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ELECTROLYTIC SURFACE TREATMENT OF STEEL

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This invention relates to metal articles and products, more especially to an art of producing black coated stainless steel products, and to the resulting treated products themselves, representing an improvement to the process and product of the pending application of Irvine C. Clingan, Serial No. 470,853, filed December 31, 1942, and entitled Stainless Steel and Method, now Patent 2,394,899 of February 12, 1946.

An object of my invention is the rapid, efficient and economical production of black oxide coated stainless steel articles and products, for example, machine and equipment parts, accessories, ornamental objects and parts, utensils, implements, instruments and instrument parts, trim and furnishings, or the like, by which the coating produced is resistant to corrosion and mechanical wear.

Another object is the production of coated stainless steel of the character indicated in a simple, practical and thoroughly reliable manner including the utilization of readily available materials and known and tried equipment.

A further object of my invention is the provision of stainless steel products and articles having a high quality black oxide coating which is resistant to corrosive attack and wear such as by abrasion.

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

The invention accordingly consists in the combination of elements, composition of materials, and conditions of operation, in the various steps, and in the relation of each of the same to one or more of the others 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 the stainless steels by definition comprise carbon ranging from negligible amounts up to 0.25% in the relatively low-carbon varieties and more for the higher-carbon grades, 10% to 35% or more chromium, in many instances nickel, and frequently supplemental additions of manganese, silicon, cobalt, copper, molybdenum, tungsten, vanadium, columbium, titanium, sulphur, and the like, for special purposes, and the remainder substantially all iron.

The stainless steels most frequently are put into use having a natural metallic surface finish, which in the absence of polishing is gray and somewhat dull, or which with polishing as by means of rubbing, buffing or electrolytic polishing treatment is highly reflective and bright. In

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natural metallic finish, the stainless steels far surpass ordinary carbon steels in corrosion resistance, the extent depending upon such factors as composition, treatment prior to use, and corrosive environment. Even so, it is at times desirable to provide other than natural metallic finishes on stainless steel products for such reasons as to gain further resistance to corrosion, a light absorbing finish, or a departure from natural metallic appearance. As a result of existing needs, a number of stainless steel treating processes which have for their object the provision of protective coatings or films on the metal surfaces now form a part of the prior art.

Many of the heretofore known coating processes, however, fall short of acceptance for providing desired types of coatings on stainless steel. In particular, some of the processes give coatings which are removed too readily in use, especially by rubbing, or by abrasion such as with sand, grit, coarse cloth, leather or other abrasive substances. The removal by rubbing or by abrading often is more pronounced when the coated products are additionally exposed to a wetting agent as for example oil or water instead of being utilized in dry surroundings. A further prior art treatment of stainless steel such as painting gives coatings which are so thick as to be objectionable in producing coated products within close dimensional tolerances.

There are certain known processes which include the production of stainless steel coated with chemical reaction compounds of the steel itself. A number of these processes, however, require an extensive time of coating treatment of the steel, evolve dangerous or obnoxious fumes, are extremely difficult to control for consistent effectiveness, or entail other matters which are objectionable such as speedy deterioration of the treating chemicals and too frequent need for replacement of spent bath constituents. Some of the chemical processes do not yield desired corrosion resistant coatings or ones which are adherent to the stainless steels, while other known processes are inefficient in view of inertness of the metal to certain types of treating chemicals and accompanying conditions of coating treatment.

Quite some few of the chemically coated stainless steels are not resistant to abrasion or rubbing, instead are soft and rub off or wear away too readily for most purposes. This is true of the heretofore known hydroxide coatings, which in addition are affected by moisture to such extent as to undergo a change in appearance.

An outsanding object of my invention, accordingly, is the provision of a method for producing black oxide coated stainless steel products, or other alloy steel products, and the products themserves, which coating is hard, adherent, and resistant to abrasion in wet or dry environments, which is corrosion resistant, dense, and of uniform texture and appearance, and which, being hard and substantially free of chalkiness, does not rub off or wear away during extensive use.

Referring now more particularly to the practice of my invention, I obtain hard-surface blackened ferrous metal, for example, stainless steel, by treatment which includes both immersing the same in a strong blackening salt bath of sodium dichromate and/or potassium dichromate, and then subjecting the metal in blackened condition to electrical cathodizing current, preferably in a separate dichromate bath. The quality of black coating which I achieve, including physical depth of the coating and hardness and abrasion resistance of the same, depends to a large extent upon such factors as time of immersion, temperature of the immersion bath, and conditions of the cathodizing treatment. Likewise, the actual appearance of the coating importantly reverts to such controls as initial finish of the article or product before treatment. A dull gray unpolished piece responds to my blackening and cathodizing treatment by assuming a resulting dull black appearance, while a polished piece assumes a smooth black finish as a result of the treatment.

As illustrative of the practice of my invention, I provide stainless steel articles and products for black coating treatment, for example, those in the form of telephone equipment parts, door and window trim, light switch plates, gun parts, vacuum cleaner or electric toaster casings, handles and bumpers, photographic and optical equipment parts, or in the form of any of a wide variety of other stainless steel products and articles to serve such functions after blackening as entail rubbing, abrasion, corrosive attack, or some further need for endurance of black coating. Before continuing with my coating treatment, I prefer to preliminarily cleanse the stainless steel articles or products, such as by pickling, to eliminate substantially all scale, oxide film, grease, dirt, or the like, often present on the metal surfaces as a result of earlier treatment or fabrication. At times, I resort to mechanical cleaning methods such as sand blasting or grinding with or without the pickling treatment.

For the pickling of stainless steel products, I find that dipping in an aqueous solution of 20% nitric acid and 1% hydrofluoric acid usually is sufficient. Thereafter, I subject the products to rinsing in clean water, finally obtaining a scale-free and otherwise clean metal surface which usually is of dull gray or satin-like appearance. I subsequently dry the products which then are ready for coating especially where a dull black finish is sought.

In preparing the products for a smooth black finish, I usually introduce a polishing step before the blackening operation. Mechanical polishing methods such as rubbing or buffing often are satisfactory for this purpose. An even better polishing step which I frequently employ involves electrolytic polishing treatment of the metal, as for example, polishing in accordance with the process described and claimed in U. S. Patent No. 2,335,354 of James N. Ostrofsky, entitled Polishing Stainless Iron and Steel, in which the stainless steel

products are made the anode of an aqueous electrolyte comprising an aliphatic carboxylic acid such as citric acid and a soluble compound having a sulphate radical such as sulphuric acid, or subject 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 Serial No. 460,296 of Alexander L. Feild, entitled Electrolytic Polishing of Stainless Steel, now Patent 2,442,591 of June 1, 1948. I usually wash the electrolytically polished products in clean water to remove traces of the electrolyte. The polished products are dried, which then are in excellent condition for treating steps more fully described hereinafter.

For the coating of stainless steel articles and products, or other alloy products, in accordance with my invention, I prepare in a melting vat or the like having a suitable heater, a molten salt bath consisting of sodium dichromate and/or potassium dichromate. The preferred dichromate bath which I form and utilize for blackening the metal consists substantially entirely of fused sodium dichromate and/or potassium dichromate. The dichromate salts are heated to temperatures which are sufficient to give a molten bath. In general, I maintain the blackening bath usually within the approximate temperature range of 320° C. to 500° C.

To effect a blackening treatment in accordance with my invention, I immerse a stainless steel product, for example, in the dichromate bath for a period of time ranging from about 2 to 30 minutes or more. The bath temperature preferably is substantially constant throughout the blackening period. In immersing the metal in the fused dichromate, I resort to such practices as holding the metal immersed during the entire blackening treatment or to dipping the product repeatedly into the bath. The blackening treatment results in the achievement of a dense, adherent black coating on the metal which in the instance of the stainless steel product consists of chromic oxide (Cr_2O_3) as determined by X-ray analysis.

Where the metal, such as the stainless steel product is blackened by dichromate bath treatment, I effect a further step which materially and importantly contributes to the achievement of a hard, abrasion-resistant black finish, as on the stainless steel product surface. In carrying out this step, I subject the metal to direct current cathodizing treatment within a fused dichromate bath after the blackening operation proper. Following the cathodizing treatment, the product is removed from the bath, rinsed and dried. Experience indicates that the abrasion resistance of the resulting coating thus obtained usually is superior as compared with results of blackening the metal without cathodically treating the blackened product.

In cathodizing, I conveniently provide the treating current from a suitable source of direct current electrical supply to an anode illustratively of stainless steel, for example 18–8 chromium-nickel or 17% chromium steel, in one of the dichromate baths described hereinbefore, heated to within temperature limits as already defined, the work itself being made the cathode.

To cathodize and enhance surface hardness of the stainless steel product referred to, for example, as after the product has been subjected for at least about 2 minutes' time to dichromate bath blackening treatment, I supply direct current through the dichromate usually for 5 to 10

minutes or more to the product as cathode. In so doing, I maintain a current density of about 0.05 ampere per square inch to approximately 4 amperes per square inch with respect to area of product surface under cathodizing treatment. A preferred cathodizing current density range which I use in this connection extends from about 0.05 ampere per square inch up to about 0.25 ampere per square inch. The optimum current density for maximum abrasion resistance of the resulting products is about 0.10 ampere per square inch, but this, of course, may vary somewhat with the grades of blackened metal which I cathodize, or it may be influenced by the condition of the bath. With the stainless steel product black coated, and the cathodizing treatment complete, I withdraw the same and thereafter rinse and dry the coated metal surface.

The black coated and cathodized stainless steel product possesses a durable and beautiful black oxide finish which in no manner impairs the ruthless or corrosion-resisting properties of the underlying metal. My black oxide film or coating itself is adherent, hard, and resistant to abrasion, rubbing or wiping whether exposed to wet or dry environments, and is dense and resistant to corrosion. The black oxide coating does not fade in atmospheres of varying humidity or even after extensive rubbing or abrasion, and maintains its natural appearance for a long period of time in the outdoor elements.

By actual test on a "Taber abraser," under dry conditions, using a standard abrading wheel (No. CS–17F) loaded at 1000 gms. and running at 60 R. P. M. comparative results were had of my black coated and cathodized products, as compared to a product black coated but not cathodized, as follows:

Sample No.	Cathodizing Current	Rev. to Failure
1A	none	110
2A	.05 amp./sq. in.	250
3A	.10 amp./sq. in.	900
4A	.25 amp./sq. in.	250

Similarly, by test under water of my black coated and cathodized products, as compared to a product black coated but not cathodized, with conditions otherwise the same as noted, the results are even more pronounced:

Sample No.	Cathodizing Current	Rev. to Failure
1B	none	400
2B	.05 amp./sq. in.	700
3B	.10 amp./sq. in.	7,500
4B	.25 amp./sq. in.	950

In providing black coated products, and in improving the same by cathodizing, I find it advantageous to employ a molten salt bath comprising substantially all sodium dichromate at temperatures of bath ranging between 320° C. and 400° C., the melting and decomposition temperatures, respectively, of sodium dichromate. The bath is particularly useful for providing high quality cathodized coatings on chromium-nickel stainless steel products such as the 18–8 chromium-nickel grades, but also is capable of contributing to the achievement of abrasion-resistant, cathodized black oxide finishes on straight chromium stainless steel products as well as on other alloy steel products. I find that the oxidizing strength of the bath increases with temperature

increases. By holding the bath in a temperature range well above the decomposition temperature, however, satisfactory black coatings on stainless steel are no longer rapidly achieved, although good coatings are achieved by extending the treating time. In treating with the sodium dichromate baths of the character just mentioned, I therefore prefer a process range of about 360° C. to approximately 380° C. In the blackening treatment a highly satisfactory black oxide coating or film develops on the products in about 2 to 15 minutes' time. The same temperatures are suitable for the cathodizing treatment which, for example, I effect immediately following the blackening treatment proper.

For coating and/or cathodizing stainless steel products such as those of chromium or chromium-nickel steel, at bath temperatures higher than those which are practical in using sodium dichromate alone, a molten bath containing substantial amounts of sodium dichromate and potassium dichromate is advantageous. The sodium dichromate of the bath is a more active oxidizing agent for stainless steel than is potassium dichromate, and, therefore, preferably is included in predominating amount, especially for effecting the blackening treatment in combination with the cathodizing operation or followed by the same. In treating the products, temperatures of approximately 400° C. to 500° C. are employed with the mixed salt bath.

Thus, it will be seen that there are provided in this invention an art and 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 made with assistance of cathodizing treatment to have a durable, abrasion-resistant and corrosion-resistant black oxide coating in a simple and thoroughly reliable manner without in any way impairing the rustless or corrosion resistant characteristics of the metal. Moreover, it will be seen that my process is readily practiced with stable and highly effective chemicals which are easy to obtain and to handle.

While my process is described as being particularly useful in the provision of cathodized black oxide finishes on stainless steel articles and products, it will be understood that the coatings achieved may serve 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 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 as my invention:

1. In treating alloy steel articles containing at least 10% chromium to obtain a hard, adherent, abrasion-resisting surface, the art which comprises, surface-blackening such articles in a fused salt bath consisting of salt of the group consisting of sodium dichromate and potassium dichromate, and then subjecting the same to electrical cathodizing treatment for at least about five minutes in a fused salt bath consisting essentially of salt of the group consisting of sodium dichromate and potassium dichromate.

2. In treating stainless steel articles to obtain a hard, adherent, abrasion-resisting surface, the art which comprises, surface-blackening such articles in a fused bath consisting of salt of the group consisting of sodium dichromate and potassium dichromate heated to a temperature of

320° C. to 500° C., and subjecting the blackened articles to electrolytic cathodizing treatment for about five to ten minutes in said fused salt bath at a current density of 0.05 to 0.25 ampere per square inch of article area immersed.

3. In treating stainless steel articles to obtain a hard, adherent, abrasion-resisting surface, the art which comprises, surface-blackening such articles in a fused salt bath comprising substantially all sodium dichromate heated to temperature within the range of 360° C. and 380° C., and then subjecting the same to electrolytic cathodizing treatment for about five to ten minutes in a fused salt bath at a current density of about 0.10 ampere per square inch of article area immersed.

4. In treating alloy steel articles containing at least 10% chromium to obtain a hard, adherent, abrasion-resisting surface, the art which comprises electrolytically polishing such articles, then surface blackening the polished articles in a fused salt bath containing substantially all salt 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, and after at least said 2 minutes' blackening time subjecting the articles to electrolytic cathodizing treatment in said fused salt bath at a current density of 0.05 to 4 amperes per square inch of article area immersed for a period of at least 5 minutes.

5. An alloy steel product containing at least

10% chromium and having an adherent and abrasion-resistant cathodized black oxide surface film thereon, produced by immersion in a fused salt bath consisting of salt of the group consisting of sodium dichromate and potassium dichromate, and subjected to electrical cathodizing treatment in a fused salt bath essentially consisting of salt of the group consisting of sodium dichromate and potassium dichromate.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,795,512	Schmidt et al	Mar. 10, 1931
1,845,978	Hosenfeld	Feb. 16, 1932
1,927,773	Chittum	Sept. 19, 1933
1,975,239	Ungelenk	Oct. 2, 1934
2,261,744	Ostrofsky	Nov. 4, 1941
2,394,899	Clingan	Feb. 12, 1946
2,426,962	Witchger	Sept. 2, 1947

FOREIGN PATENTS

Number	Country	Date
695,366	France	of 1930

OTHER REFERENCES

Hackh's Chemical Dictionary, 3d edition (1944), pages 198, 199.