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2,861,906

METAL TREATMENT

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The present invention relates to metal treatment and particularly to treatment for increasing the corrosion resistance of the metal and/or the adhesion of paint, varnish, lacquer, and other organic finishes to the metal.

This application is in part a continuation of prior applications Serial No. 277,286, filed March 18, 1952, now Patent No. 2,768,103, granted October 23, 1956; Serial No. 278,481, filed March 25, 1952, now Patent No. 2,768,104, granted October 23, 1956; Serial No. 371,427, filed July 30, 1953, now Patent No. 2,777,785, granted January 15, 1957; Serial No. 433,698, filed June 1, 1954, now Patent No. 2,733,623, granted December 11, 1956; and Serial No. 592,552, filed June 20, 1956.

Among the objects of the present invention is the provision of novel treating methods which improve the uniformity of treatment.

The above, as well as additional objects of the present invention will be more completely understood from the following description of several of its exemplifications.

According to the present invention, an extremely uniform corrosion-resistant and organic finish-retaining coating is formed on corrodible ferrous metal that is first etched in nitric acid and then has applied to the etched surface a film of an in situ dried aqueous solution of partially reduced chromic acid, if the etching is preceded by an activation treatment to minimize passivation during the etching.

The etching step should be as uniform as practicable and a metal removal of at least about 100 milligrams per square foot of metal surface is very effective. There appears to be no upper limit for the amount of metal removal that will provide a sharp increase in corrosion resistance and organic film adhesion. However, an etch of more than about 1000 milligrams per square foot will tend to leave a roughened surface that does not make a good appearance. Furthermore, in the interest of economy the etch is preferably kept down to not more than about 400 to 450 milligrams per square foot. Furthermore, an etch removal of more than 450 milligrams per square foot produces a surface that even after the final coating does not have the maximum corrosion resistance when tested by some standards such as the synthetic corn test used by canners.

In use the etching bath accumulates a relatively large amount of dissolved iron and may then deposit a rust-like coating on the metal, especially when the dissolved iron is in the ferric form. Before this build up, however, the nitric acid treatment can be at any desired concentration, time and temperature so long as it effects a uniform metal removal. A bath temperature of about 120° F. is a preferred upper limit for this purpose.

An etching bath that deposits a rust-like coating can be used providing this coating is not so tenaciously held that it cannot be brushed off as by means of felt pads or fiber-bristle brushes.

When etching is carried out by merely dipping the metal in the etch bath, a two to seventy second dwell at a temperature of 60 to 150° F., the bath having a nitric

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acid concentration of from 1 to 20% by weight, can be used. The etching bath can also be sprayed or jetted against the metal, in which case the treatment conditions are at the lower ends of the above ranges.

The nitric acid treatment is sometimes effected under conditions in which ferrous metal becomes passive. When this takes place, the etching either does not occur or is only spotty over the surface of metal being treated. The passivating effect is serious with high concentrations of nitric acid but will be troublesome even with lower concentrations of this acid where the etching bath has picked up a sizeable amount of dissolved iron. In many instances, the development of passivity is unpredictable.

According to the present invention, the etching bath is advisedly preceded by an activating treatment. Examples of such treatments are the contacting of the metal with a liquid non-oxidizing etchant such as solutions of acids including

HCl
H₂SO₄
H₃PO₄
H₃PO₃
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 plus a small amount of acetic acid
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 this etch is preceded by a thorough rinse. 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% by weight NaHSO₃ solution 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. In general, the activation treatment, if carried out with an etching agent, should not dissolve more than about 30 milligrams of metal per square foot of surface.

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.

The activation step is also effective when the etching is carried out by solutions of picric acid or ammonium persulfate. Aqueous or alcoholic solutions containing 1 1/2% picric acid by weight will etch corrodible ferrous

metal and at 155° F. for 12 seconds removes about 370 milligrams of metal per square foot. Concentrations of from ¼ % to saturation can be used at temperatures varying from about room temperature to the boiling point of the solution.

With ammonium persulfate aqueous solutions containing from ½ % to saturation at temperatures from the freezing to the boiling point of the solution are effective. A 4 % aqueous solution by weight will at 75° F. remove in 15 seconds about 380 milligrams of metal per square foot.

The picric acid, the ammonium sulfate and the nitric acid etch the metal in such a way as to preferentially attack the grain boundaries, and this type of treatment seems to be required in order to obtain the added corrosion resistance that the etch provides. Etching with acids like sulfuric acid or hydrochloric acid does not cause preferential grain boundary attack and also does not provide the added corrosion resistance.

Where the metal to be coated is not perfectly clean, it should be subjected to a careful cleaning operation before the activation step. 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.

The partial reduction of the chromic acid is best effected by a reducing agent dissolved in the chromic acid solution but compatible with it for the length of time elapsing before the drying is completed. The reducing agent should be one that is not rapidly oxidized by the chromic acid in the bath at the temperature to which the bath is exposed before it is applied to the metal. In most cases, the reducing agent is compatible with the chromic acid for at least about one day at 80° F.

Examples of such reducing agents for this purpose are:

Organic polyalcohols such as sugars, including:

Invert sugar

Sucrose

Dextrose

Glycol and polyethylene glycols

Glycerine

Mannitol

Sorbitol

Triethanolamine

Hydroxylamine as well as its salts such as its sulfate or hydrochloride

Phosphorous acid

Hydroquinone

Phenol

Potassium iodide

The reducing agent incorporated with the chromic acid solution should not be so volatile that it is evaporated away from the film before it completes the desired reduction. A boiling point higher than that of water is accordingly desired.

The chromic acid bath itself will gradually undergo deterioration, apparently by reason of the gradual reduction of the chromic acid. When a precipitate appears in a bath, it can no longer be used commercially inasmuch as the precipitate deposits on the metal in spots and renders the final coating non-uniform.

The life of the bath is greatly prolonged if the bath also contains a negative catalyst such as a dissolved manganese compound, in the amount of from 0.01 to 0.5 % by weight. Examples of such a compound are manganese salts such as manganese carbonate, $Mn(H_2PO_4)_2$, manganese nitrate, manganese chloride, manganese acetate, as well as potassium permanganate, ammonium permanganate, sodium permanganate, and potassium man-

ganate. Without the manganese compounds a precipitate will form at 80° F. in about two weeks or slightly less when

the reducing agent is cane sugar. With as little as 0.06 % of manganese carbonate originally incorporated in the bath the precipitate formation is delayed for an additional period of at least a week or more. An eleven day extension of life is provided by 0.1 % potassium permanganate.

The reducing agent can be added to the chromic acid solution immediately before the solution is applied to the metal, so that the compatibility period can be reduced to only a few minutes or even less. By way of example, the reducing agent can be supplied as a solution mixed with a chromic acid solution while these solutions are fed to a spray gun.

When the added manganese compound has its manganese in heptavalent or hexavalent condition or in valences above 4, there will sometimes form for a short period of time a slight precipitate apparently of manganese dioxide during the first few days the bath is kept. However, this precipitate will go back into solution a few hours after it is formed and after redissolving will not deleteriously affect the coating.

The chromic acid film should be uniformly applied over the surface of the metal to be protected. To this end it is preferred to flood or spray the solution over the metal or pass the metal through a suitable bath, and then between rubber rollers. A very effective distribution of the film is obtained at low rolling speeds when the rubber rollers have a rough or coarse outer surface. At higher speeds, about 700 feet per minute or more, roughened surfaces are not needed and can be omitted. Natural or synthetic rubber or other resilient materials such as plasticized resin can be used as roll surfaces with equally beneficial results. Roller surfaces of the more resilient type should be somewhat rougher than those of the lesser resilient type to obtain corresponding film distribution. When spraying is used it can be plain or electrostatically assisted.

The most resistant and adherent forms of coating are obtained when the chromic acid film is heated during the drying to a temperature above 212° F. Above 350° F. very little additional advantage is obtained. At drying temperatures of 450 to 550° F. the coating appears to be adversely affected, depending upon the particular reducing agent used and its concentration. At 212° F. or higher, the aqueous coating film is converted to the final protective coating in about two to five seconds. The final coating is a very light grayish, and slightly greenish, more or less transparent layer that is very adherently held on the metal and does not scratch off very easily. The folding of a sheet of metal back on itself so as to produce a sharp crease does not loosen the coating either on the inside or outside of the crease.

The corrosion resistance of the coating can be further improved by quenching the coated metal from the drying temperature down at least 25° F. in a liquid such as water or oil. This treatment lengthens by about 50 % the period in which the coated metal can be exposed to a hot humid atmosphere without showing corrosion. Even better corrosion resistance is obtained by quenching in water containing up to about 1 % chromic acid. The lacquer adhesion of the coating is also improved in water quenching where about 0.05 % or more of chromic acid is dissolved in the quench water. At lower concentrations of chromic acid the lacquer adherence is slightly diminished.

A particularly effective coating operation is one that ends with a drying step performed at 250 to 450° F. followed by a quenching down to 200° F. in a ½ % chromic acid solution in water. In some cases the chromic acid bath is more uniformly applied if it contains a wetting agent. When the bath is applied by a roller that transfers the liquid to another roller which in turn transfers it to the metal, about 0.1 % of a wetting agent is very helpful. Non-ionic, cationic or anionic wetting agents can be used but those of the non-ionic type such as the condensation product of 3 mols of ethylene oxide with

1 mol of p-n-octyl phenol, as described in U. S. Patent No. 2,115,192, are preferred. Other wetting agents as described in copending application Serial No. 587,388, filed May 25, 1956, are also suitable.

Without limiting the invention in any way, the following specific examples are given of effective coating operations.

Example I

A strip of full bright finish sheet steel (black plate) ten mils thick is subjected to the following treatment in the order given:

- A. A one second dip in 1% H_2SO_4 in water at 70° F.
- B. Rinsed with tap water at 70° F.
- C. Immersed for 5 seconds in 2½% solution of HNO_3 in water at 70° F.
- D. Rinsed with tap water at 70° F.
- E. Brushed to assure that adherent reaction products or contaminants are removed.
- F. Passed through a water solution containing 2½% CrO_3 , 0.9% sucrose and 0.1% KMnO_4 at 70° F., and then rolled between smooth rubber rollers wet with the same solution.
- G. Cured by passing the resulting filmed metal through a drying unit having a set of ceramic gas burners heated red hot by burning gas, a 5 second exposure to the incandescent units being used, and the metal reaching a temperature of 300 to 350° F.
- H. Quenched in tap water containing 0.5% CrO_3 and held at 200° F.

Example II

An elongated strip of No. 7 finish black plate 11 mils thick was subjected to the following treatments in order, by continuously moving the strip through each one:

- A. Dip for ½ second in ½% H_2SO_4 by weight, at 65° F.
- B. Spray rinse with tap water at 65° F.
- C. Pass for 2½ seconds before a series of jets of 75° F. aqueous 1.2% HNO_3 by weight, the jets impinging on the metal surface at a velocity of 40 feet per second, each jet being ¼ inch wide and the individual jets being 1 inch apart both longitudinally and transversely of the strip.
- D. Spray rinse with tap water at 65° F.
- E. Roll between rotating brushes having stainless steel wire bristles.
- F. Pass between rubber rollers over which is poured an aqueous solution of 3% CrO_3 and 1% triethanolamine.
- G. Pass for 10 seconds through air oven, the air having a temperature of 1000° F., the metal reaching a temperature of 350° F.
- H. Quench with tap water at 200° F.

The coated metals of these Examples are more corrosion resistant and show better organic finish adhesion than similar products made without the activation step.

The coatings and coating processes described above are highly suited for all corrodible ferrous metal and particularly plain carbon and low alloy steels, that is those containing not more than about 5 to 6% alloying metals, and whether hot rolled or cold rolled. A very desirable use of the present invention is in the manufacture of metal containers such as those used for oil, foods including milk as well as dried foods, and chemicals. For this purpose cold-rolled sheet or strip carbon steel containing from about 0.05 to 0.2 carbon is coated in the manner pointed out above and then formed into a container such as the usual crimped seam food can, after which a layer of lacquer can be applied to the outside of the can surface. An application of the lacquer coating in this manner helps to seal the crimped joints against leakage. If desired, however, the lacquer can be applied to the inside as well as to the outside, or alternatively only to the crimped areas, preferably before the crimping is effected so that the lacquer has a gasket-like leak-reducing effect on the joint. Such leakage reduction can also be pro-

vided with other plastic materials such as resins that are not in lacquer form.

In some cases, however, these coatings may show a tendency to brittleness caused by sudden impact, as for example when a coated metal is subjected to a high speed stamping operation. This tendency to brittleness can be considerably diminished by using reduced CrO_3 coatings weighing not more than about 50 milligrams per square foot of metal surface, as well as by decreasing the ratio of reducing agent to the chromic acid. A good ratio for this purpose is about the lower limit of the range suitable to form a coating that gives the effective corrosion resistance. By way of example, an aqueous solution containing 3% chromic acid and 0.75% sucrose produces a coating that is extremely resistant to mechanical shocks and can be stamped at any desired stamping speed without showing significant damage. About half the CrO_3 is reduced in this coating.

The proportion of reducing agent to chromic acid in the coating bath is such that the chromic acid is not completely reduced. Where sucrose is the reducing agent a proportion within the range of from 1 part of chromic acid for 1 part of sucrose, to about 7 parts of chromic acid for 1 part of sucrose by weight is suitable. With triethanolamine a range from 2 parts of chromic acid for 1 part reducing agent to about 10 parts of chromic acid for 1 part of reducing agent by weight is suitable. In accordance with the invention about 40 to 95% of the chromium in the final coating is in the trivalent form, as determined by dissolving the coating in hot concentrated aqueous NaOH, adding excess potassium iodide and titrating with a standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ to give the hexavalent chromium content. The total chromium content is found by taking a different portion of the dissolved coating, adding excess H_2O_2 and boiling to convert the trivalent chromium to hexavalent condition, and then adding excess potassium iodide and titrating. Regardless of the reducing agent, proportions giving about the same results are used.

The reduced chromic acid coatings of the present invention contribute a substantial amount of increased adhesion and wear-resistance for such organic coatings as well as resistance to corrosion. Suitable organic layers are those usually loosely referred to in the art as enamels, sanitary enamels or lacquers, such as the oleo-resinous, phenolic or vinyl resin varnishes. Particularly effective forms of such organic type coating are described in U. S. Patents Nos. 2,231,407, 2,299,433, 2,479,409 and 2,675,334.

The coating of the present invention can also be used to protect ferrous metal that is subjected to high temperature treatment, as for example annealing or the like. During such annealing, the steel usually becomes covered with oxide scale to varying degrees, and the scale is generally removed by a pickling operation. A coating of 20 to 50 milligrams per square foot of the partially reduced chromic acid before the high temperature treatment will cause the scaling to take place with much more uniformity and in such a form that it is much more readily removed by pickling. Furthermore, the pickled surface is not as deeply eaten away and gives a much more desirable finish with a higher strength. By way of example, gears cold forged from AISI 8620 steel, when coated as in Example I with reduced chromic oxide coating of 30 milligrams per square foot and then heated at 1700 to 1800° F. for 20 minutes, readily descale after 15 minutes pickling in uninhibited 5% aqueous sulfuric acid by weight. The above steel is a corrodible low alloy steel having the following composition:

	Percent
Carbon	0.18 to 0.23
Chromium	0.4 to 0.6
Nickel	0.4 to 0.7
Manganese	0.7 to 0.9
Molybdenum	0.12 to 0.25

A similar improvement is obtained from articles that are annealed or tempered after other cold-forming operations, such as the conventional drawing. In this phase of the invention the steel is not made absolutely corrosion resistant and the maximum degree of protection is not necessary. The preliminary etching step can accordingly be omitted along with the preliminary activation. On the other hand, the amount of scaling can be further diminished by covering the reduced chromic acid coating of the invention with ordinary clay such as kaolinite in finely powdered form and in a layer of from 1/8 to 1/2 inch thick.

Cold forming operations also tend to leave the metal surface somewhat more porous than normally. Cans made of sheet steel by the usual drawing operations to provide seamless and strong containers, will therefore not be too well suited for containing liquid chemicals because of a tendency for the chemicals to pick up iron from the metal surface. Aqueous or non-aqueous chemicals and even hairdressing lacquers, will become contaminated from containers so made and from steel that has also been tin-plated with up to 1/2 pound or more of tin per base box. The reduced chromic acid coatings of the present invention are very effective in diminishing such contamination. Here the preliminary etching of the grain boundary type gives a better corrosion resistance, both for the tin-plated as well as the unplated steels and the preliminary activation is also advantageous.

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. In a method of coating corrodible ferrous metal by first etching the metal surface in aqueous nitric acid having a concentration of from 1 to 20% by weight for a period of from 2 to 70 seconds to a temperature of 60 to 150° F., and then applying to the etched surface a film of an in situ dried aqueous solution of partially reduced chromic acid, at least about half but less than all the chromic acid in the film being reduced, the improvement by which the etching is preceded by a step in which

the metal surface is subjected to an activation treatment to minimize passivation by the nitric acid.

2. A method for forming a corrosion-resistant, lacquer-adhering surface on ferrous metal, which method comprises subjecting the metal to an activating treatment to keep it from becoming passivated by nitric acid, then contacting the metal with an aqueous nitric acid bath having a concentration of from 1 to 20 percent HNO₃ by weight for a period of from 2 to 70 seconds at a temperature of 60 to 150° F., rinsing the contacted metal, applying to the rinsed metal a film of a bath consisting essentially of water having dissolved in it about 1/2 to 30 percent CrO₃, from about 1/4 to 25 percent of a reducing agent for the chromic acid, said reducing agent being one that co-exists in the bath with the chromic acid without producing a precipitate at the contacting temperature for at least one day, and about 0.01 to 0.5 percent of a manganese compound, and then drying the filmed metal by heating to about 250° F. to eliminate all free water from the film and to cause the reducing agent to be completely oxidized by the chromic acid in the film.

3. The invention of claim 2 in which the heated coated metal is water quenched to 200° F.

4. The invention of claim 1 in which the activating treatment is with a liquid nonoxidizing etchant that dissolves no more than about 30 milligrams of the metal per square foot of metal surface.

5. The invention of claim 4 in which the liquid non-oxidizing etchant is aqueous sulfuric acid.

6. The invention of claim 1 in which the activation treatment is effected by contact of the metal with aqueous sulfuric acid, and the in situ drying is carried out at a temperature of from 250 to 450° F.

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