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2,853,406

METAL COATING

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8 Claims. (Cl. 148—6.2)

This invention relates to the coating of metal surfaces, more particularly the surfaces of corrodible ferrous metal, as well as the coated product thereby produced.

The present application is in part a continuation of application Serial No. 251,450, filed October 15, 1951, now abandoned.

Among the objects of the present invention is the provision of novel coating methods which impart to ferrous metal surfaces coatings that make very good anchorages for lacquer and other organic films, and which possess high corrosion resistance with or without a covering organic film. Further objects of the present invention include the provision of novel corrosion resistant surfaces for corrodible ferrous metal. Additional objects of this invention will become apparent from a consideration of the following description of several of its exemplifications.

The above objects are achieved in accordance with the present invention by first etching the ferrous metal surface with an etching acid such as nitric acid, picric acid and soluble persulfates, that preferentially attack the metal grain boundaries, wetting the resulting surface with a dilute aqueous solution of chromic acid, and drying the chromic acid solution on the so-treated surface.

The etch should dissolve away at least about 50 milligrams of metal per square foot of etched surface. This is most readily obtained by contacting the surface with nitric acid having a concentration of from 1 to 20% by weight for a period of 2 to 70 seconds at a temperature of 60 to 150° F. The etching conditions can be varied throughout this range, although best results are obtained with at least about 100 milligrams of metal removed per square foot of etched surface. For some purposes, as when the coated metal is covered with an organic resin film and then subjected to salt type corrosion conditions, the best protection is obtained if the etch removal is not over 450 milligrams per square foot of etched surface. When the etching agent is applied by spray or other arrangement that continually brings a fresh etching solution into intimate and forceful contact with the surface, etching times, temperatures and/or etchant concentrations can be on the low side, since such a technique generally causes the etchings to proceed more vigorously.

Under some nitric acid etching conditions the ferrous metals may tend to become passivated, or may not be fully active, so that the etching results may vary over different parts of the surface. Improved uniformity is obtained by subjecting the ferrous metal to an activation either during or before the nitric acid treatment. One simple activation treatment is dipping in:

Acids such as—

HCl
H₂SO₄
H₃PO₄
H₃PO₃

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H₃BO₃ plus a small amount of HNO₃

Citric acid

Acetic acid

Trichloroacetic acid

Tartaric acid, and even

Tannic acid

Acid reacting salts including—

NaHF₂

Al₂(SO₄)₃

Fe₂(SO₄)₃

And reducing agents such as—

NaHSO₃

MnCl₂

Potassium thiocyanate plus a small amount of hydrochloric acid

Hydroxylamine or its salts such as the sulfate

Hydroquinone plus a small amount of formic acid

A dip in an aqueous solution of any of the above materials at concentrations as low as 1/10% by weight will so affect the metal that it will not show any passivity in the nitric acid etch, even if the activating dip is followed by a thorough rinse before the nitric acid etch is begun. In fact, where the activating dip tends to introduce water soluble materials into the final coating, it is preferred to have such a rinsing effected before the nitric acid etch. Not more than a second or two, and sometimes only a fraction of a second, are required for the passivity inhibiting treatment to insure the desired results. Thus, a 3 second treatment at 50° F. or at 70° F. in a 10% NaHSO₃ in water will prevent passivity. A 2.3% solution of HCl in water will also produce the desired results with a 1/2 second dip at 35° F.

Other passivity inhibiting treatments such as dipping the ferrous metal in a bath, as for example a solution of copper sulfate slightly acidified with sulfuric acid, that chemically applies a coating is also effective, as is mechanical working of the metal surface as by scratch brushing, and cathodic electrolytic treatment of the metal. The mechanical working and the cathodic treatment can be performed either before or during the nitric acid treatment.

Because of the greater effectiveness of the nitric acid etch after the metal is subjected to an activating step, the etching can be very effectively carried out in a very uniform manner without using the highest etching times, temperatures or acid concentrations.

Where the metal to be coated is not perfectly clean, it should be subjected to a careful cleaning operation before the etch. The cleaning can be of any kind such as degreasing with organic solvents like trichloroethylene, treatment with an alkaline cleaner such as aqueous solutions of sodium carbonate, sodium hydroxide and/or sodium silicate, or electrolytic treatment in the above type of alkaline cleaning solutions.

When the metal to be treated possesses a considerable amount of scale or rust it may be advantageously pickled in a conventional manner with an acid such as sulfuric or hydrochloric acid in order to improve the surface characteristics. Care should be taken that this pickling step (which is optional) is not carried to the point where the entire surface of the metal is deeply pocked or etched. Thus, a moderate etch obtained as by treatment in 10% by weight sulfuric acid in water, at a temperature of 160° F. for a period of 15 minutes, does not impair the advantageous results of the invention. Further pickling than this, however, should generally be avoided. When pickling is used, the etching it produces can in general be ignored in considering the metal removal to be obtained by the grain-boundary etch of the present invention.

Inorganic impurities and slight amounts of organic impurities can sometimes be removed by the nitric acid or persulfate etch without any pre-cleaning step. Any soluble persulfate such as ammonium, potassium or even barium persulfate will give the desired etch. However, nitric acid is the least expensive of the above grain-boundary etchants, and is preferred for this reason.

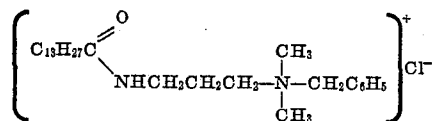
During etching with nitric acid, if the etchant is used as a dip or as a recirculated spray, it gradually accumulates a large amount of dissolved iron and eventually has to be dumped or sent to salvage. The use of lower etching temperatures, below 100° F. for example, seems to give the bath a somewhat longer life, that is enables it to be used with a somewhat larger content of dissolved iron. When higher temperatures are used, there is also a tendency for the bath to begin to generate rapidly increasing amounts of nitrogen oxide fumes. At that time the bath should be changed since its etching ability is sharply reduced and furthermore the fumes are highly toxic.

Inasmuch as the etching operation generates heat, it is helpful to cool the bath with running water or with refrigeration for example, in order to keep the temperature from rising unduly.

Following the nitric acid treatment, the etched metal is rinsed in cold water. This minimizes contamination of the succeeding chromic acid bath with residues from the nitric acid treatment. In many cases the surface of the rinsed metal will show some smut brought out by the etch. This smut should be removed as by wiping or brushing. Brushes with stainless steel bristles are very effective smut removers, particularly when used in the form of revolving brushes. Other types of bristles such as hog hairs can also be used, and stationary wipers such as rubber, plastic or cellulose sponges are effective if the metal surface is brushed over them.

Next, the article being treated is immersed in a dilute solution of chromic acid for a sufficient period to completely wet its surface. Concentrations of chromic acid of from about ½ % to about 10% by weight give the most advantageous results. If the chromic acid concentration is too high, the resulting coating after drying loses some of its desirable water-repellent characteristics as well as corrosion resistance. Concentrations in the neighborhood of 1½ to 5% are preferred. Concentrations below ½ % do not provide a coating that is sufficiently protective.

The chromic acid solution need not be applied for any particular time or at any particular temperature. So long as the surface to be treated is covered with an unbroken film of the solution and the drying is carried out without breaking the film, the desired results will be obtained. The inclusion of wetting agents in the chromic acid solution or of elevated treating temperatures promotes the uniform wetting of the surface. Wetting agents so used should be relatively inert to the chromic acid. Polyethylene oxide ethers of alkyl phenols, such as described in U. S. Patent 2,115,192, long-chained alkyl sulfates such as sodium lauryl sulfate and quaternary ammonium compounds such as myristo amido propyl dimethyl benzyl ammonium chloride



are suitable in concentrations as low as 0.05%. Even tertiary butyl alcohol is satisfactory but in somewhat larger concentrations, e. g. 0.5%.

Mixtures of wetting agents, especially nonionics with other nonionics or nonionics with cationics or anionics are particularly useful. A mixture of the above alkylated aryl polyethers with a medium length solubilized alkyl phosphate gives particularly well regulated wetting and forming characteristics.

To better assure a uniform application of the chromic

acid solution, it can be sprayed on for example with spray nozzles through which air is blown under pressure. Alternatively, if a chromic acid dip is used on a metal sheet or plate, the metal, after removing from the dip, can be passed between roughened or smooth rubber or resilient plastic rolls that are squeezed toward each other. In rolling over the chromic acid film on the metal, the rolls act to spread it around uniformly. At the same time, heavy dip coatings are squeezed out somewhat and reduced in amount. The squeezing rolls can be wet beforehand with some of the same coating solution on the metal. Where spraying of the chromic acid is employed an electrostatic field helps provide better coating uniformity.

The chromic acid treated metal can be dried as soon as the solution is applied. Oven drying or drying with a blast of hot air is preferred, although mere standing at room temperature is effective. The time required for drying varies with the source of heat used but can be as low as about 1 minute, or even a second or two. The use of hot chromic acid solutions reduces the drying time.

Best results are obtained when the chromic acid coating reaches a temperature of 250° F. during the drying. A slightly lower corrosion resistance results if the drying is at lower temperatures.

A peculiar characteristic of the final dried coating is that it does not show its maximum corrosion resistance when it is first formed. The coating seems to undergo spontaneous internal changes on standing and after 2 or 3 days becomes a very high quality protective layer that is strongly water-repellent. Before that time its water-repellence is much lower and in the first 3 hours it is actually readily wet by water. In fact, wetting it during the first 3 hours causes the coating to dissolve at least in part, so that another drying operation is needed, followed by another 2 or 3 day cure to bring out the maximum protection.

The curing can be shortened or entirely eliminated by covering the coating with a film of lacquer or other organic resin such as paint, and drying the resin film. If this drying or the previous drying of the chromic acid is effected at a temperature of at least 250° F. the resulting resin-coated surface can be immediately immersed in water and will show substantially its maximum corrosion resistance while so immersed. Since the application and drying of resin films can be completed in a few minutes or less, this is a particularly desirable after-treatment in accordance with this invention where the protected metal is to be produced commercially on a continuous production line, for example, and the 3 hour avoidance of liquid water is difficult to assure.

The following illustrative examples, in which the quantities are stated in parts by weight unless otherwise noted, will more clearly show different techniques for practicing the present invention.

Example I

Black plate panels (SAE 1010 cold rolled steel) 10 mils thick and with a No. 7 finish were cleaned by dipping for one minute at 180° F. in water containing 3% trisodium phosphate and 1% sodium gluconate and then rinsed in fresh water. The cleaned panels were then etched by dipping in a solution of 10% nitric acid in water for 5 seconds, at a temperature of 75° F. Following this, the panels were rinsed in fresh water, and then immersed in a solution of 1.5% chromic acid (CrO₃) in water for 5 seconds, at a temperature of 180° F. They were then passed through a set of rough rubber rolls to remove excess solution, and dried at room temperature (70° F.) with an air blast.

The final panels, after aging for three days out of contact with water, have a tough, corrosion-resistant film over the entire surface. A one hundred hour exposure to an atmosphere of 95% relative humidity at 115° F. produced no appreciable corrosion.

The coated panels also showed an unusually good lac-

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quer adherence. Unaged panels were dipped in a solution of a lacquer prepared by adding one hundred pounds of Congo gum (preheated about 50° above its melting point until it loses about 20% of its weight and attains the so-called run off state) to twenty gallons of China-wood oil at 400° F., cooking these ingredients together at 400° F. for one-half hour after which the mixture is cooled to 75° F. and thinned to a solids content of 50%. The lacquer is diluted with benzene to obtain a viscosity of 76 seconds at 75° F. as measured with a Parlin viscosity cup #7 AMD, and then baked for 10 minutes at 410° F. The average weight of the baked lacquer was 900 milligrams per square foot.

Lacquer coated panels produced as aforesaid were immersed in boiling solution of 3% sodium chloride and 1½% acetic acid for a period of from ½ to 2 hours. They were then rinsed, wiped dry, and the lacquer adherence tested by firmly pressing against the lacquered surface the adhesive surface of a piece of pressure-sensitive tape. To make the tests more rigorous the panels were bent along a line across which the tape was secured. The tape was then quickly pulled off and examined. If the lacquer adherence is not excellent, patches of it can be readily seen on the tape. In this test all panels showed excellent lacquer adherence.

In Examples II to IX inclusive, the procedure and tests of Example I were repeated without change except for the particular variations noted in the respective examples. All of the tests for lacquer adherence showed superior result, ranging from very good to excellent. Tests for corrosion resistance likewise ranged from very good to excellent.

Example II

1% nitric acid was used at 150° F. for 70 seconds, instead of 10% nitric acid at 85–90° F. for 5 seconds.

Example III

Picric acid in a 1.5% solution in water at 155° F. was used for 12 seconds, instead of the nitric acid etch.

Example IV

A fresh 4% solution of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ —sometimes called ammonium peroxydisulfate) in water at 75° F. was used for 15 seconds as the etching step.

Example V

3% nitric acid was used.

5% chromic acid was used.

Example VI

5% chromic acid was used.

The panels were aged 3 days before being tested for lacquer adherence after the lacquer baking was completed. The lacquer adhesion was about the same as in the product of Example V.

Example VII

20% nitric acid was used, and in place of the black plate a SAE 1025 cold rolled steel stamped into the shape of a handle was treated, the rolling step being omitted.

Example VIII

20% nitric acid was used.

5% chromic acid was used.

The panels were aged 3 days before the lacquer coating was applied. The lacquer adhesion was substantially the same as in Examples V and VI.

Example IX

10% chromic acid was used.

Example X

Several eight inch by four inch panels of 0.0095 inch thick #7 finish black plate were cleaned by immersing in

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an aqueous solution of alkaline cleaner (water containing 5% NaOH and 5% Na_2SiO_3) at 200° F. and then carefully rinsed with water. The rinsed panels were immersed in a 1% by weight aqueous solution of nitric acid at 75° F. for 5 seconds and then again rinsed thoroughly with water and wiped to remove any smut that developed from the nitric acid treatment. The wiped panels were immersed for 15 seconds in a ½% solution of CrO_3 in water, then drained for ½ minute and then placed for 3 minutes in an air oven maintained at 250° F.

After aging for 2 days, the coated metal showed very little corrosion when subjected to an accelerated cold-hot humid cycle test, with alternate periods of 2 hours at 32° F. and 24 hours at 125° F., all of 98% humidity. Similar panels treated in the same way but having the chromic acid solution of only ¼%, show at least four times as much corrosion and are in fact substantially entirely covered with corrosion, whereas the coating in accordance with the present invention (½% CrO_3) has large areas entirely free of corrosion.

Example XI

The process of Example X is repeated but the steel, after cleaning, is subjected for 0.25 second to a 1% solution of H_2SO_4 at 70° F., followed by a rinse. The nitric acid bath was applied in the form of jets impinging on the steel with a velocity of 25 feet per second, and the time of the nitric acid treatment was reduced to 2.25 seconds. A spray was also used for the application of the chromic acid. The final panels were more uniform in appearance than the panels of Example X, but otherwise showed about the same corrosion resistance.

Example XII

Hot rolled SAE 3140 steel (containing 1.4% nickel and 0.5% chromium) in 11 mil thick sheets, was subjected to the treatment of Example XI and resulted in coated sheets with an unusually high corrosion resistance.

It has also been discovered that a nitric acid etching bath can be made to have an exceedingly long life if there is bubbled through it a non-reactive gas such as air, nitrogen, carbon dioxide, helium or even hydrogen. Thus, by blowing air through the bath at the rate of 25 cubic feet per minute for each square foot of mean horizontal cross-sectional area the bath occupies, that is enough to create continuous turbulence in the bath, the need to dump the bath is entirely eliminated. All that is required is the gradual addition of fresh nitric acid to make up for the acid consumed by the etching. The metal etched will generally drag out enough bath to keep the bath volume down, but extra amounts of the bath can be removed if desired.

A preferred way to adjust the drag out is to add the fresh nitric acid in such a concentration that it counteracts any tendency for the bath volume to change. Thus, where the volume is increasing a high concentration (70% by weight) of replenishing acid can be used, and vice versa.

If no replenishing is made, the bath can generally be used about half again as long as without blowing.

It is believed that the blowing or bubbling acts to remove volatile nitric acid reduction products from the bath as fast as they are formed, and thereby keeps them from reacting with the ferrous iron, a relatively large quantity of which accumulates in the bath. In any event, when no blowing is used, the bath which originally turns green, gradually becomes more reddish and after 16 to 18 hours of continual use suddenly begins to liberate large quantities of NO_2 fumes and has to be dumped. If before it gets too red, air is bubbled through, the sudden fume evolution is delayed or completely avoided.

The proximity of the sudden change is usually indicated by the etching becoming uneven and streaky. The bubbling avoids this unevenness as well as the bath dumping.

For commercial operations it is preferred to continually bubble air or other non-reactive gas through the bath so that no other precaution need be taken. As little as 15 cubic feet per minute for each square foot of mean horizontal cross-sectional area of the bath can be used to advantage. The bubbling of very large quantities of gas provides no better results than 25 cubic feet per minute figure given above, and is therefore more wasteful. Where the smaller bubbling rates are used it is important to distribute the bubbling over the entire bath as by having bubbling orifices spread no more than about 5 inches apart all over the bottom of the bath. Greater separation such as 8 to 10 inches can be used with the 25 cubic foot per minute figure, and at the same time the bubbling need not extend to the very bottom of the bath but can stop six inches or so above the bottom. If the etching is limited to the upper portion of the bath, this can be considered the bottom limit of the bubbling. Although hydrogen is listed above as a suitable bubbling gas, it is highly inflammable and care should be taken with it to avoid ignition, as by providing good ventilation.

The above bubbling technique is useful wherever a ferrous metal is to be partially or completely dissolved by nitric acid, and particularly where the nitric acid is at a temperature of not over 100° F.

A feature of the present invention is that there appears to be some peculiar coaction between the chromium oxide coating and the grain boundary etch. Thus, if the process of the invention is modified by substituting a sulfuric acid etch for the grain boundary etch, the final coated metal is much more readily corrodible even though exactly the same amount of metal is removed by the etching.

The desirable characteristic of the new coating is obtained with any corrodible ferrous metal including plain carbon and low alloy steels, that is steels having no more than about 2% of alloying metals. They can have a carbon content varying from extremely low values, 0.05% or even less, to as much as 1.4% or higher. The phosphorus and sulfur contents can range from substantially zero to several tenths of a percent. Generally phosphorus maxima are about 0.15% and sulfur maxima about 0.3%. These materials include the steels ordinarily considered as carbon steels (SAE 1010 to 1095), free cutting steels, plain carbon tool steels, including those that have up to several percent of silicon, and casting metals.

The metal can be in any shape, including sheet, foil, wire, plate, bar, rod, tube, or fabricated forms such as girders, beams, machined elements, etc. Where the surfaces being treated are contoured, as in forgings or machined members, the chromic acid solution is preferably applied in the form of a uniform spray since dipping generally produces nonuniform coatings by reason of the drainage problems.

This invention may be used for a wide variety of purposes. Wherever corrosion resistance is important it is of particular value. Thin sheets of these materials may be bonded to underlying bases of dissimilar metals to impart desired properties thereto. When coated with lacquers, sheets of these products are ideally adapted for use as substitutes for so-called tin cans in the food industry and wherever else tin coated ferrous materials have been employed. Because of their low cost they are of particular interest to the canning and other industries.

The excellent adhesion of resin layers on the chromium oxide coatings of the present invention makes itself manifest with all types of resins such as ordinary paints including those with straight linseed oil vehicles, either raw or blown, or in mixtures with tung oil, oiticica or tung oil paints or varnishes, resin-modified linseed, oiticica or tung oil paints or varnishes and nitrocellulose or cellulose

acetate, or cellulose acetate-butyrate lacquers. High quality paints such as melamine resin-modified drying oil and alkyd resin-modified drying oil paints are very effective. Reference is made to the type of organic coatings described in Paint and Varnish Technology (1948) by William Von Fisher, page 334, as particularly suitable.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A method for improving the surface of corrodible ferrous metal which comprises etching the surface of said metal with nitric acid having a concentration of from 1 to 20% by weight for a period of 2 to 70 seconds at a temperature of 60 to 150° F., applying on the etched surface an aqueous chromic acid solution having a concentration of from ½ to 10% by weight, and drying the chromic acid solution on said surface.

2. The method of claim 1 in which the drying is carried out at an elevated temperature, the dried chromic acid solution reaching a temperature of at least 250° F.

3. A method for improving the surface of corrodible ferrous metal which comprises treating said surface with an etching agent selected from the group of nitric acid, picric acid and soluble persulfates to etch away at least about 50 milligrams of metal per square foot of etched surface, thereafter wetting said surface with an aqueous chromic acid solution having a chromic acid concentration of from ½ to 10% by weight, and drying the chromic acid solution on the metal surface.

4. A method for improving the surface of a plain carbon steel which comprises the steps of etching said surface with an etching agent from the group of nitric acid, picric acid, and soluble persulfates, to etch away from about 100 to 450 milligrams of metal per square foot of etched surface, rinsing the etched surface, wetting the rinsed surface with an aqueous solution of chromic acid containing from ½ to 10% by weight of chromic acid, drying the chromic acid solution on the surface of the metal, and then keeping the resultant product out of contact with liquid water for at least three hours.

5. A method for improving the surface of a plain carbon steel which comprises the steps of etching said surface with an etching agent selected from the group of nitric acid, picric acid, and soluble persulfates, to etch away from about 100 to 450 milligrams of metal per square foot of etched surface, rinsing the etched surface, wetting the rinsed surface with an aqueous solution of chromic acid containing from ½ to 10% by weight of chromic acid, drying the chromic acid solution on the surface of the metal, and then applying a resin coating on the dried surface.

6. The product produced by the method of claim 3.

7. In a process for prolonging the effectiveness of an aqueous nitric acid etching bath in the etching of ferrous metal the step of bubbling a non-reactive gas through the bath during the etching, the bubbling being in quantities of at least 15 cubic feet per minute for each square foot of mean horizontal cross-sectional area of the bath.

8. The combination of claim 7 in which the bath is kept at a temperature below 100° F.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,853,406

September 23, 1958

Ludwig K. Schuster et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 2, for "NoOH" read -- NaOH --.

Signed and sealed this 9th day of December 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents