

UNITED STATES PATENT OFFICE

2,327,870

METAL SURFACE FINISHING

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No Drawing. Application December 16, 1939,
Serial No. 309,576

4 Claims. (Cl. 204—36)

This invention relates to the process of finishing ferrous metal surfaces and more particularly to the finishing of components of guns such as the exterior surfaces of the barrels, although it is to be distinctly understood that it is not limited thereto and may also be applied to items of hardware and other similar objects.

It is desirable in the finishing of such ferrous metal surfaces to provide a pleasing appearance and, at the same time, a rust resistant surface.

It is also desirable that the process be one which will be economical to use and that can be easily and quickly applied in the course of manufacture.

There have been many ways suggested and used to coat or prepare surfaces for the purpose of coloring or "browning" the surface and to give it the rust resisting properties desired. One of these processes is that, for illustration, which is used for the "browning" of gun parts, wherein a coating of black iron oxide is caused to be formed on the surface. This may be done, for example, by rusting the part in a humidifying oven, boiling in a logwood solution, and then carding or holding the part by hand against a rotating wire wheel, the operation being repeated from three to seven times, depending upon the quality of finish to be obtained. The finish thus produced is very hard and wear-resistant, but it is not as satisfactory a rust preventative as desired, nor is it an economical process to perform.

It is desirable that the finish for gun components, for example, be a rich dark color with a metallic or semi-metallic luster, and have a smooth matte surface. The finish should be hard and resistant to abrasion and scarring, should resist discoloration, and protect the metal from rusting. It must also withstand cleaning with oils and solvents in the case of gun components. It is also desirable that the finish be such that it will not require too high a polished surface on which to be placed in order to obtain a satisfactory final coat, as otherwise the cost of producing the polished under-surface might be too high.

The phosphate films which are formed by the reaction of various phosphates with the surface of the metal to be protected are not entirely satisfactory, partly because of the resultant color which is lacking in the rich fine texture and metallic sheen that is desired for gun parts, the phosphate coating usually giving a light gray color. Attempts to dye or color the phosphate coating have not been satisfactory because the coloring apparently did not penetrate through the layer of phosphate. One method tried was

the dyeing of the phosphate coat in a boiling logwood solution, followed by a dip in pyrolignite of iron solution. With subsequent polishing or buffing, the dye would be removed unevenly so that a non-uniform coloring resulted.

The electrolytic application of the phosphate film by applying alternating current to the work while immersed in a hot solution of mono-zinc phosphate also did not give the desired finish.

The application of an electro-plated metal finish subsequently blackened also did not give the desired finish. It was found that black nickel could be electro-plated over a bright zinc surface under carefully controlled conditions, giving a deep rich color, but such a finish is not as hard as the browned finish. It was also difficult to prevent white flowering of the zinc on the surface.

By the use of current densities of about 10 amperes per square foot or enough to produce gassing, a mottling similar to cyanide mottling can be obtained, but the white flowering of the zinc is not prevented. The flowering of the zinc is prevented when the zinc is subjected to alternating current in a chromic acid solution; but the wear resistance of the resultant coat is not good.

In the field of oxide films, it was found possible to produce a surface by the use of a strong sodium hydroxide solution (1.4 specific gravity) with a small quantity of any one or a combination of several oxidizing agents, such as sodium nitrate, sodium nitrite, or potassium permanganate. The solution is kept at a boiling temperature and the work is immersed therein for 5 or 10 minutes. The wear resistance, however, of this coating is not satisfactory.

This invention relates particularly to the electrolytic production of an oxide film on the article. The surface of an iron article becomes passive when the iron article is placed in and made the anode of an electrolytic cell wherein the electrolyte is a basic solution in which iron oxide is slightly soluble.

The passivity is believed to be due to an impervious microscopic film of oxide isolating the metallic iron from the electrolyte, the anode liberating oxygen. This process of passivating and oxidizing the iron surface may be referred to as anodic oxidation. Instead of keeping the article as the anode throughout the process, it may be made the cathode of the cell for short periods by means of manual switch means, and when it is made the cathode, the surface of the article apparently becomes cleaner or has metallic deposits placed thereon from the electrolyte. When the

article is again made the anode, the passivation and liberation of oxygen continues.

It is also possible to superimpose an alternating current on the direct current used in the electrolytic cell in such a manner as to cyclically depassivate the surface of the article, the ratio of voltages of the alternating current to the direct current being made such that the article becomes a cathode during a part of the cycle. When an alternating current is used in this manner, the anode cycle or time during which the article to be coated is made the anode should be of greater duration and higher voltage than during the time when it is the cathode.

By using a sufficiently high current density for a sufficiently long period of time, a coating is formed on the metal which is composed of a hard tenacious lustrous film next to the metal and which will be covered by a softer coating or film on the exterior thereof. By removing this exterior coat, the hard tenacious surface is left on the metal article and is a coating having the desired color, metallic sheen, wearing, and rust resistant properties. It is also produced on the surface of the article by a single immersion and cycle in the electrolytic cell, which can be seen to be a distinct advantage.

A satisfactory coating is also produced when a phosphate film is first placed upon the surface of the article and then subjected to the anodic oxidation process. Anodic oxidation when used herein is to be construed to mean either the direct process wherein the article is the anode at all times, or the process wherein an alternating current is superimposed upon the direct current, or a process wherein the direction of the current is reversed by any suitable means.

In one example of the practice of the invention, a suitable electrolyte or alkaline solution may be made with sodium hydroxide having a specific gravity of 1.3 to 1.4, equivalent to 3.1 to 4.1 pounds of sodium hydroxide per gallon. It can be theorized that the high sodium hydroxide concentration allows growth of the oxide film due to the fact that a slightly soluble sodium ferrate is probably formed by the reaction of the iron oxide and the sodium hydroxide, which tends to depassivate the anode. The oxide formed is the difference between the rate of formation of the oxide and the rate of solution thereof. Metallic iron and hydrogen are liberated at the cathode. In order to obtain the desired coating, the article is placed in this solution, the solution having been brought to a temperature of between 248° F. and 266° F., and is kept in said solution for a period of 30 minutes with a current density of 100 amperes per square foot of surface of the article, the article being the anode. It may then be taken from the anodic oxidation bath and immersed in hot water, after which it can be boiled in a logwood or other similar coloring solution for 20 minutes or as long as is desired. The article is then carded on a wire wheel to remove the softer exterior film, which will leave the hard tenacious film upon the metal article. Following this, the article may be placed in a hot oil bath to complete the process, which, for example, may be paraffin oil with a temperature of 300° F., and may be held in this bath for a period of 45 minutes. In the event that the logwood step is omitted, instead of the richly colored surface, a lighter steely colored surface is obtained after the carding. The oil or paraffin soak increases the corrosion and wear resistance, and is to be preferred to merely an oil wipe.

Another example is the placing of the article in a 3 normal sodium hydroxide solution having a specific gravity of approximately 1.112 with 120 grams per liter of sodium chlorate, the bath being kept at the boiling temperature thereof. A direct current of 60 amperes per square foot and having an alternating current transformer with the secondary thereof connected in series with the direct current source, the alternating current having a voltage ratio of 2 to 1 to the direct current, is applied to the article for two hours. The article is then processed as in the first example. It is to be noted that the alternating current depassivation of the article does not speed up this process to that of the higher sodium hydroxide concentration. In place of sodium chlorate (NaClO_3), other alkali metal salts of an oxidizing acid may be used. Potassium, etc., may be used for example, as the alkali metal, and perchloric acid, nitric acid, manganic acid, etc., may be used as the oxidizing acid.

In the process wherein a phosphate film is placed upon the surface of the article before the electrolytic or anodic oxidation takes place, the article may, for example, be subjected to a hot solution of phosphoric acid and manganese oxide and/or dioxide for one hour. The film is composed of iron phosphate, possibly with the addition of other metal phosphates according to the oxide used in the phosphoric acid solution, and can be formed by any of the well-known "Parkerizing" processes. In these processes, phosphoric acid is the principal ingredient of a solution into which has been placed oxides or mixtures thereof of a metal such as manganese, zinc, iron, and which forms a metal phosphate or a mixture thereof in the solution. The article is then taken from the phosphate bath with a phosphate film thereon and placed into the anodic oxidation bath, and the process completed as outlined above.

It is to be understood that one of the essential features of this invention is the subjection of the article to the anodic oxidation for a sufficient length of time and current density, such, for example, as that shown, to produce the hard tenacious coating on the surface of the metal, this coating being exposed after the removal of the softer oxide coating by any suitable means. The type of coloring and solution densities and method of treatment may be changed, and still come within the scope of the invention.

A process has been disclosed herein which produces a satisfactory and economical coating for ferrous articles, and particularly gun components.

As many different embodiments of this invention may be made without departing from the scope thereof, it is to be understood that the invention is not limited to the embodiment given, except as defined by the appended claims.

What is claimed is:

1. The process of finishing the surfaces of ferrous articles comprising: subjecting the articles to anodic oxidation in a sodium hydroxide solution with a specific gravity of substantially 1.3 to 1.4 and at a temperature between substantially 248° and 266° F. for substantially 30 minutes with a current density of substantially 100 amperes per square foot of article surface to form a steely gray hard tenacious oxide film covered with an exterior softer oxide film on the surface of the articles; and then removing the exterior oxide film leaving exposed the steely gray hard tenacious oxide film.

2. The process of finishing the surfaces of ferrous metal articles comprising the steps of subjecting the articles to anodic oxidation in a hot alkali metal hydroxide solution of more than 1.112 specific gravity for substantially two hours, using a direct current of 60 amperes per square foot of article surface with a superimposed alternating current with substantially twice the voltage of the direct current, thereby producing a hard tenacious oxide covered with an exterior softer oxide film; and then removing the exterior oxide film leaving exposed the hard tenacious oxide film.

3. The process of finishing the surfaces of ferrous metal articles comprising the steps of subjecting the article to anodic oxidation in a substantially 1.1 specific gravity sodium hydroxide solution containing a small quantity of an alkali metal salt of an oxidizing acid for substantially two hours, using a direct current of 60 amperes per square foot of article surface with a superim-

posed alternating current with substantially twice the voltage of the direct current, thereby producing a hard tenacious oxide film covered with an exterior softer oxide film; and then removing the exterior oxide film leaving exposed the hard tenacious oxide film.

4. The process of finishing the surfaces of ferrous metal articles comprising the steps of subjecting the article to anodic oxidation in a substantially 1.1 specific gravity sodium hydroxide solution containing a small quantity of sodium chlorate for substantially two hours, using a direct current of 60 amperes per square foot of article surface with a superimposed alternating current with substantially twice the voltage of the direct current, thereby producing a hard tenacious oxide film covered with an exterior softer oxide film; and then removing the exterior oxide film.

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