My invention relates to a process of coating metallic products and more especially to the coating of stainless steel products.

An object of my invention is the provision of a simple, economical and thoroughly practical process of coating metallic products, such as products fashioned of stainless steel.

Another object is the provision of tough, durable and corrosion-resistant blackened metallic articles, such as stainless steel articles, having a surface of high quality which retains its finish over a prolonged period of time.

A further object of my invention is the provision of a wide range of coated articles such as machine and equipment parts, implements, trim, fittings, furnishings, articles of apparel, and the like.

Other objects in part will be obvious and in part pointed out heretofore.

The invention, accordingly, consists in the combination of elements, composition of ingredients and mixture of materials, and in the several steps and the relation of each of the same to one or more of the others, and in the products resulting therefrom, as described herein, the scope of the application of which is indicated in the following claims.

As conducive to a clearer understanding of certain features of my invention, it may be noted at this point that stainless steel is defined as a low-carbon steel comprising 10% to 35% chromium, with or without nickel, and with or without supplemental additions of manganese, silicon, cobalt, copper molybdenum tungsten, vanadium, columbium, titanium, and the like, for special purposes, and a balance which is substantially all iron.

It further may be noted that stainless steel is widely used in the form of products having natural metallic finish. In natural unpollished condition the products present a dull gray or satin-like appearance and, when polished, possess an unusual mirror-like brilliance. There is wider demand for coated stainless steel products having surfaces differing in appearance from the usual metallic. In meeting this demand, a number of coating processes of the prior art are employed, for achieving non-metallic coatings or films on the metal surfaces. The more popular coatings of those heretofore obtained are chemical compounds of stainless steel, which coatings differ from paint or like coatings partly in that they are more adherent and durable.

The heretofore known chemical processes of coating stainless steel have, for the most part, been of limited success, one reason being that the time of processing required is too long to be practical. In this connection, it should be noted that stainless steel is quite inert and does not respond readily to many types of coating treatment. Oftentimes, the processes necessarily create dangerous or obnoxious fumes or other working conditions which are objectionable. Certain known coating processes, moreover, involve the use of chemicals which deteriorate in a short time. In such event replacement of the chemicals, usually at considerable expense, is quite essential in order to achieve uniformly treated stainless steel products.

Some of the heretofore known processes are wholly incapable of giving satisfactory coatings on stainless steel products or, as pointed out heretofore, are not easily controlled to give an expected quality of coating in a consistent manner. The coatings obtained often are porous, lack hardness and toughness, or are insufficiently resistant to corrosion. Soft coatings, such as heretofore known hydroxide coatings, are chalky and rub off or wear away too readily to be of practical use. They also undergo change of appearance in the presence of moisture. Other known coatings are not sufficiently adherent to the underlying metal. They crack, chip, or spall-off, especially where stressing such as bending or flexing are encountered. Another class of coatings heretofore achieved on stainless steel are thick and materially affect the final dimensions of finished products, thus making the products unsuitable for an originally intended use requiring accurate dimensions.

An outstanding object of my invention, accordingly, is the provision of a method for producing stainless steel products, or other alloy steel products, and the products themselves, which coating is stable, durable and corrosion-resistant under a wide variety of conditions and even is adherent where the metal is bent, which coating is hard and tough and uniform both in texture and appearance, and which, being substantially free of chalkiness, does not rub off or wear away during extended use.

Referring now more particularly to the practice of my invention, stainless steel articles, for example, are provided with black oxide coatings of exceptional quality by immersion in a strong oxidizing bath of sodium dichromate and/or potassium dichromate. The quality and physical depth of coating obtained are controlled primarily by the time of immersion and temperature of the immersion bath. As for actual appearance
of coating achieved, initial finish of an article or product prior to treatment is important. A dull gray unpolished piece when treated comes out a dull black, while a polished piece receives a lustrous black finish as a result of treatment.

As illustrative of the practice of my invention, stainless steel products and articles to be coated preferably are given a preliminary cleansing treatment such as pickling to eliminate substantially all scale, oxide film, grease, dirt, or the like often present on the product surfaces as a result of earlier treatment or fabrication. Where desired, mechanical cleaning methods are resorted to such as sandblasting or grinding with or without pickling.

In pickling the stainless steel products, quick dipping in an aqueous solution of 20% nitric acid and 1% hydrofluoric acid usually is sufficient. Thereafter, it is preferable to rinse the product in clean water, finally obtaining a scale-free and otherwise clean metal surface which is usually of dull gray or satin-like appearance. The products subsequently are dried and then are ready for coating especially where a dull black coated finish is sought.

To prepare the products for receiving a lustrous black finish, I find advantage in introducing a polishing step before coating. The polishing conveniently is accomplished by buffing or like mechanical methods. A better polish, however, is achieved electrolytically as, for example, in accordance with the process described and claimed in the copending application Ser. No. 254,888 of James N. Ostrofsky, now Patent No. 2,335,354, Nov. 30, 1943, entitled Polishing stainless iron and steel, in which the stainless steel products are made the anode of an aqueous electrolyte comprising an allphatic carboxylic acid such as citric acid and a soluble compound having a sulphate radical such as sulphuric acid; or by anodic treatment in an aqueous solution of concentrated perchloric acid as covered in my copending application Ser. No. 319,057, entitled Electrolytic polishing of stainless iron and steel; or by subjecting the products to alternating current treatment in a concentrated acid bath including a substantial amount of nitric acid as set forth in the copending application Ser. No. 440,296 of Alexander L. Feld, entitled Electrolytic polishing of stainless steel. After the stainless steel products are subjected electrolytically, I wash them in clean water so as to remove traces of the electrolyte employed. The products are dried and thereafter present evenly polished metallic surfaces which are in excellent condition for coating.

In coating stainless steel articles and products, or other alloy steel products, in accordance with my invention, I prepare, in a melting vat or the like, equipped with a suitable heating unit, a molten salt bath consisting of or comprising substantial amounts of sodium dichromate and/or potassium dichromate. The bath advantageously is prepared at temperatures substantially below decomposition temperature of the final melt. A bath consisting of fused sodium dichromate and/or potassium dichromate is preferred.

After melting, the bath is adjusted to treating temperature preferably substantially below decomposition temperature and usually in the approximate range of 320°C to 500°C. I then immerse a stainless steel product, for example, in the bath for a period of time usually ranging from about 30 to 300 minutes or more. Temperature of the bath preferably is maintained substantially constant throughout the immersion period. The product conveniently is left immersed in the bath during the treatment period or is immersed periodically as by dipping. In any event, it appears that a strong oxidizing action is set up and a coating or film rich in oxides of iron and chromium accordingly forms on the stainless steel product.

The coated product or article is withdrawn from the salt bath and is washed free of salt and cooled to room temperature. The product or article provided has the many beneficial characteristics of stainless steel such as its corrosion resistance, hardness and strength, yet possesses a durable and beautiful black oxide finish which in no manner impairs the rustless or corrosion-resisting properties of the underlying metal.

The oxide film or coating is dense, hard, tough and corrosion resistant and thus does not wear away readily or wipe off and, moreover, is highly adherent and flexible and does not crack, chip or spall-off even upon being subjected to flexing or bending stresses. The coating, whether dull or lustrous black in appearance depending upon initial finish of the steel before treatment, is uniform and of stable quality. My black oxide coating does not fade in atmospheres of varying humidity or as a result of rubbing, but maintains its initial beauty for a long period of time even when exposed to the outdoor elements.

In connection with the practice of my process, a molten salt bath comprising substantially all sodium dichromate is used to good advantage especially at temperatures ranging between 320°C, the melting point of sodium dichromate, and 400°C, the decomposition point of sodium dichromate. The bath is particularly useful for providing high quality coatings on chromium-nickel steel products such as of the 18-8 chromium-nickel grade, but also is capable of giving a fine oxide finish on chromium steel products as well as on other alloy steel products. I find that the oxidizing strength of the bath increases with temperature increased below the decomposition point. Where the bath is held in a temperature range above decomposition temperature, it no longer rapidly produces coatings on stainless steel, although good coatings have been achieved by extending the treatment time. In all, I prefer a processing range of about 320°C to approximately 380°C, for within this range substantially no decomposition occurs to affect the oxidizing power of the bath and a highly satisfactory oxide coating or film is obtained on the products in about 2 to 15 minutes time.

In coating stainless steel products, such as those of either chromium or chromium-nickel steel, at bath temperatures higher than those achieved practicably in using sodium dichromate alone, a molten bath containing substantial amounts of sodium dichromate, and potassium dichromate is employed to good advantage. The sodium dichromate of the bath is a more active oxidizing agent for stainless steel that is potassium dichromate and, therefore, preferably is included in predominating amount; the potassium dichromate serving primarily to elevate the decomposition point of the bath. A bath thus provided has a decomposition point ranging from about 400°C to 500°C or more depending upon the amount of potassium dichromate used. In treating the products, temperatures of approximately 400°C to 500°C are preferred without encountering substantial decomposition of the bath. To illustrate, a bath composed substantially of 80 parts by weight sodium dichro-
mate and 20 parts potassium dichromate was made up and worked, and it was possible to employ temperatures within the approximate range of 430° C. to 470° C. without encountering decomposition to any material extent. This same bath later was used at 500° C., being worked each day, and after one month was still very effective despite showing considerable decomposition.

Thus it will be seen that there has been provided in this invention an art and a product in which the various objects hereinbefore noted, together with many thoroughly practical advantages, are successfully achieved. It will be seen that the product is strong, durable and corrosion-resistant, and that it is given a permanent and attractive black oxide finish in a direct and thoroughly reliable manner without in any way impairing the rustless or corrosion-resistant characteristics of the metal. Moreover, it will be seen that in the practice of my process, stable and highly effective chemicals are employed which are readily available and which are handled with considerable ease.

While my process is described as being particularly useful in providing black oxide finishes on stainless steel articles and products, it will be understood that the coatings achieved may be employed as a base for subsequent coatings or films such as paint, enamel, and the like. As many possible embodiments may be made of my invention and as many changes or alterations may be made in the embodiment hereinbefore set forth, it will be understood that all matter described herein is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. The art of blackening stainless steel articles and products which includes, treating the stainless steel articles or products by immersing the same in a molten salt bath consisting essentially of sodium dichromate and potassium dichromate, the while holding said bath at a temperature in the range of 400° C. to 500° C.

2. The art of blackening stainless steel articles and products which includes, treating the stainless steel articles or products in a molten salt bath consisting essentially of one or more salts of the group consisting of sodium dichromate and potassium dichromate, said bath treatment being continued over a period ranging from about 2 to 30 minutes time.

3. The art of blackening stainless steel articles and products which includes, treating the stainless steel articles or products in a molten salt bath consisting of one or more salts of the group consisting of sodium dichromate and potassium dichromate, said bath treatment being continued over a period ranging from about 2 to 30 minutes time.

4. The art of blackening alloy steel articles and products which includes, treating the alloy steel articles or products by immersing the same in a molten salt bath consisting of potassium dichromate in substantial amount and a predominating amount by weight of sodium dichromate at a temperature of at least 320° C.

5. The art of blackening metallic articles and products which includes, polishing the metallic articles or products and then treating said polished articles or products in a molten salt bath consisting essentially of one or more salts of the group consisting of sodium dichromate and potassium dichromate.

6. The art of blackening alloy steel articles and products which includes, electrolytically polishing the articles or products, and then treating said polished articles or products in a molten salt bath consisting essentially of one or more salts of the group consisting of sodium dichromate and potassium dichromate at a temperature of 320° C. to 500° C. for a period ranging from about 2 to 30 minutes time.

7. The art of blackening stainless steel articles and products which includes, treating the stainless steel articles or products by immersing the same in a molten salt bath comprising substantially all sodium dichromate, the while holding said bath at a temperature in the range of 320° C. to 500° C.

8. The art of blackening stainless steel articles and products which includes, treating the stainless steel articles or products in a molten salt bath comprising substantially all sodium dichromate, the while holding said bath in the range of 360° C. to 380° C.

9. The art of blackening stainless steel articles and products which includes, treating the stainless steel articles or products in a molten salt bath consisting by weight of approximately 80 parts sodium dichromate and about 20 parts potassium dichromate, the while holding the bath in an approximate range of 430° C. to 470° C.

10. A coating bath composition of the character described, consisting of a major portion of molten sodium dichromate and a minor portion of molten potassium dichromate.

11. A molten coating bath composition of the character described, consisting, by weight, of substantially 80 parts sodium dichromate and 20 parts potassium dichromate heated in a temperature range from approximately 430° C. to 470° C.

12. In manufactures of the class described, an alloy steel product of high chromium content having an adherent, flexible, black oxide surface film thereon, said oxide consisting substantially of chromium oxide produced by immersion in a molten salt bath consisting of salt of the group consisting of sodium dichromate and potassium dichromate.

13. In manufactures of the class described, a chromium-nickel stainless steel product having an adherent, flexible black oxide surface film thereon, said oxide consisting substantially of chromium oxide produced by immersion in a molten salt bath consisting essentially of sodium dichromate.

14. In manufactures of the class described, a chromium stainless steel product having an adherent, flexible black oxide surface film thereon, said oxide consisting substantially of chromium oxide produced by immersion in a molten salt bath consisting of substantial amounts of sodium dichromate and potassium dichromate.

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