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METHOD OF TREATING STAINLESS STEEL

Edgar A. Hahn, Grosse Pointe Park, Mich., assignor to Lyon Incorporated, Detroit, Mich., a corporation of Delaware

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This application is a continuation-in-part of application Serial No. 259,286, filed November 30, 1951, and now abandoned, and application Serial No. 448,749, filed August 9, 1954, and now abandoned.

This invention relates to the treatment of metal surfaces, and more particularly, the treatment of stainless steel surfaces to remove metal oxide films and/or coatings therefrom, and also the subsequent application of chrome plating to such cleaned surfaces.

Particularly in the fabrication of stainless steel hub caps, trim rings and the like, where appearance is an essential feature, there is often encountered a certain amount of difficulty in perfecting the de-oxidation or cleaning of the stainless steel surfaces, for example, to remove oxides therefrom. Pickling of certain ferrous metal materials is, of course, old; but the pickling procedures heretofore used in the art, which involve the use of strong acids, have left something to be desired in connection with the surface treatment of stainless steels, and particularly, the wrought stainless steels of the 300 to 400 series. The difficulty apparently resides in the peculiar nature and extent of oxide formation which takes place in connection with certain of the metals other than iron which are present in these stainless steels. Such steels contain about 12–30% chromium and the chromic oxide is one of the more difficult oxides to handle. In general, the stainless steels have very high resistance to corrosion and the oxides formed from certain of the metals present in stainless steel are equally resistant to chemical action in many cases and can be removed from the stainless steel surface only with difficulty.

The instant invention is based, in part, upon the discovery of a unique type of electrochemical action which can be obtained through anodic action in the presence of strong aqueous alkali, so as to remove substantially all of the oxide contaminants or surface films without any apparent attack upon the metal per se. In contrast, using the various acid pickling solutions heretofore used there was almost invariably a severe attack upon the metal which took place as a necessary part of the oxide removing pickling process.

It is important that anodic cleaning be used, since if cathodic cleaning is used, an undesirable effect is obtained and, in the case of a subsequent chrome plating operation, it will be noted that the cathodic cleaned stainless steel will not accept a bright chromium plate, but will give a gray deposit when chromium plated. After the anodic cleaning step, the stainless steel is rinsed in plain water to remove most of the alkaline constituents remaining from the anodic cleaning step. The stainless steel is then also immersed in an acid dip, particularly an aqueous solution of 1–5 N sulphuric acid. The time of immersion in the acid dip is only sufficient to completely remove all traces of alkalinity from the surface of the stainless steel; but again it is important to use a dilute acid dip such as that here mentioned, if one is to avoid obtaining a subsequent dull gray chromium plating or a chromium plating containing a number of brown spots.

It is, therefore, an important object of the instant invention to provide an improved stainless steel de-oxidation process.

It is a further important object of the instant invention to provide a method whereby austenitic stainless steel can be directly plated in a conventional chromium plating bath to receive a bright chrome plate.

Another object of the instant invention is to provide a method wherein austenitic stainless steel is first anodically cleaned in an alkaline bath, then, after rinsing, subjected to a dilute acid dip to prepare it directly, after a further rinse, for receiving a bright chromium plate in a conventional chromium plating bath.

It is a further object of the instant invention to provide an improved electrochemical process for the removal of metal oxide and contaminants from the surface of 12–30% Cr stainless steel which comprises subjecting the surface to anoidic action in the presence of strong aqueous alkali for a time sufficient to remove substantially all of said oxide contaminants.

The instant invention is uniquely adapted to the preparation of stainless steel surfaces for receiving a chrome plating and it is also an important object of the instant invention to provide an improved chrome plating process for a 12–30% Cr stainless steel surface containing metal oxide contaminants which comprises subjecting the surface to anodic action in the presence of strong aqueous alkali for a time sufficient to remove substantially all of said oxide contaminants, and immediately after rinsing to free the surface of the strong alkali electroplating a chromium layer onto the surface.

Other objects, features and advantages of the present invention will become apparent to those skilled in the art from the following detailed disclosure of preferred embodiments thereof.

The instant invention consists in an improved process for the treatment of stainless steel surfaces having oxide films thereon, and particularly the wrought stainless steels. Wrought stainless steels are a well known class of materials including austenitic, martensitic and ferritic stainless steels, all of which contain a substantial amount of chromium (at least about 11% and preferably 12–30%). Wrought austenitic stainless steels are characterized by the presence of nickel or manganese and chromium therein in a total amount of at least 23% (and not more than about 50%), the Cr content being at least about 14–16% and the Ni and/or Mn content being at least about 7%. Preferred austenitic steels for use in the invention are AISI type No. 301 (0.08–0.2% C; 16–18% Cr; 6–8% Ni; and max. 2% Mn) and "chrome-manganese" steel (0.05–0.15% C; 16–18% Mn; and 14–16% Cr). The martensitic steels have 11–18% chromium and up to about 1.25–2.5% nickel, an example being AISI type 431 (max. 0.2% C; 15–17% Cr; and 1.25–2.5% Ni). The ferritic steels have about 11–27% chromium, an example of a particularly preferred steel for use in the invention being AISI type No. 430 (max. 0.12% C and 14–18% Cr).

Most preferably the steel used is in sheet form (18–22 gauge) and it is formed into sheet-like articles such as hub caps, wheel covers, etc. Steels which have been found to be preferred for use in the instant invention and the above identified "chrome-manganese" steel and the No. 301 steel, although the other steels above identified may also be treated with distinct advantage by the use of the instant solution.

The stainless steels treated in the instant process contain preferably about 12–30% chromium, and this results in a corresponding proportion of chromic oxide on the surface of the stainless steel. Although it is not de-

sired to limit the instant invention to any particular theory and the precise physical and chemical phenomena which take place during the instant process cannot be fully understood, it is believed that there is a unique cooperation between the anodic action and the strong alkali present in effective removal of the chromic oxide layer. The anodic action is particularly important in this process. As those skilled in the art will appreciate, anodic as well as cathodic "cleaning" has been used for some metals at one time or another. In general, these procedures have been considered to be substantially interchangeable, the anodic cleaning involving the use of the surface to be cleaned as the anode and the cathodic cleaning involving the use of the surface to be cleaned as the cathode. Alkaline or acid anodic cleaning and alkaline or acid cathodic cleaning are also known, the alkaline or acidic type of cleaning depending upon the use of an alkaline or an acid bath, respectively. Since the cathode gas (hydrogen) is ordinarily given off at a greater rate than the anode gas (oxygen) most workers in the art indicate that they prefer to use cathodic cleaning because of the additional cleaning effect of the gas formation and movement through the solution.

In general, oxide removal from metal surface was heretofore carried out using an acid pickling solution, with or without anodic or cathodic action. The alkaline baths have been used heretofore primarily for the purpose of removing oils, greases, soil and the like contaminants from the surface of metal as a preliminary cleaning process. In such processes, alkaline salts such as the sodium orthosilicates, metasilicates, phosphates, pyrophosphates, etc., are used primarily for their cleansing effect upon the metal surface.

In contrast, the instant invention contemplates an electrochemical reaction that is entirely different from the mere removal of oil or the like contaminants, in that the actual removal of oxides is accomplished by anodic action in the presence of a strong aqueous alkali.

The instant process is believed to be specific in its action on one of the most difficultly handled oxides, namely chromic oxide (Cr_2O_3). In an acid system which is customarily used in removing oxides, the Cr_2O_3 is slightly soluble and a substantial amount of metal is etched during oxide removal. In an alkaline system, however, it is possible by the use of anodic action (i.e. presumably through action of nascent oxygen) to increase the Cr valence from three to six, thereby obtaining the chromate anion $(CrO_4)^=$. This valence change alone, however, is not enough to effect removal of the chromium-oxygen complexes from the surface, since it has been found that free alkali must be present. Unless alkali as sodium hydroxide, in excess, is present, presumably so as to form soluble sodium chromate, there is apparently no way of taking advantage of this valence change in the chromium. For this reason strong aqueous alkali, i.e. at least about pH 13 and preferably at least about pH 13.5, must be maintained in the bath continuously during the anodic action. Subjection of the surface to anodic action is thus only part of the instant process, and the excess alkali (i.e. alkali metal hydroxide or base) must be available for reaction.

Other metal oxides such as the iron oxides and the oxides of nickel, manganese, etc., which will also be present on the surface of the sainless steel are believed to be effectively removed by electrochemical reactions comparable to those just described in connection with the chromic oxide; but the chromic oxide is one of the most difficult oxides to remove and the removal thereof is a principal concern. The various oils and other surface contaminants will, of course, be removed rather readily during the instant process; but effective removal of the metal oxides, and particularly chromic oxide, will not be obtained in the absence of the strong aqueous alkali reactant and the other operating conditions which will be described.

In carrying out the invention, the stainless steel is first anodically treated in an alkaline bath which may contain alkali metal orthosilicate, metasilicate, phosphate, carbonate, pyrophosphate, etc., or mixtures thereof, but which contains an excess of alkali metal hydroxide, and preferably caustic soda, so as to have a total alkalinity equivalent of from 8 ounces to 20 ounces per gallon of alkali metal hydroxide, and preferably 10 to 16 ounces per gallon. It is particularly important that the amount of alkali metal hydroxide present in excess, is such that the solution is continuously maintained at a pH of at least 13 and preferably at least 13.5 during the entire anodic cleaning process. The presence of this excess alkali is necessary to the solubilizing of the chromate anion, for example, and oxide removal, in the absence of this excess of alkali, will either fail to be initiated during the anodic action or will terminate almost as quickly as it starts. In the instant process, the effective reaction conditions are maintained for a time sufficient to remove substantially all of the oxide surface contaminants. The current density employed for the anodic action should be at least about 10 amperes per square foot in order to get an effective rate of reaction and may be as high as 100 to 200 amperes per square foot for fast reaction rates. Preferably a current density of about 30–50 amperes per square foot is used at immersion or reaction times ranging from ¼ minute or ½ minute, as a practical minimum, to about 2½ minutes (above which the processing time becomes unnecessarily prolonged). The tanks which may be used commercially to hold the alkaline solution may be made of ordinary boiler plate and the cathodes for introduction of the current therein may be made of the same material. The stainless steel articles to be treated are, of course, the anodes (which are subjected to the instant "anodic action"). In general, the anodic action required to remove the usual oxide layers of about 0.0001 to about 0.0004 inch in thickness involves the use of current densities of 30–50 amperes per square foot for 15 to 60 seconds, which amounts to from 450 to 3000 coulombs input.

Another feature of the instant invention involves the use of relatively high bath temperatures. The bath temperature should be at least about 160° F. and may be as high as the boiling point of the bath, but preferably the bath temperature is at least about 175° F., and within the range of 175° F. to 200° F. In general, the upper bath temperature and/or the upper current density to be used is a matter of selection in order to effect conveniently rapid removal of the oxide layers. Excessive treatment of the metal surface in accordance with the instant procedure does not appear to be harmful, since the surfaces have been treated in accordance with the preferred procedure using as much as 30 minutes of treatment without any evidence of attack on the metal per se.

Using an 18% chromium–8% nickel stainless steel of the 300 series, and subjecting the same to anodic action at a current density of 30 to 50 amperes per square foot in the presence of an aqueous sodium orthosilicate bath using a sodium hydroxide concentration equal to 12 to 16 ounces per gallon, at 190° F., it is found that oxide layers of 0.000013 inch thick are removed in 15 seconds and oxide layers of 0.000033 inch thick are removed in thirty seconds, although no evidence of attack on the metal per se is noticeable even after thirty minutes of treatment. The treatment time in practice is ½ to 2½ minutes.

Immediately after the alkaline anodic treatment just described, the stainless steel is thoroughly rinsed in cold water to remove the residue of the aqueous alkaline bath therefrom buffed, and the stainless steel piece is then ready for the direct application of a chromium plate by electrodeposition. If desired, a slight amount of acid may be included in the rinsing solution solely for the purpose of neutralizing all traces of alkalinity on the

surface, but the acid treatment should be mild so as to avoid the possibility of any additional oxidation. Actually, the advantage of the instant invention resides in the fact that the single anodic alkaline treatment is sufficient to completely remove the oxide contaminants and no subsequent acid pickling step or similar treatment is required.

A particularly important aspect of the instant invention with respect to neutralization of the residual alkaline material after the anodic cleaning step resides in the use of a dilute or mild aqueous acid system. For this reason, an aqueous solution of 1–5 N sulphuric acid is employed.

The chromium plating is carried out in a conventional chromium plating bath for obtaining a bright chromium plate. For this purpose, the temperature of the bath should be at least 120° F., and preferably 124° F., or higher, and the current density should be at least 50 amps. per square foot, with higher current densities being used when the temperature is higher. The chromium plating, in general, is carried out in accordance with the disclosure in the Fink Patent No. 1,802,463. The chromium plate may be from 1 to 5 hundred thousandths of an inch in thickness. A bright plate is obtained, without the necessity of any undercoat, which is free from tendency to peel.

The instant invention may be demonstrated as follows:

(1) Pieces of an 18% chromium–8% nickel stainless steel sheet of the 300 series were subjected to anodic action at a current density of 30–50 amperes per square foot in the presence of an aqueous sodium orthosilicate bath using a sodium hydroxide concentration of 10 ounces per gallon at 190° F.; and it was found that oxide layers of 0.000013 inch thick were removed in 15 seconds and oxide layers of 0.000033 inch thick were removed in 30 seconds, although no evidence of attack on the metal per se is noticeable even after 30 minutes of treatment. During this treatment the pH was continuously maintained at 13.5–13.6. It was further noted that the surface of the stainless steel thus treated was completely cleaned of oxides and there were no local areas of oxide layers on the surface of the metal.

(2) A procedure was carried out that is the same as that described in paragraph (1) except that the sodium hydroxide concentration was 12 ounces per gallon and the results were the same as those described in paragraph (1).

(3) A procedure was carried out that is the same as that described in paragraph (1) except that the sodium hydroxide concentration was 16 ounces per gallon and the results were the same as those described in paragraph (1).

(4) A procedure was carried out that is the same as that described in paragraph (1) except that the sodium hydroxide concentration was 4 ounces per gallon; and it was found that a number of localized portions of the oxide layer were retained on the surface of the metal even after treatment for 2½ minutes, which is considered a practical maximum period of time for commercial operation. More extensive treatment for as long as about 10 minutes results in a reduction but not elimination of the size and number of retained oxide layers on the metal surface. During this treatment it was noted that the pH of the bath dropped below 12.

(5) A procedure was carried out that is the same as that described in paragraph (1) except that the sodium hydroxide concentration was 8 ounces per gallon and it was found that the cleaning effect obtained was substantially better than that obtained in the procedure of paragraph (4), although not quite as good as that obtained in the procedures of paragraphs (1), (2) and (3). Substantially all of the oxide layer is removed during treatment periods within the range of ½ to 2½ minutes; and during such treatments the pH remains at at least 13.

(6) One way of observing the cleanliness or removal of oxide layers from the surface of the metal pieces treated in the foregoing procedures involves mere physical examination of the surfaces before and after a buffing operation, and this procedure was employed in obtaining the results hereinbefore described; but another method involves the use of a rinsing treatment followed by chrome plating. The pieces treated in accordance with the procedures of paragraphs (1–5) were immersed in a 3 N aqueous sulphuric acid solution for a time of about 1 minute sufficient only to completely remove all traces of alkalinity from the surface of the metal pieces and this treatment was followed by plating in a chrome plating bath (having 270 g./l. CrO_3 and 2.8 g./l. H_2SO_4 content) maintained at 125° F., using a current density of 100 amperes per square foot, to obtain a chrome plate of about $^{30}/_{1000}$ of an inch in thickness. In the case of the pieces treated originally according to the procedures of paragraphs (1), (2), (3) and (5), it was found that a bright chrome plate was obtained which is free from any tendency to peel. In the case of the pieces treated initially according to the procedure of paragraph (4), it was found that a number of brown spots were apparent on the chrome plated surfaces and these spots are actually bare spots which did not plate properly because the base metal had not been adequately cleaned in these localized areas.

(7) A procedure was carried out that is the same as that described in paragraph (6) except that nitric acid was used in place of the sulphuric acid in the rinsing step; and it was found that a spotty chromium layer was obtained in the plating of all of the pieces, such chromium layers containing a number of brown spots rendering them defective.

(8) A procedure was carried out that is the same as that described in paragraph (6) except that the rinsing solution employed was 8% aqueous nitric acid and 1% aqueous hydrofluoric acid; and it was found that a dull gray chromium plating was obtained on all of the pieces. Such dull gray coating is clearly defective and clearly distinguishable from the bright lustrous chrome plating obtained carrying out the procedure of paragraph (6).

My method of preparing austenitic stainless steel for receiving a bright chromium plate has been successfully carried out in connection with the chromium plating of stainless steel hub caps, trim rings, and the like, to give a very bright chromium plate, free from any tendency to peel.

The instant process is similarly effective with each of the various other stainless steels hereinbefore mentioned.

As has been explained hereinbefore, the instant invention is uniquely adapted to the preparation of a stainless steel surface (subsequently buffed) for receiving chromium by the conventional electroplating process. Because of the superior oxide removing properties of the instant treatment and the selective manner in which oxides only are removed, the bond between the chromium and the stainless steel surface is superior in a number of respects, even though the chromium plating step per se is carried out in a conventional manner.

Still another very important aspect to the instant invention resides in the fact that the instant alkaline anodic treatment may be used merely for the purpose of cleaning a stainless steel surface to the extent that deoxidation thereon is carried out. If, for example, it is desired to obtain a buffed stainless steel surface which does not have oxide components thereon, the instant alkaline anodic treatment may be employed, followed immediately by buffing at sufficiently low temperatures, etc., so as not to induce oxide formation, and the resulting buffed stainless steel surface will not contain oxide components. On the other hand, if a stainless steel surface containing oxide components has been buffed, and the instant alkaline anodic treatment applied thereto, the surface will be dulled (because the oxide components

also serve to assist in the formation of the smooth buffed surface), but this surface may be rebuffed so as to contain only metal. In many instances, subsequent finishing operations are carried out at another plant or by another user, after the initial stainless steel forming operations have been carried out. In the practice of the instant invention, such initial forming operation may be carried out and followed by the instant alkaline anodic cleaning process, so that the stainless steel articles thus obtained will have oxide contaminant free surfaces which may be used advantageously in the next plant or by the next user.

It is emphasized that the instant process actually takes the place of "pickling" by acids as heretofore carried out, and it is superior thereto in that it removes the oxides without removing metal per se (as is done in acid pickling). The instant process is carried out in the presence of excess alkali or base as indicated, preferably with an anion content (i.e. silicate, phosphate, etc.) equivalent to an alkali salt content (i.e. sodium orthosilicate) of about 1 to 10 or 15% salt, plus the excess alkali here specified. The excess alkali herein set forth is based on alkali hydroxide (as stated) and not on mere alkaline salts, hence the resulting pH.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

I claim as my invention:

1. The method of preparing austenitic stainless steel for receiving a chromium plate, which consists essentially in subjecting said stainless steel to anodic cleaning in an alkaline bath containing an alkali metal salt selected from the group consisting of silicates and phosphates and having an alkalinity equivalent to from 10 to 16 oz./gal. of NaOH to remove grease and surface oxides, with drawing said steel after a short period of time in the neighborhood of ½ to 2½ minutes, rinsing, dipping the steel in a dilute sulphuric acid bath and again rinsing before chromium plating said steel and without further processing said steel bright chromium plating the same.

2. The method of preparing austenitic stainless steel for receiving a chromium plate, which consists essentially in subjecting said stainless steel to anodic cleaning in an alkaline bath containing an alkali metal salt selected from the group consisting of silicates and phosphates and having an alkalinity equivalent to from 10 to 16 oz./gal. of NaOH to remove grease and surface oxides, withdrawing said steel after a short period of time in the neighborhood of ½ to 2½ minutes, rinsing, dipping the steel in a 1 to 5 N-sulphuric acid bath and again rinsing before chromium plating said steel and without further processing said steel bright chromium plating the same.

3. The method of preparing 18–8 stainless steel for receiving a bright chromium plate directly thereon, which consists essentially in anodically cleaning said steel in an aqueous bath having an alkalinity equivalent to from 10 to 16 oz./gal. of NaOH and containing an alkali metal salt selected from the group consisting of silicates and phosphates, continuing the anodic cleaning for from ½ to 2½ minutes, rinsing the steel, immersing the same in an aqueous 1 to 5 N-sulphuric acid dip, and again rinsing and thereafter without further processing bright chromium plating said steel in a chromium plating bath maintained at at least 120° F. while passing electrical current to said steel as the cathode at a current density of at least 50 amps. per sq. ft.

4. An electrochemical process for the removal of metal and contaminants from the surface of 12–30% Cr stainless steel which comprises subjecting said stainless steel to anodic cleaning in an alkaline bath containing an alkali metal salt selected from the group consisting of silicates and phosphates and having an alkalinity equivalent to from 8 to 20 ounces per gallon of alkali metal hydroxide to remove grease and surface oxides, withdrawing said stainless steel from the bath after a short period of time in the neighborhood of ¼ to 2½ minutes, rinsing, dipping the stainless steel in a dilute sulfuric acid bath, and again rinsing.

5. A process as claimed in claim 4, wherein the alkaline bath contains 8 to 20 oz./gal. of NaOH.

6. A process as claimed in claim 5, wherein the sulfuric acid bath is a 1 to 5 N-sulfuric acid bath.

7. A process as claimed in claim 4, wherein the sulfuric acid bath is a 1 to 5 N-sulfuric acid bath.

8. The method of preparing austenitic stainless steel for receiving a chromium plate, which consists essentially in subjecting said stainless steel to anodic cleaning in an alkaline bath containing an alkali metal salt selected from the group consisting of silicates and phosphates and having an alkalinity equivalent to from 8 to 16 oz./gal. of alkali metal hydroxide to remove grease and surface oxides, withdrawing said steel after a short period of time in the neighborhood of ½ to 2½ minutes, rinsing, dipping the steel in a dilute sulphuric acid bath and again rinsing before chromium plating said steel and without further processing said steel bright chromium plating the same.

9. A process as claimed in claim 8, wherein the alkaline bath contains 8 to 20 oz./gal. of NaOH.

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