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COLORATION OF STAINLESS STEEL

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My invention relates to a method of coloring stainless steels containing 7% or more of chromium, and also to the product resulting from such treatment.

Stainless steels produced on the modern strip and sheet mills by both hot and cold rolling may, either by reason of the method of rolling or by subsequent treatment, have such highly polished or polished surfaces as almost to equal silver or chromium plate in smoothness and reflecting properties. This ability to take and substantially permanently to retain a high polish, together with the fact that they are now commercially available in thin gauge strips or sheets of a width of from 2 to 4 feet, is widely increasing their use in the general building and construction industries for such purposes as wall tiles, panel sheets, moldings and the like. However, when such tiles or panels are applied to relatively large wall areas the effect created, due to the more or less uniformity of color, is extremely monotonous. My invention, therefore, has to do with the aesthetic coloration of stainless steels for decorative purposes, and to break up large areas of bright metal by means of interspersed color.

Any process of coloring stainless steels, in order to be practicable and commercially acceptable, must be certain in its operation to the extent that any given grade or type of steel can be consistently and repeatedly given the same color tone effect, and, furthermore, such process must be capable of producing the color desired within a reasonable and commercially acceptable interval of time. Hence, the principal object of my invention is to provide a controlled method of permanently coloring, within a reasonable period of time, stainless steels containing 7% or more of chromium and having substantially any surface finish from that produced by fine polishing to the more or less dull finishes produced by pickling or etching. A further object is to produce a stainless steel product having a color film thereon or therein which is so coherent and so tenaciously adherent to the surface of the steel as properly to be described as substantially integral therewith, and which is substantially permanent in character.

With these objects in view, I have discovered that steels containing 7% or more of chromium and which are therefore of so-called "stainless" grade or quality may be positively and permanently colored by the reactions which take place when such steels are immersed in a water-acid

perature as would normally dissolve the steel but which also contains one or more substances which not only definitely inhibit such destructive dissolution but also prevent the strong acid solution from visibly etching the surface of the steel.

Generally speaking, my treating solution may be prepared by first forming a sulphuric acid solution of such concentration that, at the temperature selected for the treatment, it will rapidly attack and quickly dissolve a thin specimen of the steel to be colored when immersed therein, and then adding to the acid solution a sufficient quantity of an appropriate oxidizing agent to prevent the acid from etching the surface of another test specimen of said steel when immersed therein.

As an oxidizing agent which serves as an etching inhibitor, I may use any of the manganates or permanganates of the alkali metals of Group I, the manganates or permanganates of the alkaline earth metals of Group II, or manganese dioxide. Commercially, only the commoner and therefore cheaper manganates and permanganates, such as those of ammonium, barium, calcium, lithium, potassium, sodium and strontium will be employed.

The solutions which may be used to color stainless steels according to my process contain water, sulphuric acid, and an etching inhibitor, within about the following limits for commercial practicability:

Parts by weight	
Etching inhibiting oxidizing agent	1-25
Sulphuric acid (1.84 sp. gr.)	23-54
Water	35-64

In the above formula, the minimum quantity of sulphuric acid in the acid-water solution is 23 parts in a total of 23+64 or 87 parts of acid and water, which is about a 27% acid solution; and the maximum quantity of acid is 54 parts in a total of 54+35 or 89 parts of acid and water, which is about a 61% acid solution.

It may be said generally that any steel containing chromium in sufficient quantity to resist etching when immersed in a solution containing the above ingredients within the ranges set forth can be colored thereby, but the intensity or depth of color imparted to the steel, the character of the color film and the time required for coloring depend on many factors such, for example, as the temperature of the solution, the acid concentration, the quantity of etching inhibitor, the time of immersion, the presence in the steel of other alloying elements in addition to chromium,

and the character and condition of the surface of the steel.

With the lower concentrations and particularly with the lower temperatures, the time required to produce a definite color is so prolonged as to raise a serious question as to the commercial practicability of the process. On the other hand, with the higher concentrations, and particularly with temperatures closely approaching the boiling point of the bath, the color film formation takes place so rapidly that the film is not always completely coherent or adherent, and the commercial practicability of the process in this phase may likewise be questionable.

It is in the intermediate ranges of my formula that the process is unquestionably highly practicable, and I point out the above facts merely to afford a foundation for claims of a scope which will adequately protect the invention.

Where it is desired to produce a permanent, brown-black, coherent and tenaciously adherent color film on a stainless steel, I prefer to use a bath or solution of the following ingredients within about the limits set forth:

Parts by weight	
Etching inhibiting oxidizing agent-----	3-15
Sulphuric acid (1.84 sp. gr.)-----	36-50
Water-----	40-50

In the above formula, the minimum quantity of acid in the acid-water solution is 36 parts in a total of 36+50 or 86 parts of acid and water, which is about a 42% acid solution; and the maximum quantity of acid is 50 parts in a total of 50+40 or 90 parts of acid and water, which is about a 56% acid solution.

By heating the above solution and maintaining it within a temperature range of from about 190° F. to 210° F., a specimen of polished stainless steel of the 18-8 type or the straight 17-18 chromium type when immersed therein will acquire a color ranging from a very light gold to a brown approaching black depending on the time of immersion and the smoothness of the surface. If the solution is well stirred, it will decrease the coloring time and insure a smoother color. Such color film upon critical examination will be found to have a smoother texture and a more highly polished surface than the surface of the specimen before treatment. In this respect, it compares very favorably with the finest electroplating.

If any color film forms on the steel within a few minutes after its immersion in the solution, such film cannot be detected by the naked eye. The color "build up" is very gradual during the earlier stages of the processing but progresses very rapidly during the last few minutes up to what is apparently its maximum color and film depth.

The surface lustre of the color film is dependent upon the initial lustre and finish of the steel or, in other words, the more highly polished steel surfaces produce the more lustrous color films. However, it is to be understood that my process is not limited in its application to highly polished steel surfaces but is equally applicable to steel which has been previously submitted to a pickling or an electro-etching process to dull its surface, in which case a more or less satin finished color film is produced having a minimum of reflectibility.

Where the temperature of the solution is permitted to approach the boiling point (which in my high gravity solution is around 250° F.-260°

F.), it is extremely difficult, if not impossible, to control the coloration because of the very rapid rate of film formation. Furthermore, the surface of the steel may be destructively etched by the high acid concentration and the aesthetic qualities of the product thus destroyed. This latter effect is apparently due to a marked reduction in the inhibiting action of the salt at such elevated temperatures.

Where the acid content of my solution is materially reduced below that stated in the above formula, it is difficult to produce a colored film within a reasonable time. Where the acid content in the formula is substantially increased beyond the upper limit given in my formula, the tendency is to produce a solution which will etch the surface of the steel and destroy the lustre of the finished product.

While I have indicated above that the temperature of the treating solution should be maintained between about 190° F. and 210° F., because this is the best temperature to produce rapidly and economically a permanent deep brown-black color, I have also discovered that a comparable result can be obtained by treating the steel in a solution at normal room temperature. In this case, however, the time necessary to produce a brown-black color film of equivalent thickness to that produced by my preferred treatment requires many hours. Solutions at a temperature of say 70° F., are, therefore, workable but their commercial practicability may be open to question because of the long time factor.

The color film produced by the treatment is largely composed of oxides and/or hydrated oxides of chromium and iron with lesser quantities of oxides and/or hydrated oxides of nickel and copper, when these metals are present in the steel undergoing treatment. Such oxides and/or hydrated oxides are, of course, understood to be formed by reason of the very strong oxidizing effect of the solution upon the constituents of the steel.

In checking the formation of the film by using, in the solution, chemically pure ingredients free from iron, precisely the same results are attained as with the use of commercial ingredients.

It has been observed, during the continued operation of a bath whose initial composition was within the limits above specified, that the free acid concentration is gradually diminished; that the concentration of the oxidizing agent (inhibitor) is gradually reduced; that the concentration of iron salts is gradually increased; and that salts of nickel appear in the bath, if nickel is a constituent of the steel undergoing treatment.

It has been observed, when chromium-bearing steels of the above compositions are treated in baths as hereinbefore specified, and at such temperatures as I have recommended, that no visible color film is produced during the initial stages of the treatment, neither is there any visible action within the bath. It is believed, however, that the oxidizing action starts immediately, but that the film of iron and chromium oxides initially produced is so thin as to be invisible to the eye. It is, of course, understood that the terms "oxide" and "oxide film" as herein used mean either the anhydrous, or the hydrated oxides of the metal mentioned therewith, and films produced of such anhydrous or hydrated oxides. As the treatment proceeds, the thickness of the oxide film is gradually increased, as the active oxidizing agent of the bath gradually pene-

trates the film and attacks the underlying alloy steel. Simultaneously, the iron and nickel (where nickel is a constituent of the alloy) oxides, which are more soluble in sulphuric acid than chromium oxide may be dissolved from the film in part by the strong acid. Should the treatment be continued unduly, there results a film of such character as to be non-coherent and non-adherent.

Due in all probability to the well known high resistance of most stainless steels to nitric acid attack, I find that the sulphuric acid in my formula cannot be satisfactorily replaced with nitric acid. Hydrochloric acid in any moderate concentration in water solutions, as well as the "1c" iron salt of this acid is very destructive to stainless steels in general, and therefore this acid cannot be used in my process. The organic acids which I have tried, including glacial acetic acid, have also been found unsuitable. I have also found phosphoric acid unsuited to my process.

It is to be understood that my invention is applicable only to alloy steels containing chromium in quantities (7% or more) sufficient to bring the steel into the well known and so-called stainless grades. So long as the chromium is present in sufficient quantities, the presence of the other well known elements such as nickel, molybdenum, copper, etc., in steels is immaterial. Very excellent results are obtained with straight chromium steels containing chromium in the range of 16% to 18% by weight, with the so-called 18-8 steels containing about 18% of chromium and 8% of nickel, and also with stainless steels containing copper and/or molybdenum.

My process cannot be used to produce color upon ordinary carbon steels and irons, or metals of the yellow group such as brass or bronze, or on such metals as aluminum and zinc or alloys such as Monel metal.

My invention is in no sense limited to stainless steel in the form of sheets, strips or plates but may be applied to wire or steel in any other form.

This application is a continuation in part of my application Serial No. 206,043 filed May 4, 1933.

What I claim is:

1. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing sulphuric acid and a manganese-containing oxidizing agent and etching-inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide, and for a sufficient length of time to form in said surface a coherent and adherent color film; the sulphuric acid solution being sufficiently concentrated, if used alone, to dissolve said steel, and the oxidizing agent being present in a sufficient quantity to prevent the etching of said surface by said solution.

2. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing sulphuric acid and a manganese-containing oxidizing agent and etching-inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide, at a comparatively high temperature but below the boiling point and for a sufficient length of time to form in said surface a coherent and adherent color film; the sulphuric

acid solution being sufficiently concentrated, if used alone, to dissolve said steel at the temperature employed, and the oxidizing agent being present in a sufficient quantity to prevent the etching of said surface by said solution.

3. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing sulphuric acid and a manganese-containing oxidizing agent and etching-inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide, at a temperature of from about 190° F. to about 210° F., and for a sufficient length of time to form in said surface a coherent and adherent color film; the sulphuric acid solution being sufficiently concentrated, if used alone, to dissolve said steel at said temperature, and the oxidizing agent being present in a sufficient quantity to prevent the etching of said surface by said solution.

4. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing, by weight, from about 23 to about 54 parts of concentrated sulphuric acid, from about 35 to about 64 parts of water, and from about 1 to about 25 parts of a manganese-containing oxidizing agent and etching-inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide, and for a sufficient length of time to form in said surface a coherent and adherent color film; the sulphuric acid solution being sufficiently concentrated, if used alone, to dissolve said steel, and the oxidizing agent being present in a sufficient quantity to prevent the etching of said surface by said solution.

5. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing, by weight, from about 23 to about 54 parts of concentrated sulphuric acid, from about 35 to about 64 parts of water, and from about 1 to about 25 parts of a manganese-containing oxidizing agent and etching-inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide, at a comparatively high temperature but below the boiling point and for a sufficient length of time to form in said surface a coherent and adherent color film; the sulphuric acid solution being sufficiently concentrated, if used alone, to dissolve said steel at the temperature employed, and the oxidizing agent being present in a sufficient quantity to prevent the etching of said surface by said solution.

6. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing, by weight, from about 23 to about 54 parts of concentrated sulphuric acid, from about 35 to about 64 parts of water, and from about 1 to about 25 parts of a manganese-containing oxidizing agent and etching-inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide, at a

temperature of from about 190° F. to about 210° F., and for a sufficient length of time to form in said surface a coherent and adherent color film; the sulphuric acid solution being sufficiently concentrated, if used alone, to dissolve said steel at said temperature, and the oxidizing agent being present in a sufficient quantity to prevent the etching of said surface by said solution.

7. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing, by weight, from about 36 to about 50 parts of concentrated sulphuric acid, from about 40 to 50 parts of water, and from about 3 to about 15 parts of a manganese-containing oxidizing agent and etching inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide and for a sufficient length of time to form in said surface a coherent and adherent color film.

8. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing, by weight, from about 36 to about 50 parts of concentrated

concentrated sulphuric acid, from about 40 to 50 parts of water, and from about 3 to about 15 parts of a manganese-containing oxidizing agent and etching inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide at a comparatively high temperature but below the boiling point and for a sufficient length of time to form in said surface a coherent and adherent color film.

9. The method of coloring the surface of an alloy steel containing at least 7%, by weight, of chromium which comprises subjecting said surface to the action of a solution containing, by weight, from about 26 to about 50 parts of concentrated sulphuric acid, from about 40 to 50 parts of water, and from about 3 to about 15 parts of a manganese-containing oxidizing agent and etching inhibitor selected from the group consisting of the manganates and permanganates of the alkali metals of Group I, the alkaline earth metals of Group II, and manganese dioxide at a temperature of from about 190° F. to about 210° F. and for a sufficient length of time to form in said surface a coherent and adherent color film.

CLEMENTS BATCHELLER.