both appearance and performance of the finished product. The coarse, grainy, or even discontinuous coatings which are frequently attained are known to be subject to corrosion, adhesion failure, or both. Further, it is becoming an increasing industrial problem to dispose of the wastes generated by chemical methods of cleaning.

Prior art phosphatizing techniques based on mechanical methods of surface preparation have consistently proved inferior to chemical methods because of excessive substrate removal, surface contamination, stresses introduced into the metal, danger to operating personnel, and less effective corrosion prevention.

The present invention provides a novel coating process including a method for pretreating surfaces which overcomes the disadvantages of previously known prior art methods. This process makes it possible to prepare coated metal surfaces which are conspicuous for their uniformity and—depending upon the specific substrate and material coated—luster, corrosion resistance, and other desirable qualities. The novel process of this invention is simple, extremely rapid, may be carried out at room temperature, and renders technically and economically feasible

the attainment of unusual or unique coatings. The amount of substrate removed is minimum, and the process is subject to wide deviation in operating conditions without significant change in the quality of the work produced. Coatings applied to a surface pretreated in accordance with this invention generally adhere with greater tenacity than coatings applied to surfaces pretreated by any conventional chemical or mechanical technique.

In accordance with the invention, a coating is applied to a substrate by forcing against the surface of the substrate a tough flexible resilient low density abrasive structure, imparting relative motion to the contacting surfaces, and promptly applying a protective, decorative, or modifying coating material to the substrate. The abrasive structure contains abrasive granules which are harder than the substrate and which are firmly bonded to a matrix which is itself resilient. Although this process typically removes no more than about 5×10^{-5} inch of bulk substrate under widely varying operating conditions, surprisingly the resultant coating is more uniform, continuous, and adherent than was heretofore obtained with any commercial mechanical or chemical method of surface preparation.

One type of abrasive structure which may be used to practice this invention is a tough, resilient low density polyurethane foam wheel having abrasive granules distributed throughout within the polyurethane itself. Such products tend to generate more heat than the low density abrasive products described in the succeeding paragraph and also are somewhat less conformable, but they may be used in operations where low operating temperature and high conformability are not of primary importance.

A preferred embodiment of the abrasive structure used to practice this invention is disclosed in U.S. Patent No. 2,958,593, issued to Howard L. Hoover, Eugene J. Dupre, and Walter J. Rankin, on Nov. 1, 1960. This patent discloses a resilient low density abrasive article containing, distributed substantially uniformly throughout, a large number of intertwined flexible tough organic fibrous members bonded together at junctures which are widely spaced along said members so that there are comparatively long sections of fibrous members free from attachment to other fibrous members. Abrasive granules are randomly distributed at spaced points throughout the article and bonded to the fibrous members. Products of this type are available from Minnesota Mining and Manufacturing Company of St. Paul, Minn., under the trade designation "Scotch-Brite" low density abrasive material.

Prior to the present invention, low density abrasive products as disclosed in the Hoover et al. patent were known to be excellent cleaners, removing scale and rust from metal surfaces and imparting unique appearance thereto while simultaneously removing very little base metal. When the base metal was to be provided with a subsequent coating, however, low density abrasive products were considered less desirable than more aggressive abrading means, which were believed to expose a highly reactive virgin metal surface. For example, a coated abrasive belt, which is more effective in removing stock, was also considered more effective in generating a metal surface to which adhesion of subsequent coatings could be expected. Metal workers had previously found, however, that even coated abrasive belts were far less effective than chemical treatment in preparing a surface

for coating. Hence, the use of the even less aggressive low density abrasive products was contraindicated. Surprisingly, however, we have found that a process wherein coatings are applied to metal surfaces following pretreatment with low density abrasives, yields products having unique and unexpected properties not attainable by any prior art technique.

With the view in mind of illustrating our invention without limiting it in any way, several representative examples are listed below:

EXAMPLE I

To compare several surface preparation techniques, twelve 2-inch x 6-inch coupons of 20 gauge galvanized steel were pretreated in each of the following ways:

(a) Low density abrasive.—An 8-inch diameter roll approximately 3 inches wide was formed by ganging low density abrasive discs on a shaft and compressing them to a density of 12 discs per inch of width. The low density abrasive material was the type disclosed in Hoover, Dupre, and Rankin 2,958,593, specifically "Scotch-Brite" Type A, Very Fine, in which Grade 280–600 aluminum oxide particles were bonded to 15 denier nylon fibers with phenol formaldehyde resin, the material being about ¼ inch thick and having a void volume upwards of about 90%. The roll was then mounted on a "Speedsander" machine and driven at 1200 r.p.m. while the coupons were twice passed beneath it at a rate of 30 feet per minute. In conducting this test, double-coated pressure-sensitive adhesive tape was used to adhere first and second coupons to the conveyor belt, in line with its direction of movement, a third coupon being positioned between the first two coupons but not adhered to the belt. After pretreatment, the first and second coupons were discarded and the third (middle) coupon was retained for test. A meter connected to the driving motor indicated that the power consumption was approximately 0.5 horsepower per inch of coupon width above that required to drive the motor under no-load conditions.

(b) Coated abrasive belt.—A Grade 320 aluminum oxide coated abrasive belt was mounted on a "Speedsander" machine, where it was entrained over a 9½-inch diameter serrated 40-durometer rubber contact wheel and driven at 1200 r.p.m. Each coupon was passed beneath the belt at a feed rate of 30 feet per minute, the negative clearance between the panel and the abrasive belt being set at the minimum to obtain a visually clean coupon in a single pass.

(c) Wire brush.—Two 1-inch wide x 8-inch diameter No. 154 stainless steel wire brushes were mounted on the "Speedsander" machine and driven at 1200 r.p.m. The approximate bristle diameter was 0.011 inch. The coupons were passed under the brushes twice at a rate of 30 feet per minute, power consumption being approximately 0.5 horsepower per inch of coupon width above no-load conditions.

(d) Grit blast.—Grade 180 aluminum oxide granules were ejected from the ¼ inch nozzle opening of a small grit blast gun, air pressure being approximately 90 lbs. gauge. The coupons were held 12 inches away from the source and moved until no contamination was evident and the surface appeared uniform in both finish and cleanliness.

(e) Chemical.—Coupons were immersed for 2 minutes in a 2½% solution of "Parco Cleaner 341" at 180–190° F. (The cleaner contained by weight approximately 2% NaHCO₃, 1.3% Na₃PO₄, sodium borate equivalent to a boron content of 0.084% and a small amount of wetting agent.) The coupons were then thoroughly rinsed in running water and acid-pickled by immersion in a 6% solution of H₂SO₄. Each coupon was then rinsed and allowed to dry.

Each of the sixty coupons was numbered, desiccated, weighed and immersed in an agitated 6% solution of

"Bonderite 37," maintained at 155° F. ("Bonderite 37" is a proprietary phosphatizing solution available from Parker Rust Proof Company containing, per liter, approximately 3.34 grams of Zn+++, 2.63 grams of Ni+++, 0.53 gram of SO₄⁼, and phosphate ions equivalent to 4.12 grams of P. It is believed to consist essentially of zinc dihydrogen phosphate, nickel sulfate, and oxidation-reactive materials.) Three coupons from each set were removed after each of the following times: ½, 1, 2, and 4 minutes. After removal from the phosphate bath, the coupons were rinsed for 30 seconds in 155° F. dilute conventional chromic acid-phosphoric acid solution (0.2 gram of "Parcolene 8B," available from Parker Rust Proof Company, per liter of water), and dried for 10 minutes at 350° F. All 60 coupons were then weighed to determine the amount of phosphate coating which had been applied. Data from representative coupons are tabulated below:

TABLE 1

Pretreatment	Coupon weight gain, gram, vs. immersion time			
	30 sec.	1 min.	2 min.	4 min.
Low density abrasive.....	0.0160	0.0187	0.0191	0.0201
Coated abrasive belt.....	0.0138	0.0346	0.0387	0.0313
Wire brush.....	0.0134	0.0140	0.0145	0.0141
Grit blast.....	0.0295	0.0310	0.0303	0.0311
Chemical.....	0.0129	0.0226	0.0239	0.0222

Photomicrographs (360×) were then taken of one coupon from each set of three which had been phosphatized for 4 minutes. Prints of these photomicrographs were then measured to determine the average phosphate crystal size; results are set forth in Table 2:

TABLE 2

Pretreatment	Accelerator in PO ₄	Average crystal size, microns
Low density abrasive.....	No.....	2.33 x 2.33
Coated abrasive belt.....	No.....	18.1 x 9.4
Wire brush.....	No.....	52.8 x 25.4
Grit blast.....	No.....	36.6 x 12.5
Chemical.....	No.....	47.2 x 14.8

Over the phosphate-coated surface of the coupons was then poured a composition consisting of 250 parts raw linseed oil, 500 parts mineral spirits and 6 parts metal drier solution (52.45% mineral spirits; 6.75% cobalt naphthenate solution containing 6% Mn; 22.80% lead naphthenate solution containing 24% Pb), after which the coupons were held in an upright position for one hour at 75° F. to facilitate draining, and cured 24 hours at 185° F., all according to the procedures described by R. C. Ulmer in Uhlig, "The Corrosion Handbook" (John Wiley & Sons, New York, 1948) at page 870. The bottom end of the coupons was marked, and the edges of the coupons were then protected with masking tape to prevent edge failure in a corrosive environment.

Comparative corrosion resistance of the various samples was then determined by placing twenty galvanized steel coupons (one from each set of three) in an ASTM B117 chamber and subjecting them to a "salt fog" corrosion test in accordance with ASTM Test Procedure No. 117–57T. The coupons were inspected at regular intervals, an estimate being made at each inspection as to the percent of the exposed coated surface which had failed by rust formation. The test was then repeated twice (once with each of the two remaining coupons from each set of three), placing the corresponding coupons in a different location in the chamber to cancel out any placement

variable. Results of this test, averaged for the three coupons in each set, are summarized in Table 3:

TABLE 3

Pretreatment	PO ₄ immersion time	Percent surface failure vs. time in salt for chamber, hours							
		4	8	12	16	24	56	88	116
Low density abrasive.....	30 sec.....	0	0	0	0	0	0	0	2
	1 min.....	0	0	0	0	0	0	0	1
	2 min.....	0	0	0	0	0	0	0	0
	4 min.....	0	0	0	0	0	0	0	0
Coated abrasive belt.....	30 sec.....	25	50	90	100	100	100	100	100
	1 min.....	0	40	95	100	100	100	100	100
	2 min.....	10	45	90	100	100	100	100	0
	4 min.....	0	10	30	30	35	40	60	65
Wire brush.....	30 sec.....	0	10	30	35	40	50	60	65
	1 min.....	0	2	15	15	20	40	50	60
	2 min.....	0	0	0	2	5	20	25	30
	4 min.....	0	0	0	0	5	10	20	25
Grit blast.....	30 sec.....	0	5	65	65	70	70	70	70
	1 min.....	2	5	60	70	70	70	70	70
	2 min.....	5	5	5	10	15	35	50	55
	4 min.....	0	0	0	2	5	30	30	50
Chemical clean.....	30 sec.....	0	2	15	25	70	95	95	95
	1 min.....	0	10	30	85	85	85	85	85
	2 min.....	0	20	70	95	95	95	95	95
	4 min.....	0	2	35	80	95	95	95	95

EXAMPLE II

One hundred twenty 2-inch x 6-inch coupons of 18 gauge cold rolled steel were pretreated in the same manner as the galvanized steel coupons of Example I; except that the chemically pretreated samples were acidpickled 2 minutes in 12% H₂SO₄. Each coupon was then numbered, desiccated, and weighed.

Half of the coupons were phosphatized in exactly the same way as the galvanized steel coupons in Example I, while the other half were phosphatized in a bath containing, in addition to the phosphate solution, 0.0375 part of a conventional proprietary accelerator (Parker Rust Proof Company No. 131) per 100 parts of water. All the coupons were then weighed to determine the amount of phosphate coating which had been applied. Data from representative coupons are tabulated in Table 4:

TABLE 4

Pretreatment	Accelerator in PO ₄	Coupon weight gain, grams, vs. immersion time			
		30 sec.	1 min.	2 min.	4 min.
Low density abrasive.....	No.....	0.0109	0.0178	0.0234	0.0245
Coated abrasive belt.....	No.....	0.0016	0.0104	0.0167	0.0176
Wire brush.....	No.....	0.0014	0.0151	0.0238	0.0348
Grit blast.....	No.....	0.0093	0.0200	0.0401	0.0324
Chemical.....	No.....	0.0013	0.0052	0.0176	0.0275
Low density abrasive.....	Yes.....	0.0107	0.0186	0.0231	0.0234
Coated abrasive belt.....	Yes.....	0.0069	0.0163	0.0271	0.0271
Wire brush.....	Yes.....	0.0023	0.0122	0.0239	0.0356
Grit blast.....	Yes.....	0.0098	0.0215	0.0396	0.0339
Chemical.....	Yes.....	0.0014	0.0069	0.0228	0.0396

Photomicrographs (360X) were then taken of one coupon from each set which had been phosphatized for 4 minutes. Prints of these photomicrographs were then measured to determine the average phosphate crystal size; results are tabulated in Table 5:

TABLE 5

Pretreatment	Accelerator in PO ₄	Average crystal size, microns
Low density abrasive.....	No.....	13.3 x 6.6
Coated abrasive belt.....	No.....	17.8 x 3.9
Wire brush.....	No.....	19.2 x 8.6
Grit blast.....	No.....	21.2 x 16.6
Chemical.....	No.....	75.2 x 15.0
Low density abrasive.....	Yes.....	2.4 x 1.86
Coated abrasive belt.....	Yes.....	15.6 x 4.9
Wire brush.....	Yes.....	29.6 x 8.3
Grit blast.....	Yes.....	10.2 x 6.0
Chemical.....	Yes.....	25.0 x 9.3

The phosphatized coupons were then linseed-oil coated and tested for corrosion resistance as in Example I. Cold-rolled steel is, of course, more susceptible to corrosion

than is galvanized steel; hence dried linseed-oil coated cold rolled steel coupons are inherently less corrosion-

resistant than their galvanized steel counterparts. Corrosion results are summarized in Tables 6 and 7:

TABLE 6.—COLD ROLLED STEEL, NO ACCELERATOR

Pretreatment	PO ₄ immersion time	Percent surface failure vs. time in salt fog chamber, hours				
		2	4	6	8	10
Low density abrasive.....	30 sec.....	5	10	70	90	100
	1 min.....	0	0	0	30	65
	2 min.....	0	0	0	0	0
	4 min.....	0	0	0	0	0
Abrasive belt.....	30 sec.....	0	50	100	100	100
	1 min.....	0	20	25	85	95
	2 min.....	0	0	10	70	90
	4 min.....	0	5	35	50	60
Wire brush.....	30 sec.....	10	75	95	100	100
	1 min.....	0	0	10	50	70
	2 min.....	40	70	85	95	100
	4 min.....	10	40	70	80	85
Grit blast.....	30 sec.....	0	65	95	100	100
	1 min.....	0	10	35	95	100
	2 min.....	0	0	15	35	90
	4 min.....	0	15	50	70	85
Chemical clean.....	30 sec.....	70	90	95	95	100
	1 min.....	0	95	100	100	100
	2 min.....	10	80	100	100	100
	4 min.....	0	0	30	85	96

TABLE 7.—COLD ROLLED STEEL, ACCELERATOR

Pretreatment	PO ₄ immersion time	Percent surface failure vs. time in salt fog chamber, hours				
		2	4	6	8	10
Low density abrasive.....	30 sec.....	0	0	0	30	85
	1 min.....	0	0	0	5	20
	2 min.....	0	0	0	0	0
	4 min.....	0	0	0	0	0
Coated abrasive belt.....	30 sec.....	0	95	100	100	100
	1 min.....	0	10	25	55	95
	2 min.....	0	25	50	70	80
	4 min.....	0	5	20	50	90
Wire brush.....	30 sec.....	10	50	90	100	100
	1 min.....	0	60	95	100	100
	2 min.....	20	75	95	100	100
	4 min.....	10	15	25	45	55
Grit blast.....	30 sec.....	0	40	90	95	100
	1 min.....	0	10	70	95	100
	2 min.....	0	20	35	50	80
	4 min.....	0	20	50	75	90
Chemical clean.....	30 sec.....	20	95	100	100	100
	1 min.....	10	95	100	100	100
	2 min.....	10	60	90	100	100
	4 min.....	10	65	95	97	97

Comparison of Tables 6 and 7 reveals that the panels pretreated with the low density abrasive wheel and immersed in accelerator-free phosphate for at least 1 minute had corrosion resistance far better than samples pretreated by any other method and immersed in either accelerator-free or conventional accelerated phosphate. Since the nature of accelerated phosphate solutions is both unpredictable and subject to change with the passage of time, pretreatment with low density abrasives thus offers a way to simplify phosphatizing of cold rolled steel while simultaneously obtaining improved results.

The phosphate solution may be sprayed on the metal surface at the same time that treatment with the low density abrasive material is taking place to obtain results which are substantially similar to those obtained in the process of the preceding examples. Excellent results are also obtained when an organic solvent solution of a phosphate and a sealer (e.g. "Kephos 92") are used in place of the aqueous phosphate solution, the sealer serving to improve corrosion resistance still further and provide a base for subsequent lacquer or enamel coats.

Analysis of Examples I and II shows that:

For identical phosphate solutions and base metal, the phosphate crystals formed on metal pretreated with low density abrasive were generally smaller and more nearly equiaxial than those formed following any other method of pretreatment. Significantly, however, corrosion resistance was not necessarily inversely proportional to phosphate crystal size. Thus the average crystal size when an accelerator-free phosphate solution was applied to low density abrasive-pretreated cold rolled steel coupons was 13.3 x 6.6 microns, while the average crystal size when an accelerated phosphate solution was applied to grit blasted coupons was only 10.2 x 6.0; however, when these two types of coupons (2-minute phosphate immersion in each case) were coated with linseed oil and tested for corrosion resistance, the low density abrasive-pretreated coupon showed no rust after 10 hours in the salt fog, while the grit blast-pretreated coupon showed 80% rust.

Corrosion resistance was not necessarily directly proportional to the weight of phosphate deposited on the coupons. Thus, although Table 4 shows that the weight of phosphate deposited in 4 minutes was generally lower for coupons pretreated with low density abrasives than for coupons pretreated in any other way, Tables 6 and 7 show that the corrosion resistance of coated coupons having a low density abrasive pretreatment was vastly superior to that of coated coupons having any other type of pretreatment.

For identical base metal, the corrosion resistance of low density abrasive-pretreated coupons coated with accelerator-free phosphate solution for at least 2 minutes was vastly superior to the corrosion resistance of coupons pretreated in any other way and treated with either accelerated or accelerator-free phosphate solution for as long as 4 minutes.

The results of these two experiments lead to the conclusion that pretreatment with low density abrasive products imparts a unique effect to the surface of steel and galvanized steel which is to be phosphatized and painted. The reason for this phenomenon is not known.

EXAMPLE III

Twenty-gauge cold rolled steel having a black oxide coating was degreased in trichloroethylene and tinplated by processing it as follows:

(1) Abraded by being held in the hand of an operator and forced against a rotating 12" diameter x 3" wide low density abrasive wheel,¹ which was driven at 1,100 r.p.m.

¹ The low density abrasive wheel was formed by accordion-folding a 3-inch x 39-foot strip of the same type of low density abrasive material described in Example I, lightly compressing it into a block having a 3-inch x 3-inch cross-section, forming the block into an annulus and adhering it to the periphery of a 5-inch diameter steel core, the folded edges of the strip defining the sides of the resultant wheel.

at a power demand of 0.1 horsepower per inch of width above no-load conditions.

(2) Rinsed in room temperature water.

(3) Electroplated in a conventional manner, i.e., by being immersed in plating solution for 15 seconds at 12.6 volts and a current density of 450 amperes per square foot. (The plating solution was prepared by dissolving the following materials in 4 liters of water: stannous sulfate, 400 grams; concentrated H₂SO₄, 120 grams; tartaric acid, 120 grams; gelatin, 20 grams; beta-naphthol, 4 grams.) For purposes of comparison two sets of cold-rolled steel samples were prepared in the same manner; in one set, abrading Step 1 was replaced by pickling 12 seconds in 180° F. 6% H₂SO₄, and in the other set this pickling step was inserted between Steps 1 and 2. The experimental and control samples were then subjected to the "pickle lag" test, an empirical but widely used method of checking the quality of electroplating. In accordance with this test, the samples were first detined by immersion in Clarke's reagent (20 grams of antimony trioxide dissolved in 1 liter of hydrochloric acid having a specific gravity of 1.16), until one minute after all gas evolution had ceased. The samples were washed in water and the residue rubbed off with a cloth. The cleaned samples were then oxidized by immersion for 30 seconds in a 90° C. 10% sodium hydroxide solution to which hydrogen peroxide was added in sufficient amounts to produce oxygen gassing. The oxidized samples were next immersed in 6 N hydrochloric acid, heated to 90° C., and the time recorded before a steady rate of iron dissolution or hydrogen evolution was attained. Corrosion resistance is inversely proportional to this "pickle lag" time; a maximum of 10 seconds, and preferably no more than 5 seconds, is considered the dividing line between good and questionable quality. Results are tabulated in Table 8:

TABLE 8

Pre-plating treatment			Pickle lag time, seconds
Low density abrasive	Pickling	Rinse	
x	-----	x	3
-----	x	x	12
x	x	x	7

It is apparent that improved results are obtained when the conventional pickling step is preceded by abrasion with a low density abrasive; however, the best results are obtained when there is no intervening chemical treatment between abrasion and plating.

EXAMPLE IV

Twenty samples of a steel commonly referred to as "black plate," were electroplated with tin as follows:

(1) Cleaned cathodically for 5 seconds at 160°-180° F. in electrolyte consisting of 4-6% Na₂CO₃ at a current density of 50 amperes per square foot with a carbon rod anode. (Degreasing, normally required before cathodic cleaning, was not necessary because no oil had been applied to the surface of the steel prior to shipment.)

(2) Rinsed in hot water, 160°-180° F., for several seconds.

(3) Abraded with low density abrasive material of the type described in Example I, in which discs compressed on a shaft formed a roll having 14 discs per inch of width. As the steel was passed beneath the roll at 50 feet per minute, the roll was driven in the opposite direction at 1100 r.p.m. and water sprayed between the roll and workpiece. A meter connected to the driving motor indicated that the power consumption was approximately 0.1 horsepower per inch of workpiece width above that required to drive the motor under no-load conditions. Substrate removal was approximately 200 milligrams per square foot.

- (4) Pickled for 5 seconds in 3-3½% H_2SO_4 at 160° F.
 (5) Rinsed in demineralized water at 80° F.
 (6) Electroplated for 15 seconds at 135°-150° F. at a current density of 100 amperes per square foot in a stirred electrolyte prepared by dissolving the following chemicals in 1 gallon of demineralized water:

NaF and $NaHF_2$ (mixed in a 1:1 ratio) ---oz---	4.5
$SnCl_2$ -----oz---	4
$Na_4Fe(CN)_6 \cdot 10H_2O$ -----g---	0.5-1.5
Commercial brightener -----ml---	300
for tin plate halogen baths, e.g., "AA2," available from Du Pont NaCl -----oz---	4.5-5

The pH of the electrolyte was held between 3 and 3.3 by adding HCl.

- (7) Dipped for 2 seconds in 120° F. solution containing ½ oz./gal. of $NaHF_2$.

- (8) Rinsed for 1-2 seconds in 160° F. demineralized water.

- (9) Rinsed for 1-2 seconds in 160°-180° F. solution containing 0.2 oz./gal. of NH_4Cl .

- (10) Dried with forced air at room temperature.

- (11) Tinplate flow-melted by clamping the electroplated sample securely between two copper bus bars, applying 90 volts A.C. across the sample until the typical dull plate of electroplated tin began to flow and become bright. The molten tin was then air cooled 0.35 second and quenched in room temperature water.

The quality of the tin plate was then checked according to the industrially accepted Alloy Tin Couple, or ATC, test² as follows:

- (12) Cleaned cathodically according to the procedure outlined in Step 1.

- (13) Detinned electrolytically in 5% NaOH solution at a constant voltage of 0.4 volt D.C. to expose the iron-tin alloy layer adjacent to the steel base, a 0.1-ohm shunt being connected across the power supply. The tin was selectively dissolved anodically by employing a stainless steel cathode ten times as large as the area of tin plate being detinned.

- (14) Dried sample by immersing in ethyl alcohol and evaporating alcohol at room temperature.

- (15) Placed rear of sample on a piece of plastic backing and completely masked the front of the sample with molten wax except for an inscribed elliptical area of 2.33 square centimeters.

- (16) Positioned sample so that the exposed iron-tin alloy layer faced a pure tin anode in a specially constructed air-tight cell into which grapefruit juice, previously purged of any dissolved oxygen and containing 100 p.p.m. of $SnCl_2$, had been introduced. The cell was maintained under a positive pressure of purified N_2 gas at room temperature during the entire testing period. The current flowing between the test sample and pure tin anode was measured after 20 hours by breaking the short circuit between the electrodes and quickly reading the potential drop across a 27.9-ohm resistor. The reading was then converted to microamperes per square centimeter, the ATC value.

The grapefruit juice electrolyte used in the ATC Test is regarded as typical of a large class of products including citrus fruits, peaches, pineapple, pears, and tomato products. The test, which is believed to measure the effect of alloy discontinuities and nature of the base steel exposed through the alloy, correlates with the galvanic detinning of cans containing acidic products in pack performance tests which may require two years. Low ATC values insure good corrosion resistance. Grade A acid tin

plate is defined as a plate having an average value of 0.050, and 95% of the values below 0.085 microampere per square centimeter.

- The twenty samples prepared according to this example were compared to twenty control samples (identical, except for omission of abrading in Step 3). No values of the experimental samples were found in the uppermost range, 0.081-0.100 microampere per square centimeter, whereas 10% of the values of the control samples fell therein. Although 90% of the experimental samples had ATC values below 0.060, only 60% of the control samples fell in this range. The average ATC values for experimental and control samples were respectively 0.38 and 0.54. Thus, steel treated in accordance with this example produced tin plate well within the limits for Grade A, while the same base steel, when conventionally treated, produced acid tin plate not acceptable for Grade A rating.

- Comparable experimental and control samples were then analyzed electrolytically³ to determine the iron-tin alloy weight. The control samples averaged 0.172 lb. of iron-tin alloy per base box, while the experimental samples averaged 0.143 lb. of tin per base box. Thus, despite a lower iron-tin alloy weight, the experimental tin plate showed superior corrosion resistance, as indicated in the preceding paragraph. Although the reason for these results is not known, it is felt that perhaps the surface pretreated with low density abrasives somehow beneficially affects the formation of the iron-tin-alloy crystals so a thinner layer covers the steel more uniformly, thereby affording greater corrosion protection.

EXAMPLE V

A test was conducted on a commercial electrolytic acid tin plate line following the process for manufacturing bright tin plate, 0.25 lb. of tin per base box, described in McGannon, *The Making, Shaping and Treating of Steel*, 8th Edition, United States Steel, pp. 954-962. Between the pickling and electroplating sections of the line, the steel strip was contacted by a rotating roll formed by mounting 12-inch diameter discs of ¼-inch thick low density abrasive material having a void volume upwards of about 90%, on a hollow shaft and compressing them to a density of 16 discs per inch of roll width. The steel strip was traveling at 600-700 feet per minute; the abrasive roll was driven at 900 r.p.m. in a direction opposite to the movement of the steel strip, contacting the steel at a pressure resulting in a power consumption of 0.05 HP (above no-load conditions) per inch of steel strip width. Cooling water, at 65° F., was pumped into the hollow shaft of the abrasive roll and thrown centrifugally outward.

- During this experimental run, a control sheet of finished tin plate was prepared by lifting the roll from the steel strip, this representing the conventional method of bright acid tin plating. Forty-two tin-plated samples each were randomly selected from the control sheet and the experimentally prepared sheets and subjected to the ATC test described in Example IV. Whereas 83.4% of the experimental samples had an ATC value below 0.060 microampere per square centimeter, only 54.7% of the control samples fell within the same range. Over 97% of the ATC values for the experimentally processed steel strip fell below 0.085 microampere per square centimeter, and none were above 0.090; in contrast, 7.2% of the ATC values for the control samples were above 0.090, and 2.4% actually exceeded 1.2. Average ATC values for the experimental and control samples were respectively 0.49 and 0.60 microampere per cm.². It is thus noted that the experimentally produced tin plate met the

² Details of the test, and its electrochemical effects are described extensively in "The Alloy-Tin Couple Test—A New Research Tool," *Corrosion*, National Association of "Corrosion Engineers," February 1961, volume 17, pp. 85t-92t, and in U.S. Patent #3,087,871.

³ Method described in the article, "Electrolytic Determination of Tin and Tin-Iron Alloy Coating Weights on Tin Plate," C. T. Kunze, and A. R. Wiley, *Journal of Electrochemical Soc.*, vol. 99, September 1952.

requirements for Grade A, while the tin plate produced by the conventional process did not.

EXAMPLE VI

Low carbon enameling steel panels containing a maximum of 0.003% carbon were prepared as follows:

(1) Thoroughly degreased in trichloroethylene and thereafter scrubbed in a strong detergent solution. As a final check all panels were wetted with water, tilted, and examined for water breaks. The panels were then dried and weighed.

(2) One side of each panel was abraded twice under water lubrication, at a dwell time of 1 second or less, with a roll formed of 8-inch diameter low density abrasive discs compressed to 16 discs per inch of roll width. The shaft was driven at 1100 r.p.m., with power being supplied at 0.4 HP/in. above no-load conditions. A total of about 2.25 grams of metal per square foot was removed. The panels were dried, reweighed, and stored in a desiccator for one day.

(3) The desiccated panels were pickled for 10 minutes in 6% H_2SO_4 at 160° F. with no agitation but occasional stirring.

(4) The pickled panels were rinsed and immersed for 10 minutes in a 170° F. nickel flash-plating bath containing 2 oz. of $NiSO_4$ per/gal. and acidified with H_2SO_4 to maintain a pH of 3.2–3.4.

(5) The weight of nickel deposited was then determined by emission spectrography.

Control panels were prepared in the same manner except that abrasion as in Step 2 was omitted.

The nickel deposition weight of panels prepared in accordance with Steps 1 through 5 was 0.095 gram per square foot, whereas the nickel deposition weight on the control samples was only 0.050 gram per square foot. To obtain the same 0.095 gram of nickel on the control samples necessitated an additional 10 minutes of pickling.

EXAMPLE VII

Gold was deposited on the surface of No. 430 stainless steel as follows:

A plating bath prepared by dissolving 0.1 gram of gold chloride in 100 cc. of ethyl alcohol was maintained at 75° F. The stainless steel sample was placed in the bath and, while submerged, vigorously cleaned by hand with a 4-inch x 6-inch pad of low density abrasive material. After 1 minute, the stainless steel was removed from the bath and a layer of gold was found to be deposited on the entire surface. This layer remained after the sample was rinsed in hot water and wiped dry vigorously with a towel. In contrast, gold deposited in the same manner, except that a low density abrasive pad was not employed, was readily wiped off.

EXAMPLE VIII

A layer of platinum was deposited on a 30:70 zinc:copper brass in the following manner:

A brass sheet was cleaned in the same manner as described in Example III and immediately dipped into a plating bath maintained at 75° F., the bath having been prepared by dissolving 3 grams of platinum chloride in one liter of water and adjusting the pH to 4.6 with HCl. After 3 minutes, the sample was removed from the plating bath; it was found that a thin platinum coating uniformly covered the entire surface of the brass and was not removed when a strip of pressure-sensitive adhesive tape was forced against the surface and subsequently pulled off. In contrast, brass which is prepared by a method in which a standard 160° F. pickling treatment (aqueous solution containing by weight 6% H_2SO_4 plus enough H_2O_2 to produce oxygen gassing, thus enabling the oxidation of the Cu_2O on the surface of the brass to CuO) and

a water rinse are substituted for the low density abrasive treatment does not plate within 3 minutes.

Further experimentation at a lower pH of 3.3 with similarly prepared samples gave platinum coatings on the control and low density abrasive burnished samples. However, the low density abrasive prepared samples had a brighter and smoother finish. A 60° reflectometer gave reflected light readings of 75% for the low density abrasive prepared samples and 14% for the control samples.

EXAMPLE IX

Copper was plated on aluminum (Reynolds 2014-0) as follows:

The aluminum sample was cleaned in the same method as described in Example III, after which it was immersed in a plating bath prepared by dissolving 10 grams of copper sulfate and 10 grams of sodium citrate in one liter of water and adjusting the pH to 10.8 with ammonium hydroxide, the bath temperature being maintained at 80–92° F. After 3 minutes a satin-like uniform copper plate was observed. A control sample of aluminum was conventionally cleaned in a trisodium phosphate solution (5 oz./gal.) at a temperature of 165° F., rinsed with water and immediately immersed in the copper sulphate bath for two minutes. The control had a bright, blotchy copper coating when removed from the bath. Although the adhesion of the copper coating was excellent on both the control and low density abrasive prepared samples, the even, satin-like finish on the latter was far superior to the bright, blotchy appearance of the control sample.

Satisfactory coatings having an attractive appearance were also obtained by following the same general procedure in this example (except for appropriate changes in the coating bath and/or the substrate), by plating bronze on steel, silver on brass, copper on steel, copper on zinc, molybdenum on aluminum, aluminum on steel, zinc on steel, chromium on steel and palladium on brass. Spot tests and X-ray diffraction or fluorescence analytical procedures also revealed the successful plating of silver on aluminum, chromium on aluminum, zinc on aluminum, nickel on aluminum, nickel on brass, tin on zinc, cobalt on steel, and molybdenum on steel. In cases where the metal being plated is significantly higher in the electromotive series than the substrate, reducing agents are included in the plating bath.

Another way in which one metal may be coated on another—irrespective of which metal is higher in the electromotive series—is by the incorporation of finely divided particles of the plating metal in the low density abrasive structure. The incorporation can be effected either by supplying the metal particles at the abraded interface or by actually lightly bonding the particles in the abrasive structure.

EXAMPLE X

Nickel was plated on brass in the following manner:

Sheet brass was cleaned by the method described in Example III and thereafter immersed for 5 minutes in a bath containing 8 ounces of nickel sulfate, 8 ounces of nickel ammonium sulfate, and 8 ounces of sodium thiosulfate dissolved in sufficient water to make 1 gallon. A smooth uniform highly adherent nickel coating resulted, the plating rate being substantially faster than that obtained by conventional means and the coating being generally more uniform.

Procedures similar to those illustrated by the preceding examples are also useful in such diverse operations as: production of "passivated" surface on stainless steel by application of various chromate chemicals, nitric acid, hydrogen peroxide, and the like; application of corrosion inhibitors such as alpha-mercapto-stearic acid to metal surfaces; coating of surfaces with "release" chemicals of the fluorochemical type or "adhering" chemicals of the chelating ("Cyquest") type; "poisoning" of metal surfaces for oxygen-hydrogen recombination by appli-

cation of lead substance; application of depolarizers, inhibitors and the like to base steel, as before tin plating; application of acid inhibitors, as before and/or during pickling operations; polishing; application of chrome oxide coat to less noble metal surfaces; application of chemicals from "three-phase" (fluorochemical/water/oil) system; preparation of surfaces for subsequent application of abrasive/adhesive composition or abrasive-containing paint formulation; reduction of "fingerprinting" tendency of stainless steel, aluminum, copper, and the like by reaction with peroxides, chromates, polymers produced by reacting salts of molybdenum, chromium, copper, or such like with chelating polymers typified by poly-N-vinyl-5-methyl-2-oxazalidinone and a copolymer of N-vinyl-5-methyl-2-oxanelidinone and vinyl acetate; production of "release" surface by forming Werner-type chrome complex polymers in situ by reaction of appropriate conversion coated metal surfaces or properly passivated chromium-containing steels; application of drawing agents to the surface of metal to be dimensionally reduced; dyeing or adhesion of colored pigments to chromate conversion coated or "zeolitized" surface obtained by sodium aluminate-sodium silicate reaction on metals, especially silicon steels; staining and/or other surface treatment of steel with permanganates, perchlorates, and the like; or electro-chemical/abrasive treatment by means of an electrically conductive low density abrasive wheel flooded with chromic acid or sulfuric acid. The same principles and concepts may also be useful in such further diverse procedures as calorizing, sherardizing, cementation-coating, chromizing, metal-cladding, spraying of molten metals, cathode sputtering, vapor coating, anodization, welding, coloring steel, carburizing, cyaniding, nitriding, siliconizing, browning, bluing, barfing, and the like.

EXAMPLE XI

A sample of one-coat enameling grade steel having a carbon content of less than 0.003% was coated with vitreous enamel as follows:

A cobalt "flashplate" was applied to the surface of the steel by abrading it as in Example III and then immersing it in a plating bath maintained at 200° F., having a pH of 8.0, and containing 11.2 grams of cobalt chloride, 2.9 grams of sodium hypophosphite, 19.6 grams of ammonium chloride, 37.5 grams of sodium citrate and 378.5 grams of water. After immersion in the bath for one minute the sample was removed, rinsed in hot tap water, and air dried. The dried sample was then sprayed with an aqueous dispersion of a mill addition which contained "Chi-vit" white frit No. CV 430 T5 and which had an analysis of 4% ball clay, ¼% bentonite, ¾% potassium carbonate, ½% sodium aluminate, and ¼% gum tragacanth. The coated samples were air dried and then placed in an electric furnace for 10 minutes at 1,450° F., after which they were removed and allowed to cool. The porcelain had satisfactory adhesion as evaluated by bending the sample, porcelain side out, until the coating began to chip off. A major advantage imparted by the use of the low density abrasive material is the reduction in the time to prepare the sample for porcelainizing, to about half the time required in the conventional method of pickling.

Other pre-porcelainizing metal plates which are useful in this process include chromium, nickel, tin, and molybdenum, depending upon the mill addition employed.

EXAMPLE XII

Steel was primed with a bronze flash-plate prior to the application of an organic adherend as follows:

Six panels of 20-gauge cold rolled steel, AISI C1008, were abraded on a commercially available low density 6-inch diameter x 1-inch wide polyurethane foam wheel having a high void volume and containing aluminum

oxide granules distributed and bonded throughout within the polyurethane resin. The wheel was designated "Poly-bond Abrasive Wheel, Grade 150, Medium Hardness." The panels were lightly forced by hand against the wheel, which was driven at 1200 r.p.m. Three of these panels were "flash-plate" with bronze by dipping them, immediately after the abrasion step, for 0.5 second in a solution consisting of 11.2 grams of copper sulfate and 1.4 grams of tin sulfate dissolved in 378.5 grams of water, adjusted to a pH of 1 with sulfuric acid. Immediately after the plating step the three bronze-plated samples were rinsed with water and dried.

All six samples were then again forced against the low-density wheel as before, except that even lighter pressure was employed. Immediately after this second abrasion step, each of the panels was immersed in a mixture of 100 parts of a commercial epoxy resin (the diglycidyl ether of bisphenol "A"), and 22 parts of Bakelite ZZL0812 hardener (an aliphatic amine cyanoethylation product). After immersion in the catalyzed resin for 5 seconds, each panel was withdrawn and held in a vertical position until the excess resin draining from the panel no longer flowed in a steady unbroken stream but formed drops at the panel edge. All panels were allowed to dry in air at 75° F. for 40 minutes, baked at 250° F. for 20 minutes, and allowed to cool at room temperature.

Two days after the baking operation, all panels were tested for adhesion of the cured epoxy film to the metal substrate. When bent, coated side out, at an angle of about 15° from its original flat plane over a ⅞" mandrel on the Gardner Mandrel Adhesion Tester, failure of the bond between the cured epoxy film and the unplated steel samples occurred in every case. Adhesion of the epoxy to the bronze-plated steel samples was considerably better; all three panels could be bent at least 15° on the ⅞" mandrel without failure, and one panel was bent at 90° on a ⅝" mandrel without failure.

When subjected to 20 inch-pounds of impact on the Gardner Variable Impact Tester, the bond between the cured epoxy film and the unplated steel substrate failed in every case; in contrast, the bond between the epoxy film and the bronze-plated substrate in every case withstood at least 30 inch-pounds of impact before failure. In every case, it was noted that adhesion of the epoxy film to the unabraded portions of the steel panels was so poor that adhesion failed at negligible level of metal deformation.

The adhesion of epoxy resins (as well as other coatings) to seams in metal tanks, tin cans, etc., may similarly be improved by first buffing the area to be coated with a low-density abrasive wheel and, either concurrently or shortly afterward, spraying a solution of CuSO₄ on the surface to deposit a thin priming layer of copper.

EXAMPLE XIII

This example demonstrates the way in which this novel process may be adapted to the galvanizing of ferrous metals, a process which is ordinarily costly and dependent upon the use of reducing furnaces and attendant equipment or double salt fluxing baths.

A 20-gauge 2" x 6" cold rolled steel coupon was degreased in trichloroethylene and processed in an inert helium atmosphere, to obtain a galvanized coating, as indicated below:

The coupon was forced by hand against a low density abrasive wheel of the type described in Example III, due care being taken to avoid contaminating either side of the coupon. It was then galvanized by partial immersion in a bath prepared by melting analytical grade zinc bars in a graphite crucible equipped with spiral electrical strip heaters which maintained the zinc at 450-460° C., any contamination which appeared as dross being removed by skimming. The coupon was held with a pair of tongs and partially immersed in the galvanizing bath for five min-

utes, after which it was removed and hung on a drying rack by means of a nail inserted through a hole in that end of the coupon which had not been immersed in the molten zinc.

The galvanized coupon was subjected to ASTM adhesion test No. A93-58T, in which it was bent back on itself with from 0 to 6 20-gauge steel plates interposed. No crazing occurred until the number of plates was decreased to 1, and only slight crazing resulted when the plates were eliminated altogether. Such adhesion is above the minimum tolerated by the galvanizing industry and thus illustrates how this novel process can effect significant savings.

Similar improvement over conventional galvanizing procedures may also be effected by providing, in the same inert atmosphere, flash plates of copper, nickel, or other metals; such flash plates serve the additional function of changing corrosion resistance.

Procedures similar to those of Example XIII may also be followed to provide hot dip coatings of other metals, e.g., tin or aluminum.

EXAMPLE XIV

Two 1" x 6" coupons of 20 gauge No. 2024 aluminum were held by hand and forced against the surface of an 8-inch diameter x 3-inch wide low density abrasive wheel driven at 1100 r.p.m. until a uniform finish was obtained. Within 20 minutes a 1" x 11" strip of 10-mil "FEP Teflon" fluorocarbon film was placed on the treated surface of each coupon, one end of the film being coterminous with the first end of the coupon and the other end of the film extending beyond the second end of the coupon. A silicone-treated ferrotype release plate was then placed on the opposite side of the film to form a sandwich.

The release plate-film-coupon sandwiches were then placed in a press, the platens of which were heated to 575° F. The sandwiches were so positioned in the press that only the 5 lineal inches immediately adjacent the first end were actually subjected to heat and pressure. After 10 minutes at 200 p.s.i., the sandwiches were removed from the press, quenched in room temperature water, and the release plates removed. One coupon:film laminate was then immersed for 2 hours in boiling water, removed, and dried.

For purposes of comparison, pairs of identical aluminum coupons were prepared in the same manner, except that the treatment with the low density abrasive wheel was replaced by one of the following treatments: sand-blasting—a stream of Grade 100 silicon carbide particles was directed at one face of the coupons for 15-20 seconds, until a uniform appearance was obtained; chemical etch—4 ounces of Na_3PO_4 was dissolved in 1 gallon of water, heated to 190° F., and the coupons immersed therein for 10 seconds; solvent cleaning—coupons were immersed for 2-5 minutes in trichloroethylene, removed, squirted with trichloroethylene, and wiped on a clean towel; wire brush—coupons were held by hand and forced against a 6-inch diameter x 1-inch wide steel brush with .011-inch bristles, driven at 1200 r.p.m., until a uniform appearance was obtained; coated abrasive—coupons were held by hand and forced against the surface of a 1-inch x 21-inch Grade 320 silicon carbide belt mounted on an expandable wheel driven at 1200 r.p.m. until a uniform appearance was obtained.

Adhesion tests were performed on the various laminates by clamping the second end of the coupon in the upper jaw of an "Instron" tensile testing machine, doubling the free end of the film back on itself at 180° and clamping it in the lower jaw of the machine. The jaws were then moved apart at a rate of 20 inches per minute, and the force required to strip the film from the

coupon measured in lbs. per inch of width. Results are tabulated in Table 7:

TABLE 7

Pretreatment	Film-coupon adhesion, lbs. per inch of width	
	Initial	After 2 hours in boiling water
Low density abrasive.....	11.0	10.0
Sandblasting.....	4.0	0
Chemical etch.....	1-2	0
Solvent cleaning.....	1.3	0
Wire brush.....	4.0	1.0
Coated abrasive.....	3.9	2.4

It is noted that where a pretreatment with low density abrasives was included the initial adhesion was over 2½ times that obtainable in any other way. After subjection to boiling water, the adhesion for this product was nearly as good as before—and over four times that obtained when any other pretreatment was used. The reason for this superiority is not understood.

Over a period of years, resin and paint systems have been developed which are comparatively unsaturated for use with surfaces, particularly metallic surfaces, which are coated with an oxide of some kind. When such resins or paints are applied to surfaces in accordance with our invention, it is likely that the optimum material is not being applied. Thus, it may be possible to employ less expensive—e.g., more highly saturated—paints on the surface resulting from treatment with low density abrasive material in accordance with the hereindescribed invention; under many conditions, such paints should cure to a better, e.g., harder state.

Because of the myriad applications of this invention, it is not feasible to exhaustively list all possible ways in which it may be practiced. Many applications for the process set forth will readily suggest themselves to those persons who are skilled in the art and wish to take advantage of this teaching. To illustrate, two metal surfaces may be abraded in a vacuum following the procedure taught herein and brought together to achieve a welded composite. In still another variation of the invention a hollow cylinder may be lined with radially inwardly extending strips of low density abrasive material, the radially inner ends of the strips defining a chamber in which plating material and objects to be plated may be introduced, such a device providing a high degree of utility in tumbling operations.

What we claim is:

1. The method of providing a metallic substrate selected from the class consisting of steel and galvanized steel with a uniform, firmly-adherent inorganic phosphate coating comprising the steps of pretreating the surface of said substrate by abrading with a low density abrasive product to achieve a uniform appearance, said low density abrasive product comprising a tough, flexible resilient three-dimensional fibrous structure containing a multiplicity of abrasive granules randomly distributed throughout and firmly adherently bonded thereto, and thereafter, without any intervening chemical treatment, applying an aqueous solution of an inorganic phosphate to the pretreated surface.

2. The method of providing a ferrous metal structure selected from the class consisting of steel and galvanized steel with a firmly-adherent uniform corrosion-resistant organic coating comprising the steps of pretreating the surface of said structure by abrading with a low density abrasive product to achieve a uniform appearance, said low density abrasive product comprising a tough, flexible resilient three-dimensional fibrous structure containing a multiplicity of abrasive granules randomly distributed throughout and firmly adherently bonded thereto, thereafter without any intervening chemical treatment, applying an aqueous solution of inorganic phosphate to the

pretreated surface to form a phosphate coating thereon, applying a curable film-forming organic coating over the phosphate-coated surface, and curing the said organic coating.

3. The method of providing a steel substrate with a uniform, firmly-adhered fine-grain inorganic phosphate coating, comprising the steps of pretreating the surface of said substrate by abrading with a low density abrasive product to achieve a uniform appearance, said low density abrasive product comprising a tough, flexible, resilient three-dimensional fibrous structure containing a multiplicity of abrasive granules randomly distributed throughout and firmly adherently bonded thereto, and thereafter applying an accelerator-free inorganic phosphate solution to the pretreated surface to form a phosphate coating thereon.

4. The method of providing a galvanized steel substrate with a uniform, firmly-adhered fine-grain inorganic phosphate coating, comprising the steps of pretreating the surface of said substrate by abrading with a low density abrasive product to achieve a uniform appearance, said low density abrasive product comprising a tough, flexible, resilient three-dimensional fibrous structure containing a multiplicity of abrasive granules randomly distributed throughout and firmly adherently bonded thereto, and thereafter applying an inorganic phosphate solution to the pretreated surface to form a phosphate coating thereon.

5. A phosphate-coated ferrous substrate made by the method of claim 1.

6. A corrosion-resistant organic resin-coated ferrous metal structure made by the method of claim 2.

References Cited

UNITED STATES PATENTS

1,007,069	10/1911	Coslett	148—6.15 X
1,247,668	11/1917	Gooding	148—6.15 X
2,514,149	7/1950	Amundsen	148—6.15
2,958,593	11/1960	Hoover et al.	51—295
2,976,169	3/1961	Streicher	117—50 X
2,992,131	7/1961	Bricknell et al.	148—6.15 X
2,997,405	8/1961	Huck	117—51 X
3,012,904	12/1961	Baer et al.	117—50
3,033,703	5/1962	Schneble et al.	

OTHER REFERENCES

Streicher, Metal Finishing, August 1948, p. 65.

RALPH S. KENDALL, *Primary Examiner*.

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