May 8, 1945. C. BATCHELLER 2,375,613

METHOD FOR PRODUCING DESIGNS ON STAINLESS STEEL

Filed Oct. 28, 1939

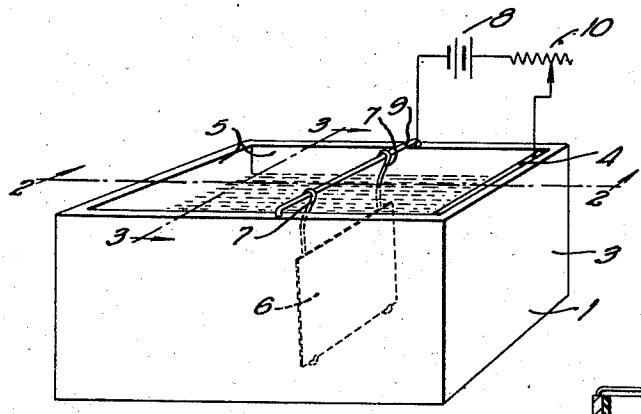


FIG. 1

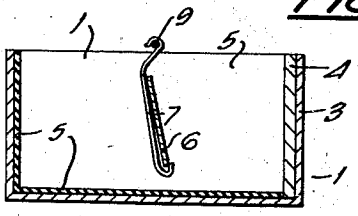


FIG. 2

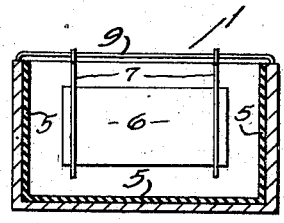


FIG. 3

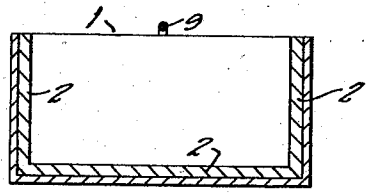


FIG. 4

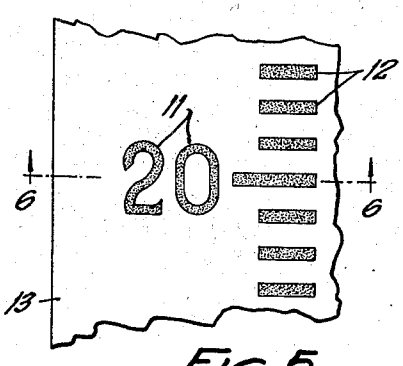


FIG. 5

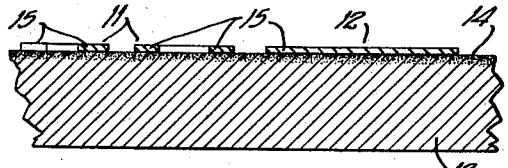


FIG. 6

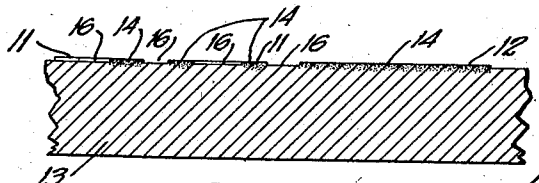


FIG. 7

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METHOD FOR PRODUCING DESIGNS ON STAINLESS STEEL

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Application October 28, 1939, Serial No. 301,805

6 Claims. (Cl. 204—143)

In my Letters Patent Nos. 2,172,353, 2,219,554, and 2,243,787, I have disclosed methods of treating stainless steels whereby a color film containing oxides of the metals in the steel itself is formed in and substantially integral with the surface of the steel.

The processes are applicable to all alloy steels belonging to what is commonly termed the "stainless group" and all of which contain chromium in quantities of 6% or more, by weight, either alone or with other alloying elements, such as nickel, silicon, molybdenum and the like. Steels colored by any of these methods are rendered extremely resistant to corrosion and the color film, under ordinary conditions, is only removable with such difficulty, as by abrasives, that it may be said to be substantially permanent. Such color films offer unusual possibilities for producing permanent decorative or utilitarian designs, such as signs and the like, on stainless steel surfaces. While it would seem possible to mask certain portions of the steel surface and thus color only the unmasked portions to produce the desired design, the coloring process is preferably performed at comparatively high temperatures, and no masking substance which will satisfactorily withstand the treatment has been discovered.

In my copending applications, Serial No. 216,719 filed June 30, 1938 now Patent No. 2,243,787 and Ser. No. 380,241 filed February 24, 1941, now Patent No. 2,283,171, I have disclosed a method of producing color designs on stainless steel by first forming a color film of metallic oxide over the entire surface of the steel, then cutting a stencil of the desired design which is used as a mask to permit the color film to be rubbed off through the openings in the stencil by means of a suitable abrasive. This method produces very beautiful designs but is quite expensive, and it is impossible to produce in this way a design involving fine details. Furthermore, due to the facts that the color film is in and integral with the surface of the steel, rather than merely on the surface thereof, and is extremely thin, it is impossible to rub it off or out with an abrasive without materially changing the original physical texture and finish of the steel. Thus, if the surface of the steel before coloring has a highly polished, mirror-like finish, this finish is not affected by the coloring treatment but, in rubbing off the color, this finish is destroyed and the surface is dulled where the color is removed.

The present invention concerns the production of colored designs either for decorative or utilitarian purposes on stainless steels by a method which can not only be cheaply and quickly performed but by means of which it is possible to produce on the steel a design having details substantially as fine as those of an etching or engraving.

In the preparation of such a design the surface of the stainless steel is first given the desired finish such as that produced by any of the various types of pickling, cold rolling, belt sanding, or polishing by any of the methods well known in the art. The entire surface of the steel is then colored by forming a film of metallic oxides therein. Such a film may be formed by treating the steel in a solution containing sulphuric acid and water together with an etching-inhibiting, oxidizing agent at any temperature from ordinary room temperature up to somewhat below the boiling point of the solution; the preferred temperature being between about 170° F. and about 220° F.

The solution should preferably contain from 23 to 54 parts, by weight, of sulphuric acid (1.84 sp. g.) and from 35 to 64 parts, by weight, of water, or in other words, have an acid concentration of from about 25% to about 60%; the best results being obtained with acid concentrations above about 40%. Sulphuric acid solutions of this strength will immediately attack and quickly dissolve a specimen of stainless steel immersed therein, and an etching inhibitor and oxidizing agent, such for example as chromic acid, the chromates and dichromates of aluminum, ammonium, barium, bismuth, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, mercury, nickel, potassium, sodium, strontium or zinc; the vanadates or metavanadates of ammonium, potassium or sodium, vanadic acid or metavanadic acid; the manganates or permanganates of the alkali metals of Group 1, the manganates or permanganates of the alkaline earth metals of Group 2 or manganese dioxide; is therefore added to the acid solution in a quantity at least sufficient to prevent etching of the steel at the temperature employed in the treatment. Anywhere from 4 to 25 parts, by weight, may be used, but I prefer to use a quantity not greatly in excess of that necessary to prevent etching of the steel at the temperature selected for the treatment. This quantity can be easily determined by adding the etching-inhibiting oxidizing agent to the sulphuric acid solution in small quantities and testing the mixture after each addition with a specimen of the steel to be colored.

The addition of any of the above mentioned

chromates or dichromates to the sulphuric acid solution forms chromic acid and a sulphate or bisulphate of the chromate or dichromate-forming element; the addition of any of the above mentioned vanadates or metavanadates forms vanadic or metavanadic acid together with a sulphate or bisulphate; and the addition of a manganate or permanganate forms manganic or permanganic acid and a sulphate or bisulphate.

The treating solution made up as above described is maintained at the temperature selected for the treatment and the steel is simply immersed therein until it acquires the desired color, whereupon it is removed, washed and dried. For any given acid concentration, the time required depends upon the temperature. Usually 15 to 30 minutes with the preferred solutions and preferred temperatures will be found sufficient.

The design to be imparted to the steel is then printed or painted thereon with a resist such as common paint, lacquer, varnish, or a printing or lithographing ink. The comparatively new art of screen painting through silk is admirably adapted for imparting the desired design to the colored surface of the steel. The paint, ink, or other resist employed, when dry, need merely form a waterproof, non-porous film capable of withstanding the solution hereinafter described, and be readily removable by suitable solvents after treatment without damage to the color film. After the resist has dried the steel is subjected to an electrolytic treatment whereby the color in the unpainted or unprinted zones is removed.

In the electrolytic treatment any controlled source of direct current may be used and, in the accompanying drawing, I have illustrated in a diagrammatic way an apparatus suitable for removing the color,

In the drawing—

Fig. 1 is a perspective view showing an arrangement for removing the color from one side only of the steel;

Fig. 2 is a section of Fig. 1 in the plane 2—2;

Fig. 3 is a section of Fig. 1 in the plane 3—3;

Fig. 4 is a section similar to Fig. 2 showing a modified type of vat which may be used for removing the color from both sides of the steel;

Fig. 5 is a fragmentary elevation view of a thermometer scale;

Fig. 6 is a section of Fig. 5 in the plane 6—6 drawn to a somewhat enlarged scale; and

Fig. 7 is a section similar to Fig. 6 showing the finished product.

Referring to the drawing, 1 represents a tank or vat which may be a pickling tank such as is commonly used in the metal industry except that the lining thereof must be formed of some substance which will resist destruction by the action of the electrolyte used therein. For my purpose a lining 2 of 18–8 (18 chromium–8 nickel) stainless steel has been found satisfactory. In my process such a lining may serve as either the anode or cathode. However, the lining of the tank may be so constructed as to limit the electrical removal of the color film to one side of the steel thus leaving intact the color on the opposite side. Such a construction is shown in Figs. 1 and 2. Here one side or end 3 only is provided with a lining 4 of 18–8; the other portions of the tank being lined with an insulating material 5 such as rubber, gutta percha, asphalt or the like.

It may be said generally that the electrolyte in which the electrodes are immersed and which carries the current from electrode to electrode may contain any substance which will impart good electrical conductivity to the solution, and will not detrimentally affect either the surface of the steel or the functioning of the resist. In other words, a solution to which the surface of the steel itself is substantially immune from destructive attack, such as by etching or pitting, when immersed therein. Substances which result in the evolution of chlorine, for example, are generally not satisfactory. Since the surface condition of the stainless steel after the removal of the color film is of extreme importance, it may be preferable to use only those solutions that are adapted for or commonly used in the electrolytic pickling of stainless steel. It must be understood that the removal of my color film is not at all dependent upon a pickling of the surface of the steel because, by selecting a proper electrolyte the color may be removed without in any way altering the physical texture and finish of the surface of the steel from its condition prior to coloring, however, the surface of the steel may be given a desired pickle finish as an incident to the removal of the color film by using a pickling solution as the electrolyte. In any event, a solution is chosen which will leave the desired finish on the surface of the steel; for example, a water solution containing 10% nitric acid and 5% hydrofluoric acid imparts a slight whitish tinge to the steel due to a very fine etching thereof, and thus, by means of such a solution a silver-like color may be imparted to the steel. On the other hand, a solution of household lye containing approximately 75 grams per liter of water leaves the stainless steel surface in its original condition before coloring with no evidence of pickling. A solution containing approximately 75 grams of sodium nitrate per liter of water also leaves the stainless steel surface unmarred by pickling. Where an extremely bright surface is desired on the stainless steel after the removal of the color film of metallic oxides, any "bright pickling solution" may be employed. For example, a solution containing 70% of phosphoric acid and 30% of sulphuric acid with citric acid dissolved therein may be employed, as well as 85% phosphoric acid solutions. While I prefer to maintain the electrolyte at a temperature of from 50° to 100° C. during the treatment, electrolytes at room temperature work very well.

The character of the surface of the stainless steel from which the color is removed may also depend to a considerable extent upon the amperage of the current used and the duration of the treatment. In general, better control is attained if either the voltage or amperage is so regulated that no gas is visibly given off from the surface of the anode. For instance, when using a solution containing 10% nitric acid and 5% hydrofluoric acid good results are obtained by using a current of from 1.0 to 1.1 amperes and treating the steel for approximately 20 seconds for each square inch of film to be removed. Violent evolution of gas from the surface of the colored steel which forms one electrode may remove or injure the resist, particularly in the marginal zones thereof, and, if permitted to continue after the removal of the color film may etch or pit the surface of the steel.

In any particular solution the proper current and duration of the treatment may be easily determined as follows: Immerse in the solution a sample 6 of the colored stainless steel having a

known surface area. Such a sample may be suspended in the solution by means of stainless steel hooks 7 as shown in Fig. 1. 8 is a source of direct current, here indicated as a storage battery, the proper terminal of which is electrically connected to the specimen 6 through the bar 9 and hooks 7 to make the specimen 6 the anode in the electrolyte. The other terminal of the battery is connected through the adjustable rheostat 10 to the lining 4 at one end of the tank which here forms the cathode. It will be noted that the anode and cathode are opposed to each other and that the cathode is entirely on one side of the anode, or, in other words, every straight line that can be drawn from the cathode towards the anode will intersect the plane of the face of the anode before passing through the specimen 6 and intersecting the back thereof. With this arrangement the color will be removed only from that side of the specimen 6 which faces the cathode. By adjusting the rheostat the current may be gradually increased until the surface of the specimen 6 begins to lighten in color. Current is permitted to flow at this amperage until the color film is removed or becomes easily removable by light rubbing. Since with this set-up the color is removed from only one side of the anode the area of this side only should be considered. By dividing the time required to remove the film, or to render it easily removable, by the area in square inches of one side of specimen 6, the time required per square inch may be ascertained. For any piece thereafter the proper total time required for the treatment will be the total area of the surface from which the color is to be removed, multiplied by the required time per square inch. If the color is to be removed from all sides of the specimen, the specimen should be entirely surrounded by the other electrode which serves as a cathode. After the removal of the color the paint, ink or lacquer used as a resist may be removed with a suitable solvent.

The voltage employed does not seem to be material except that it may affect the amperage which is preferably kept low enough to prevent the visible evolution of gas from the anode where the surface of the steel from which the color is removed is to be maintained free of visible pickling or etching.

One of the recent applications of my process is in the making of stainless steel thermometer scales. Such scales, which must stand the action of certain chemicals, have usually been produced of 18—8 stainless steel. Heretofore, in the preparation of these scales, the polished steel face of the scale has been first printed with a special resist, such as a mixture of asphalt and dragon's blood or the like, over all areas of the face not intended to be etched. That is to say, the numerals and graduations are not covered with the resist so that they may be exposed to the action of an etching solution, such as an aqueous solution of iron perchloride. After the etching of the numerals and graduations has progressed to a desired depth, usually three or four thousandths of an inch, the resist is removed with a suitable solvent to produce the thermometer scale in its first stage. The etched numerals and graduations are then filled in, by a tedious and exacting hand operation, with a special black paste. Thereafter the scale is subjected to a baking treatment to harden the inlaid color. Even under the most favorable conditions this color fill does not last long in immersion thermometers.

In my treatment the numerals 11 and the graduations 12 are printed with a resist such as ink or paint 15 upon a strip of stainless steel 13 having a color film 14 thereon, thus leaving exposed all of the colored steel in and about the numerals and graduations. The strip is then subjected to the electrolytic treatment above described, as an anode, and the color film is thus removed from all of the exposed zones 16. The paint or ink used in the printing is then removed with a suitable solvent and the scale is finished.

Obviously, if it is desired to have the numerals and graduations appear in the color of the stainless steel on a dark field, the field is printed instead of the numerals and graduations and the color is removed only from the numerals and graduations.

By the term "stainless steel" as used herein, I mean a corrosion of resisting ferrous alloy containing 6% or more of chromium.

What I claim is:

1. Those steps in the method of producing a design in color on a polished surface of a corrosion-resisting, alloy steel containing a substantial quantity, by weight, of chromium and having therein and substantially integral therewith a film containing oxides of iron and chromium imparting a distinctive dark coloration to said surface which comprise, coating those portions of said surface which it is desired to preserve in color with a resist, and thereafter removing the color film from the uncoated portions of said surface by subjecting said uncoated portions to electrolytic action as anode in an aqueous electrolyte having good electrical conductivity.

2. Those steps in the method of producing a design in color on a polished surface of a chromium-containing, corrosion-resisting alloy steel as set forth in claim 1 in which the electrolyte employed is an aqueous alkaline electrolyte.

3. Those steps in the method of producing a design in color on a polished surface of a chromium-containing, corrosion-resisting alloy steel as set forth in claim 1 in which the electrolyte employed is an aqueous acid electrolyte.

4. Those steps in the method of producing a design in color on a polished surface of a corrosion - resisting, chromium - containing steel which comprise first forming in and substantially integral with the surface of said steel, but without changing the physical texture and finish thereof, a thin film containing oxides of chromium and iron to impart a distinctive coloration to said surface by treating said steel in a solution of sulphuric acid, water and an etching-inhibiting-oxidizing agent; the sulphuric acid-water solution being of such acid concentration, in the absence of the inhibitor, as quickly to attack and dissolve a specimen of said steel when immersed therein, and the inhibitor being present in a quantity at least sufficient to prevent said solution from etching said steel by chemical attack; coating those portions of said colored surface which it is desired to preserve in the finished design with a resist, and removing said film from the uncoated portions of said surface without substantially affecting the surface finish and texture of the steel itself by subjecting said steel to electrolytic action as anode in an aqueous electrolyte of good electrical conductivity and under conditions which do not cause the surface

of the steel to be attacked during the removal of said film by said anodic treatment.

5. Those steps in the method of producing a design in color on a polished surface of a chromium-containing, corrosion-resisting alloy steel as set forth in claim 4 in which the electrolyte employed is an aqueous alkaline electrolyte.

6. Those steps in the method of producing a design in color on a polished surface of a chromium-containing, corrosion-resisting alloy steel as set forth in claim 4 in which the electrolyte employed is an aqueous acid electrolyte.

CLEMENTS BATCHELLER.