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POLISHING STAINLESS IRON AND STEEL

James N. Ostrofsky, Baltimore, Md., assignor to Rustless Iron and Steel Corporation, Baltimore, Md., a corporation of Delaware

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The present invention relates generally to the art of manufacturing stainless iron and steel and more particularly to the finishing of stainless iron and steel products such as wire, rods, plates, sheets, strip, rounds, bars and the like and the articles fabricated therefrom. By the present invention I provide an improved method of polishing such material and a composition to be employed therefor.

Manufactured stainless iron and steel products have surfaces that are of such character that the products have a characteristic grayish appearance which is quite objectionable in some cases. Even where cold rolling or drawing to size is effected without either intermediate or final annealing a satisfactory polish cannot be obtained. Furthermore, where articles are fabricated from such products by further rolling, drawing or forging they still possess this grayish appearance. This objectionable grayish appearance is particularly prevalent where it has been necessary to remove the oxide scale formed during annealing operations.

The most common method of removing the fire scale is to subject the material to pickling in a suitable bath. In most cases a somewhat rough surface results from the pickling of the material but in some cases where electrolytic pickling has been used lustrous surfaces have been obtained. However, so far as I am aware none of the known commercial pickling processes provided by others will give the material a sufficiently high finish. In order to obtain a material or article having a sufficiently polished or mirror-like finish it has been necessary to resort to mechanical finishing such as grinding or buffing. Furthermore, in the fabrication of articles from such products, if any welding of parts is necessary an oxide scale forms adjacent the weld and it has been necessary heretofore to remove it by similar grinding or buffing operations. As is well known in this art, all of such grinding and buffing operations are difficult and extremely costly, adding materially to the cost of the finished article. Frequently in grinding or buffing such articles the material is ruined due to lack of sufficient care in the carrying out of these difficult operations and the material has to be scrapped.

In my copending application Serial No. 254,888 filed February 6, 1939, I have disclosed a method which overcomes the objectionable features of the prior art polishing methods and whereby stainless iron and steel (i. e., iron and steel having a high chromium content) may be given a high, mirrorlike finish without resort to any of the mechanical methods discussed above and at greatly reduced cost. In accordance with the invention set forth in said application, the material is subjected to electro-chemical treatment. The material is used as the anode and the cathode may be in the form of one or more lead sheets of suitable configuration. The electrolyte is a solution of an organic acid such as an aliphatic carboxylic acid the stainless iron or steel salts of which will permit ready flow of corrosion products away from the anode during the treatment and a soluble compound having a sulphate radical, such for example as sulphuric acid or sulphate salts. The preferable solution, as set forth in said application, comprises approximately 55% citric acid, 15% sulphuric acid and 30% water by weight. The proportions of the bath may be varied within relatively wide limits depending upon the current density employed, the temperature at which the treatment is carried out and the time of the treatment. The citric acid content of the preferable solution can be varied from approximately 10% to 70% by weight. The sulphuric acid content can be varied from approximately ¼% to 70% by weight and the water content can be varied from approximately 5 to 50% by weight. Little or no water is necessary if the treatment is carried out at an appropriate temperature to maintain the ingredients of the bath in a fused condition, but it is better to use at least a small amount of water due to the fact that appreciably lower operating temperatures can be utilized. The current densities employed can be varied from approximately ½ ampere per square inch of material to at least as high as 40 amperes per square inch. The current density utilized is regulated according to the desired time of treatment, the character of the bath, the temperatures employed and the nature of the material. The controlling factor with regard to the current density is that it should be sufficient to overcome the gray etching action of the electrolyte. The temperatures employed likewise may be varied throughout a substantial range. As stated in said application I preferably maintain the bath at a temperature between approximately 50° C. and 125° C. The temperature should be sufficiently high to maintain the organic acid in solution and the highest temperature which may be employed will vary according to practical limitations arising out of the nature of the electrolyte. The time of treatment likewise may be varied over a substantial range. I have found that extremely high polishes can be obtained in

a relatively short period of time, for example, from ½ minute to 3 minutes.

While, as stated above, I preferably employ a solution of citric acid, sulphuric acid and water as the electrolyte, I have found that any of the organic acids the stainless iron or steel salts of which will permit ready flow of corrosion products away from the anode during the treatment, will give satisfactory results in the bath. Other aliphatic carboxylic acids which will work entirely satisfactorily are acetic acid, tartaric acid, formic acid, lactic acid, maleic acid, malic acid, succinic acid and glyceric acid. While I prefer to use sulphuric acid in the bath I have found that satisfactory results can be obtained where any soluble compound containing a sulphate radical is used.

In carrying out the method of polishing stainless iron and steel pursuant to the invention disclosed in the aforesaid copending application, difficulty has been encountered where the temperature of the bath for one reason or another has been permitted to drop below approximately 50 to 55° C. In operations it is sometimes necessary to lower the temperature of the bath to below such temperatures and where this is done a hard, glassy, difficultly soluble salt is formed. This hard, glassy substance is in the form of crystals and builds up in the bottom of the tank and along the sides thereof as the electrolyte is cooled down and an extremely long period of time is required to redissolve this material so as to permit further electro-chemical treatment. Of course, these salts remain in solution at the higher temperatures but if the temperature of the bath, which is generally a saturated solution at elevated temperatures, is lowered, these hard, difficultly soluble crystals form and are relatively insoluble at the lower temperatures.

In one instance where the preferred electrolyte mentioned above was used and the electrolytic treatment carried out at approximately 90–95° C. the temperature of the bath, which was saturated at about 70° C., was lowered to below that temperature and the objectionable crystals started forming. When the bath was permitted to cool down to room temperature and to remain there for several days it required approximately one week after the heat was again turned on to redissolve the crystals and permit further polishing operations.

I cannot state definitely the nature of the salt crystals which are formed but I believe that they are mostly salts of the organic acid used although there may be some sulphuric salts and some combined salts formed.

I have found that where any of the electrolytes mentioned in my aforesaid copending application are employed the formation of objectionable crystals upon the cooling down of the electrolyte is either delayed or prevented by the addition thereto of an alcohol and that a sufficient amount of alcohol can be added without detrimentally affecting the polishing of the material. I preferably employ a relatively small proportion of the alcohol for the reason that if an excessive amount of alcohol is added to the electrolyte it detrimentally affects the polishing of the material. In some cases if too much alcohol is added the polish obtainable is not as good as that obtainable with the same bath without any alcohol present therein. In fact, under some circumstances if an excessive amount of alcohol is added to the bath no polishing effect whatever will be obtained on the material. On the other hand, where only a relatively small amount of alcohol is embodied in the electrolyte a better polish is obtained than can be obtained with the same electrolyte without any alcohol therein.

The amount of alcohol which should be used in the bath in any particular case depends somewhat upon the constituents of the bath, the temperature to which the bath may be cooled and the effect it has upon the polishing of the material. A very small amount of alcohol, such as ½% by volume, will give entirely satisfactory results if the electrolyte is to be or may be cooled only part way to room temperature. This amount prevents the objectionable crystals from forming at the higher temperatures and does not detrimentally affect the polishing of the material. However, a greater quantity of alcohol should be used if the bath is to be cooled to lower temperatures, for example, to room temperature. The quantity of alcohol included in the bath and the temperature to which the bath is cooled determine the amount of crytals formed and also the rate of solubility of the formed crystals. In general, if approximately 10% or less by volume of alcohol is used the formation of the objectionable crystals is prevented or retarded to such an extent that they can be redissolved readily.

In all cases it is desirable to use an amount of alcohol in the electrolyte which will not detrimentally affect the polishing of the material being treated. It is, of course, preferable to use an amount which will enhance the polishing of the material if that amount can be used and the objectionable crystals prevented from forming when the bath is cooled. From the standpoint of polish the quantity of alcohol embodied in the electrolyte should be relatively low. I have found that best results as to polishing of the material are obtained where less than 10% and preferably less than 5% by volume of alcohol is used. When approximately 4% of alcohol is used an excellent polish is obtained. Some mushy crystals form upon cooling of such a bath to room temperature but they are of such character that they will readily redissolve upon reheating.

I have found that any of the alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, amyl alcohol, the glycols or the glycerols give entirely satisfactory results. The monohydric alcohols, however, are preferable.

Where methanol is used in a bath consisting of approximately 60% citric acid, 15% sulphuric acid and 25% water, the proportions being by weight, excellent results are obtained where approximately 4% by volume of methyl alcohol is used in the bath. Where this amount of alcohol is used and the bath is cooled down to approximately 20 to 21° C. (room temperature) only a very small amount of rather mushy crystals (approximately 1/10th the normal crystallization) will be formed. In addition, where this proportion of alcohol is used a better luster is obtained on the finished product than where the alcohol is not used in the solution. 2% methyl alcohol gives a slightly better luster to the material than does the treatment without the alcohol in the bath but a greater proportion of mushy crystals is formed if the bath is cooled to approximately room temperature. Where 2% methyl alcohol is used I would say that the crystals formed constitutes approximately 1/4th the normal crystallization and that that 1/4th consists of rather

mushy, fine crystals. Where approximately 5% methyl alcohol is used the polish on the material is not quite as good as where only 4% is used, although this amount of alcohol in the bath gives considerably better results so far as crystallization at lower temperatures is concerned. Very few crystals form upon cooling to room temperature where this proportion of alcohol is used. Where 10% methyl alcohol is used in this bath no crystals are formed upon cooling it down to room temperature but this quantity of alcohol in the bath detrimentally affects the polishing of the material.

From the standpoint of preventing crystallization the other alcohols set forth above give approximately the same results as those stated above with regard to the use of methyl alcohol in a citric acid-sulphuric acid bath. However, these alcohols do not give as good results from the standpoint of the polishing of the material. Where 4% or more of these higher alcohols is included in the electrolyte it adversely affects the polishing of the metal. Where such alcohols are used not more than approximately 2–3% should be used in the bath in order to obtain satisfactory polishing.

While I have referred generally to the alcohols, I find that the aliphatic alcohols are preferable. It will be understood by those skilled in the art that variations in the amount of the alcohol employed and the particular alcohol to be employed will be dependent upon the organic acid employed and also upon the relative proportions of the constituents of the bath. A suitable alcohol and suitable proportion thereof should be chosen in accordance with the result desired and the operating conditions to be encountered.

While I have described the presently preferred electrolyte, and the presently preferred proportions of the alcohol to be used in the polishing of stainless iron and steel it will be evident that my invention is not to be limited to the preferred process or solution stated above and that my invention may be otherwise practiced or embodied within the scope of any of the appended claims.

I claim:

1. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in an aqueous bath consisting essentially of a water-soluble aliphatic carboxylic acid, ½% to 10% by volume of a member of the group consisting of the mono-, di-, and trihydric aliphatic alcohols and mixtures thereof having one to five carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, a soluble compound having a sulphate radical providing a sulphate ion in the bath, and water in an amount less than approximately 50% by weight of the bath and passing direct current of sufficient density to polish the metal through the bath using the metal as the anode.

2. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in an aqueous bath consisting essentially of a water-soluble aliphatic carboxylic acid, less than 10% by volume of a member of the group consisting of the mono-, di-, and trihydric aliphatic alcohols and mixtures thereof having one to five carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, sulphuric acid, and water in an amount less than approximately 50% by weight of the bath, and passing direct current of sufficient density to polish the metal through the bath using the metal to be treated as the anode.

3. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in an aqueous bath consisting essentially of citric acid, less than 10% by volume of a member of the group consisting of the mono-, di-, and trihydric aliphatic alcohols and mixtures thereof having one to five carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, a soluble compound having a sulphate radical providing a sulphate ion in the bath, and water in an amount less than approximately 50% by weight of the bath, and passing direct current of sufficient density to polish the metal through the bath using the metal to be treated as the anode.

4. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in an aqueous bath consisting essentially of citric acid, sulphuric acid, methyl alcohol less than 10% by volume, said alcohol serving to inhibit crystallization upon chilling the bath, and water in an amount less than approximately 50% by weight of the bath, and passing direct current of sufficient density to polish the metal through the bath using the metal as the anode.

5. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in an aqueous bath consisting essentially of acetic acid, less than 10% by volume of a member of the group consisting of the mono-, di-, and a trihydric aliphatic alcohols and mixtures thereof having one to five carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, a soluble compound having a sulphate radical providing a sulphate ion in the bath, and water in an amount less than approximately 50% by weight of the bath, and passing direct current of sufficient density to polish the metal through the bath using the metal as the anode.

6. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in an aqueous bath consisting essentially of tartaric acid, less than 10% by volume of a member of the group consisting of the mono-, di-, and trihydric aliphatic alcohols and mixtures thereof having one to five carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, a soluble compound having a sulphate radical providing a sulphate ion in the bath, and water in an amount less than approximately 50% by weight of the bath, and passing direct current of sufficient density to polish the metal through the bath using the metal as the anode.

7. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in a bath consisting essentially of 10% to 90% by weight of a water-soluble aliphatic carboxylic acid, ½% to 70% by weight of a soluble compound having a sulphate radical providing a sulphate ion in the bath, ½% to 10% by volume of a member of the group consisting of the mono-, di-, and trihydric aliphatic alcohols and mixtures thereof having one to five carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, and water in an amount less than approximately 50% by weight of the bath, and pass-

ing direct current of sufficient density to polish the metal through the bath using the metal as the anode.

8. As an electrolyte for the anodic polishing of stainless iron and stainless steel, a mixture consisting essentially of citric acid, ½ to 10% by volume of a member of the group consisting of the mono-, di-, and trihydric aliphatic alcohols and mixtures thereof having one to five carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, a soluble compound having a sulphate radical providing a sulphate ion in the bath, and water in an amount less than approximately 50% by weight of the bath.

9. The method of polishing stainless iron and stainless steel by anodic treatment comprising immersing the metal to be treated in an aqueous bath consisting essentially of citric acid, sulphuric acid, less than 4% by volume of a member of the group consisting of mono-, di- and trihydric aliphatic alcohols and mixtures thereof having 1 to 5 carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, and water in an amount less than approximately 50% by weight of the bath, and passing through the bath direct current of sufficient density to polish the metal, using the metal as the anode.

10. As an electrolyte for the anodic polishing of stainless iron and stainless steel, a mixture consisting essentially of a water-soluble aliphatic carboxylic acid, less than approximately 10% by volume of a member of the group consisting of the mono-, di- and tri-hydric aliphatic alcohols and mixtures thereof having 1 to 5 carbon atoms, said alcohol serving to inhibit crystallization upon chilling the bath, a soluble compound having a sulphate radical providing a sulphate ion in the bath, and water in an amount less than approximately 50% by weight of the bath.

JAMES N. OSTROFSKY.