My invention relates to a method of blackening stainless steels or high alloy chromium steels by the formation on their surfaces of a black film of oxide.

It has hitherto been discovered, as set forth in Patent No. 2,394,899, issued February 12, 1946, to Irvine C. Clingan, that a tightly adherent and abrasion resistant coating of black color could be formed on the surfaces of high alloy chromium steels by a procedure which involves the dipping of the steel articles beneath the surface of a fused bath of sodium dichromate, potassium dichromate, or mixtures of the two, maintained at temperatures, roughly, between 320° C. and 500° C., and holding the articles beneath the surface of the fused bath for a length of time, approximately 2 to 30 minutes, sufficient to cause the formation of a satisfactory black oxide coating. The coating is believed to be one rich in oxides of iron and chromium.

A disadvantage of the above process lies in the fact that relatively expensive equipment is required for dipping and maintaining submerged the stainless steel articles for the required length of time, and that production cannot be increased except by increasing the capacity of the equipment.

It is a principal object of my invention to produce black oxide coatings on the surfaces of high chromium steel articles with less equipment, more cheaply, and at a very much higher rate of productivity for the equipment involved.

It is also an object of my invention to provide a way of forming the black oxide coatings on stainless steel articles which is available to the ordinary fabricator, without the installation of any great quantity of expensive equipment, and through the use, in part at least, of equipment which the fabricator had in his plant for other purposes.

The and other objects of my invention, which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, I accomplish by that procedure of which I shall now describe certain exemplary embodiments.

In the practice of my process, the nature of the coatings produced is in all respects the equal of those produced in accordance with the teachings of Patent 2,394,899. They are black in color, tightly adherent, hard, tough, and uniform in texture and appearance, and highly resistant to abrasion. The actual appearance of the finished coating will vary with the initial finish of the article or product prior to the treatment. Thus, a dull gray, unpolished piece of high chromium steel, when treated in accordance with my process, has produced upon it a dull black coating, while more highly reflective initial finishes will affect the appearance of the final coating, so that a satiny initial finish will produce a satiny black coating, and a highly polished initial finish will produce a lustrous or equally highly polished black coating.

The stainless steels or chromium alloy steels to which my invention is applicable are defined as any low carbon steel comprising 10% to 35% of chromium, with or without nickel, and with or without other alloying ingredients, such as manganese, silicon, cobalt, copper, molybdenum, tungsten, vanadium, columbium, titanium, and the like, as well as those impurities ordinarily found in stainless or chromium steels. In other words, the only necessary qualification for the base steel or article is that it shall be a ferrous body containing substantially 10% to substantially 35% of chromium. Contents of other substances do not affect the formation of the black oxide coating herein described, the color and characteristics of that coating being due to its high content of the oxides of iron and chromium.

I have found that under the conditions of procedure hereinafter outlined, it is not necessary to immerse the article or piece of chromium steel in a bath of the fused dichromates and hold it there until the required oxide coating has been formed. Instead, it is readily possible to coat the surfaces of the cleaned article with dichromate and then effect the formation of the oxide coating in a separate furnace, such as an annealing furnace. This is surprising, inasmuch as it has hitherto been understood an atmospheric or gaseous oxidation occurring prior to or along with the formation of the black oxide coating, impairs its character and appearance. The danger of atmospheric oxidation is avoided in the process of Patent 2,394,899 by cleaning the articles and then submerging them in the bath of the fused dichromate, holding them there until the desired oxide layer has been formed. In the practice of my invention, I have found it is readily possible by several procedures so to coat the surfaces of a clean piece or article of chromium steel with a dichromate, that atmospheric oxidation will be prevented during the heating-up period of a subsequent treatment of the coated articles in a furnace, while the coating of dichromate will remain in place during the heat treatment and will be sufficiently continuous and imperforate to prevent atmospheric oxidation, in
As in the practice of the process of Patent 2,394,899, the articles or pieces must first be cleaned, so as to eliminate substantially all scale, oxide, grit, and the like, and the chemical cleaning methods may be employed such as sand blasting, grinding and the like, with or without pickling. If a pickling is employed, any pickle suitable for use with high chromium steels may be adopted. In pickling stainless steels, a quick dipping in an aqueous solution of 30% nitric acid and 1% hydrofluoric acid is usually sufficient. This is followed by a rinse in clean water.

In addition to pickling, or as a substitute therefor, where a highly polished surface is desired, this may be secured by buffing or other mechanical methods; but I prefer to use any one of those methods of electrolytically polishing stainless or chromium steels, such as the process of Ostofsky, Canadian Patent 2,353,984, Filed Patent Re. 23,068, or Patent 2,424,674 in the name of Harold I. White. Electrolytic cleaning, as distinct from electrolytic polishing, may be employed if desired. Any of these processes, after the piece has been suitably rinsed, will tend to leave its surfaces adequately clean. The cleaning procedure does not, as to its nature, form a limitation upon the present invention.

One of the ways of securing a coating of dichromate on the surfaces of a stainless steel material or article suitable for my purpose is by dipping the article in a bath of the molten dichromate. The bath may consist of sodium dichromate, potassium dichromate, or mixtures of the two. All that is necessary is to immerse the piece or article in the molten bath for a sufficient length of time to permit the adherence of a coating of the dichromate. This dipping may be done very rapidly in a bath of the salt or salts maintained at any temperature above the melting point of the bath, and below the point at which decomposition is encountered. In general the temperature of the bath will be over about 320° C., and while the decomposition temperature will vary with the ratio of sodium dichromate to potassium dichromate, if both are used, the decomposition temperature of potassium dichromate being the higher, and tending to raise the decomposition temperature of the bath), ordinarily the temperature of the bath will be less than about 500° C. Temperatures even above decomposition temperature may be tolerated; but are preferably avoided in order to avoid chances in the bath. Since the black oxide coatings are, in my process, not formed while the article or piece is submerged in the bath of fused salt, there is no advantage in using the highest possible temperatures in order to speed up the chemical attack.

I have found that if an article is dipped in a bath of sodium or potassium dichromate or mixtures thereof for a long enough time to reach the thickness of product or minimum thickness will adhere to the surfaces of the article, and will be sufficiently imperforate and continuous for my purpose, while at the same time drag-out or loss will be at a minimum. The molten salt may be otherwise introduced, however, as by spraying it in a suitable spraying apparatus capable of handling a liquid at a temperature above the melting point of the dichromate or dichromates, or by swabbing the surface of the piece or article with the molten salt. When swabbing, spraying or the like is practiced, it becomes possible to apply the material selectively, as by coating only one side of the article, and by altering the temperature, the productivity of any piece of apparatus in which a molten dichromate bath is maintained is greatly increased since the time cycle has been greatly shortened, as will now be evident. The stainless steel strip, or piece, by spraying it in suitable spraying apparatus capable of handling a liquid at a temperature above the melting point of the dichromate or dichromates, or by swabbing the surface of the piece or article with the molten salt. When swabbing, spraying or the like is practiced, it becomes possible to apply the material selectively, as by coating only one side of the article, and by altering the temperature; the productivity of any piece of apparatus in which a molten dichromate bath is maintained is greatly increased since the time cycle has been greatly shortened, as will now be evident. The stainless steel strip, or piece, by spraying it in suitable spraying apparatus capable of handling a liquid at a temperature above the melting point of the dichromate or dichromates, or by swabbing the surface of the piece or article with the molten salt. When swabbing, spraying or the like is practiced, it becomes possible to apply the material selectively, as by coating only one side of the article, and by altering the temperature; the productivity of any piece of apparatus in which a molten dichromate bath is maintained is greatly increased since the time cycle has been greatly shortened, as will now be evident. The stainless steel strip, or piece, by spraying it in suitable spraying apparatus capable of handling a liquid at a temperature above the melting point of the dichromate or dichromates, or by swabbing the surface of the piece or article with the molten salt.
fused salt and then into and through a continuous furnace in which the chemical reaction will take place.

When the chemical reaction is complete, any residue of salt may be washed from the surfaces of the article with conventional equipment. The black coatings formed in my process are suitable not only for decorative uses, but there are many utilitarian uses in which they have importance. By way of a single example, the metal bodies of television tubes require to be blackened, and my process is particularly adapted to this end. The tube bodies have a thin wall section making possible a very short time of immersion in the molten salt bath to bring the body up to bath temperature to obtain, as set forth above, a suitable thin film of the fused salt or salts with minimum drag-out.

The greater part of the time required for the chemical reaction occurs in the subsequent furnace which may be any suitable type of heat treating furnace. Where dipping is practiced, I prefer to accomplish this at temperatures around 400° C. to 450° C. to employ a water solution at any around 455° C. in the subsequent furnace or oven. The atmosphere in the furnace does not require control and can even be reducing, although this involves unnecessary expense. A neutral or oxidizing atmosphere is preferred. The atmosphere may be an atmosphere of products of combustion in a fuel-fired furnace, or where other heating means are used, such as radiant tubes or electric heating elements, a furnace atmosphere of air is entirely satisfactory. The temperature for furnace heating may be varied over a wide range, and it is even possible to tolerate a temperature above the decomposition temperature of the fused salts since the chemical reaction occurs very rapidly and ordinarily there is an excess of the dichromate or dichromates acting as oxidizing agents over and above that required for the formation of the desired black coatings.

I have further found that the salt or salts may be applied to the cleaned metal articles or pieces otherwise than in a fused condition. It is readily possible to apply them in a water solution as at any temperature below the boiling point. The articles may be dipped into a tank containing such a water solution, or they may be treated by swabbing, spraying and the like. In the use of water solutions, the problem becomes more complex in that the temperature and concentration of the dichromate or dichromates in solution as well as the conditions of coating should be controlled to obtain large spangled crystals on the surfaces of the metal pieces or articles.

In the formation of satisfactory black coatings by my method, the cleaned chromium steel pieces should be protected from atmospheric oxidation, since this is productive of a heat tint which may give an undesirable color and is likely to impair the continuity of the coating. A film of dichromate solution which dries on the metal pieces in the form of tiny separate crystals will protect the work from heat tinting during the heating-up cycle in the furnace or oven and prior to the complete melting of the salt or salts. As a consequence, I prefer to employ aqueous solutions which are to coat the pieces under such circumstances that a large or spangled crystal formation is obtained upon drying. One way of producing such large spangles is to make up an aqueous solution of the salt ranging from 5% to nearly 100% saturated at room temperature and to apply it to the article as by dipping, swabbing or spraying. I have found that such a coating is sufficiently impervious for my purpose and that it will remain so during the heating-up cycle in the oven or furnace. A preliminary heating of the pieces to a temperature approaching, equal to, or slightly above the boiling point of the solution is helpful in the obtaining of impervious coatings. Where the solution is sprayed on, using a solution saturated at elevated temperatures, so that the tendency is to form the minute, discrete crystals referred to, it is within the scope of my invention to coat it a plurality of times in order to obtain an impermeable black coating. Furthermore, whenever an aqueous solution is applied to the articles or pieces by spraying, I prefer to employ two or more coats as a precautionary measure to assure complete coverage.

While in a dipping procedure in fused salt some chemical reaction may be begun in the bath, there is no detectable chemical reaction or blackening which takes place when the articles or pieces are coated with an aqueous solution by dipping and spraying at any temperature up to their boiling point and are then dried at normal temperatures or by means of heated air. Under these circumstances the entire chemical reaction will take place in the subsequent furnace or oven.

The use of water solutions of the dichromates which are not so easily brought to become supersaturated during application, the use of elevated solution temperatures, and the warming of the pieces, all contribute to the formation of a spangled crystal condition which I have found to be inhibitive of atmospheric oxidation. It is within the scope of my invention to add to water solutions of the dichromate or dichromates surface active agents to increase the wetting and assist in the formation of air impervious crystalline coatings.

Modifications may be made in my invention without departing from the spirit of it. Having thus described my invention in certain exemplary embodiments, what I claim as new and desire to secure by Letters Patent are:

1. A process of producing a black oxide coating on chromium steel articles which comprises coating the cleaned articles with an imperforate layer of salt chosen from a class consisting of sodium dichromate and potassium dichromate and mixtures thereof, passing the articles into a furnace maintained at a temperature between substantially 300° C and 500° C for a heat treatment having a duration of substantially 2 to substantially 30 minutes, and thereafter washing the articles to remove from the surfaces thereof any residue of unreacted substance.

2. The process claimed in claim 1 in which the furnace atmosphere is oxidizing.

3. The process claimed in claim 1 in which the coating of salt is applied to the steel articles by dipping them into a bath of fused salt and withdrawing them therefrom.

4. The process claimed in claim 1 in which the coating of salt is applied to the steel articles by dipping them into a bath of fused salt and withdrawing them therefrom, and in which the articles are left in the bath for such length of time as to cause them to reach substantially the temperature of the bath, whereupon they are withdrawn therefrom and drained.

5. The process claimed in claim 1 in which the coating of salt is applied to the steel articles by dipping them into a bath of fused salt and withdrawing them therefrom, and in which the articles are left in the bath for such length of time
as to cause them to reach substantially the temperature of the bath, whereupon they are withdrawn therefrom and drained, and in which the said furnace has an oxidizing atmosphere.

6. The process claimed in claim 1 wherein the fused salt is applied to at least one surface of the cleaned article by swabbing.

7. The process claimed in claim 1 in which the fused salt is applied to the surface of the cleaned article by spraying.

8. The process claimed in claim 1 in which the salt is applied to the surface of the cleaned article in water solution, a film of the water solution being subsequently dried on the surface of the article.

9. The process claimed in claim 8 wherein the solution is less than saturated at and is applied at an elevated temperature.

10. The process claimed in claim 8 wherein the solution is 5% to 100% saturated at the temperature of application, and is applied to the surface of the cleaned article by spraying.

11. The process claimed in claim 8 wherein the dried coating of salt on the surface of the article is crystalline and is characterized by a spangled crystalline condition.

12. A process of producing a black oxide coating on the surface of a chromium steel article which comprises dipping the cleaned article in a fused bath of salt at a temperature of substantially 400° C., said salt being chosen from a class consisting of sodium dichromate, potassium dichromate and mixtures thereof, maintaining the said article in said bath until it reaches substantially bath temperature, withdrawing and draining it, passing it into a furnace wherein it is maintained at a temperature of substantially 455° C. for a time between substantially 2 to 30 minutes, and thereafter washing the article to remove from the surface thereof any residue of unreacted substance.

13. A process of producing a black oxide coating on the surface of a chromium steel article which comprises dipping the cleaned article in a fused bath of salt at a temperature of substantially 400° C., said salt being chosen from a class consisting of sodium dichromate, potassium dichromate and mixtures thereof, maintaining the said article in said bath until it reaches substantially bath temperature, withdrawing and draining it, and passing it into a furnace wherein it is maintained at a temperature of substantially 455° C. for a time between substantially 2 to 30 minutes, thereafter withdrawing the said article from the said furnace, cooling it and washing from its surface any residue of unreacted substance.

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The following references are of record in the file of this patent:

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