

UNITED STATES PATENT OFFICE

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SURFACE TREATMENT OF METALS

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4 Claims. (Cl. 41-42)

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This application is a continuation in part of my application Serial No. 484,767 filed April 27, 1943, now abandoned, which was a continuation in part of my application Serial No. 447,435 filed June 17, 1942, now abandoned.

This invention relates to the art of finishing ferrous metal or zinc, generally in sheet or strip form, and is particularly directed toward minimizing the defects commonly attributed to the presence of hydrogen in the structure of the metal. It is known that such gas as it exudes over a period of time may result in weakness and corrosion; and if the metal is painted or enameled may cause the coating to blister or flake off. These ultimate defects have been attacked in the past by using oxidizing solutions such as nitric, sulfuric or chromic acid to form a film or coating of oxide over the metal which would seal the pores thru which the hydrogen might escape, and to form a rust resistant base.

In the present invention I use similar chemicals, but in a different manner and for a different immediate purpose; that is, rather than providing a coating, I seek to remove any coating and do away with the unduly compacted surface particles of the metal itself that obstruct its normal porosity. Yet I do not visibly etch or destroy the surface finish to the average eye, since my treatment merely touches the microscopic outer layer, which I mechanically remove as fast as oxidized, and no oxidized film remains.

The essence of the invention is a quick acid treatment accompanied by vigorous mechanical scrubbing to continuously remove the oxide as created, followed immediately by rinsing and drying so that oxidation by the air is avoided. This produces a metal whose microscopic surface pores are about the same as its internal intermolecular or intercrystalline spaces, that is, there is normal metal structure at the surface as well as under the surface. This has the double advantage of permitting the hydrogen to escape without building up undue pressure, and at the same time providing better anchorage or bonding below the surface for better adhesion in case paints or enamels are later applied. This not only prevents blisters, but also permits such metal when so coated to be bent in later fabrication without cracking the enamel.

My particular invention however is not in any coating, but in the treatment of the metal itself, which may also be used without painting or enameling, since the treatment leaves a fair luster and good resistance to corrosion, as compared with the bare metal not so treated. The beneficial effects flow from the removal of the

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microscopic layer of compacted surface metal without visibly etching or destroying the finish, and are fundamentally due to the increase in the means of escape for the hydrogen from within the metal, whereby the building up of excessive internal pressures is avoided.

In brief the invention consists in running the metal strip or sheet quickly thru an aqueous acid bath such as ordinarily used for oxidizing, but while submerged scrubbing it vigorously with rotating brushes to remove any oxide as fast as it is formed, the treatment being so brief and superficial that the surface is not sufficiently etched to impair its marketable quality, since merely the microscopic compacted surface is affected; the sheet being then promptly rinsed and thoroughly dried before contact with the air can impair it. In the prior art the acid always left some form of coating intended to protect the metal. I have found that the metal without any compacted or occlusive surface is largely self-protecting.

To give a specific example of my process as applied to practice in a mill, the metal sheet or strip as it passes rapidly thru the usual rolls is conducted thru an aqueous bath such as ordinarily used for oxidizing; and while submerged it is vigorously scrubbed by rotating brushes placed among the conveyor rollers, these brushes being preferably surfaced with wire or Tampico bristles, which whisk away the oxidized particles as fast as they are formed, thus obtaining a clean surface free from deposits and removing the microscopic outer skin or film of amorphous metal. This skin as ordinarily found consists of densely compacted and enlarged flattened particles produced by the crushing and smoothing of the disrupted portions of the metallic grains of the body of the material in the ordinary rolling mill operations.

Such smooth and compacted surfaces under the microscope appear non-crystalline and contain relatively few breaks, cracks, discontinuities or pores. By my treatment a more uniform porosity is restored and the metal made more susceptible to the release of hydrogen gas at myriad points over its whole area. In carrying out the process, the action of the rotating brushes keeps the solution well agitated and thus accomplishes the purpose of exposing unencumbered metal surfaces constantly to the action of unimpoverished treating solution. The action, while brisk, is so brief in point of time as to be strictly superficial, for we are dealing only with surfaces of microscopic thickness. The general finish of the strip is not appreciably impaired. The time may vary with the strength of the solu-

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tion, composition and temperature, from about 5 seconds to possibly as long as 5 minutes; a typical time in preferred practice being about 10 seconds at say 180° F.

Immediately after this scrubbing bath the moving sheet or strip of metal is rinsed and promptly dried. The sheet or strip is kept wet between the acid bath and the rinsing bath at all times so that air will not touch the metal surface until the moment of drying is reached. Once freed from the acid and dry, the metal surface is remarkably stable, and may then be exposed to other operations such as polishing, enameling or painting without losing its desirable properties. In any event the surface treatment described has a definite and permanent effect. Sheets from which the compacted microscopic surface has been so removed have remained uncorroded very much longer than untreated sheets of the same original material and appearance.

A wide variety of acidified solutions may be used, as will be apparent to those familiar with oxidizing processes in the steel business. An illustrative solution contains chromic acid, a dichromate, preferably sodium, and a chloride, such as sodium chloride; approximate proportions by weight in dry form may be 57% of chromic acid, 6% of sodium dichromate, and 37% of rock salt; dissolved in water in the proportion of from 2 to 6 ounces by weight of the dry ingredients to one gallon of water. Temperatures may run from say 180° F. to 212° F.; cooler temperatures give slower action while boiling represents the upper limit.

Other illustrative solutions are as follows, to be dissolved in water in approximately the proportions above mentioned.

Example 2

	Percent
Chromic acid -----	47
Rock salt -----	47
Potassium ferricyanide -----	3
Sodium dichromate -----	3
	100

Example 3

	Percent
Chromic acid -----	47
Rock salt -----	45
Sodium fluoride -----	2
Potassium ferricyanide -----	2
Sodium dichromate -----	3½
Sodium sulphate -----	½
	100

Example 4

	Percent
Chromic acid -----	40
Rock salt -----	57
Sodium fluoride -----	1
Sodium dichromate -----	2
	100

Example 5

	Percent
Chromic acid -----	40
Rock salt -----	56
Sodium fluoride -----	1
Potassium ferricyanide -----	1
Sodium dichromate -----	1¾
Sodium sulphate -----	¼
	100

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Example 6

	Percent
Chromic acid -----	57
Rock salt -----	31
Sodium fluoride -----	3
Potassium ferricyanide -----	3
Sodium dichromate -----	5
Sodium sulphate -----	1
	100

It is solutions of compounds of the above mentioned types that I prefer to employ, principally because they are relatively inexpensive, readily available on the market, and easily brought into solution; and also because it is possible to use relatively low concentrations.

In the event that an additional passivating treatment is desired, the metal may be further treated with a solution containing a suitable passivating agent such as chromic acid or a chromate, but one which preferably contains no chlorides or other activating compounds. Such known passivating agents are for example about 8 ounces of either chromic acid or chromates per gallon of water; or I may use a solution containing from 3 to 8 ounces of both chromic acid and sodium dichromate per gallon of water. These are preferably used at about 180° F. and the treatment may last about 10 seconds, more or less. The sheets or strip should then be rinsed and dried as before. The result remains a sheet having uniformly distributed microscopic pinhole porosity. In some of the examples I have included the ingredient sodium sulphate; this may be omitted, but is used to achieve a mottled effect where the metal is to be provided with a ceramic or vitrified coating.

While I have in the foregoing described certain specific embodiments by way of example, it will be understood that they are merely for purposes of illustration to make clear the principles of the invention, which is not limited to the particular forms shown, but is susceptible to various modifications and adaptations in different installations as will be apparent to those skilled in the art, without departing from the scope of the invention as stated in the following claims.

I claim:

1. A method of treating sheet steel in a rolling mill to remove microscopic compacted surface particles resulting from the rolling mill treatment, which consists in running the sheet quickly thru an aqueous acid washing bath containing chromic acid and scrubbing it vigorously with rotating brushes while immersed therein for a sufficient time to loosen compacted surface particles but insufficient to remove any substantial amount of the base metal, the scrubbing removing any oxide that may be formed by the acid so that the sheet remains uncoated, the time of immersion being from five seconds to five minutes, immediately thereafter passing it thru a rinsing bath, and then promptly drying it, whereby the surface is conditioned to more freely release occluded hydrogen.

2. A method of treating sheet steel in a rolling mill to remove microscopic compacted surface particles resulting from the rolling mill treatment, which consists in briskly scrubbing the sheet with rotating brushes while immersed in an aqueous acid washing bath containing chromic acid for a sufficient time to loosen compacted surface particles but insufficient to remove any substantial amount of the base metal, the scrubbing

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removing any oxide that may be formed by the acid so that the sheet remains uncoated, the time of immersion being from five seconds to five minutes, then without permitting it to dry passing it thru a rinsing bath to remove the acid, and then promptly drying it so as to retain the surface condition created by the scrubbing, whereby the surface is conditioned to more freely release hydrogen from the pores of the metal.

3. A method of treating sheet steel in a rolling mill to remove microscopic compacted surface particles resulting from the rolling mill treatment, which consists in rapidly passing the sheet thru an aqueous acid washing bath containing chromic acid while simultaneously scrubbing the surface to remove any results of the acid treatment as fast as they are formed and to free the surface of the steel from occlusions, said scrubbing being for a sufficient time to loosen compacted surface particles but insufficient to remove any substantial amount of the base metal, the scrubbing removing any oxide that may be formed by the acid so that the sheet remains uncoated, the time of immersion being from five seconds to five minutes, then promptly rinsing it to remove the acid, and immediately drying the sheet so as to preserve the surface of the steel in its free natural state, whereby the escape of hydrogen from within the steel is facilitated.

4. The method of treating metal of crystalline structure bounded externally by a skin-like layer of amorphous metal which hinders the escape of internally-held hydrogen, which consists in providing substantially uniformly distributed pores of substantially microscopic size through said amorphous metal skin-like layer by running the metal in a rolling mill under submerged engagement with an aqueous solution of a metal-reactive agent containing chromic acid that reacts with the metal of said amorphous metallic layer, and during movement of the metal physi-

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cally removing solid reaction products of said solution with the metal thus removing any oxide that may be formed by the acid so that the sheet remains uncoated, the velocity of movement of the metal while in reactive engagement with said solution and the concentration of said metal-reactive agent being such as to cause the reaction to provide substantially uniformly distributed microscopic pores thru said amorphous metallic layer without materially etching into the underlying metallic grain structure of the body of the metal and the physical removal of said reaction products insuring against obstruction and closing over of said pores at the external ends thereof, the time of submergence being from five seconds to five minutes, promptly rinsing the metal to remove the acid and immediately drying it, so as to retain the surface with the pores as described.

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